Overview of Catalytic Peroxide Bleaching Kraft Pulp
Transition metal centered activators

- Peroxomolybdate
  - ![Peroxomolybdate](image)

- Bi-nuclear Mn complexe
  - ![Bi-nuclear Mn complexe](image)

- TAML
  - ![TAML](image)

- Cu-dpa
  - ![Cu-dpa](image)

References:
- Fabian, Tappi J. 2008, 8
- Argyropoulos, Tappi J. 2002, 1(2), 1
Peroxometalates centered activators

Peroxomolybdate complexes

[MoO(O_2)_2(OH)(H_2O)]^-

Formation of peroxometalates under acidic conditions
- Enhanced electrophilic character of peroxo oxygens
- Preferably act on aliphatic C-C double bond

Ball and stick model of diperoxomolybdate anions
Op=peroxo oxygens, Ot= double bond oxygen,
O1, O2=other oxygens (e.g. H_2O, OH-)

Fabian, Tappi J. 2008, 8
Transition metal centered activators

Peroxomolybdate complexes

Lignin model compounds: isoeugenol (left), eugenol and creosol (right)

Fabian, Tappi J. 2008, 8

- HexA is generated from 4-O-methyl-D-glucuronic acid in xylan during alkaline pulping
- HexA actively reacts with permanganate, thus affecting the kappa number determination
- Contributes to higher demand for bleaching chemicals
## Delignification and HexA Removal

<table>
<thead>
<tr>
<th>Stage</th>
<th>Charge</th>
<th>pH</th>
<th>T (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>6% EDTA</td>
<td>~5</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>P</td>
<td>10%H₂O₂</td>
<td>~5.5</td>
<td>80</td>
<td>3</td>
</tr>
<tr>
<td>PMo</td>
<td>10%H₂O₂, 300ppm Mo</td>
<td>~5.5</td>
<td>80</td>
<td>3</td>
</tr>
<tr>
<td>PMoSi</td>
<td>10%H₂O₂, 300ppm Mo, 100ppm Silicate</td>
<td>~5.5</td>
<td>80</td>
<td>3</td>
</tr>
<tr>
<td>EP</td>
<td>10%H₂O₂, 10% NaOH</td>
<td>~11</td>
<td>70</td>
<td>2</td>
</tr>
</tbody>
</table>

### Kappa number and HexA removal

<table>
<thead>
<tr>
<th>Bleaching stage (BIRCH PULP)</th>
<th>Kappa number (units)</th>
<th>HexA (μmoles/g pulp)</th>
<th>Kappa number equivalence (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂-prebleached</td>
<td>10.0</td>
<td>50.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Q+P</td>
<td>8.6</td>
<td>45.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Q+P+Q+EP</td>
<td>6.8</td>
<td>45.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Q+PMo</td>
<td>5.8</td>
<td>25.8</td>
<td>2.2</td>
</tr>
<tr>
<td>Q+PMo+Q+EP</td>
<td>4.3</td>
<td>25.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Q+PMoSi</td>
<td>5.9</td>
<td>22.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Q+PMoSi+Q+EP</td>
<td>4.3</td>
<td>22.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bleaching stage (PINE PULP)</th>
<th>Kappa number (units)</th>
<th>HexA (μmoles/g pulp)</th>
<th>Kappa number equivalence (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂-prebleached</td>
<td>16.6</td>
<td>23.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Q+P</td>
<td>15.0</td>
<td>22.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Q+P+Q+EP</td>
<td>10.4</td>
<td>22.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Q+PMo</td>
<td>10.8</td>
<td>14.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Q+PMo+Q+EP</td>
<td>6.3</td>
<td>12.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Q+PMoSi</td>
<td>10.6</td>
<td>12.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Q+PMoSi+Q+EP</td>
<td>6.1</td>
<td>11.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Vanadium peroxo complexes

Oxygen transfer from peroxovanadium complexes to hydrocarbons from various possible active species

Experimental Details

- Pine kraft pulps (kappa=16.2)
- Q stage: 1.6% consistency, 0.5% DTPA, 50°C, 30min, pH~4.5
- P stage: 10% consistency, 0.2% DTPA, 0.05% MgSO₄, varying charges of H₂O₂, NaOH, varying reaction time

Suchy et al. Pulping Conference, 2008, 1277
Vanadium peroxo complexes

Optimum Conditions
- Pine Kraft pulps
- Activator charge: 0.5%
- Temperature: 80°C
- Retention time: 2h
- Peroxide and alkaline charge: 3%

Improvements
- Kappa number reduction: 16.2-6.3 (61% reduction)
- ISO brightness: 5.7% rise
H₂O₂-copper/pyridine systems

Cu(II), Cu(II)-dpa

<table>
<thead>
<tr>
<th></th>
<th>Kappa reduction</th>
<th>Viscosity loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>24.3%</td>
<td>7.6%</td>
</tr>
<tr>
<td>Cu(II)/Q</td>
<td>28.0%</td>
<td>11.1%</td>
</tr>
<tr>
<td>Cu(II)-dpa</td>
<td>26.2%</td>
<td>0.6%</td>
</tr>
<tr>
<td>Cu(II)-dpa/Q</td>
<td>29.9%</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

- High selectivity for delignification by Cu(II)-dpa complexes

Experimental Details

- Oxygen-prebleached kraft pulp (OKP)
- Cu stage: Cu/dpa ratio=1:1, 1% H₂O₂
  5% csc, pH~10, 60°C, 4h
- Q stage: 0.5% EDTA, 5% csc, 80°C

OKP-Oxygen delignified pine kraft pulp

Production of hydroxyl radicals with Cu(II) and Cu(II)-dpa

\[ 2\text{Cu}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow 2\text{Cu}^+ + \text{O}_2 + 2\text{H}_2\text{O} \]

\[ \text{Cu}^+ + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{OH}^- + \text{HO} \]

- Fenton reaction: produce hydroxy radicals in the presence of free metal ions
- Cu-dpa has altered the redox potential to prevent hydroxy radical production

Nitrogen Centered Peroxide Activators: TAED

![Chemical Structure of TAED, DAED, and PAA](image)

*R. Patt, Tappi Pulping Conference Proceedings, 1998, 1, 111*

**TAED-Tetra acetic ethylenediamine**

- Colorless, odorless, nontoxic and nonmutagenic compound and was widely used since 1980s
- Generate PAA or peracetate anion in-situ, which is more powerful oxidants than peroxide
- Benefits can be achieved under milder bleaching conditions (e.g. lower alkalinity, low temperature)
**In-situ Generated Peracetic Acid (PAA)**

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\delta^- & \quad \delta^+ \\
\text{Nucleophilic} & \quad \text{Electrophilic} \\
\text{site} & \quad \text{site}
\end{align*}
\]

\[
\text{pKa} \approx 8.25
\]

\[
\text{pH} < 8.25
\]

\[
\text{pH} > 8.25
\]

*Neil et al, TAPPI International Pulp Bleaching Conference, 2002*

- TAED works best at pH 10~10.5, but still effective at pH~8

- Disproportionation of PAA at medium alkalinity
  \[
  \text{AcOO}^- + \text{AcOOH} \rightarrow \text{AcOH} + \text{AcO}^- + \text{O}_2
  \]

- Improve pulp properties by reducing fibre degradation caused by longer, less efficient bleaching
Effectiveness of TAED on different pulps

<table>
<thead>
<tr>
<th>I. OPTICAL AND PHYSICAL PROPERTIES FOR THERMOMECHANICAL PULP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleaching, % GE</td>
</tr>
<tr>
<td>TAED, %, H₂O₂, %, pH Pre-aging, Post-aging, PC*, Bulk, cm²/g</td>
</tr>
<tr>
<td>0, 1.0, 1.0, 11, 68.5, 65.1, 4.22, 2.674</td>
</tr>
<tr>
<td>0.5, 1.0, 10, 68.1, 65.4, 3.36, 2.839</td>
</tr>
<tr>
<td>1.0, 1.0, 8, 65.5, 63.5, 2.81, 3.37</td>
</tr>
<tr>
<td>*Post-color number.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II. OPTICAL AND PHYSICAL PROPERTIES FOR RECYCLED PULP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleaching, % GE</td>
</tr>
<tr>
<td>TAED, %, H₂O₂, %, DTPA, %, pH Pre-aging, Post-aging, PC*, Bulk, cm²/g, Tensile strength, N</td>
</tr>
<tr>
<td>0, 1.25, 1.25, 0, 0, 11, 55.5, 54.6, 1.74, 2.07, 50.7</td>
</tr>
<tr>
<td>0.625, 1.25, 0.05, 0.05, 10.5, 53.4, 53.4, 2.02, 0.75, 51.8</td>
</tr>
<tr>
<td>0.625, 1.25, 0.05, 0.05, 8, 53.4, 53.1, 1.91, 0.76, 53.8</td>
</tr>
<tr>
<td>1.25, 1.25, 0.05, 0.05, 8, 54.3, 53.9, 2.04, 0.97, 54.6</td>
</tr>
<tr>
<td>*Post-color number.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>III. OPTICAL AND PHYSICAL PROPERTIES FOR CHEMICAL PULP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleaching, % GE</td>
</tr>
<tr>
<td>TAED, %, H₂O₂, %, pH Pre-aging, Post-aging, PC*, Bulk, cm²/g, Tensile strength, N</td>
</tr>
<tr>
<td>0, 1.0, 11, 26.3, 25.4, 12.57, 2.8, 48.2</td>
</tr>
<tr>
<td>1.0, 0, 10.5, 8.1, 27.4, 8.39, 3.12, 39.2</td>
</tr>
<tr>
<td>0.3, 0, 10.5, 24.3, 23.0, 21.95, 2.76, 44.3</td>
</tr>
<tr>
<td>0.3, 0, 8, 23.8, 23.1, 12.03, 4.11, 38.4</td>
</tr>
<tr>
<td>*Post-color number.</td>
</tr>
</tbody>
</table>

With TAED treatment

- pH, TAED charge influence the optical and physical properties of each pulp type

- Both H₂O₂ and PAA produce quinones (methoxy-hydroquinone) and vanillin derivatives (e.g. homovanillic acid, veratric acid)

- Increase in bulk and improvement of color reversion, with a possible brightness tradeoff (9% loss~8% increase)

Jeffery, TAPPI J. 2006, 5(9), 27
TAED oxidation kinetics

Reaction of acetovanillone with peroxide

\[ \ln C = -kt + \ln C_0 \]

- TAED assisted system (rate constant \( k=0.34\text{min}^{-1} \)) proceeds 100 times faster than that without TAED (\( k=0.0035\text{min}^{-1} \))

Conditions
- \( C(\text{acetovanillone})=0.12\text{mmol/L} \)
- \( C(\text{H}_2\text{O}_2)=12\text{mmol/L} \)
- Peroxide system
  - pH~11.0-11.5, 60°C
- TAED assisted system
  - pH~7.9-8.3, 60°C, TAED/H\(_2\)O\(_2\)=0.5

pH dependence of TAED/H₂O₂ systems

- A higher pH (~10.8) is desired to increase production of peroxycetic acid at the beginning of the reaction.

- A much lower pH (~8) is required to minimize decomposition of the peroxycetic acid and improve its bleaching efficiency at the second phase.

- Optimium pH ~8.3

DMD Activated peroxide bleaching

DMD can be generated from acetone and peroxymonosulfate (PMS) in-situ.

- Activated Oxygen (AO), effective in transferring a single activated oxygen atom onto aromatic and unsaturated substrates.

- Advantageous compared with ClO₂, O₂, H₂O₂ which can only oxidize phenolic hydroxyl groups.
DMD Activated peroxide bleaching

**General Conditions**

- Acetone/oxone
  - \((2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4)\) ratio, 1.5
- Temperature, 25°C
- Retention time, 60-110min
- 10% consistency
- 1.5~2.5 AO charge on o.d. pulp
- pH 7-7.5 (bicarbonate or phosphate)

- Spruce kraft pulp
- Bicarbonate buffer

- Delignification conditions:
  AO charge: 1.5% on o.d. pulp
  final csc: 10%
  acetone/AO ratio: 1.5
  Temperature: 25°C

The presence of bicarbonate has maximized the delignification efficiency in pH 7~8

DMD Activated peroxide bleaching

- Birch kraft pulp
- M stage: varying acetone/oxone molar ratio, pH~7-7.5, 25°C, 60min, csc 10%
- E stage: 8% NaOH, 70°C, 60min, csc 10%
- Ep stage: 0.8% \( \text{H}_2\text{O}_2 \), the other conditions are the same as E stage
- Op stage: \( \text{O}_2 \) 0.3Mpa, 100°C, 60min, csc 10%, 2% NaOH, 0.8% \( \text{H}_2\text{O}_2 \), 0.5%MgSO\(_4\), 3% NaSiO\(_3\)
- Q stage: 0.5% EDTA, pH~5, 70°C, csc10%, 60min
- P stage: 3% \( \text{H}_2\text{O}_2 \), 2% NaOH, 0.5% MgSO\(_4\), 3% NaSiO\(_3\), 70°C, csc10%, 70min
- A stage: 2.5% \( \text{H}_2\text{SO}_4 \), 0.6% sodium hexametaphosphate, 25°C, csc 10%, 60min

- The optimum AO charge in this condition is considered to be \(~2.5\%
- DMD reduced viscosity loss in a great extent

**DMD Activated peroxide bleaching**

<table>
<thead>
<tr>
<th></th>
<th>Brightness (%ISO)</th>
<th>Alpha-cellulose (%)</th>
<th>Degree of Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original Pulp</td>
<td>37.8</td>
<td>90.1</td>
<td>1449</td>
</tr>
<tr>
<td>M-E-Q-M-P-A</td>
<td>68.0</td>
<td>94.5</td>
<td>1460</td>
</tr>
<tr>
<td>M-Ep-Q-M-P-A</td>
<td>73.5</td>
<td>94.6</td>
<td>1390</td>
</tr>
<tr>
<td>Op-Q-M-P-A</td>
<td>82.0</td>
<td>93.8</td>
<td>804</td>
</tr>
<tr>
<td>Op-(AQ)-M-P</td>
<td>78.1</td>
<td>93.5</td>
<td>944</td>
</tr>
<tr>
<td>Op-(AQ)-M-P-A</td>
<td>80.2</td>
<td>93.5</td>
<td>928</td>
</tr>
</tbody>
</table>

AQ: pulp will not be washed between the stage A and the stage Q.

- DMD is both effective and selective as a delignifying agent but not as a brightening agent.
- The stage M made it possible to achieve a high DP and cellulos content, but the brightness is still far away from 90%ISO.