Hydrogen Peroxide Bleaching
Highlights

State of the Art and Research Direction

Art J. Ragauskas
Hydrogen Peroxide Bleaching

- Background
- Mill Applications
- Research Directions
Peroxide Bleaching: Background

- active bleaching species is $\text{HOO}^-\text{O}^-$ and derivatives
Peroxoide Bleaching: Background

\[
\begin{align*}
H_2O_2 + M & \rightarrow HO\cdot + HO^- + M^+ \\
H_2O_2 + HO^- & \rightarrow HO_2^- + H_2O \\
HO_2^- + M^+ & \rightarrow HO_2\cdot + M \\
HO_2\cdot + HO^- & \rightarrow O_2^- + H_2O \\
O_2^- + M^+ & \rightarrow O_2 + M \\
O_2^- + HO\cdot & \rightarrow O_2 + HO^- \\
2O_2^- + H_2O & \rightarrow O_2 + HO_2^- + HO^- \\
HO\cdot + HO_2^- & \rightarrow H_2O + O_2^- \\
HO\cdot + M & \rightarrow HO^- + M^+ \\
HO\cdot + HO\cdot & \rightarrow H_2O_2
\end{align*}
\]

Peroxoide chemistry strongly influenced by metals.
Peroxide Bleaching: Background

- Dakin reaction

- Dakin-like reaction

Lignin fragmentation reactions
Peroxide Bleaching: Background

- Addition to quinone structures

Destruction of color bodies
Peroxide Bleaching: Background

Formed during pulping

- 30-50% of Southern HW Kappa #
- 10-20% of Southern SW Kappa #
Peroxide: Mill Applications

Eop
- Peroxide 0.1 - 0.5%
- Temp.: 55 - 85°C
- Time: 50 - 134 min
- O₂: 0.5 - 0.7% consumed
- first extraction stage
- P is largely brightening chemistry

• Ep
- Peroxide: 0.1 - 0.2%
- Temp. 65- 85°C
- Time: 45 - 120 min.
- second extraction stage
- Brightening chemistry

• P
- Peroxide: 0.5 - 1.5%
- Temp. 65- 85°C
- Time: 45 - 120 min.
Peroxide: Mill Applications

- **PO**
  - Requires pre Q-stage
  - Peroxide: 0.5 - 3.0%
  - Temp: 100 - 110°C
  - Time: 60 - 120 min
  - O₂: 75 - 120 psi
  - Stabilizer
  - Brightening & delignifying

- **P<sub>HT</sub>**
  - Pre Q stage preferred
  - Peroxide 0.5 - 3.0%
  - Temp.
    - 105 - 110°C for 5-15 min
    - 90 - 98°C for 180 - 240 min
  - O₂: 70 - 120 psi
  - Stabilizer
  - Brightening & delignifying
Peroxide: Mill Applications

- North America
  - Primarily ECF
    - D(Eop)DED
    - D(Eop)DEpD,
    - OD(Eop)D or OD(Eop)DEpD
    - D(Ep)DED
  - HD storage (0.1 - 0.2% P, pH approx. 9)
P-Stage Mill Applications

• Europe
  – Greater bleaching sequence diversity in ECF & TCF
    • OD(Eop)DED
    • O/OD(Eop)DP
    • OQ(Op)PaaQ(PO)
    • ODQ(PO)
    • OAZQ(Eop)(PO)
    • OQPZP
Peroxide Bleaching: Role of metals

2.5% P, Q vs. no Q for SW Kraft Pulp

- P-delignification requires metal management via Q-stage
- Favorable M: Mg$^{2+}$
- Harmful: Fe, Cr, Ni
  - Mn favorable/harmful
- Note: C/D or D not M sensitive
Peroxide Bleaching: Role of Temperature

2.5% P Q HW Kraft Pulp

- P* significantly improves peroxide
- P* not just increase in rates
- Capital intensive
- Sensitive to M+
  - Q stage
  - yield
P-Stage  Future Research Directions

• Peroxide Efficiency
  • Improved Conditions
  • Catalysis
  • Modification of fibers
Brightening After OD(EPO)D Kraft HW

![Graph showing brightness as a function of chemical charge for different treatments: Chlorine Dioxide, Peroxide, and Ozone.](image)

- **Brightness** on the y-axis ranges from 84 to 92.
- **Chemical Charge, % o.d. pulp** on the x-axis ranges from 0.0 to 2.5.

- **Chlorine Dioxide** represented by black circles.
- **Peroxide** represented by black triangles.
- **Ozone** represented by black squares.
Peroxide Brightening Effects

- D-stage generates active lignin structures for P-stage
Peroxide Activation - Catalyst
Peroxide Bleaching: Research

• Bleaching properties of $P_{HT}$ and PO suggest that a catalyst could improve delignification and/or brightening

• First generation
  – $HO_3SOOH$, $CH_3CO_3H$
Peroxide Bleaching: Research P-activators

Pentacetyl Glucose

Diacetin

Diethyl Pyrocarbonate

DAED

TAED

RAc + H-O-O -  →  RH + -O-O-Ac

All improve a P-stage by 15 - 40% >>stoichiometrically
Peroxide Bleaching: Research P-catalyst
Catalytic Peroxide Activation: Use of Mn-catalyst to improve alkaline peroxide bleaching of Do SW kraft.
Peroxide Fiber Modification
Strength Effects of O and (PO) on (OZE) SW Kraft

Use an OZE pulp and apply O or (PO)

Bleaching stage enriched acid groups content of pulp fibers

(PO) increased acid groups by 65%
(O) increased acid groups by 37%
Practical Application - Bleaching
CONCLUSIONS

• Additional acid groups on or near fiber surfaces increased specific bond strength.

• Strength benefit mechanism is not known, but could be intermolecular diffusion.

• The possibility exists to produce stronger, bulkier sheets than by conventional processes.
Peroxide Summary

- Current peroxide bleaching chemistry has dramatically advanced.
- P-stage delignifies but destroys color bodies more effectively.
- Environmentally compatible.
- Sensitive to certain metals.

- Peroxide research is directed at reducing capital requirements.
- Improved peroxide delignification will be achieved.
- New research opportunities in fiber modification.
Acknowledgments

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