TAML™ Oxidant Activators:
Green Bleaching Agents for Paper Manufacturing

A Green Chemistry Module
Background

• Paper making 2000 years old, started in China
• World Consumption 300 million tons/year
• Highest consumption in the US - 700 lbs/person, followed by Finland
• 500 paper mills in operation in the US, 10,000 worldwide
Regional Paper Consumption

Figure 1: 1999 Regional Paper Consumption

- 35% North America
- 25% Asia/Australia
- 31% Europe
- 5% Rest of World
Paper Industry Trends

• 1999, growth of 5% in the newsprint/magazine market
• Overall, newsprint has been declining
• Marketing and stationery have been taking a bigger market share since 1990
• Significant growth expected in developing countries, especially in Southeast Asia, Africa, and Latin America
Paper Manufacturing

- Made from the natural fibers in wood - cellulose
- Fibers from both hard and soft woods
- Softwoods have long fibers, hard woods short fibers
- Long fibers add strength - used for grocery bags and boxes
- Short fibers used to make paper smoother
• Fibers are often blended to combine physical properties
• Hardwood fibers blended with softwood to make paper strong yet smooth
• Plants other than trees can be utilized in paper making - straw, cotton, bamboo, eucalyptus, kenaf have all been used
• Over 45% of paper in the US is recovered for use in the paper industry
General Schematic of Paper Making

Wood or Recycled Papers

Mechanical or Chemical Pulping

Paper Machining

Bleaching

Final Paper Products
Paper Making Process

- First Step - wood chips or recycled paper broken into individual fibers in a process called *pulping*
- Pulping takes place either chemically or mechanically
- Mechanical - grinding fibers, leaves lignin
- Chemical - heating with water and chemicals until fibers separate
Bleaching Process

• Removes lignin - which would cause the final paper product to have a brown discoloration

• Conventional bleaching - Kraft Process

• Consists of several processing steps combining acid, base, hydrogen peroxide, oxygen, dithionate salts, and sodium bisulfite followed by chlorinating treatments
Lignin Structure
Dioxin Formation and Properties

- Bleaching of pulp produces 2,3,6,7-tetrachlorodibenzo-4-dioxin (TCDD) as a by-product
- TCDD is tetratogenic and is acutely toxic
- Stored in the fatty tissues of animals
TAML™ Activators

• Work performed in the labs of Terrence Collins at Carnegie Mellon University
• Awarded a Presidential Green Chemistry Challenge Award in 1999
• Based on a macrocyclic tetraamide coordinated ligand and an iron center
• Catalyzes hydrogen peroxide of pulp
TAML™ Complexes
Fenton’s Reagent Mechanism

Fe$^{3+}$ + H$_2$O$_2$ → Fe$^{2+}$ + -OH + OH
OH + H$_2$O$_2$ → HOH + HO$_2$
HO$_2$ + HOOH → HOH + O$_2$ + OH
Fe$^{3+}$ + H$_2$O$_2$ → Fe$^{2+}$ + HO$_2$ + H$^+$
Fe$^{3+}$ + HO$_2$ → Fe$^{2+}$ + O$_2$ + H$^+$
Fe$^{3+}$ + OH → FeOH$^{2+}$
OH + S → P

• In the final step substrate S is oxidized to form product P.
Fenton’s Reagent vs TAML™

- Oxidizing power of Fenton’s Reagent is due to the formation of hydroxyl radicals as seen in the elementary steps of the reaction

- TAML™ is a Non-Fenton’s based oxidation
Focus of Current Work

- Collins’ recent work has focused on the design of multidentate ligands that release electrons and stabilize the metal-oxo species.
- Ligands must be resistant to oxidation.
- Collins has developed a series of ligand protection rules.
Rule 1

'For chelate rings, a hydrogen atom should not be placed on an atom that is $\beta$ to an oxidizing metal center, if the $\alpha$-atom can support an increase in the bond order with the $\beta$-atom.'
Rule 2

'A heteroatom should not be attached to a five-membered chelated ring on an atom that is \( \gamma \) to an oxidizing metal center, if the heteroatom has an available lone pair to stabilize forming cationic character on the \( \gamma \)-atom as the endocyclic \( \beta-\gamma \) bond is oxidatively cleaved by the metal.'
Rule 3

'A heteroatom should not be employed as an \( \alpha \)-donor atom in a five-membered chelate ring, if it has an available lone pair to stabilize forming cationic character on the \( \beta \)-atom as the endocyclic \( \beta-\gamma \) bond is oxidatively cleaved by the metal.'
Rule 4

'If the goal is to produce a strong electron transfer oxidant, amido-N donors should be avoided as internal ligands in acyclic chelate ligands.'
Savings with TAML™

• 38.9 x 10^{12} BTU’s per year from lower water temperatures for bleaching
• Billion of $US that would have been spent on pollution abatement and emission reduction equipment
Other TAML™ Uses

• Purification of drinking water through oxidative catalysis

• Laundry applications- reduces the problem of dye transfer by oxidizing loose dye molecules in the wash water before they can adhere to fabrics