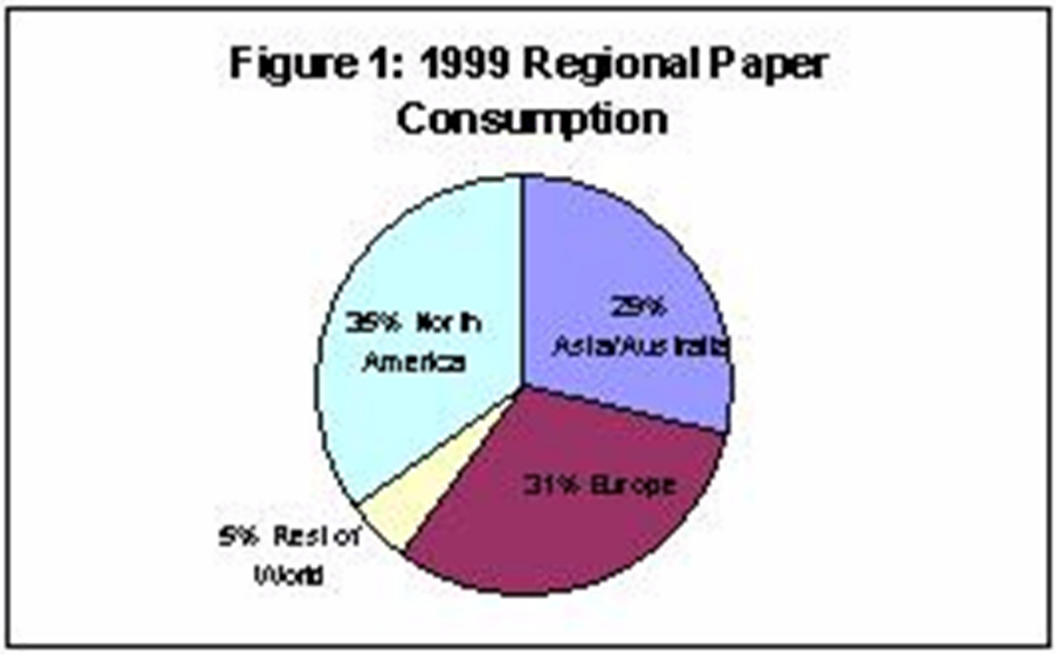
TAML™ Oxidant Activators:
Green Bleaching Agents for Paper Manufacturing

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



Paper Industry Trends

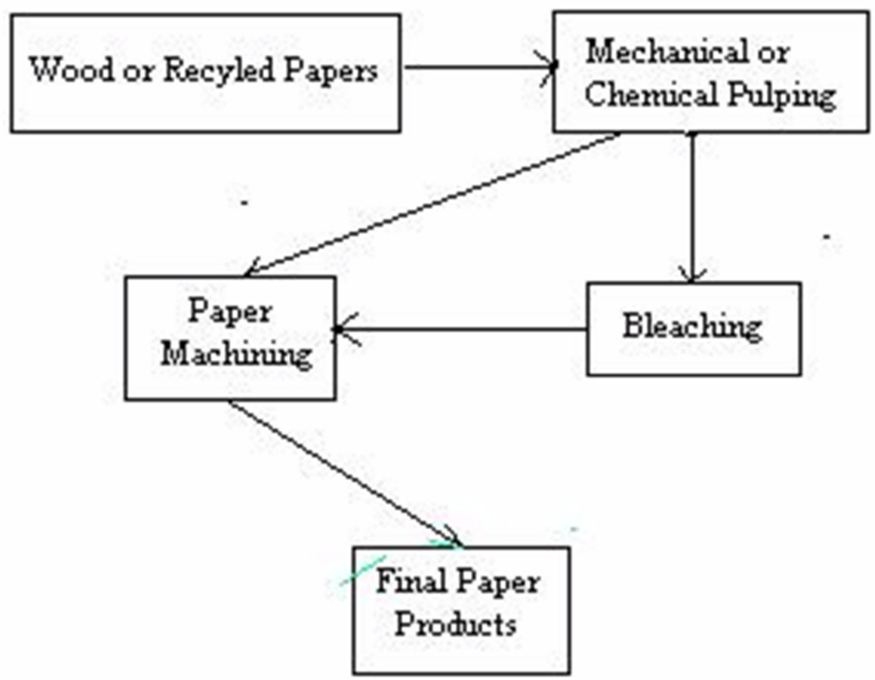
- 1999, growth of 5% in the newsprint/magazine market
- Overall, newsprint has been declining
- Marketing and stationery have been taking a bigger market share since 1990
- Significant growth expected in developing countries, especially in Southeast Asia, Africa, and Latin America

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



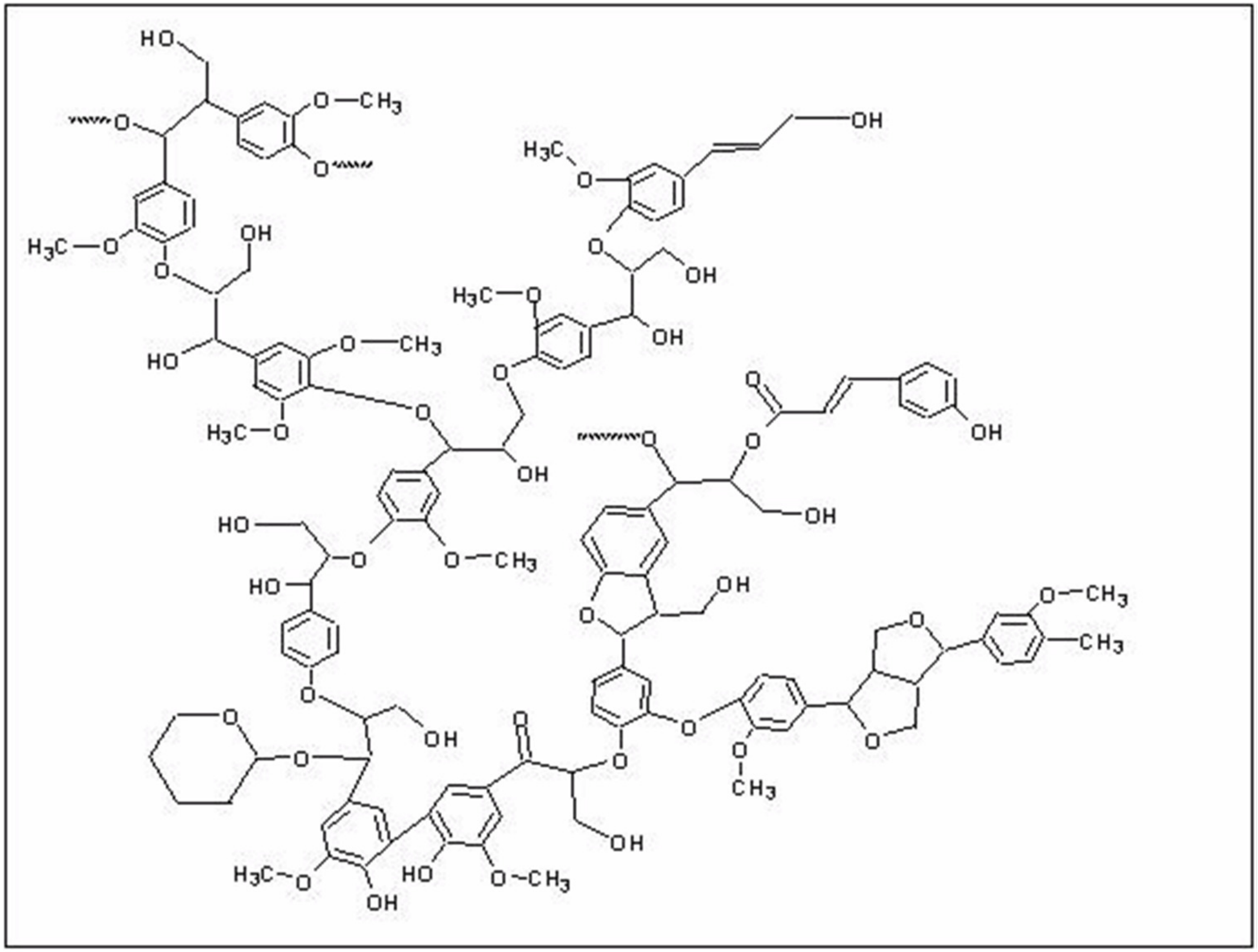
Paper Making Process

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

Bleaching Process

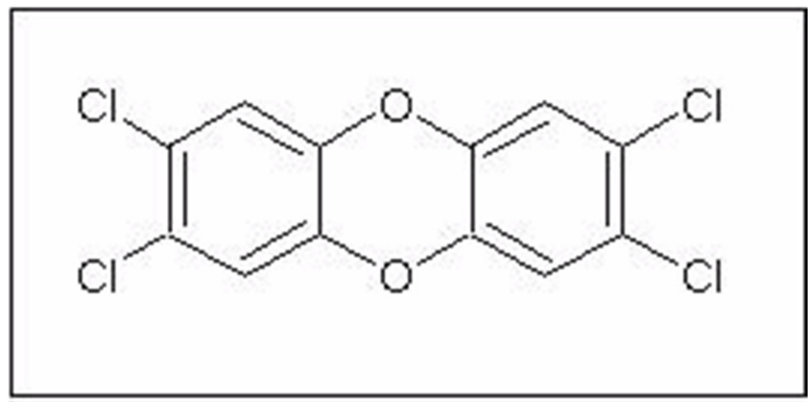
- Removes lignin -which would cause the final paper product to have a brown discoloration
- Conventional bleaching -Kraft Process
- Consists of several processing steps combining acid, base, hydrogen peroxide, oxygen, dithionate salts, and sodium bisulfite followed by chlorinating treatments

Lignin Structure



Dioxin Formation and Properties

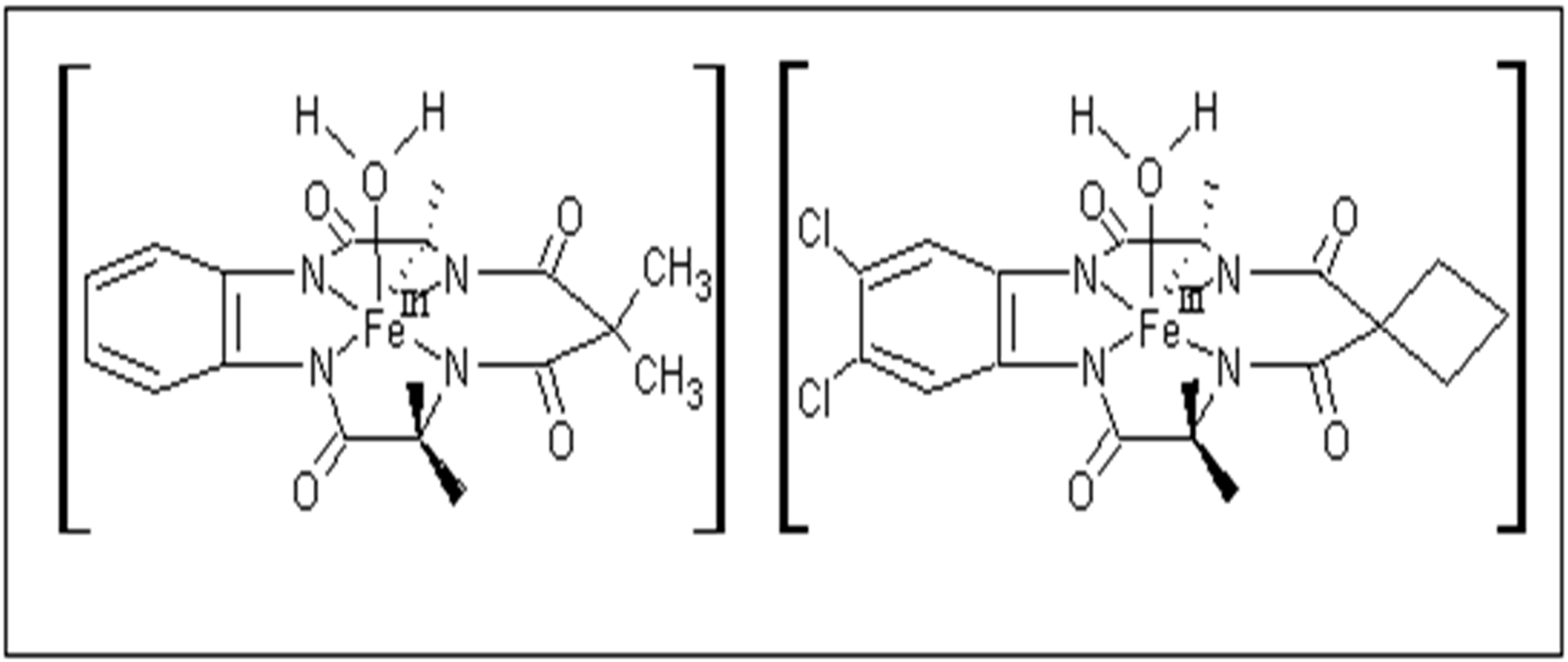
- Bleaching of pulp produces 2,3,6,7-tetrachlorodibenzo-4-dioxin (TCDD) as a by-product
- TCDD is tetratogenic and is acutely toxic
- Stored in the fatty tissues of animals



TAML^{TM} 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

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + -OH + OH$$

$$OH + H_2O_2 \longrightarrow HOH + HO_2$$

$$HO_2 + HOOH \longrightarrow HOH + O_2 + OH$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2 + H^+$$

$$Fe^{3+} + HO_2 \longrightarrow Fe^{2+} + O_2 + H^+$$

$$Fe^{3+} + OH \longrightarrow FeOH^{2+}$$

$$OH + S \longrightarrow P$$

- 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 β to an oxidizing metal center, if the α-atom can support an increase in the bond order with the β-atom.'

Rule 2

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

Rule 3

'A heteroatom should not be employed as an α-donor atom in a five-membered chelate ring, if it has an available lone pair to stabilize forming cationic character on the β-atom as the endocyclic β–γ 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