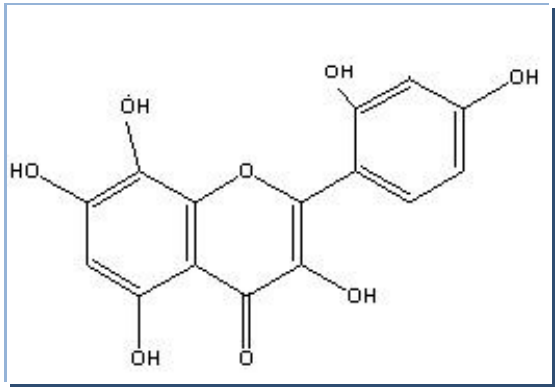
Bleaching

Introduction to bleaching



The source of the colour:

- Flavone pigment in case of cotton
- Soil and dirt acquired from atmosphere
- Contact with plant parts and seeds, etc.
- Colour acquired during mechanical processing e.g. grease, oil, etc.

Objectives

To destroy the natural or acquired coloring materials to bring the textiles in a white state.

❑ This may be necessary when:

- The fabric has to be supplied in white colour
- It needs to be dyed in pastel shades
- It needs to be printed

For dyeing in dark shades –it is an optional process

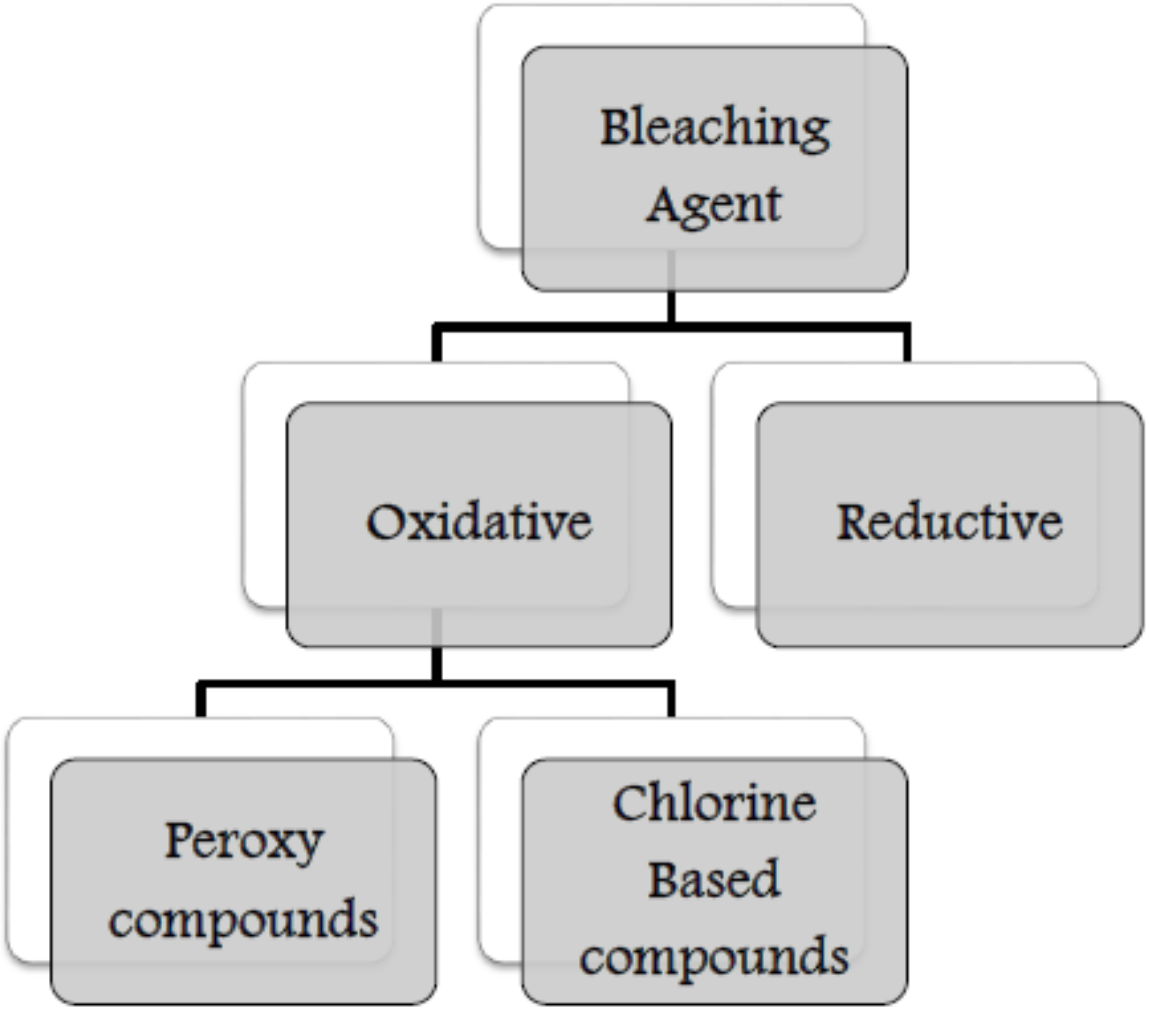
❑ Additionally:

❖ To destroy the motes or the seed coat fragments

❖ To remove residual impurities left by other pretreatment processes like desizing, scouring, etc.

❑ Increased absorbency

Classification of Bleaching Agents



Different Bleaching Agents

Peroxy Oxidative Bleaching Agents	Chlorine based Oxidative Bleaching Agents	Reductive Bleaching Agents
Hydrogen peroxide	Bleaching powder	Sulphur dioxide
Potassium permanganate	Sodium hypochlorite	Sodium hydrosulphite
Peracetic acid	Lithium hypochlorite	Acidic sodium sulphite
	Sodium chlorite	Sulphoxylates

Main Bleaching Agents

- ✓ **Sodium hypochlorite (NaOCl)**
- ✓ **Sodium chlorite ($NaClO_2$)**
- ✓ **Hydrogen peroxide (H_2O_2)**

Sodium Hypochlorite (NaOCl)

- NaOCl is sodium salt of Hypochlorus acid (HOCl) having redox potential of 1400-1550 mV.

- Strongest oxidizing agent

❑ NaOCl solution in water undergoes the following reaction:

$$NaOCl + H_2O \longrightarrow NaOH + HOCl \text{ (}\mathbf{Weak\ acid)}$$

(pH of 11-11.5)

❖ Bleaching occurs due to the following reaction:

$$HOCl \longrightarrow HCl + [O]$$

Sodium Hypochlorite (NaOCl)

- What happens in acidic pH?

In acidic medium the consumption of hypochlorite is very fast and can lead to cellulose degradation by oxidation. The reaction is given below:

$$NaOCl + HCl \longrightarrow NaCl + HOCl$$
$$HOCl + HCl \longrightarrow H_2O + Cl_2$$
(Excess acid)

Process Parameters:

- pH
- Temperature
- Time

In practice, cotton is bleached with NaOCl solution containing 1 - 3 gpl available chlorine at room temp. in the pH range 9.5 - 11.

Sodium Hypochlorite (NaOCl)

Active Chlorine

- Active chlorine is a unit of concentration used for hypochlorite bleaching
- Active chlorine is determined by adding excess potassium iodide to sample of bleach solution
- Titration of iodine with standard sodium thiosulfate solution

Sodium Hypochlorite (NaOCl): Active Chlorine

$$\underset{\text{(Hypochlorite ion)}}{ClO^-} + \underset{\text{(Potassium iodide)}}{2I^-} + \underset{\text{(Acidic solution)}}{2H^+} \rightarrow \underset{\text{(Iodine)}}{I_2} + H_2O + \underset{\text{(Common salt)}}{Cl^-}$$

Similarly,

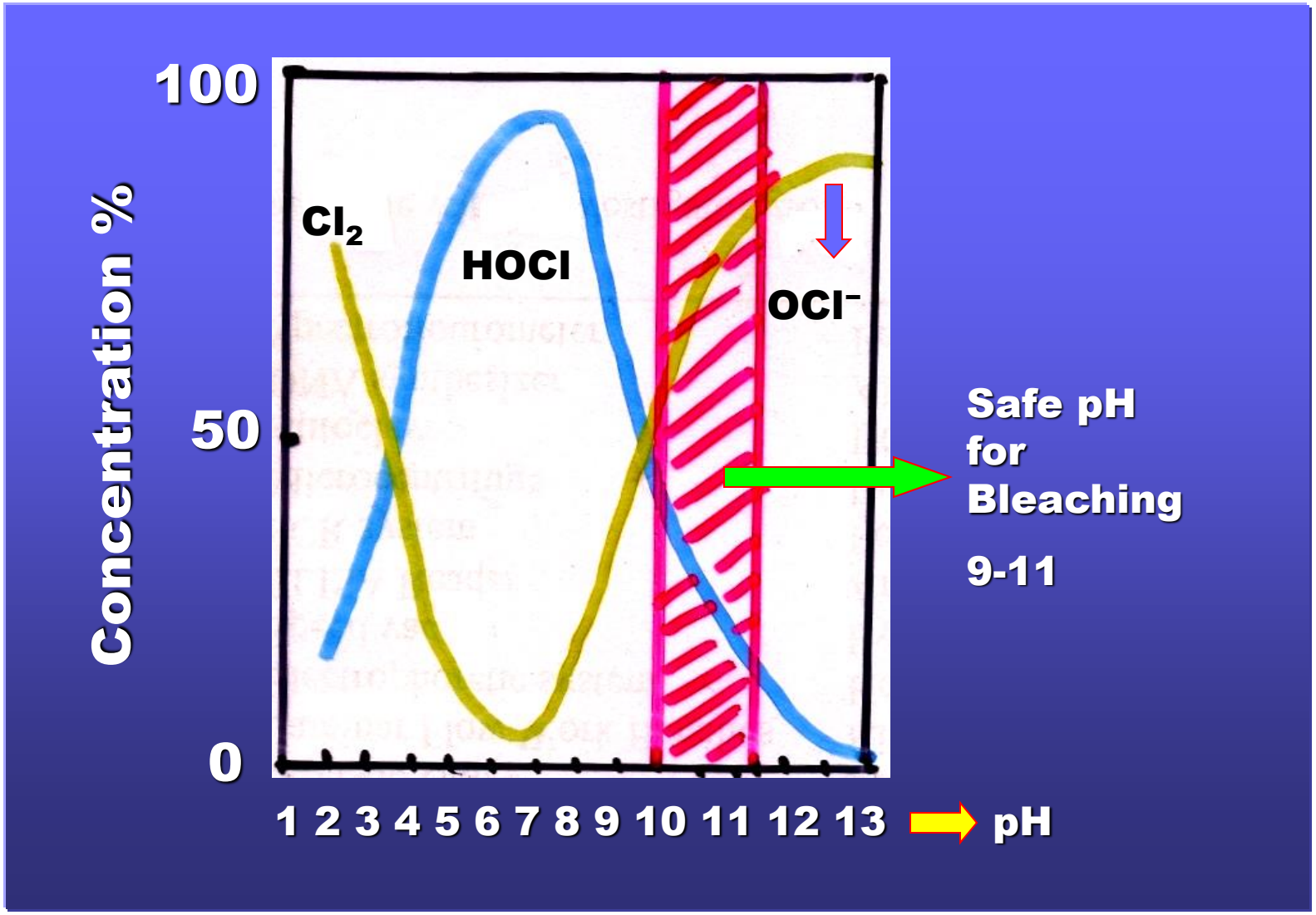
$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

Determination of liberated I_2 by titration:

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

2 moles of thiosulfate are equivalent to 70.9 grams (1 mole) of active chlorine or 51.5 g of hypochlorite ions. In other words a 51.5 gpl solution of OCl− (or 75 gpl NaOCl) is equv. to 70.9 gpl solution of available Cl_2.

Bleaching with Sodium Hypochlorite (NaOCl): pH effect



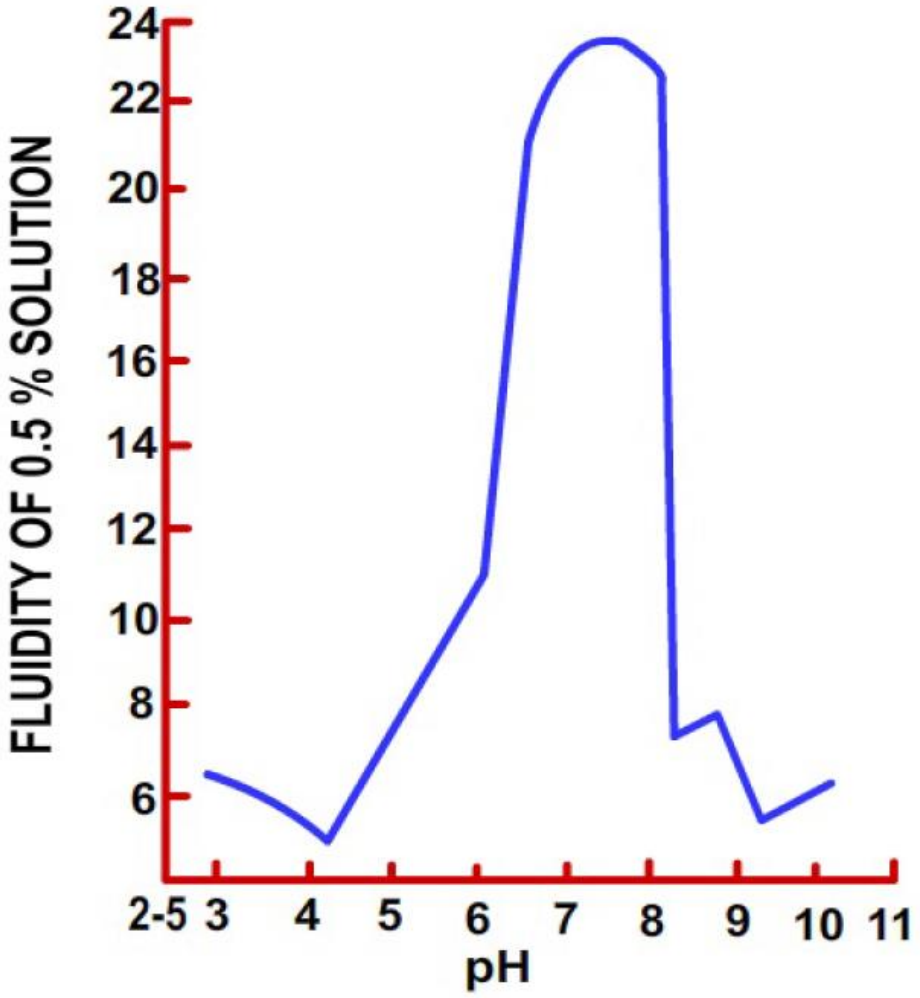
Bleaching with Sodium Hypochlorite (NaOCl): pH effect

- Fraction of HOCl with change in pH
- Between pH 5 to 10, drastic change in concentration of free acid

pH	Fraction of hypochlorite as HOCl
10.0	0.003
9.0	0.03
8.0	0.21
7.43	0.50
7.0	0.73
6.5	0.91
6.0	0.96
5.0	0.997

Free acid (HOCl) with change of pH

Bleaching with Sodium Hypochlorite (NaOCl): pH effect



✓ The degradation of cotton measured by Cupra-ammonium Fluidity test

✓ Maximum degradation is at near pH 7 region

Practical Bleaching Conditions

Parameters	Conditions
pH: 9.0	Time to bleach: 45 min
pH: 11.0	Time approximately: 4 hrs
Temperature	Room temperature
Concentration	2-3 gpl available chlorine

Sodium Hypochlorite Bleaching

Advantages & Disadvantages

Advantages:

- Economical
- Room temperature process

Disadvantages:

- Fibre damage
- Formation of AOX
- Yellowing on storage
- May degrade many dyes and FBAs
- Not used for bleaching of synthetic or protein fibres
- Not very satisfactory white is produced
- Unused NaOCl can form chloroform and affect the sea-life

Antichlor Treatment

Residual hypochlorite is removed by treatment with Reducing agent:

- ❑ 2 - 2.5% of a reducing agent
- ❑ Time: 15 min
- ❑ Temperature: 40 ^{o}C

✓ **Reducing agent:**

Sulphites, bisulphites, hydrosulphites, thiosulphates, etc.

Sodium Chlorite Bleaching

Sodium Chlorite Bleaching

- Fibre-gentle Bleaching Agent
- Redox Potential : 1040 – 1200 mV

$$NaClO_2 + H_2O = NaOH + HClO_2 \text{ (pH 8.5)}$$

$$HClO_2 = HCl + 2 <O>$$

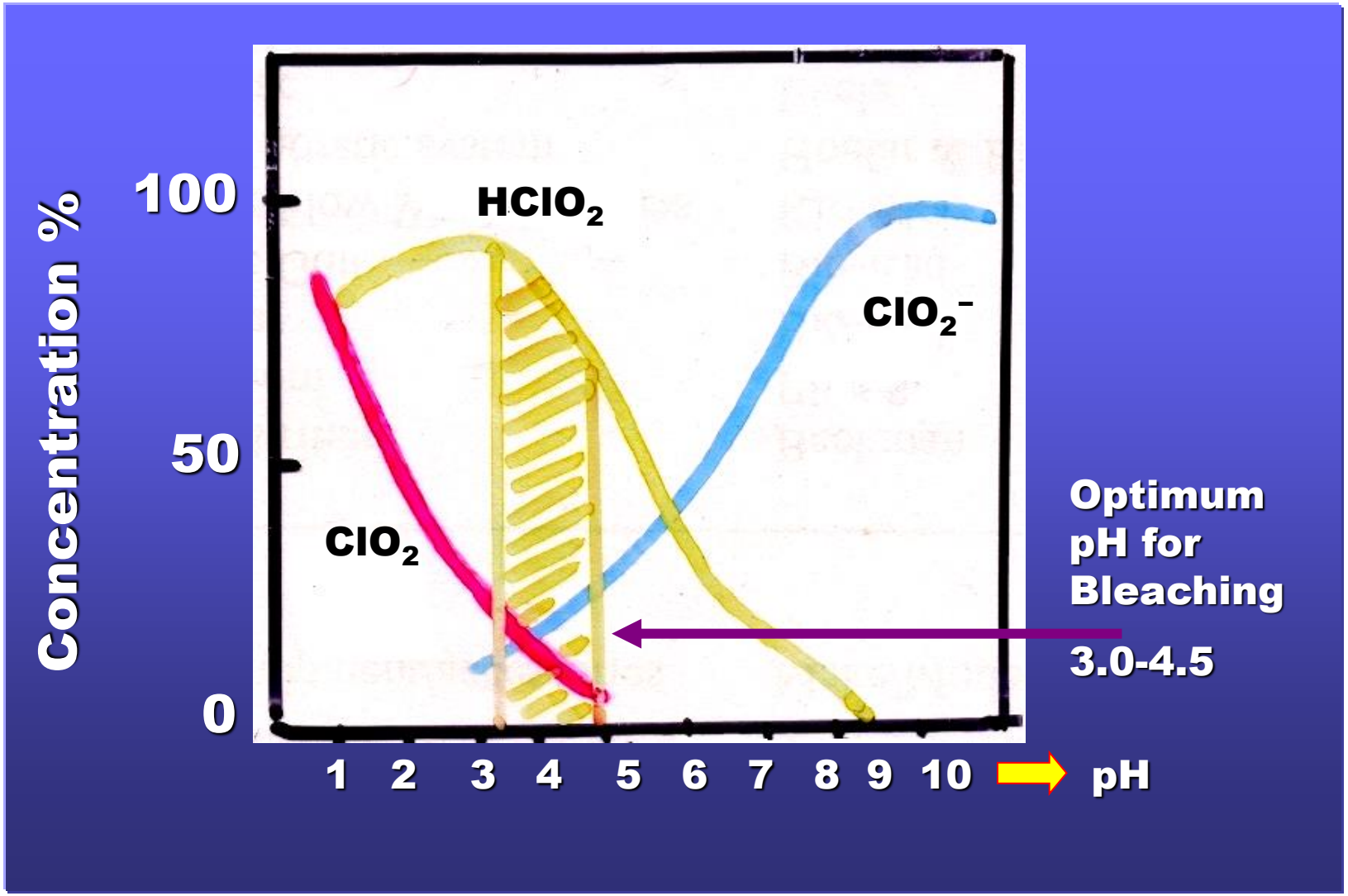
$$NaClO_2 + HCl = NaCl + HClO_2$$

(pH 2.5 – 3.0)

$$5\ HClO_2 = 4ClO_2 + HCL + 2H_2O$$
$$3\ HClO_2 = 2HClO_3 + HCl$$

(@ Lower pH)

Sodium Chlorite Bleaching



Sodium Chlorite Bleaching

Process Parameters: pH, Temperature, Time

- ❖ Stabilized at higher pH
- ❖ At pH 1-2, evaporation of ClO_2
- ❖ Balanced pH around 3.5 - 4

- ✓ Bleaches at high temperature (80 – 90 ^{0}C)
- ✓ At boil, the bleaching time is a few hours (1- 4)
- ✓ The rate of bleaching doubles for every 10 ^{o}C rise in the process.

Sodium Chlorite Bleaching: Corrosion Problem

ClO_2 is a toxic corrosive gas

- **Corrosion resistant materials**: Stainless Steel with 2.5% Molybdenum, Titanium / Ceramic lining
- **ClO_2 scavenging chemicals**: $(NH_4)H_2PO_4$, sodium and ammonium nitrate, nitric acid, melamine, urea, etc.
- **Chlorite stable surfactants**: foam of the surfactant can trap the ClO_2 gas formed.

Sodium Chlorite Bleaching

Advantages & Disadvantages

Advantages:

- Both cotton and synthetic fibres can be bleached.
- Hardness of water does not impair the process (unlike H_2O_2)
- For knitted fabrics, soft feel is retained
- Good white color with excellent mote removal
- Little or no cellulose degradation

Disadvantages:

- Expensive than NaOCl or H_2O_2
- No silk and wool (yellowish pink color) bleaching possible
- Corrodes the metals
- ClO_2 is a toxic gas
- Wax removal is not very satisfactory

Hydrogen Peroxide Bleaching

Hydrogen Peroxide Bleaching

- An eco-friendly bleaching agent: by-products only water and oxygen
- Redox potential: 810 – 840 mV
- Universal bleaching agent–most of the fibres can be bleached
- Provides permanent bleaching action

H-O-O-H

Hydrogen Peroxide Bleaching

$H_2O_2 \longrightarrow H^+ + HO_2^-$ (pH: ~ 3)

$2HO_2^- \longrightarrow 2HO^- + O_2$

Bleaching species: **Perhydroxyl ion (HO_2^-)**

In alkaline medium H_2O_2 decomposes as:

$H_2O_2 + OH^- \longrightarrow OOH^- + H_2O$

Above pH 10.8, formation of HO_2^- ions is rapid.

- ❑ Stable in acidic pH
- ❑ Decomposes in presence of alkalis or UV light.

Hydrogen Peroxide Bleaching: Auxiliaries

Activators:

✓ Stabilized at acidic pH
✓ Unstable in basic pH

• Sodium hydroxide (NaOH) is commercially used as an activator

Stabilizers:

✓ Regulate the formation of perhydroxyl ions formation
✓ Prevent rapid decomposition of bleach bath
✓ Prevent fibre damage

Hydrogen Peroxide Bleaching: Stabilizers

Act by-

- ✓ Buffering action (pH regulation)
- ✓ Sequestering of heavy transition metal ions
- ✓ Complexing with perhydroxy ions

Commonly used Stabilizer: **Sodium Silicate**

- ✓ Easily available, economical and effective
- ✓ Na_2O :SiO_2 ratio (1:1)
- ✓ Stabilizing action of silicates is improved by Ca or Mg ions
- ✓ Water of hardness should be controlled

Hydrogen Peroxide Bleaching: Sequestering Agents

- Metals or UV light causes **fission of H_2O_2**
- The rate may be so high that cellulose is oxidized
- Oxycellulose has poor mechanical properties

To prevent harmful effects of metal cations:

Sequestering agents are often used to minimize the harmful effects of metal cations.

Example:

- Poly phosphonates
- Poly hydroxyl carboxylic acids
- Amino polycarboxylic acids
- Phosphonic acids
- Polyacrylic acids

Hydrogen Peroxide Bleaching: Sequestering Agents

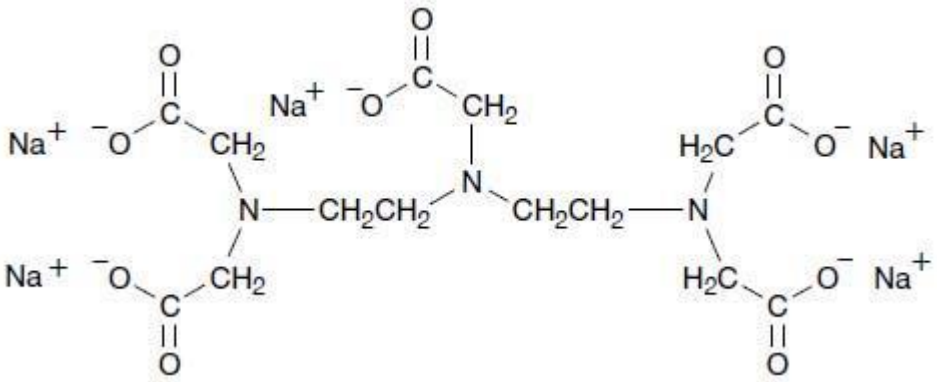
Common sequestering agents:

- Di-ethylene tri-amine penta acetic acid (DTPA)
- Ethylene di-amine tetra acetic acid (EDTA) as sodium or magnesium salts

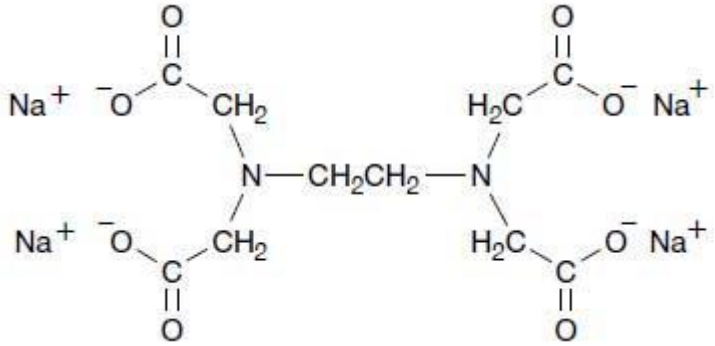
These compounds can form Chelates or metal complexes with metal ions

The complexes formed may have complicated 3-D structures.

Hydrogen Peroxide Bleaching: Sequestering Agents



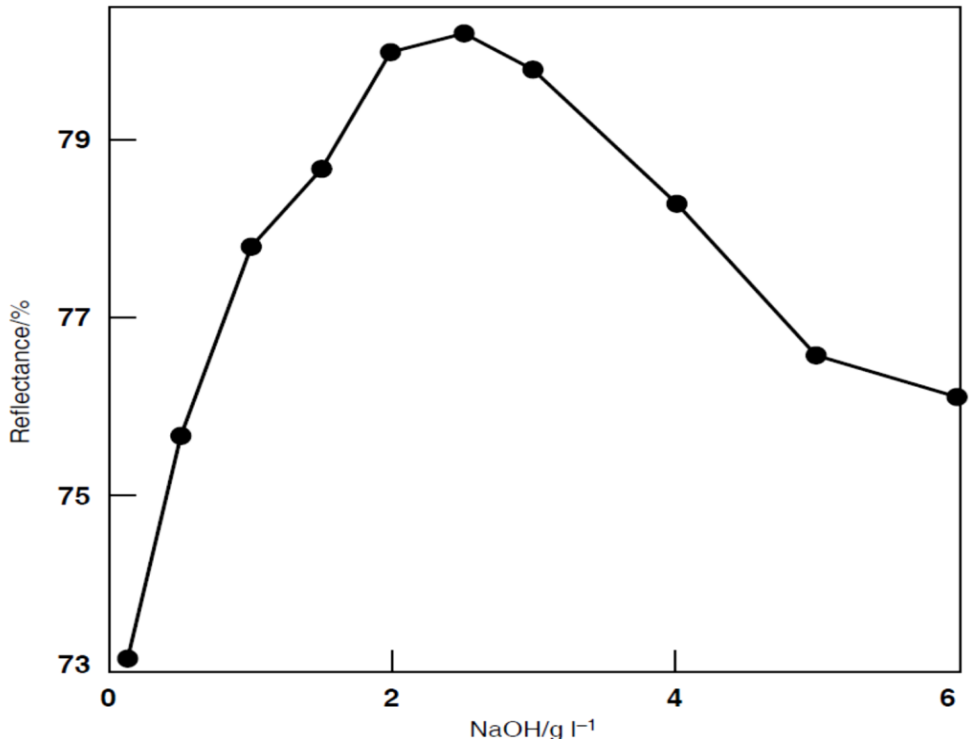
DTPA (Di-Ethylene Tri-Amine Penta Acetic Acid)



EDTA (Ethylene Di-Amine Tetra Acetic Acid)

Hydrogen Peroxide Bleaching: pH effect

In acidic pH, H_2O_2 is stable, so alkaline pH is used for bleaching



Desired pH: 10.5 (cotton)

Effect of concentration of alkali on whiteness

Hydrogen Peroxide Bleaching: Temperature effect

- Bleaching of cotton is carried out at boil (90-100 ^{o}C)
- Rapid bleaching in pressurized equipment at 120 ^{o}C
- Bleaching at low temperature (~80^{o}C) increase process time

Flexibility: from 30 ^{o}C – 130 ^{0}C

Hydrogen Peroxide Bleaching: Recipe for cotton

- H_2O_2 (50%) : 1 – 2%
- Activator (TSP): 2 – 3% (to adjust the pH 10.5)
- Stabilizer (Sodium silicate): 1 – 2%
- Non-ionic surfactant: 3 gpl
- Metal chelating agent (EDTA): 0.01%
- Temp: 1-2 hrs.(@ 95 ^{0}C)

Activated Bleaching Process

Bleaching with Hypochlorite followed by Peroxide bleaching

- NaOCl: 3 gpl
- Temperature: 30 ^{0}C
- Time: 30 – 45 min

1st Bleaching J-Box

H_2O_2 (50%) : 0.5 – 0.8%

Activator (TSP): pH (10.5)

Stabilizer (Sodium silicate)

Metal chelating agent (EDTA)

Temp: 2 hrs.(@ 95 ^{0}C)

2nd Bleaching J-Box

Hydrogen Peroxide Bleaching

Advantages & Disadvantages

Advantages:

- Universal bleaching agent.
- Combine scouring and bleaching
- No antichlor treatment
- Non-corrosive and no unpleasant odour
- No AOX problem
- Improved absorbing and TEWEGA rating

Disadvantages:

- ❖ Silicates as stabilizers
- ❖ Catalytic damage to cotton
- ❖ Not effective for synthetic fibres