

CHAPTER 4

BLEACHING

Natural fibers, i.e. cotton, wool, linen etc. are off-white in color due to color bodies present in the fiber. The degree of off-whiteness varies from batch-to-batch. Bleaching therefore can be defined as the destruction of these color bodies. White is also an important market color so the whitest white has commercial value. Yellow is a component of derived shades. For example, when yellow is mixed with blue, the shade turns green. A consistent white base fabric has real value when dyeing light to medium shades because it is much easier to reproduce shade matches on a consistent white background than on one that varies in amount of yellow.

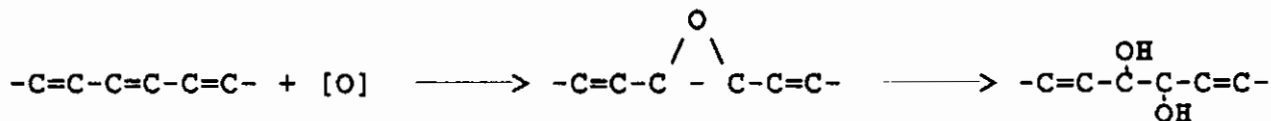
Bleaching may be the only preparatory process or it may be used in conjunction with other treatments, e.g. desizing, scouring and mercerizing. The combination of such treatments for an individual situation will depend on the rigorousness of the preparation standard and economic factors within the various options.

Other chemicals will be used in addition to the bleaching agent. These serve various functions such as to activate the bleaching system, to stabilize or control the rate of activation, to give wetting and detergent action, or to sequester metallic impurities. This section gives consideration to the selection of bleaching agents and to the role of the various chemicals used in conjunction.

I. MAJOR BLEACHING AGENTS

The mechanism of bleaching is very complicated and not completely understood. One opinion is that the color producing agents in natural fibers are often organic compounds containing conjugated double bonds. It is known in dye chemistry that conjugation is necessary for an organic molecule to perform as a dyestuff. Decoloration can occur by breaking up the chromophore, most likely destroying one or more of the double bonds within the conjugated system. Oxidative bleaches oxidize color bodies into colorless compounds. For example, double bonds are known to be oxidized into epoxides which easily hydrolyze into diols. The major bleaching agents used in textile preparation are sodium hypochlorite, hydrogen peroxide and sodium chlorite. Other bleaching agents, of lesser importance to textile preparation

but important in consumer laundry products, are perborates, percarbonates and peracetic acid. All of these are oxidative bleaches. Oxidative bleaches are also known to degrade cellulose so the objective in bleaching is to optimize whitening and minimize fiber damage.

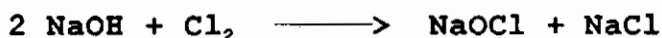


Reductive Bleaches reduce color bodies into colorless compounds. Most textile fibers are bleached with oxidizing bleaches.

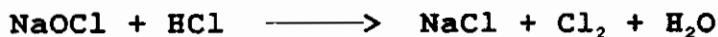
II. SODIUM HYPOCHLORITE

Hypochlorite bleaching (OCl^-) is the oldest industrial method of bleaching cotton. Originally, calcium hypochlorite, $\text{Ca}(\text{OCl})_2$ was used. Most cotton fabrics were bleached with sodium hypochlorite up until 1940. Today it accounts for only 10 % of the cotton bleaching agents in the U.S. It is however the main stay of home laundry bleaching products. Hypochlorites are excellent cidal agents for mildew and other bacteria and are used as disinfectants and to control bacteria in swimming pools. Sodium hypochlorite is the strongest oxidative bleach used in textile processing. Prior to bleaching with hypochlorite, it is necessary to thoroughly scour fabrics to remove fats, waxes and pectin impurities. These impurities will deplete the available hypochlorite, reducing its effectiveness for whitening fabric.

Sodium hypochlorite is made by bubbling chlorine into a solution of sodium hydroxide.



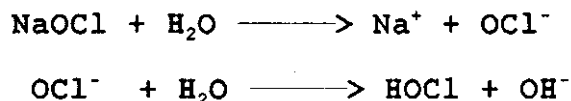
Conversely, when acid is added to a hypochlorite solution, chlorine gas is liberated. Product strength of hypochlorites is generally expressed as the available chlorine content. This relates to the chlorine formed on reaction with acid.



Commercial sodium hypochlorite will have 12 to 15 % active chlorine. Household bleach is 5 % active chlorine. Calcium hypochlorite is sold as a solid material and contains 65 % active chlorine.

A. Bleaching Mechanism

Sodium hypochlorite is the salt of a moderately strong base (OCl^-) and a weak acid (HOCl). Solutions are therefore alkaline. The species present in a solution can be understood from the following:



Note: Hypochlorous acid (HOCl) is the active bleaching agent.

B. Effect of pH

pH has a profound effect on bleaching with hypochlorite. 1. If caustic is added to the solution, the equilibrium shifts to the left favoring the formation of the hypochlorite ion (OCl^-) at the expense of hypochlorous acid (HOCl). Under strongly alkaline conditions ($\text{pH} > 10$), little to no bleaching takes place. 2. When acid is added, the equilibrium shifts to the right and the HOCl concentration increases. At a pH between 5 and 8.5, HOCl is the major specie present so very rapid bleaching takes place. However, rapid degradation of the fiber also takes place. 3. When the pH drops below 5, chlorine gas is liberated and the solution has no bleaching effectiveness at all. 4. The optimum pH for bleaching is between 9 and 10. Although the concentration of HOCl is small, it is sufficient for controlled bleaching. As HOCl is used up, the equilibrium conditions continue to replenish it. This pH range is used to minimize damage to the fiber. Sodium carbonate is used to buffer the bleach bath to pH 9 to 10.

C. Effect of Time and Temperature

Time and temperature of bleaching are interrelated. As the temperature increases, less time is needed. Concentration is also interrelated with time and temperature. Higher concentrations require less time and temperature. In practice, one hour at 40°C is satisfactory for effective bleaching.

D. Effect of Metals

Copper and iron catalyze the oxidation of cellulose by sodium hypochlorite degrading the fiber. Fabric must be free of rust spots or traces of metals otherwise the bleach will damage the fabric. Stainless steel equipment is required and care must be taken that the water supply be free of metal ions and rust from pipes. Prescouring with chelating agents becomes an important step when bleaching with hypochlorites.

E. Antichlor

Fabrics bleached with hypochlorite will develop a distinctive chlorine odor. This odor can easily be removed with an aftertreatment consisting of sodium bisulfite and acetic acid.

F. Uses

Hypochlorite is used mainly to bleach cellulosic fabrics. It cannot be used on wool, polyamides (nylon), acrylics or polyurethanes (spandex). These fibers will yellow from the formation of chloramides.

Bleaching with hypochlorite is performed in batch equipment. It is not used in continuous operations because chlorine is liberated into the atmosphere. Over time, the pad bath decreases in active chlorine causing non-uniform bleaching from beginning to end of the run.

G. Typical Batch Procedure

a. Formulation:

NaOCl	2.5 %	active bleach
Na ₂ CO ₃	1.0 %	pH buffer

b. Bleach Cycle:

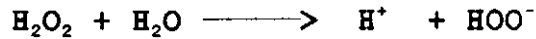
1. Run one hour at 40° C.
2. Drop bath, rinse
3. Add antichlor chemicals
4. Rinse

III. HYDROGEN PEROXIDE

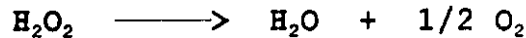
Hydrogen peroxide was first used to bleach cotton in the 1920's. By 1940, 65 % of all cotton fabrics were bleached with hydrogen peroxide, largely brought about by the invention of the J-box which lead to continuous processing. Today, it is estimated that 90 to 95 % of all cotton and cotton/synthetic blends are bleached with hydrogen peroxide. It is available commercially as 35, 50 and 70 % solutions. It is a corrosive, oxidizing agent which may cause combustion when allowed to dry out on oxidizable organic matter. Decomposition is accelerated by metal contamination and is accompanied by the liberation of heat and oxygen, which will support combustion and explosions in confined spaces. The material is an irritant to the skin and mucous membranes and dangerous to the eyes

A. Mechanism

Hydrogen peroxide is a weak acid and ionizes in water to form a hydrogen ion and a perhydroxyl ion. The perhydroxyl ion is the active bleaching agent.



Hydrogen peroxide can also decompose. This reaction is catalyzed by metal ions e.g. Cu^{++} , Fe^{++} . This reaction is not desired in bleaching because it is an ineffective use of hydrogen peroxide and causes fiber damage.



B. Effect of pH

Hydrogen peroxide is an extremely weak acid, $K_a = 1.5 \times 10^{-12}$. Since the perhydroxyl ion is the desired bleaching specie, adding caustic neutralizes the proton and shifts the reaction to the right. Therefore: 1. at $\text{pH} < 10$, hydrogen peroxide is the major specie so it is inactive as a bleach. 2. At $\text{pH} 10$ to 11 , there is a moderate concentration of perhydroxyl ions. $\text{pH} 10.2$ to 10.7 is optimum for controlled bleaching. Sodium hydroxide is used to obtain the proper pH . 3. At $\text{pH} > 11$, there is a rapid generation of perhydroxyl ions. When the pH reaches 11.8 , all of the hydrogen peroxide is converted to perhydroxyl ions and bleaching is out of control.

C. Effect of Time and Temperature

Stabilized hydrogen peroxide does not decompose at high temperature therefore faster and better bleaching occurs at 95 to 100 °C. This feature makes it ideal for continuous operations using insulated J-boxes or open-width steamers.

D. Stabilizers

Stabilizers must be added to the bleach solution to control the decomposition of hydrogen peroxide. Stabilizers function by providing buffering action to control the pH at the optimum level and to complex with trace metals which catalyze the degradation of the fibers. Stabilizers include sodium silicate, organic compounds and phosphates.

1. Sodium Silicates

Sodium silicates are the most commonly used and most effective hydrogen peroxide bleach stabilizers. They may be used as colloidal silicate (waterglass), ortho silicate or metasilicate. The mechanism by which silicate stabilize is not completely

understood, however it is known that silicates have a natural affinity for ferrous ions and ferrous ions are naturally present in cotton. It is possible that the silicates are adsorbed onto the ferrous ions in the fiber, producing a species that catalytically enhances bleaching while reducing bleach decomposition and fiber damage. Stabilization by silicates is enhanced by the presence of magnesium ions. Magnesium serves as a pH buffer. As the concentration of OH^- rises during bleaching, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) precipitates, reducing the OH^- concentration. Bleach solutions containing only magnesium ions have good stability but the bleaching effectiveness is not as good as when silicates are included.

Silicates as stabilizers have one drawback, they tend to polymerize and form insoluble silicates. They become hard deposits which build-up in the machines causing the fabric to be abraded. Also some of the deposits will form in the cloth, giving it a harsh, raspy hand, a real negative for terry toweling.

2. Organic Stabilizers

Organic stabilizers avoid the problems associated with sodium silicates. These products are often referred to as silicate free or non-silicate stabilizers. They may be based on sequestering agents, protein degradation products or certain surfactants. The commercial products are of two types, those designed only to be stabilizers and those which combine stabilization with other properties such as detergency and softening. For some bleaching methods, organic stabilizers may be used alone, while in others, they are best used in combination with silicates.

3. Phosphates

Tetrasodium pyrophosphate (TSPP) and hexametaphosphates are of interest as stabilizers in alkaline bleach baths under the following conditions: 1. The alkalinity of the bleach must not be higher than pH 10 since above this, the stabilizing effect decreases rapidly. 2. Temperature of the bleach bath is limited to 60 °C. Higher temperatures reduce stabilizing properties. They should be used with ammonia, not caustic soda or soda ash.

TSPP at high pH and temperature is converted to trisodium phosphate which has little stabilizing effect. The use of TSPP is limited to bleaching wool and silk which are sensitive to high pH and high temperatures. As opposed to silicates, pyrophosphates are precipitated from solution in the presence of calcium and magnesium and therefore do not develop full stabilizing power.

E. Uses

Hydrogen peroxide is the bleach most widely used for cellulosic fibers [cotton, flax, linen, jute etc.) and well as wool, silk, nylon and acrylics. Unlike hypochlorites,

peroxide bleaching does not require a full scour. Residual fats, oils, waxes and pectines do not reduce the bleaching effectiveness of hydrogen peroxide. Additionally it can be used on continuous equipment. Since it ultimately decomposes to oxygen and water, it doesn't create effluent problems.

F. Typical Bleaching Procedures

1. Batch

a. Bath Formulation

	<u>%</u>
Hydrogen peroxide (35 %)	3 - 5
Wetting agent	0.1 - 0.5
NaOH	0.3 - 0.8
Sodium silicate	2 - 3
Magnesium sulfate (Epsom's salt)	0.5

b. Bleach Cycle

1. Run 60 to 90 minutes at 95 to 100° C.
2. Drop bath
3. Rinse

2. Continuous

a. Bath Formulation

Double above formulation

b. Bleach Cycle

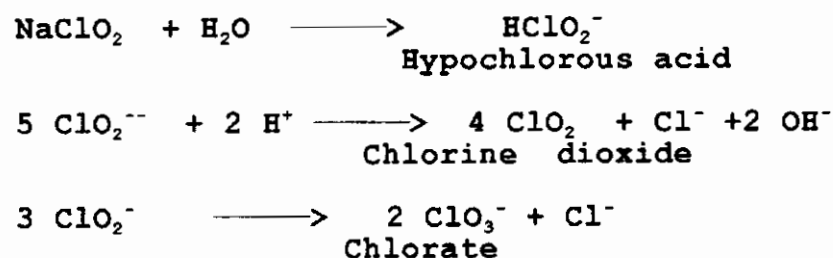
1. Saturate goods to 100 % wet pick up
2. Steam in J-box or steamer for one hour
3. Wash thoroughly

IV. SODIUM CHLORITE (NaClO₂)

Bleaching with sodium chlorite is carried out under acidic conditions which releases chlorine dioxide, a toxic and corrosive yellow-brown gas. Sodium chlorite is sold as an 80% free flowing powder. Chlorine dioxide is thought to be the active bleaching specie. It is not used much in the USA for bleaching but it is sometimes used to strip dyed goods and is often described as the bleach of last resort. One advantage of sodium chlorite bleaching is that it leaves the fabrics with a soft hand.

Because of the gaseous nature, toxicity and corrosiveness of chlorine dioxide, special attention must be paid to the equipment. It must be designed so as to not allow the gas to escape into the work place. Emissions into the atmosphere are of concern too. The gas corrodes even stainless steel so special passivating treatments must be carried out to prolong the life of the equipment.

When a solution of sodium chlorite is acidified, chlorine dioxide (ClO₂), hypochlorous acid (HClO₂), sodium chlorate (NaClO₃) and sodium chloride are formed. Chlorine dioxide and hypochlorous acid are bleaching species, sodium chlorate and sodium chloride are not. The reactions may be written:



A. Effect of pH

Chlorine dioxide is favored at low pH - 1 to 2.5. It is a more active bleaching agent than hypochlorous acid which is favored at pH 4 to 5. However chlorine dioxide is a corrosive and toxic gas. When generated too rapidly, it escapes from the bleaching bath into the atmosphere creating an explosion and health hazard. Once the chlorine dioxide is out of solution, its effectiveness as a bleach is lost.

B. Bleaching Mechanism

Chlorine dioxide only reacts with aldehyde groups without affecting hydroxyls or glucosidic linkages. Aldehydes are converted to carboxylic acids. This is of practical importance because cellulose is very slightly damaged, even when high degree of whiteness is obtained. When strong acids are used, the low pH will damage the fiber at the glucosidic linkage so buffers like sodium dihydrogen orthophosphate are commonly used. Sodium acetate and the other sodium phosphate salts are also effective buffers. The acid is added incrementally over the bleach cycle, not all at once. This too controls the bath pH and avoids rapid evolution of chlorine dioxide.

C. Effect of Temperature

Little or no bleaching takes place at temperatures below 50° C, however the bleaching rate increases considerably up to 90° C. Going to the boil is not recommended because it leads to excessive loss of chlorine dioxide with the steam.

V. OTHER OXIDATIVE BLEACHES

Some other oxidative bleaches are persulfates, perborates, percarbonates and peracetic acid.

A. Persulfates

Ammonium, potassium and sodium persulfates are oxidizing agent that find use in textile processing. They are used to: 1. bleach protein fibers in combination with hydrogen peroxide, 2. activate cold bleaching of cellulose with sodium chlorite, 3. oxidize vat and sulfur dyes, and 4. bleach fur and skins in combination with hydrogen peroxide.

B. Perborates and Percarbonates

Both perborates and percarbonates are used when full whites are not necessary such as for improving the ground color when dyeing light or pastel shades. They are often found as solid bleaches in home laundry products when fabric care require mild bleaches.

C. Peracetic Acid

Peracetic acid as a textile bleach is used mainly in bleaching nylon and acetate.

V. REDUCTIVE BLEACHES

Reductive bleaches work by reducing colored impurities into colorless forms. Reductive bleaches can be generalized as compounds which supply hydrogen for hydrogenating or reducing color bodies. For example, aldehydes are reduced to alcohols by the addition of one mole of hydrogen, double bonds are saturated by the addition of one mole of hydrogen. Both reactions can account for the decoloration of color bodies by breaking up resonance.

A. Sulfur Dioxide

In the early days (prior to 1940), sulfur dioxide was used to bleach wool. Moistened fabrics were hung on poles in a sealed chamber (called a stove). A pot of sulfur was ignited and the goods exposed overnight to the sulfur dioxide vapors. The bleached goods were rinsed in water containing sodium sulfite which removed the retained sulfur dioxide by forming sodium bisulfite. A disadvantage of this method of bleaching wool was that the white was not permanent when exposed to sun and air.

B. Sodium Dithionate (Sodium Hydrosulfite)

Sodium hydrosulfite, better known as "*hydro*" finds major usage as a reducing agent in textile processing. One of its main use is to reduce vat and sulfur dyes into the water soluble leuco form. As such it can be used to strip dyed goods, ergo bleach dyed goods. In water and with heat, hydro is oxidized into sodium bisulfite, liberating hydrogen - the reducing agent.



Hydro can also be used to bleach wool. It's not used much because it tends to impart a harsh handle. Reducing agents also are known to break cystine crosslinks in protein fibers. When the crosslinks are reformed by oxidation (oxygen in air or hydrogen peroxide) the protein fiber can be given a "permanent set". This has been used as a finishing treatment to impart durable creases to wool fabrics and to impart permanent waves to human hair.

VII. TEST FOR DEGREE OF BLEACHING

AATCC Test Method 82, Fluidity of Dispersions of Cellulose from Bleached Cotton Cloth and AATCC Test Method 110, Reflectance, Blue and Whiteness of Bleached Fabrics are the main tests used to determine the effectiveness of bleaching.

1. Whiteness

Since yellow impurities adsorb blue light, AATCC Test Method 110 measures the amount of blue light reflected by the goods, against a white standard (usually a ceramic tile). This gives a measure of how well the yellow impurities were removed by bleaching. Whiteness is measured by reflectance of green light and by the removal of yellow impurities. The equation below is used to calculate whiteness. The standard ceramic tile is measured and set to equal 100. The other specimen are rated against this standard. Unbleached fabrics will give values in the 50 to 60 range. Well breached fabrics will rank 95 or better.

Where: W = whiteness
B = blue reflectance
G = green reflectance

B. Fluidity

The theory behind fluidity measurements is that damaged cellulose has a lower

molecular weight than undamaged cellulose. Solutions from undamaged fibers are less fluid than those from damaged fibers. Fluidity is measured by dissolving cotton in cupriethylene diamine and determining the solutions's viscosity. Viscosity of polymer solutions is directly related to the polymer's molecular weight so a fluidity measurement, in reality, is a viscosity measurement. The difference between viscosity and fluidity is the units used to express the results. Viscosity measurements use water as the reference standard, setting it equal to 1 centipoise. Therefore the higher the polymer molecular weight, the higher the viscosity number. The fluidity scale (Rhes) is just the opposite of the viscosity scale. Low numbers are used to describe high viscosity solutions while high numbers describe low viscosity (more fluid) ones. Undamaged cellulose will have low fluidity numbers and damaged cellulose will have high ones.

Table 10
Typical Fluidities

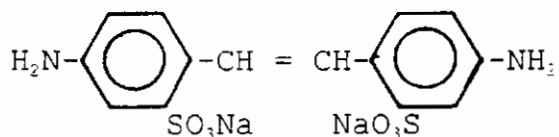
Cloth	Fluidity (Rhes)
Greige (unbleached)	0.2 - 0.4
Mild bleach	0.3 - 0.7
Average bleach	0.9 - 3.3
Over bleached	5.5 - 15.5

VIII. OPTICAL BRIGHTENERS

Certain organic compounds possess the property of fluorescence which means that they can absorb shorter wave-length light and re-emit it at longer wave-lengths. A substance can adsorb invisible ultra-violet rays and re-emit them within the visible spectrum. Therefore a surface containing a fluorescent compound can emit more than the total amount of daylight that falls on it, giving an intensely brilliant white. Compounds that possess these properties are called *Optical Brighteners or OBA's*. The effect is only operative when the incident light has a significant proportion of ultraviolet rays such as sunlight. When OBA's are exposed to UV fluorescing light bulbs, "black light", the objects glow in the dark, a sure fire way of identifying fibers that are treated with optical brighteners.

There are several classes of chemical compounds whose structure serve the purpose. These structures have dye-like properties and in essence are colorless dyes, they can exhaust onto various fibers. Anionic OBA's will exhaust onto cotton, wool and silk. Cationic ones exhaust onto acrylics and certain polyesters. Nonionic ones exhaust onto all synthetics.

1. Stilbene Type OBA



Disodium-4,4'-diamino-2,2'-stilbene disulfonate

OBA,s are not a substitute for bleaching. They are used to obtain brilliant market whites. These "white" whites can be obtained without over bleaching and damaging the fiber. On cellulose, they have poor wash fastness but most commercial laundry detergents contain OBA's so they are constantly replenished. Some OBAs have poor washfastness - some nonionics types have excellent light fastness. Fiber producers can include OBA,s in their spinning process. These can have excellent durability to both light and washing.

IX. REFERENCES