

2 The whitening of textiles

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2.1 Introduction

Textiles are whitened by the bleaching process. This process is generally applied to grey goods to finish them as white or to fabrics to prepare them for dyeing to pastel shades. Bleaching is a refurbishing step for modern textiles and a conservation/restoration procedure for historic textiles. The bleaching process removes natural colorants, water-borne stains, and oil-borne soils. Throughout history, ubiquitous bleaching practices were carried out in direct sunlight because it became apparent that the sun had a catalytic effect. In the past, bleaching agents had been identified as indigenous acids, bases, and mineral salts. They were applied as soaks and sours to achieve high whiteness levels. Up until the eighteenth century it was common practice to bleach linens and cottons in the sun and woolens in the fumes of burning sulfur. These relatively primitive bleaching practices were not only cumbersome and arduously slow, but required extensive acreage. It was not until the introduction of chlorine-based materials in the late eighteenth century that bleaching became facile. In the late 1920s, hydrogen peroxide became the most prevalent bleach. Since that time, hydrogen peroxide continues to be the prominent bleaching agent for natural fibers and blends with synthetic fibers. Synthetic fibers generally require little bleaching except for size removal, where necessary. To heighten brightness, natural and synthetic fibers, yarns, and fabrics can be treated with fluorescent whitening agents (FWAs). These optical brighteners are designed for selective emission of blue light, which gives the illusion of 'whiter than white'.

Bleaching has been the source of consumer dissatisfaction and complaint because of diminished wear-life. The dissatisfaction has prompted a plethora of research reports on textile degradation from various bleaches and bleaching protocols. These reports are not only of academic interest; they have important practical implications. Most pertinent for wear-life estimation is the damage effected during the early stages of bleaching. In the early stages, permissive degradation should be kept to a minimum level when attempting to treat the colorant selectively while avoiding oxidation of the textile.

Reference to a brand or firm name does not constitute endorsement by the US Department of Agriculture over others of a similar nature not mentioned.

Comprehensive surveys on textile bleaching can be found in Marsh (1945), Peters (1967), Trotman (1968), Cegarra and Gacén (1983), Nettles (1983), Lewin and Sello (1984), and Duffield (1986). This chapter will cover developments in bleaching systems and processes from 1986 to the present and will examine the nature of the bleaching systems currently used.

2.2 Natural and synthetic fibers

Fiber processing commonly requires removal of accompanying impurities. Natural and synthetic fibers originate commonly in an impure state. Whiteness becomes masked during growth or manufacture, processing, and fabrication of fiber to yarn and fabric. In natural fibers, impurities arise from natural exudates, local vegetation, and indigenous contaminants. In synthetic fibers, discoloration results from the by-products of manufacture, which include processing auxiliaries, spinning oils in yarn-making, and formulations for yarn sizing in weaving.

It is generally recognized that the requirements for effective bleaching are specific to fiber type. A consideration of these requirements in terms of structure and reactivity of fibers and bleaching agents is relevant.

Fibers can be classified according to origin and structure. An abbreviated scheme is as follows.

- Natural cellulosics
 - cotton, flax, jute, ramie, sisal, coir
- Regenerated cellulosic
 - rayon
- Synthetic modified cellulosic
 - acetate
- Natural polyamide
 - wool, camel, cashmere, mohair, rabbit, silk
- Synthetic polyamide
 - nylon, aramid
- Other synthetic fibers
 - polyester, acrylic, polypropylene, spandex.

Much of the chemical reactivity of fibrous polymers is derived from that of the functional groups of the monomer units. Thus, all cellulosic fibers have similar chemical reactivities, though susceptibility to attack and physical and mechanical properties are determined principally by differences in fiber morphologies. Crystalline and amorphous character define morphology. The relative content of a fiber's crystalline and amorphous regions determines its properties of strength, extension, and reagent accessibility.

2.2.1 Cellulosics

Cellulose (Figure 2.1) reacts through primary and secondary hydroxyl groups and through the glycosidic bond of the monomer unit. Typical reactions of the alcohol groups are oxidation, esterification, and etherification. These reactions take place in a heterogeneous medium, that is, in the solid substrate, which contains absorbed water. This heterogeneity stems in part from the fibril nature of cellulose itself. In cotton, a seed-hair fiber, fibrils are organized in sheets of associated polymer chains, which stack laterally and longitudinally and then spiral across the fiber axis with periodic reversal of direction. These spiral reversals give rise to the characteristic convolutions in the fiber and are responsible for reduced strength compared to flax, a bast fiber, where fibril orientation is aligned along the fiber axis. These morphological features, along with the fact that the glycosidic bonds are not easily broken, give rise to the stability of cellulose under a broad range of conditions.

All cellulosic fibers can be damaged by oxidizing bleaches. Oxidation products are termed 'oxycelluloses', whereby alcoholic —OH groups are converted to aldehyde, ketone, and carboxyl groups (Figure 2.2; Nevell, 1987). Hydrolysis reactions can occur during bleaching with the formation of chain-shortened 'hydrocellulose' (Trotman, 1968). The presence of oxycelluloses and hydrocelluloses can cause a textile to fall apart. Hydrocellulose formation ruptures glycosidic bonds and produces one reducing (aldehyde) and one non-reducing end group. Qualitative and quantitative reagents and analyses for determining the extent of degradation are Fehling's solution, copper number, Turnbull's blue test, and methylene blue absorption (Merkel, 1984).

2.2.1.1 Cotton. A typical bleach for cotton has been sodium hypochlorite. It is inexpensive and can be processed at pH 9–11, where the bleach is stable and where there is minimum fiber damage at 13–21°C (55–70°F). The process involves pretreatments for singeing and desizing with sodium hydroxides or enzymes, washing, and souring at room temperature for 10–15 min with 0.5% sulfuric acid. The material is extracted with 4% sodium hydroxide, washed, soured with 0.55–1.0% sulfuric or hydrochloric acid at room temperature and then washed. Bleaching follows by saturating the material with sodium hypochlorite at pH 9.5 for 30 min at room temperature. This process is

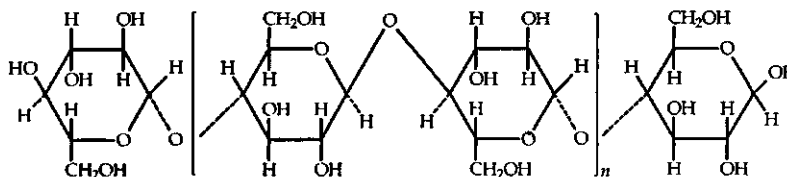


Figure 2.1 Cellulose.

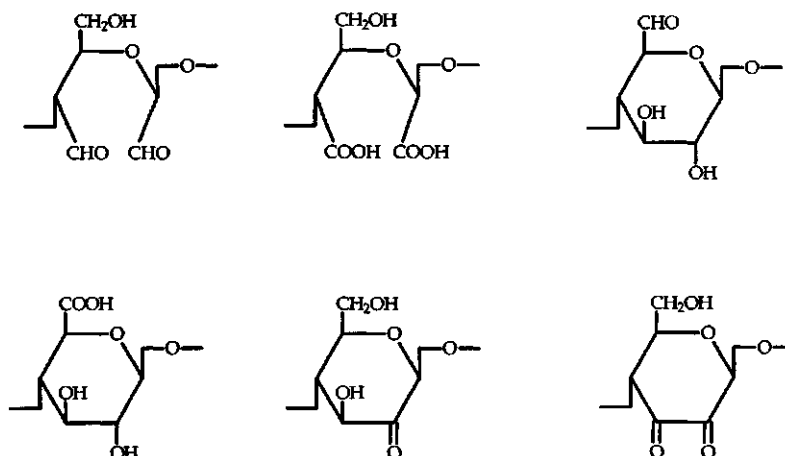


Figure 2.2 Oxycelluloses.

repeated as necessary. The material is then washed, antichlored with sulfur dioxide, and washed again at room temperature (Nettles, 1983).

Hydrogen peroxide is the most prevalent bleach. It is preferred over hypochlorite because it can be used more economically. Both hypochlorite and peroxide have been used together in one bath for scour/bleach formulations. Hydrogen peroxide serves as an antichlor and simultaneously releases oxygen for bleaching.

2.2.1.2 Flax and lignified celluloses. Flax, ramie, hemp, and coir have higher crystalline content than cotton because fibril orientation is aligned along the fiber axis. These fibers are more resistant to chemical attack. The presence of lignin, although a drawback as a source of discoloration, is somewhat beneficial, because its completely amorphous character lends stress transfer when the relatively brittle fiber is placed under stress. Bleaches can be selected to remove lignin completely or to simply decolorize it. A processing consideration is the weight loss, which can be as high as 26% from hemicelluloses and lignin (Peters, 1967). The amount of weight loss is dictated by the textile's intended end-use. There are two approaches to removing color: bleaching with sodium chlorite to remove lignin or bleaching with sodium hypochlorite by acid chlorination of lignin to make it soluble for removal in an alkaline scour. Sodium chlorite is advantageous when less weight loss is required. It requires effective bleaching in 45 min at pH 3.8–4.2 at 80°C. A second bleaching with hydrogen peroxide may be required (Peters, 1967).

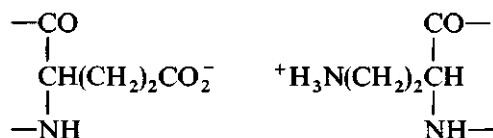
2.2.1.3 *Rayon*. Rayon lacks the highly ordered fibril character of cotton and flax. It is readily accessible and the effects of bleaching are more severe. In its preparation from xanthate-derivatized wood pulp, rayon is regenerated in an acid bath to cellulose before extrusion from a viscous solution as filament fibers. This process reduces the chain length of cellulose by one-third of the expected value for cotton and flax. Hence there are many more shorter chain lengths and thus a greater number of reducing ends. Rayon and acetate are extruded as filament fibers in the white state. Rayon is commonly cut to staple whenever bleaching may be required. Of the various forms of rayon, which include modal (rayon obtained by processes giving a high tenacity and a high wet modulus) and viscose, viscose is most vulnerable. It requires milder bleaching. Recommended procedures employ cold sodium hypochlorite at pH 10–11 with sodium carbonate. Peracetic acid can be used at 65°C for 1 h at neutral pH in the presence of sodium hexametaphosphate at neutral pH. Sodium chlorite can be used at 80°C for 30–45 min at pH 3.8–4.0. Other bleaching regimens for high wet modulus rayon and viscose have been reported elsewhere (Lewin and Sello, 1984).

2.2.1.4 *Acetate*. In the case of cellulose acetate, the reactivity of the acetate fiber is determined not by hydroxyl but by acetate groups. When cellulose is acetylated and extruded as filamentous acetate fiber, a different range of fiber properties results. Esterification conveys heat sensitivity, thermoplasticity, and solubility in acetone.

The conditions for bleaching cellulose acetate are influenced by its chemical reactions to acids and bases. Acetate is resistant to cold dilute acids, is decomposed by strong acids, and dissolves in acetic acids. It has good resistance to weak alkali. Strong alkali hydrolyzes the acetate groups and saponifies the fiber. Sodium hypochlorite and hydrogen peroxide can be used at pH lower than that used to bleach cotton. Safe bleaching can be carried out using peracetic acid in a mild alkali bath (Lewin and Sello, 1984).

2.2.2 *Natural polyamides*

2.2.2.1 *Wool*. Protein fibers are formed by the chemical combination of alpha-amino acids joined by peptide linkages. The amino acids can be liberated by alkaline hydrolysis, and this destroys the bonding between parallel polymer chains which are joined by the salt linkages of pendant amino acid groups.



Wool is keratin protein, unique because covalent intermolecular bonding

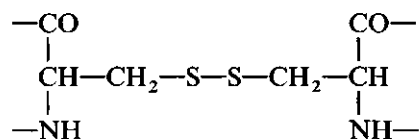
occurs through the disulfide linkages of the amino acid cystine. The salt links are a main consideration for fiber strength. They form from a weak acid and a weak base and the extent of their hydrolysis in water should increase with temperature. Fortunately, however, hydrolysis occurs at temperatures above normal processing.

Wool is not sensitive to weak acids. In fact, weak acids are used in dye applications. Moreover, dilute mineral acids are used for carbonizing wool, where the sorbed solutions do not weaken wool at the baking temperature of 120°C, at which temperature vegetable matter chars. Concentrated mineral acids do cause wool to swell and gelatinize.

Wool is sensitive to caustic sodium and potassium hydroxide, but not to sodium carbonate. Wool can be treated at the boil with ammonia without harm, but solutions of 5% sodium hydroxide cause considerable strength loss. In this case, the polymer chains are converted into sodium salts of amino acids with concomitant salt-link rupture, and cystine bonds cleave.

Attempts have been made to stabilize wool for exposure to alkali, and oxidizing and reducing agents (Speakman, 1941). Formaldehyde was used to strengthen wool by what was thought to be crosslinking of the basic amino group side-chains, represented simply as Wool—NH—CH—NH—Wool (D'yachenko and Shel'pakova, 1939). In an early report, the optimum conditions for increasing the alkali-resistance of wool with formaldehyde were 0.5%, pH 6–8, 50°C, 6 h (Brown *et al.*, 1951).

Because of wool's particular bonding characteristics, the association of keratin protein takes the form of an alpha helix or coil crosslinked with dithiol linkages through cystine's —S—S— bonds at adjacent turns in the helix, as shown.



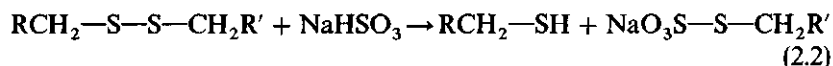
The particular challenge of bleaching wool involves the removal of dirt, vegetation, suint,* grease, and black hair impurities. The effects of oxidative and reductive bleaching processes on wool can be described as follows.

- Cleavage of —S—S— bonds by reducing agents, with the formation of thiol groups (equation 2.1) that can be readily reoxidized to the original form.

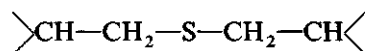


*Suint is a collection of sweat gland secretions which include potash salts of various fatty acids together with small quantities of sulphates, phosphate and nitrogenous materials (von Bergen, 1963).

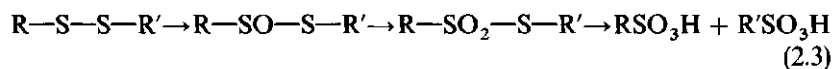
- Cleavage at these sites with formation of thiol and cysteine sulfonate (Bunte salt) groups (equation 2.2).



- Reaction with alkali to form lanthionine crosslinks.



- Cystine oxidation by hydrogen peroxide bleaching, resulting in cystine disulphide cleavage and complete conversion to cysteic acid (equation 2.3).



Oxidation of cystine during bleaching diminishes wool fiber strength. Considering the inherent low tenacity of wool, this is to be avoided. During bleaching, the selective alteration of peptide bonds and/or —S—S— linkages can be controlled by the appropriate choice of bleaching system. Although oxidation intermediates are difficult to document quantitatively because they hydrolyze to cysteine and cysteic acid, they have been recorded by infrared spectrophotometry. Absorptions at 1070 and 1120 cm^{-1} have been assigned to —SO—S— and —SO₂—S— (Nettles, 1983; Merkel, 1984). These absorptions are diagnostic for oxidation damage. Wool degradation can be monitored by percentage alkali solubility, which correlates directly with percentage cysteic acid content (Duffield, 1986).

A traditional reducing bleach for wool had been sulfurous acid (SO₂) because it leaves wool relatively unaffected but removes colored matter. The white is known to lack permanency, however, so the bleach was supplemented by a hydrogen peroxide treatment.

Often, hydrogen peroxide baths are followed by reducing bleach baths for increased whiteness. Such dual bleachings are referred to as full bleaching. Arifoglu and Marmer (see references) have perfected a single bath variation of such dual bleaching. Another variation on bleaching wool includes combining peroxide bleaching with scouring, whereby wool emerges from the last scour bowl wet with dilute peroxide; slow bleaching ensues within the wool bale.

Peroxide bleaching sometimes may be carried out within the dye bath. When wool is dyed near the boil for approximately 60–90 min, yellowing can occur during the dyeing process. For many dyes that are stable to hydrogen peroxide, clear pastel shades can be achieved without prebleaching by incorporating a bleaching agent in the dye bath.

A hydrogen peroxide bleach formulation includes a phosphate or silicate stabilizer to control the rate of peroxide decomposition and subsequent rate of bleaching. Often, chelating agents are added to bind metal ions that can

decompose the peroxide. For example, the system can include hydrogen peroxide, 35%, in the amount necessary to achieve a desired whiteness level, phosphate stabilizer, wetting agent, temperature 40–60°C, duration 1–8 h, and pH 7.5–8.5.

Because hydrogen peroxide in alkaline medium is present in excess to the amount of targetted chromophoric groups and susceptible keratin functionality, only 15–25% of the peroxide in the bleach bath is actually consumed during bleaching. Some mills therefore recycle the unspent peroxide.

2.2.2.2 Silk. Pure silk is fibroin protein. It is composed of simple amino acids and contains no disulfide (—S—S—) bonds. Without intramolecular crosslinking, silk's morphology results from the ionic bonding of amino acid groups. In contrast to wool's coil configuration, polypeptide chains of silk associate in ordered lateral sheet-arrays, which stack to build up fibril structure. These arrays convey greater strength and crystallinity to silk than does the coil configuration to wool. The permeability of silk is less than wool and there is relatively less tendency for chemical attack.

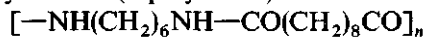
Like wool, silk has been traditionally bleached by peroxide. Because silk is not readily degradable, it can tolerate more severe conditions. Chlorine bleaching produces discoloration and is never prescribed. This discoloration has been attributed to the degradation of tyrosine residues (Earland, 1960).

When compared to wool bleaching, a typical silk bleaching system using hydrogen peroxide can be formulated for higher temperatures and alkalinity. A typical peroxide bleach bath includes alkaline hydrogen peroxide with sodium silicate and ammonia, pH 10, with tetrasodium pyrophosphate and EDTA, and processing at 40–60°C for 2–4 h.

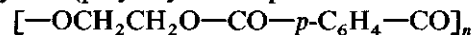
2.2.3 Synthetics

Synthetic fibres can be engineered for different mechanical behaviors. They demonstrate variable crystallinities, crosslinking densities, and thermoplasticities. Trademarks within generic fibers represent a myriad of physical and mechanical properties that have been tailored to particular end uses. Generic fibers are classified by common chemical constitution and take their name from the identity of the polymer repeat unit comprising them. Some are listed below.

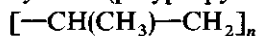
Nylon 6.10 (a polyamide):



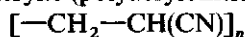
Polyester (polyethyleneterephthalate shown here):



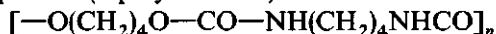
Polyolefin (polypropylene shown here):



Acrylic (polyacrylonitrile shown here):



Spandex (a polyurethane):



Synthetic fibers are generally manufactured with high levels of whiteness except when the conditions for fiber formation cause discoloration. In these cases, bleaching can include fluorescent whitening agents. Formulations are composed for safe temperatures and pH ranges that minimize acid and alkali degradation of the fiber. As an example, polyester fibers have been bleached with di- and tri-chloroisocyanuric acid at pH 3–9, at 60–65°C, for 30–45 min (Bel'tsov and Klaus, 1971).

2.2.3.1 *Nylon*. Heat setting temperatures for the various forms of nylon may cause yellowing from oxidation. Heat sensitivity is a special consideration for bleaching the nylon thermoplasts. Hydrogen peroxide is not used because the bleach bath processes at too high a temperature. Recommended bleaches are nonchlorinated types: sodium perborate, percarbonate, and peracetic acid. A peracetic acid bleach bath is processed with sodium pyrophosphate at pH 6–7. The material is introduced cold and the temperature is raised to 80–85°C over 30 min with subsequent bleaching at this temperature for 30 min. Where possible, lower temperatures and pHs are recommended (Trotman, 1968).

2.2.4 *Bleaching of fiber blends*

In 50/50 blends of natural and synthetic fibers, bleaching procedures are based on the sensitivity of the natural fiber component, provided that temperature and pH are not damaging to the synthetic fiber. When the natural fiber component represents a small percentage of the composition, it may withstand harsher conditions than would normally be prescribed for bleaching it alone. When a textile contains a fiber blend with fibers of equal sensitivity but unequal percentages, bleaching formulations are tailored to the safe requirements of the fiber present in the larger amount. For a review of bleaching methods reported on cotton/rayon, polyester/cotton, wool/cotton, wool/polyester and wool/acrylic, the reader is referred to Lewin and Sello (1984).

2.3 Bleaching agents

Natural and synthetic fibers are the essential elements of textile fabrics. The chemical, physical, and mechanical properties of fibers are directly related to yarn and to fabric behavior. When compared to fibers, yarn and fabric forms are less vulnerable substrates and after-effects of bleaching may be expected to be less pronounced.

Table 2.1 Categories of bleaching agents

Chlorine-containing oxidants	
Sodium hypochlorite	NaOCl
Sodium chlorite	NaClO ₂
Sodium dichloroisocyanurate	An <i>N,N'</i> -dichloro compound
Inorganic peroxygen bleaches	
Hydrogen peroxide	H ₂ O ₂
Ozone	O ₃
Sulfur dioxide	SO ₂
Sodium perborate	NaBO ₂ · H ₂ O ₂ · 3H ₂ O
Potassium permanganate	KMnO ₄
Sodium percarbonate	Na ₂ CO ₃ · 3H ₂ O ₂
Sodium bromate	NaBrO ₃
Sodium bromite	NaBrO ₂
Potassium peroxydiphosphate	K ₄ P ₂ O ₈
Ammonium perdisulfate	(NH ₄) ₂ S ₂ O ₈
Ammonium hydrogen permonosulfate	NH ₄ HSO ₅
Organic peroxygen bleaches	
Peracetic acid	CH ₃ CO—OOH
Peroxydodecanedioic acid	HOO—CO—(CH ₂) ₁₀ —COOH
Tetra-acetylenediamine/H ₂ O ₂	Generates CH ₃ CO—OOH
Reducing bleaches	
Sulfur dioxide	SO ₂
Sulfurous acid	H ₂ SO ₃
Sodium bisulfite	NaHSO ₃
Sodium sulfite	Na ₂ SO ₃
Sodium hydrosulfite (sulfoxylate, dithionite)	NaO ₂ SSO ₂ Na
Sodium formaldehyde sulfoxylate (sodium hydroxymethanesulfinate)	HOCH ₂ SO ₂ Na
Sodium borohydride	NaBH ₄
Thiourea dioxide (formamidinesulfinic acid)	H ₂ NC(=NH)SO ₂ H
Sodium sulfinate	HSO ₂ Na
Trisodium trithiocyanurate/H ₂ O ₂	Generates HSO ₂ Na
Photosensitizing bleaches	
Fluorescent whitening agents	

Formulations for the major bleaches listed in Table 2.1 have traditionally been tailored for selective bleaching of coloring matter without diminishing a textile's structural integrity.

Bleach formulations usually contain buffering and sequestering agents such as silicates, phosphates, or oxalates. Some formulations call for metal salts, sodium hydroxide, ammonia, or sodium nitrate. Other additives to the bleach bath are surfactants, antideposition agents and optical brighteners.

The most common bleaching is oxidative in nature, and hydrogen peroxide is the most widely used agent for stain bleaching of proteinaceous fibers, and in the past, chlorinated bleaches for cellulose. Reductive bleaching may be used alone as a substitute for oxidative bleaching, but its use is mainly confined to after-bleaching following peroxide treatment. The most widely

used reductive bleach, though not the best, is sodium hydrosulfite ($\text{NaO}_2\text{SSO}_2\text{Na}$; also known as dithionite, hyposulfite, and sulfoxylate).

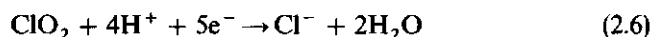
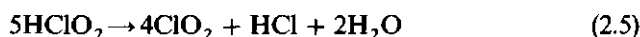
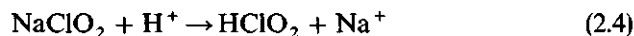
More favored as reductive bleaches are derivatives of sulfinic acid (H_2SO_2), all of which are thought to act by decomposition to a fleeting but reactive species, free sulfinate ion. The most common such derivative is sodium hydroxymethanesulfinate ($\text{HOCH}_2\text{SO}_2\text{Na}$; sodium formaldehyde sulfoxylate), but a newcomer now gaining favor is thiourea dioxide ($\text{H}_2\text{NC}(=\text{NH})\text{—SO}_2\text{H}$; formamidinesulfinic acid).

The most effective bleaching regimens for stain incorporate both an oxidative and a reductive bleaching step and are referred to as 'full' bleaching. Such full bleaching is normally a two- or three-step process carried out in separate baths. Industry, however, typically avoids full bleaching, and relies on oxidative bleaching alone; the gains from extra whiteness, it concludes, do not offset the added expenses of preparing and heating an additional bleach bath.

2.3.1 Chlorine-containing oxidants

2.3.1.1 *Sodium hypochlorite.* Sodium hypochlorite (NaOCl) is a powerful oxidizing agent, the reaction product of chlorine gas and sodium hydroxide. NaOCl is stable above pH 10. The rate of bleaching may be increased by adding acid in moderate amounts (to pH 5.0–8.5) to form hypochlorous acid (HOCl). Chlorine liberation occurs below pH 5.0. The oxidation of cellulose is greatest within the range pH 5–9.

2.3.1.2 *Sodium chlorite.* Sodium chlorite (NaClO_2) is a fairly stable solid source of chlorine dioxide (ClO_2) for bleaching. NaClO_2 can be purchased as approximately 81% solids and alkali stabilizers. The formation of ClO_2 occurs only on its dissolution in acidic medium (equations 2.4 and 2.5). ClO_2 is unstable and acts as an oxidative bleach (equation 2.6).



The formation of toxic and corrosive ClO_2 is a major industry concern. Bleaching should be carried out within the range pH 3.5–4.0 with buffer systems such as sodium dihydrogen phosphate. During cotton bleaching, when ClO_2 solutions were used at pH 1.76–6.05 at 20°C, oxycelluloses formed and were detected by increase in fluidity, copper number, and carbonyl content (Peters, 1967).

2.3.1.3 *Sodium dichloroisocyanurate*. Isocyanuric chlorine bleaches are the principal solid chlorine bleaching agents. Most common is sodium dichloroisocyanurate dihydrate, with 56% available chlorine (Farr *et al.*, 1992).

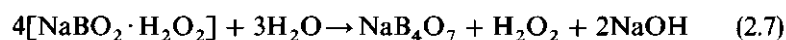
2.3.2 *Inorganic peroxygen bleaches*

2.3.2.1 *Hydrogen peroxide*. Hydrogen peroxide bleaching proceeds by dissociation into H^+ and perhydroxyl ions (HOO^-). This reaction is favored by alkaline conditions. At pH 11.5, the peroxide rapidly breaks down and molecular oxygen forms. Cotton would become severely damaged under these conditions. Activators and stabilizers are added to the hydrogen peroxide bath to control bleaching. Sodium hydroxide and sodium carbonate are the alkalis for cellulose, and ammonia and tetrasodium pyrophosphate are used for wool. Sequestering agents are used to incapacitate heavy metal ions in the bleaching solution. These ions foster the decomposition of peroxide into radical species that attack and damage the fiber.

Attention is now being given to use of enzymes to assist peroxide bleaching. In wool, proteolysis and lipolysis open channels for better penetration of peroxide. Specific enzymes are selected for their stability in an alkaline peroxide medium (Fornelli, 1994).

Ironically, the same radical process is being used to advantage to bleach pigmentation in animal fibers. Bleaching for pigmentation involves the selective decomposition of melanin pigment granules in the interior of the fiber. Industry uses one variation or other of the process first reported by Laxer and Whewell (1955) and then perfected by Bereck (1985), which involves the selective mordanting of pigmented fibers by ferrous sulfate. The fiber or fabric is first treated with $FeSO_4$ in the presence of a reducing agent (e.g. phosphorous acid, H_3PO_3 , and hypophosphorous acid, H_3PO_2) to prevent oxidation of Fe^{2+} to Fe^{3+} . Following rinsing (sometimes in the presence of a chelating agent such as ethylenediaminetetraacetic acid, EDTA, or nitrilotriacetic acid, NTA) to remove the bulk of the $FeSO_4$, small amounts of Fe^{2+} remain adsorbed specifically to the melanin granules. Subsequent treatment of the fibers with H_2O_2 causes decomposition of the melanin pigment. The localized reaction on melanin is a free-radical one, superimposed on the non-radical and non-selective interaction of H_2O_2 with stain components. The bleaching of pigmented animal fibers was reviewed by Knott (1990).

2.3.2.2 *Sodium perborate*. Sodium perborate is a white crystalline powder that dissolves in water at room temperature to form hydrogen peroxide. In practice, it is used as a 1% solution at pH 10 (equation 2.7):



2.3.2.3 *Potassium permanganate.* Potassium permanganate is unstable and decomposes in the presence of oxidizable substances; its manganese is converted into manganese dioxide, a brown solid. However, under controlled acidic conditions, soluble manganous salts form instead, and effective bleaching occurs. A formulation for permanganate bleaching to remove color from wool in acrylic or polyester blends was reported by Millson and von Bergen (1970).

2.3.2.4 *Sodium percarbonate.* Sodium percarbonate is a white powder with approximately 13% available oxygen. A 1% solution has a pH of 10.5. It decomposes above 20°C to form sodium carbonate and hydrogen peroxide.

2.3.2.5 *Sodium bromite.* Sodium bromite is used in cotton desizing as an oxidizing agent. Optimum bleaching takes place at pH 9.8–10.2 at 30°C. Without careful control of these conditions, depolymerization by glycosidic bond cleavage can occur.

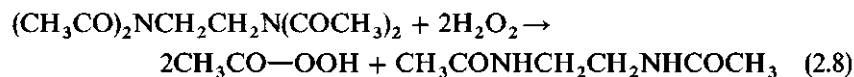
2.3.2.6 *Others.* Sodium salts of peroxygens including diphosphate, disulfate and monosulfate are used as desizing compounds in an alkaline medium. Often they are used with hydrogen peroxide in a continuous bleaching process of desizing, scouring, and bleaching (Lewin and Sello, 1984).

2.3.3 *Organic peroxygen bleaches*

2.3.3.1 *Peracetic acid.* Peracetic acid is the acetyl derivative of hydrogen peroxide. It is available as a colorless 36–40% solution in dilute acetic acid. The stability of peracetic acid is less than that of hydrogen peroxide. Radical scission will result in hydroxyl radicals (HO[•]), and when ions such as iron are present, the effect is magnified (Lewin and Sello, 1984).

2.3.3.2 *Peroxydodecanedioic acid.* Unlike such hydrophilic peracids as peracetic acid, which are very soluble in water, function in the bulk phase for bleaching, and are useful at high temperatures, peroxydodecanedioic acid, a hydrotropic peracid, is oily by nature and less soluble. It has a well-defined critical micelle concentration, which suggests it operates from within the detergent micelle and as such is highly effective in low-temperature bleachings. It is important because of its stability as a solid organic peracid.

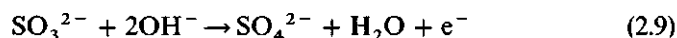
2.3.3.3 *Tetra-acetythylenediamine (TAED).* TAED has been used in over half of European detergents as a hydrogen peroxide activator to meet the demands of the European market for low-temperature processing. It activates peroxide by forming peracetic acid at the low temperatures where peroxide would normally be an ineffective bleaching agent (equation 2.8).



This bleach was introduced into normal detergent formulations in 1990 (Farr *et al.*, 1992).

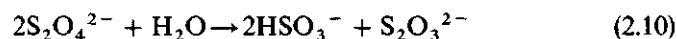
2.3.4 Reducing bleaches

2.3.4.1 *Sulfur dioxide, sulfites, and bisulfites.* Sulfur dioxide dissolves in water to form sulfurous acid, which on increasing alkalinity exists as bisulfite or sulfite. These are reducing agents, as illustrated by the half-reaction for sulfite (equation 2.9).



A bleaching formulation for wool can be found in Millson and von Bergen (1970). These agents are inexpensive, but can impart fiber damage as well as bleaching activity.

2.3.4.2 *Hydrosulfite.* Hydrosulfite (sulfoxylate, dithionite) is used as an industrial bleach for bleaching pulp and paper. It has been used on wool for less damage than bleaching with hydrogen peroxide (Millson and von Bergen, 1970). At low pH or high temperatures, aqueous solutions are unstable and bisulfite is formed (equation 2.10).



Following bleaching and rinsing, the fiber is treated with a little H_2O_2 to stem residual sulfurous odors. Full bleaching using sequential oxidation by hydrogen peroxide followed by reductive bleaching by hydrosulfite is discussed by Duffield (1986).

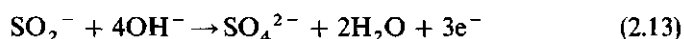
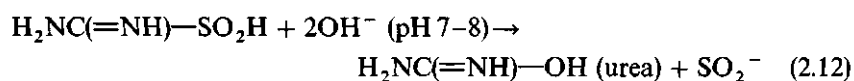
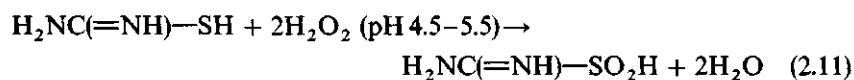
2.3.4.3 *Sodium formaldehyde sulfoxylate.* Sodium formaldehyde sulfoxylate (sodium hydroxymethanesulfinate) is formed from the reaction of hydrosulfite and formaldehyde. It can be processed at pH 3.2–3.5, is less reactive than hydrosulfite and is more stable to heat (Farr *et al.*, 1992).

2.3.4.4 *Sodium borohydride.* Sodium borohydride is a selective reducing agent for aldehyde and ketone groups. It is used for cellulose bleaching where oxycellulose formation and concomitant dehydration have produced yellowness. The reduction of aldehydic and ketone groups to alcohols reverses yellowness. Combination treatments with borohydride and ozone have been used to bleach and brighten cellulosic fibers (Wade, 1967).

2.3.4.5 *Thiourea dioxide*. Thiourea dioxide is an effective bleach when used alone or when used after hydrogen peroxide in a full bleaching process (Duffield, 1986; Cegarra *et al.*, 1988). Bleaching with thiourea dioxide is not common practice but it is effective when used alone, and the process compares favorably with hydrogen peroxide bleaching. A formulation can include a commercial thiourea dioxide product, wetting agent and EDTA sequestering agent. Reductive bleaching is carried out at pH 7.0 at 70°C for 60 min (Duffield, 1986).

Full bleaching, oxidative bleaching (e.g. with hydrogen peroxide) followed by reductive bleaching (e.g. with thiourea dioxide), can lead to superior whiteness and improved light fastness. Generally two-step full-bleaching processes incorporate rapid bleaching methods to maintain nearly similar exposure times to those of single-stage bleaching.

A series of recent reports (Arifoglu and Marmer, 1990a,b, 1992a; Arifoglu *et al.*, 1990, 1992; Cardamone *et al.*, 1992; Marmer *et al.*, 1993, 1994; Cardamone and Marmer, 1994), patents and patent applications (Arifoglu and Marmer, 1990c, 1991, 1992b,c,d, 1993a,b) disclose new approaches to full bleaching that integrate hydrogen peroxide bleaching and thiourea dioxide after-bleaching into a single-bath procedure. Residual hydrogen peroxide from the initial oxidative bleaching is utilized in a quick chemical reaction that converts the bath into a reductive medium. Thus, thiourea is added to the peroxide bath under controlled conditions, producing thiourea dioxide (equation 2.11). Thiourea dioxide is not a truly reductive agent; its hydrolysis produces sulfinate ion, the active species (equation 2.12), and reductive bleaching ensues (equation 2.13).



The proposed mechanism was supported by ¹³C NMR spectroscopy (Arifoglu *et al.*, 1992) and the monitoring of redox potential.

The above studies confirmed the advantages of full bleaching. Whiteness was vastly superior to that from peroxide bleaching. Mechanical testing showed that damage to the fabric (a wool challis) was minimal, and the fabric handle, as assessed by using the Kawabata Evaluation System (KES-F; Kawabata, 1980), was softer, more flexible, and smoother than seen from conventional bleaching.

Full bleaching could be tied into the Bereck process for bleaching of natural pigmentation. A particular advantage is the elimination of traces of any orange-colored Fe³⁺ species (from the mordanting) by reduction to soluble

Fe^{2+} (Arifoglu and Marmer, 1990a,b, 1991, 1992b,d, 1993a) during the reduction step of full bleaching.

2.3.5 *Photosensitizing bleaches*

The photo-yellowing of wool is wavelength-dependent and is influenced by the wool's previous treatment and condition. Wool can be photobleached in air in the presence of water when exposed to blue light (380–475 nm). Reducing bleaches accelerate this effect (International Wool Secretariat, 1970). Ultraviolet light (less than 380 nm) causes yellowing, especially if the wool has been hydrogen peroxide bleached, and this effect is enhanced if wool is wet. It has been reported that hydrosulfite reductive bleaching inhibits the yellowing of peroxide-bleached fabrics (International Wool Secretariat, 1970).

The spectral distribution of sunlight varies by season and by time of day within a geographical location. The effect of sunlight, therefore, is not so predictable. Supposedly, the ratio of the exposures to 300 nm ultraviolet and to 400–475 nm blue light can determine whether the exposure leads to bleaching or yellowing.

Launer (1965) examined the broad band spectrum, 331–398 nm, to simulate the effects of blue light, ultraviolet, and sunlight on wool. The work was an extension of a study in 1949 in which he and co-workers found that the yellowing and bleaching of cellulose was wavelength dependent. They reported that wool could be effectively bleached at wavelengths above 398 nm, yellowed at less than 331 nm, and simultaneously bleached and yellowed when exposed to the wavelength range 331–398 nm. Thus, wool can be made to yellow for a given time period and subsequently bleached for an ensuing period of time. Apparently, the intermediate simultaneous yellowing and bleaching proceed by different pathways with consecutive reactions in the wool molecule. Maclaren (1963) found that one such yellowing reaction involved the destruction of cystine.

These phenomena imply that the yellowing effect of light, which is a common occurrence in sunlight exposure, can mask the bleaching effect. It is most desirable to select light of appropriate wavelength for bleaching — high enough in energy to whiten but too low to break down the fibrous components to yellow substances. It should be noted that cotton, too, has been bleached by near-ultraviolet light and by visible light (Launer, 1968); the deleterious effects of accompanying heat were noted.

To address the problem of lack of stability of the whiteness obtained by hydrogen peroxide bleaching when woolen fabrics are subjected to high heat in the dye bath, Simpson (1992a) investigated the application of photobleaching wool with blue light. Exposure of wool to blue light at 470 nm imparts 60.8 kcal/einstein of energy, which is lower than the energy required for covalent bond formation in wool. Thus, blue light in photobleaching is thought to react selectively with chromophores without attacking wool.

Qualifying concepts, however, include the possibility that the presence of catalysts could lower the activation energy barrier and that the presence of 'inherent structural strain' could cause some damage to —S—S— bonds (Simpson, 1992a).

Photobleaching is viewed as color-specific, that is, only colored moieties absorb the blue light until they are destroyed. Hydrogen peroxide bleaching has no such specificity, and it can damage the fiber while bleaching it.

Reports in Wool Science Review 39 (International Wool Secretariat, 1970) indicate that the results of photobleaching can be improved when carried out in the presence of reducing bleaches, such as sodium hydrosulfite or thiourea dioxide. More recently, Simpson (1992a) showed similar photobleaching in the presence of hydrogen peroxide. He applied blue light (420 nm) to bleach peroxide-impregnated wool fabrics and found that under this exposure, pH was the most important variable affecting the rate of peroxide bleaching. A pH range of 2–12 was chosen for 20-min bleachings in 2.5% (v/v) peroxide at 30°C. At pH 11, whiteness was optimum, and at such low temperatures and short exposure times, destruction of wool in this highly alkaline medium was within acceptable limits.

When compared to conventional thiourea dioxide bleaching, the most effective in terms of brightness was peroxide photobleaching. Relatively similar results were seen with reduction photobleaching, which gave results just slightly lower in brightness than thiourea dioxide-bleached samples not subjected to photoexposure. Overall optimum conditions for achieving brightness by oxidative photobleaching were established as 2.5% v/v peroxide, pH 10.5–11, 20–30 min.

No loss in tensile strength was seen on wool fabrics treated either by conventional bleaching with alkaline hydrogen peroxide or by high-pH oxidative photobleaching. All bleached samples were within the acceptable limits for alkali solubility (24%). This value was approximately the same for conventional peroxide and photobleached (18.9% and 17.9%, respectively), and this represents an increase of 8–9% over the untreated fabrics. Weight loss for both bleaching systems was within acceptable limits. Blue light may have a catalytic bleaching effect, which allows the circumvention of the high temperatures and long exposure times generally associated with conventional alkaline peroxide bleaching (Simpson, 1992a).

2.3.6 *Fluorescent whitening agents*

'Blueing agents' had traditionally been used on cotton. The phenomenon of blueing involves the ability of the blueing agent to absorb yellow light, thereby selectively emitting blue light. When yellow chromophores are present, they are selectively absorbing blue light. When the blueing agent is added to a yellowed textile, the emitted blue light combines visually with the yellow

light. The textile will be perceived as gray–white from the additive light mixing of the complementary colors, blue and yellow.

An extension of this phenomenon is seen with fluorescent whitening agents (FWAs). These optical brighteners absorb invisible ultraviolet light and emit blue to violet light. For an effective FWA, there must be affinity of the agent for the textile substrate. The FWA must be wash-fast, except if it is a component of a laundry detergent and can thus be replenished with every laundering.

Use of FWAs, however, has a major drawback. Their presence on fabrics induces yellowing reactions by light. Fabrics that initially appear bright white may in time revert to a severely yellowed condition. This, of course, is most critical to white fabrics and fabrics dyed a pastel color.

Wool that has been brightened to FWAs tends to photo-yellow, and the effect is accelerated in sunlight. By the fact that FWAs absorb in the ultraviolet spectral region, high energy radiation can lead to degradation unless, in the design of the agent, this energy can be dissipated without causing damage. Thiourea and thiourea–formaldehyde, as well as other reducing agents, have been found to offer some protection (International Wool Secretariat, 1970). The most effective FWAs are those that are applied after peroxide bleaching but the most efficient are those that have no negative effect on the light-fastness of the dyed textile.

Many studies have addressed the design of FWAs for whitening wool without sensitizing it. Typically, a FWA is included in the last quarter of a reducing bleach bath, which follows peroxide bleaching. After the reducing bleach is consumed, acidifying the bath ensures that the last traces of brightening agent will be exhausted. Caution must be exercised, however, because pH change can cause a hue shift in some dye systems and this might be difficult to correct with after-treatment.

FWAs are used on cotton with mechanically-held finishes and with those finishes to which cotton has crosslinked. The applications of FWAs are versatile; for example, when they are added directly before or after printing, the color is brightened.

FWAs have the same specificity for fibers that dyes have. The individual application processes are similar to dyeing except that much less FWA is used than dye. A broad range of FWAs has been invented to cover the broad spectrum of substantivities found in untreated and pretreated textiles and their blends as the result of various wet-processing conditions. Other prevailing prerequisites are bath-compatibility of the FWA and penetration into the fiber.

The anionic FWAs which are substantive to cellulose and rayon are derived from stilbene. Their planar structures are similar to the planar structures of direct dyes so that the same mode of attachment applies. The incorporation of sulfonate groups, as in direct dye molecules, provides the necessary water solubility for wet-processing. Synthetic fibers can be treated with FWAs at

the melt-spin stage of filament fiber development. Cellulose acetate can be brightened with pyrazole-derived agents.

Hydrophobic polyester requires a hydrophobic FWA. Usually naphthalimides are applied as aqueous dispersions. Like disperse dyes, such FWAs can require high temperatures and carriers. Optical brighteners are applied to nylon in the manner of exhaust dyeing with acid dyes. Tailored FWAs have been developed for the various nylons. For example, some nylons can be dyed with water-insoluble disperse dyes, which suggests that insoluble FWAs can be supplied as suspensions. Acrylic textiles have affinity for cationic dyes and are thus substantive to cationic optical brightening agents of the amino or substituted amine group variety.

A comprehensive review of FWAs for textiles can be found in Sarkar (1971) and Levene and Lewin (1984).

A survey of some of the textile bleaching literature since 1986 is contained within the appendix to this chapter. Included are descriptions and evaluations of the various bleaching processes along with information on the after-effects of treatments.

2.4 Energy and the environment

Since about 1990, the textile industry in the USA and Western Europe has stepped up support for process design modifications and relevant basic and applied research designed to improve bleaching systems. These are ongoing movements to bring current wet-processing methods into compliance with those regulations governing effluents and occupational health and safety. These movements are intensifying with the ever-increasing demand by consumers for energy efficient and environmentally friendly products.

Studies on wet textile processing, including bleaching, have been directed toward conserving water, energy, and chemicals while limiting wastewater and wastewater contamination. The many reports that are summarized in the appendix show new proposed protocols for bleaching systems and processes that modify the traditional methods for increased efficiency and enhancement of textile properties with little or no loss of fiber integrity.

A current trend is to combine several process stages into a single automatically controlled continuous line with high production speed. Increased speed may require greater bleach concentration or more powerful bleaches, more effective catalysts, tailored stabilizers and activators, and higher temperatures. Some reports show the use of solar radiation and photolysis for circumventing the problem of fiber damage, which is affected by heat application (Gulrajani *et al.*, 1990; Simpson, 1990, 1992a,b; Collins and Davidson, 1993).

Various reports of investigations to modify traditional bleaching systems

such as hypochlorite (HOCl , NaOCl), peroxide (H_2O_2), and chlorite (NaClO_2) are described in the appendix. For example, the use of hypochlorite prevails because of its relatively low cost, processing ease, and high efficiency for whiteness achieved at fairly low temperatures. Drawbacks include the formation of toxic chlorinated organic byproducts and the tendering of cellulose, so modifications of the system have been examined (Nevel and Singh, 1986; Shenai and Narkhede, 1987).

An alternative to hypochlorite bleaching is chlorite. It is used on rayon, modal, acetate, polyester, acrylic, and nylon. It is preferred over peroxide for bleaching cotton because, unlike peroxide, chlorite is not affected by heavy metal ions. Strict control is essential to maintain the narrow useful pH range, 3.5–4.0, and this is difficult because liberated HClO_2 can lower the pH to the level where cotton is tendered. Advantages for the use of chlorite over hypochlorite include significant reduction in the organic halogen compound content of wastewater streams. This problem, however, is not eliminated entirely with chlorite bleaching. An added disadvantage is the production and volatility of chlorine dioxide (ClO_2), formed in solution, which contributes to corrosion of equipment and to biological irritation.

Newer systems have been designed for more energy efficient and safer usage of chlorite bleach, for example, the combined scouring/bleaching with sequential chlorite–hypochlorite–peroxide (Goswami and Mukherjee, 1993). Another approach is single-stage scouring and bleaching by padding with chlorite activated by TEA at 60°C (e.g. Gulrajani and Venkatraj, 1986; Gulrajani *et al.*, 1987; Petrick, 1988).

Generally, hydrogen peroxide is not considered a water pollutant. In wool bleaching, however, phosphate stabilizers for the peroxide do present pollution problems. There is sustained interest in reducing phosphate discharges by recycling the bleach bath. Other studies are related to phosphate replacements, and various pH buffers and amides to activate peroxide and reduce bleaching time (e.g. Sukumar and Gulrajani, 1985; Das *et al.*, 1986). In the case of cotton, another application of enzymes is seen. Enzymatic desizing is followed by hypochlorite padding and storing before actual bleaching using persulfate-activated hydrogen peroxide (Sarma *et al.*, 1989).

Peracids are stronger oxidizing agents than peroxide and consequently they are more effective in bleaching at lower temperatures. For example, peracetic acid, formed *in situ* from peroxide and acetic anhydride, has an adequate bleaching activity at 60°C . By incorporating 2,2'-bipyridine with peracetic acid, bleaching can be made effective as low as 30°C (Rucker, 1989).

Peroxide systems incorporating the enzyme peroxidase have the advantage of low peroxide concentration without high pH (Pedersen and Reesens, 1992).

Reductive bleaching is an alternative to peroxide/phosphate bleaching for wool. Although thiourea dioxide, hydrosulfite, and bisulfite bleach to an inferior whiteness level when compared to conventional peroxide, this can be compensated for by adding a surfactant. Surfactants, furthermore, offer

the added benefit of protecting wool's disulfide crosslinks (Gacén *et al.*, 1989, 1992, 1993).

The design of single-bath full bleaching, incorporating sequential oxidative (peroxide)/reductive (thiourea dioxide) steps, saves time, reagents, water and equipment when operated over the same time-frame as oxidative peroxide bleaching alone. Process parameters were chosen to reach comparable and superior whiteness to the conventional method (Arifoglu *et al.*, 1990; Cardamone *et al.*, 1992).

The following survey includes other process designs for bleaching systems which address energy and environmental concerns.

Survey of bleaching protocols

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

HOCl, catalysts: Mn(II), Co(II), Cu(I) hydroxides

Cotton staple, combed sliver

- Pretreatment of cotton by precipitation with metal salts
- Oxidative bleaching
- 30°C
- pH 4–11

Oxidation rate curves of exposure time versus cellulose oxygen consumption from hypochlorite decomposition showed a maximum rate for bleaching in the presence of manganese and cobalt at pH 7 and in the presence of copper at pH 7.5. The catalysis effect increased in the order: Co » Cu > Mn. Faster reactions produced more aldehyde groups than other oxycellulose forms. Aldehyde groups formed with copper oxidize more readily with subsequent hypochlorite bleaching (Nevell and Singh, 1986).

HOCl, cobalt sulfide

Cotton yarn

- Pretreatment of cotton by impregnation with cobalt chloride and sodium sulfide
- Oxidative bleaching at 30°C at pH 3–10

Cobalt sulfide accelerated hypochlorite oxidation of cellulose with maximum rate at pH 6.1–7.5. Maximum extent of oxidative degradation occurred at pH 7 where oxygen consumption, copper number, carboxyl value and alkali solubility (%) were greatest. Degradation increased with oxidant concentration. Oxycellulose groups were characterized by treatments with chlorous acid and sodium borohydride (Shenai and Narkhede, 1987).

NaOCl, soda ash, ammonium persulfate, sodium hyposulfite, sodium metasilicate, sodium percarbonate, hydrogen peroxide

Dyed fabric, especially blue jeans

- Two-step
- Continuous or batch processes
- Paste-form application for decolorization
- Acidic whitening
- Oxidative bleaching
- Whitening agent

Decolorization was applied to specific areas to introduce a white color area. The four-step chemical treatment process involved paste application, washing with an acidic whitening agent, oxidation bleaching, and washing in a bath containing acidic whitening agent. For sharp definition of pattern, process parameters for each step must be strictly regulated. The entire process was reported as requiring 20 min (Lin, 1989).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**HOCl, H₂O₂

Cotton hosiery knit

- HOCl/H₂O₂ separate bleaching after caustic boil, or
- H₂O₂ boil after caustic boil
- HOCl followed by cold H₂O₂ after caustic boil

Caustic boil followed by single-stage peroxide bleaching or hypochlorite bleaching followed by peroxide was recommended for required whiteness. Hypochlorite bleaching alone was not recommended to produce white hosiery (Tendulkar, 1993).

NaOCl, NaClO₂, H₂O₂

Jute fabric, grey and scoured

- NaOCl, 2 h, 30°C, 5–15 g/l, pH 11
- NaClO₂, 2 h, 95°C, 5–30% owf, pH 4.2
- H₂O₂, 30 min, 80°C, 0.5–4.0 g/l, pH 11

Bleaching jute fabric with NaOCl produced poor whiteness but this effect was reduced if scouring preceded bleaching. Scouring before NaOCl bleaching increased whiteness index by 6 units (from 40 to 46). With H₂O₂ bleaching, a value of 42.98 was obtained for whiteness index, and scouring before bleaching reduced this value. H₂O₂ bleaching was recommended as most satisfactory (Pandey et al., 1993).

NaOCl, H₂O₂, NaClO₂

Linen, grey fabric

- Bleaching sequence: NaOCl, H₂O₂, NaClO₂
- Modified sequence: NaClO₂, NaOCl, H₂O₂
- pH 4.5–11, 30–90°C, 60–180 min

Scouring/bleaching was more effective than grey-state bleaching. Fabrics scoured with 10 g/l sodium carbonate and 2 g/l surfactant, 30 min, 95°C, followed by bleaching with the combination NaOCl—H₂O₂—NaClO₂ showed 29.4% less weight loss and required 90 min less time. Whiteness index of these samples was comparable to more severe scour/bleach conditions. Fluidity was less and light fastness was the same. The modified combination NaClO₂—NaOCl—no rinse—H₂O₂ was cost-efficient and produced higher, more uniform whiteness (Goswami and Mukherjee, 1993).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

 NaClO₂ activated by triethanolamine (TEA)

Cotton cambric fabrics

- Single stage scouring/bleaching by padding
- pH 4.6
- 20–60°C
- 1–9 h
- Vary concentrations of scouring agent (emulsified perchloroethylene), NaClO₂, TEA

Optimum treatment conditions for good whiteness, absorbent fabrics, and minimum strength loss were: scouring agent 4.5% owf, 60°C, 5.5–6.5 h. At 60°C, less ClO₂ is liberated (Gulrajani and Venkatraj, 1986).

 NaClO₂, TEA, HC, (triethanolamine hydrochloride-activated sodium chlorite), scouring agent (emulsifier, perchloroethylene solvent, pine oil wetting agent)

Polyester/cotton fabrics 67/33

- Pad, store
- Combined scour and bleach
- 40–60°C
- pH 4.6
- 1–9 h
- NaClO₂, 0.0–0.8% owf

Canonical analysis from second-order polynomial equations showed that whiteness index was affected by concentration of bleaching agent, treatment time, and temperature. Bleaching agent concentration had the maximum effect on whiteness index. Sodium chlorite had a marginal effect on fabric strength. Optimal bleaching conditions: NaClO₂/TEA·HCl, 0.8/0.4% owf, treatment time 7–8 h, temperature 55°C, starting pH 4.6. Under these conditions evolution of chlorine dioxide fumes was not observed (Gulrajani et al., 1987).

 NaClO₂, formic acid, disodium phosphate, bleaching range to process 50 tons per day

Cotton knit, cotton tubular knits

- Select concentration temperature, pH to keep ClO₂ at a minimal level
- Continuous bleaching range
- Fabric in rope form
- 85°C
- 4–5 h
- Acidic

Sodium chlorite bleaching caused the least damage to cotton fiber: less weight loss, less grease, less wax from cotton in the effluent, and a fuller and softer hand. This system is recommended for bleaching fibers that are sensitive to alkali (rayon, acetate, silk) (Petrick, 1988).

Bleaching system**Textile substrate****Bleaching protocol***Remarks and reference*

NaClO₂, formic acid activator, non-ionic emulsifier, perchloroethylene

Polyester/cotton (67/33)

- Combine scour, bleach
- Padding
- Continuous high pressure steaming combined with foam
- NaClO₂, 0.2–1.8% owf
- 90–130°C

Whiteness increased with concentration of bleaching agent. This effect was greater than the effect of temperature and processing time. Temperature marginally affected whiteness. Optimal conditions: scouring agent concentration 2.0% owf; bleaching agent concentration 1.8% owf; temperature 120°C; processing speed, 68 s inside pressure chamber. Whiteness achieved was 79.88 units which was comparable to the conventional three-stage sequence: desize, scour, bleach. Wettability after treatment was satisfactory (Venkatraj and Gulrajani, 1989).

NaClO₂, formic acid, solar oven, scouring agent

Polyester/cotton suiting (67/33)

- Pad-batch
- Combined scour, bleach
- NaClO₂ concentration 0.25–1.5% owf
- pH 4.0
- 65–94°C
- 30–180 min

A solar oven was designed as a circular trough solar concentrator with a cylindrical absorber, which is a copper tube into which fabric rolls were placed. Solar radiation came directly to this tube. A quadratic polynomial was used to express the relationship among time, temperature, % NaClO₂ consumed, fabric whiteness and wetting time. Whiteness was most correlated to NaClO₂ consumed. Temperature and time made smaller contributions to whiteness. The same relationship or process variables applied to wettability. Fabric strength was retained and this represented an improvement over conventional bleaching. Optimal conditions: NaClO₂, 0.64–0.84% owf; scouring agent, 1.0% owf; pH 4.0; 150–180 min; 80–85°C (Gulrajani et al., 1990).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

 NaClO₂, H₂O₂ activator, wetting agent, Na₂HPO₄

Cotton, loomstate; cotton/polyester, loomstate

- Activation of NaClO₂ by H₂O₂ at pH 8 or 10 before bleaching
- Bleaching at 95°C at pH 8 or 10
- Concurrent desize, scour, bleach

Bleaching occurred by H₂O₂ induced activation of NaClO₂ by a free-radical mechanism. The bleaching effect of NaClO₂ increased with higher H₂O₂ concentrations. Whiteness increased with exposure time and pH, and in the absence of Na₂HPO₄. Higher H₂O₂ concentrations increased whiteness and wettability. Better results were obtained for all-cotton textiles. Copper number (aldehyde content) and carboxyl content were not greater than for unbleached textiles. Tensile strength loss was less at pH 10 but overall loss was not a detriment to recommending this system (El-Sisi et al., 1990).

 NaClO₂/K₂CrO₄, non-ionic wetting agent

Cotton, loomstate; cotton/polyester blend

- Pad, batch
- 90°C
- pH 4–8
- Concurrent desize, scour, bleach

Bleaching was based on activation of NaClO₂ by K₂CrO₄ through free-radical formation on cellulose by the interaction of Cr(VI) with OH groups. Optimum conditions for cotton: pH 6, 90 min, 90°C; optimum conditions for cotton/polyester: pH 6, 60 or 90 min, 90°C; in both cases, [NaClO₂] = 20 g/l and [K₂CrO₄] = 3 g/l. Whiteness indices of > 75 in cotton and in the blend were achieved in the presence of K₂CrO₄. Wettability improved by this treatment. Optimum conditions of time, temperature, and concentration could be chosen so that tensile strength would not fall below that of the loomstate fabric. Copper number was greater at low pH (Hafiz et al., 1991).

 NaClO₂/KMnO₄, non-ionic wetting agent

Cotton, loomstate; cotton/polyester blend

- Pad, batch
- 90°C
- pH 4–10
- Concurrent desize, scour, bleach

Bleaching occurred by permanganate-initiated hydroxyl free radicals. Whiteness was greater with $KMnO_4$ present and by increasing pH from 4 to 10. Wettability increased with $NaClO_2/KMnO_4$ concentration, exposure time, and it was greatest at pH 4. Tensile strength decreased with concentration and time and was not influenced by pH. Copper number and carboxyl group content increased with concentration and was greater at lower pH. These values were not lower than untreated fabric. Results suggested selective, primary attack of oxidant on noncellulosic colorants before attack on cellulose itself (El-Rafie et al., 1990, 1991).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

NaClO₂, sodium hydrosulfite prescour, non-ionic wetting agent

Linen, loomstate

- [NaClO₂] = 2–10 g/l
- 65–95°C
- 1–3 h
- pH 4–10

A reductive scour with Na₂CO₃ resulted in fabrics more susceptible to bleaching with NaClO₂. Maximum whiteness was with 8 g/l NaClO₂, 2.5 h, 95°C, pH 4–6. NaClO₂ bleaching after reductive scour resulted in the best bleaching effect when compared to conventional scouring that was followed by bleaching using NaOCl, NaClO₂, and H₂O₂ in succession. The cessation of bleaching at pH 8–10 was taken as evidence of a free-radical mechanism for inducing NaClO₂ activation whereby the redox system 'fiber reductant/NaClO₂, oxidant' prevails (Abou-Zeid et al., 1991).

NaClO₂/HCHO, non-ionic wetting agent

Cotton, loomstate

- Pad, batch
- 70°C
- pH 10
- Consecutive desize, scour, bleach

Bleaching was based on the activation of NaClO₂ by formaldehyde. The incorporation of formaldehyde with NaClO₂ avoided the problem of chlorine dioxide formation from an acid NaClO₂ bleach bath and increased the rate and the amount of sodium chlorite decomposition. Raising the bleaching temperature enhanced this effect. The presence of formaldehyde contributed to better wettability, higher whiteness, and greater weight loss with increasing concentration of formaldehyde. Copper number and carboxyl content of the bleached fabrics were lower than those of the unbleached fabrics. Tensile strength loss could be controlled by regulating formaldehyde concentration, time, and temperature of bleaching (Hebeish et al., 1993).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

NaClO_2 , additives, with and without buffer (ammonium sulfate/tetrasodium pyrophosphate), H_2O_2

Synthetic fibers, cellulosic fibers, viscose, linen yarns

- $[\text{NaClO}_2] = 0.75 \text{ g/l}$
- pH 3.8
- 90°C
- 30 min
- Component streams: J-box, washing machine, circulating-liquor machine
- Production unit: pretreatment, dyeing, finishing

AOX content studies of NaClO_2 bleaching liquor showed that NaClO_2 is ecologically acceptable. Without buffer, bleaching liquor from bleaching synthetic fibers was 2.6–2.8 ppm AOX, and it was 0.6–1.2 ppm AOX with buffer. These values were below the 3.0 mg/l (ppm) allowable in Germany's component streams. A bleaching NaClO_2 liquor could be selected for viscose to limit AOX to 1.3 ppm. AOX bleaching liquors from NaClO_2 bleaching of linen yarns in stage 1 were 8.0 ppm, and were 1.2 ppm in H_2O_2 stage 2 bleaching. Combined wastewaters produced a component stream below the limit AOX value. Alkaline process by boil-off before bleaching drastically reduced AOX loading and this process produced acceptable whiteness levels (Kleber, 1993).

$\text{H}_2\text{O}_2/\text{NaOH}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, EDTA, wetting agent, Fe^{3+} , Cu^{2+}

Polyester/cotton blend, (68/32) fabric, loomstate

- Simultaneous desize, scour, bleach (DSB)
- Winch-beck
- 95°C
- 60 min

Increasing $[\text{MgSO}_4]$ decreased H_2O_2 decomposition and led to higher whiteness, less wettability and no strength loss. $[\text{NaOH}]$ 4–6 g/l was preferred. Above this concentration H_2O_2 decomposition was favored, whiteness and wettability did not improve, polyester hydrolyzed, cellulose degraded, and tensile strength of the fabric was lost. $[\text{H}_2\text{O}_2, 35\% \text{ w/v}]$ 2–14 ml/l did not affect H_2O_2 decomposition. There was no improvement in whiteness above 6 ml/l. Within this range of $[\text{H}_2\text{O}_2]$, increasing concentration led to strength loss. Recommended was 4–6 ml/l $[\text{H}_2\text{O}_2]$. The effect of Cu^{2+} ions to catalyze H_2O_2 decomposition was greater at higher metal ion concentrations and resulted in whiteness loss but better wettability. Mg^{2+} and EDTA stabilized H_2O_2 decomposition in alkaline medium (Hebeish and El-Bazza, 1985).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference****H₂O₂****Cotton cambric fabrics**

- Pad fabric with H₂O₂/sodium silicate and 0.1 M buffer
- Buffer: borax (pH 9), sodium carbonate/sodium bicarbonate (pH 10), sodium hydroxide and disodium hydrogen phosphate (pH 11)
- 70–95°C
- Vary exposure time
- Sizes: acrylic and starch

pH buffers increased the rate of H₂O₂ decomposition. Fabrics with acrylic size showed a slower rate of H₂O₂ decomposition but size caused more damage to cellulose. Copper number and carboxyl content for acrylic-sized fabrics were higher than for starch-sized fabrics. In the buffered system, increase in alkalinity (pH 9–11) formed oxycelluloses of lower aldehyde content (lower copper number) and higher carboxyl content. By adding pH buffers to the bleach bath either bleaching time or amount of peroxide could be reduced (Sukumar and Gulrajani, 1985).

H₂O₂, amides: (urea, benzamide, formamide, N,N-dimethylformamide (DMF))**Cotton poplin fabric, desized, scoured**

- Pad/batch
- Room temperature, 60°C or 90°C
- 3–24 h
- pH 8

Amides were incorporated into the conventional hydrogen peroxide bleach bath to facilitate the controlled decomposition of peroxide in order to shorten bleaching time. Decomposition of peroxide was faster with amides in the bleach bath. The sequence in rate of peroxide decomposition resulting from the presence of amides was formamide > DMF > benzamide > urea. The best whiteness was obtained with benzamide, thereby indicating that the whiteness of the bleached fabrics was not the result of peroxide decomposition. The increase in whiteness index with increase in time and temperature, when bleaching in the presence of amides was most pronounced for bleaching at 20°C (increase of 5–6 units). This effect was only marginal at 60°C or 90°C. Amide activation of peroxide was recommended in cold bleaching processes (Das et al., 1986).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H_2O_2 , NaOH, borate-silicate

Jute fibers, raw and demineralized

- 80°C
- 60–240 min
- pH 8.0–10.0

Bleaching was most effective at pH < 9.0 in terms of whiteness, with 8.5 the best for demineralized fibers. At pH 8.0 there was minimum H_2O_2 decomposition. Proposed from these findings: bleaching with H_2O_2 , in the borate silicate system, is through perhydroxyl ions from H_2O_2 dissociation. Brightness increased up to 40 min bleaching time, and beyond 40 min there was strength loss. H_2O_2 consumption is minimized and brighter jute is obtained by demineralizing jute before bleaching. At pH 8.0–8.5, there was increased bleaching efficiency of H_2O_2 in the borate-silicate system. This system reduced bleaching time by 33% (Sikdar et al., 1987).

H_2O_2 , sodium silicate, sodium carbonate, emulsifying system (non-ionic detergent, trichlorethylene, pine oil)

Coir fibers

- Sequence: prewet, hypochlorite bleaching, peroxide bleaching, wash, sun dry
- H_2O_2 (50%): 6%–8%
- 5–22 h
- 80°C

Both hot and cold bleaching could be used. Subsequent peroxide bleaching nearly doubled the brightness achieved after hypochlorite bleaching. Hot bleaching required 5 h; cold bleaching 20–22 h. More strength was retained after cold bleaching. Hot bleaching caused 50% reduction in strength and cold bleaching 40% (Mandavawalla and Tendulkar, 1988).

H_2O_2 , NaOH

Cotton fabrics, grey

- Single stage cold-pad-batch for desize, scour, bleach
- 4–24 h
- 20–80 ml/l of 30% H_2O_2

Fabric weight loss did not increase when $[NaOH] = 30–40$ g/l and $[H_2O_2] = 40$ ml/l. Tensile strength decreased as NaOH and H_2O_2 concentrations increased. At 40 ml/l H_2O_2 and 40 g/l NaOH, strength loss was 6.0%, weight

loss was 5.3%, and absorbency was 5.9 s. Batching time of 8 h was minimum for good whiteness and bleaching efficiency but this time could be extended to 12 h. Adequate wettability and whiteness for dyeing pastel shades were achieved in the system without silicate stabilizer (Jamadagni et al., 1988).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H₂O₂, sodium silicate, perchloroethylene scour solvent**Cotton fabric, grey**

- Combined desize, scour, bleach
- Solar energy accelerated
- Pad-batch
- pH 10.5
- 20–110°C
- 0–90 min
- H₂O₂: 0.05, 1.8, 2.15%

Temperature was the most significant variable. Maximum whiteness was achieved at 80–95°C. Solar radiation led to high rates of H₂O₂ decomposition at temperatures above 103°C. Optimal conditions: 4% scouring agent, 1.8% H₂O₂ (100%), 2% sodium silicate, <100°C, 90 min, pH 10.5. When fabrics bleached by solar energy were compared to those bleached conventionally, all parameters (weight loss, %; strength, kg/g; whiteness index and wetting times) were approximately the same. Solar energy provided chemical and thermal energy savings (Gulrajani and Gupta, 1989).

H₂O₂, NaOH, persulfate, silicate**Cotton materials**

- Pretreatment: steaming, 5 min
- Treatment: alkaline H₂O₂, room temperature, 1–10 h
- Variables: [H₂O₂], [NaOH], [persulfate], time

Breaking strength was influenced by [NaOH] and treatment time. High breaking strength was found with 10 g/l and 5 h treatment. Increased water absorption was found at increasing [H₂O₂] and [persulfate]. Optimal values for breaking strength were found from the multiple regression equation of the dependence of water absorption on these variable pairs: [NaOH]–[H₂O₂], [NaOH]–[persulfate], [NaOH]–time, [H₂O₂]–[persulfate], [H₂O₂]–time, [persulfate]–time. Whiteness index was determined similarly, and maximum whiteness were achieved with 70 g/l H₂O₂ and 14 g/l persulfate. Optimal conditions for whiteness index were: [H₂O₂], 40 g/l; [persulfate], 10 g/l; [NaOH], 20–40 g/l. Compared to the classical two-stage hypochlorite/alkaline peroxide boiling treatment, low temperature alkaline H₂O₂/persulfate bleaching improved breaking strength by 21% but whiteness was lowered by 4%. Subsequent optical whitening increased whiteness to levels comparable to those achieved by the classical bleaching treatment (Muresan et al., 1989).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H₂O₂, persulfate activator**Cotton fabrics**

- Preparation treatment: HOCl
- Pad/batch H₂O₂, alkaline
- Vary [H₂O₂], [NaOH]
- 25–45°C

Peroxide consumption could be reduced by enzyme desizing followed by HOCl and sequential H₂O₂-activated potassium persulfate. Whiteness increased with increasing [NaOH], [H₂O₂], and temperature. Fluidity increased with increase in [NaOH]. Wicking time was in general less than after conventional H₂O₂ scouring/bleaching when done at high temperatures. Absorbency was better at 25°C with [NaOH] = 3.25 owf, [H₂O₂] = 0.6% owf. Conditions for freeing fabric from motes (immature seeds covered with fuzzy fibers): [NaOH] > 1.5%; [H₂O₂] > 0.6; T > 35°C. The H₂O₂/persulfate system was described as a one-step, low temperature scour/bleach process for enzymatically desized and 'chemicked' fabrics (Sarma et al., 1989).

H₂O₂/acetic anhydride (in situ formation of peracetic acid), 2,2'-bipyridine (bipy), sodium lauryl sulfate (SLS), transition metal cations, sodium tetraborate (borax)

Cotton plain weave, desized, scoured

- [Peracetic acid], constant
- Vary [bipy] and [SLS]
- pH 4.75–10.0
- 20–60°C

Bleaching was catalysed by tris-chelate formation from bipy/metal ion complexation with Fe²⁺ in cotton. The presence of sodium lauryl sulfate reduced peracetic acid decomposition by its association with the tris-chelate. Maximum whiteness, 73.08 WI units, was achieved at pH 7 and it decreased to 55.30 at pH 10. This indicated that increasing pH caused decomposition of peracetic acid. Higher WI was achieved with the tris-chelate at all bleaching temperatures. Maximum whiteness was obtained at 50°C (79 WI). Higher bleaching temperatures contributed to peracetic acid decomposition. The most effective metal ions used were cobaltous, ferrous, and manganous. The system was effective at 30°C (Rucker, 1989).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H₂O₂, metal salts, FeSO₄, CuSO₄, CoSO₄, sequestering agents: Na₄P₂O₇, sodium oxalate, Na₂EDTA

Wool jersey knit fabric, dark pigmented Karakul fiber

- Two-step mordant/bleach
- Mordant: 70°C, 90 min
- Bleach: pH 8.6–8.8, 55°C, 2 h

Order of increasing fiber damage: copper(II) > iron(II) > cobalt(II). Optimal conditions for mordanting and bleaching pigmented fibers were as follows: Mordanting: CoSO₄, pH 3, 80°C, 60 min; bleaching: H₂O₂/EDTA, pH 9, 65°C, 60 min. Cobalt(II) showed less damage to wool than the conventional iron(II) system. The cobalt bath was more stable, but more H₂O₂ was needed to achieve similar bleaching effects. Reductive after-treatment was not necessary because this bleaching did not discolor wool (Trollip, 1990).

H₂O₂, thiourea, thiourea dioxide, or sodium hydroxymethanesulfinate

Woolen flannel, scoured

- Single-bath sequential oxidative/reductive bleaching
- [thiourea] 3.07–7.69 g/l
- H₂O₂/alkaline, 60°C, 1 h followed by thiourea addition, pH 7.4–7.6 and continued bleaching at 60°C, 25 min

The variables [thiourea], oxidative peroxide bleaching time, reductive bleaching time and temperature were examined to optimize bleaching efficiency. Whiteness index was greatest at [thiourea] ≥ 4.61 g/l and after 15 min beyond thiourea addition. Maximum temperature for oxidative/reductive bleaching with the acceptable alkali solubility. (%) of 20.12 ± 0.34 was at 60°C. Bleaching efficiency was markedly improved with the H₂O₂ bleaching alone. In situ conversion of thiourea by reaction with residual H₂O₂ from oxidative bleaching in step 1 produced thiourea dioxide, which hydrolyzed at pH 7.5 to form the reductive species, sulfinate anion (Arifoglu et al., 1990).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H_2O_2 , Hercosett cationic resin, anionic optical brightener (OBA)

Wool knit fabric

- Pad/dry/cure
- Ternary dispersions of resin, peroxide, OBA
- 20–80°C
- 1–20 min
- pH 7.0
- Vary OBA from 1.5 to 3.5 g/g resin

Resin/OBA/ H_2O_2 aqueous systems showed acceptable loss in ball penetration resistance (BPR, %), cysteic acid content and alkaline solubility. Least damage was at lowest temperature, 20°C, and shortest exposure time, 1 min. BPR (%) after 17 min 15 s at 71°C was within the acceptable 10% level. Whiteness levels above 100% were achieved at 80°C in 10.5 min. Shrinkage increased with temperature and was highest at 71°C, 3 min 45 s (De la Maza et al., 1992).

H_2O_2 , urea, nonionic wetting agent

Linen fabrics scoured and unscoured

- Bleach grey fabric
- Separately bleach scoured fabric
- Vary H_2O_2 and urea concentrations
- pH 4–10
- 30–150 min
- 40–95°C

Optimum bleaching conditions: H_2O_2 (7 g/l), urea (8 g/l), nonionic wetting agent (1 g/l), pH 6, 95°C, 2 h. Mechanism for peroxide oxidation: free-radical, involving hydroxyl and perhydroxyl free radicals, and perhydroxyl ions, depending upon pH. This mechanism was promoted by the presence of urea. Within the concentration range for urea of 2–12 g/l, whiteness increased with urea concentration, irrespective of pH. Whiteness increased nevertheless in the order pH 6 > pH 8 > pH 4 > pH 10 (El-Rafle et al., 1992).

H_2O_2 with peroxidase enzyme and O_2 , with oxidase enzyme, bleach boosters (metal or halide ion or organic compound), cellulose, pumice

Dyed textiles; cotton denim, indigo-dyed

- Simultaneous bleaching and formation of localized color variation
- pH 4–10

The system was effective for concentrations of H_2O_2 < 100 mM. An advantage

was that the wastewater was almost colorless. The bleaching process was effective for textiles dyed with synthetic azo dyes, natural dyes or synthetic dyes that were nature-identical (such as indigo). Optimal conditions: enzyme protein per liter of bleach liquor, 0.1–10 mg/l; pH 5–9; 55°C; 60 min (Pedersen and Reesens, 1992).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H_2O_2 (alkaline), thiourea (thiourea dioxide *in situ* formation), hydrolysis of thiourea dioxide to form sulfinate reducing species and urea

Wool fabric

- Sequential oxidation/reduction
- $[H_2O_2]$ 22, 16 or 8 g/l
- 50°, 55° or 60°C
- 85 min

ARS patented bleaching showed greater whiteness than conventional alkaline bleaching. Equal whiteness was found with 16 g/l peroxide in the ARS process where thiourea was 70% ow 100% H_2O_2 and with 22 g/l conventional alkaline H_2O_2 bleaching over the same time and temperature settings. NMR spectroscopy was used to determine the amount of thiourea to add in the reductive step for complete conversion to sulfinate and urea. Multiple regression equations were predictive for establishing temperature and $[H_2O_2]$ values to achieve certain whiteness levels. By the Kawabata system (Kawabata, 1980) ARS bleached fabrics showed greater softness, flexibility, and smooth-feeling than conventional H_2O_2 bleached. Comparisons were made with conventional bleaching with alkaline H_2O_2 (22 g/l, 60°C) within the same time limits. Better whiteness was achieved using ARS bleaching under the following conditions of $[H_2O_2]$ for the oxidative step, $[H_2O_2]$ for reaction with thiourea, and run temperature: 22, then 16 g/l at 50°C; 22, then 8 or 16 g/l at 60°C. ARS bleaching resulted in some strength loss (3–14%) compared to conventional peroxide bleaching (Cardamone et al., 1992; Marmer et al., 1994).

 H_2O_2 , NaOH

Cotton fabric, sized and polyester/cotton fabric, sized

- Continuous one-stage, desize–scour–bleach
- pH 12.5
- 23–95°C
- $[NaOH]$ 0.02–2.8 g/l
- $[H_2O_2, 35\%]$ 0.1–2.8 g/l

Degree of desizing was time, temperature and $[NaOH]$ dependent. At $[NaOH]$ 2% owf, increasing the peroxide concentration reduced the rate of desizing. H_2O_2 catalytically initiated hydrolysis of size, most effectively at 0.1% owf $[H_2O_2]$. $[H_2O_2]$ was the most significant factor in whiteness; whiteness increased with time, temperature, and $[H_2O_2]$. Only fabrics treated at 65–95°C were absorbent. Increasing time, temperature, and $[H_2O_2]$ increased rate of

size removal, which was complete at temperatures below 65°C. Fluidity tests showed no chemical damage from treatments (Levene and Prozan, 1992).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H₂O₂, enzymes (xylanase and cellulase)

Jute fibers

- Enzyme pretreatment
- pH 5
- 60 min
- Room temperature

Lignin and hemicellulose content decreased by 3.9% after enzyme/bleach treatment. Loss in dry weight was 5.23%. A proper balance of xylanase and cellulase enhanced bleaching. Xylanase contributed to whiteness and cellulase to enhanced swelling or softening (Kundu et al., 1993).

H₂O₂, Na₂CO₃, NaHCO₃, urea, trisodium pyrophosphate (TSPP), ethylene diaminetetraacetic acid (EDTA), NaCl

Silk yarn, mulberry, 20/22

- Combined degumming and bleaching in one bath
- Sodium lauryl sulfate (22 g/l)
- EDTA, 1 g/l
- TSPP, 3 g/l
- Nonionic detergent, 1 ml/l
- H₂O₂ (30%), 13 ml/l
- pH 10.1
- 1 h
- 90°C

Addition of urea up to 50 g/l increased whiteness; from 50 g/l to 150 g/l, whiteness decreased. Breaking load was not affected up to addition of 100 g/l urea, but at 150 g/l urea breaking load decreased by 28%. The improvement in whiteness by 15% by urea addition was attributed to amide complexation with H₂O₂ to facilitate faster but controlled peroxide decomposition. Increased effectiveness, less time and chemicals are benefits from using combined degumming and bleaching with H₂O₂ and EDTA and TSPP. Conditions can be optimized for controlling weight loss and enhancing whiteness by the addition of urea and NaCl (Saligram et al., 1993).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

H₂O₂, alkali**Cellulose and rayon textiles (CS₂-free and modal)**

- Alkaline boiling off and cold pad-batch bleaching
- Alkaline boiling off and hot bleaching
- Alkali treatment and cold pad-batch bleaching
- Alkali treatment and hot bleaching

Carbon disulfide-free rayon had higher strengths and whiteness than cotton, viscose, and modal rayons. Abrasion resistance was comparable to modal, less than cotton, and higher than viscose. Absorbency was similar to modal and better than viscose and cotton. Least damage was with alkali/H₂O₂ cold pad-batch bleaching. No excessive strength losses were found (Hellwich et al., 1994).

Ozone, steam**Cellulosic garments, dyed and wet; applicable to vapor and cellulosic blends**

- Batchwise or continuous
- Ozone: 10–100 mg/l
- 40–100°C
- Recycle excess ozone to treat effluent

This method was proposed as an alternative method to stone washing for decolorizing or fading dyed garments. Requirement: the dye must be ozone reactive. Blocking agents on the garment determined the desired effect. Ozone-treated fabrics retained more abrasion resistance and strength than NaOCl-bleached fabrics. Shading effects were possible with ozone treatment that were not possible with stone washing. Ozone treatment corrected for yellowed background areas that result from conventional discoloration methods (Wasinger, 1992).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference****KMnO₄**

Cotton cloth, desized, scoured, cotton hanks

- KMnO₄, 0.5% owf
- H₂SO₄, $\frac{1}{4}$ part KMnO₄
- HOAc, $\frac{3}{4}$ part KMnO₄
- Room temperature
- 30 min

Tensile strength and copper number losses were less than after conventional hypochlorite bleaching. Carboxyl content was lower for KMnO₄ bleaching of cotton cloth but higher for cotton hanks. Whiteness of permanganate-bleached fabrics was comparable to fabrics bleached by hypochlorite. When considering energy and time expenditure, the permanganate process was less costly than conventional hypochlorite bleaching, followed by hydrogen peroxide bleaching. Estimate production cost saving was 16.0% and saving in process time 30% (Lokhande and Wasif, 1991a).

KMnO₄, H₂O₂

Polyester/cotton fabric (48/52) (desized, scoured, and mercerized)

Formulation I: bleach

- KMnO₄
- H₂SO₄
- HOAc
- Oxalic acid
- NaOCl
- H₂O₂
- Sodium silicate
- Sodium hydroxide
- 85°C, 2 h

Formulation II: scour, mercerize, bleach

- NaOCl
- KMnO₄
- Oxalic acid
- H₂O₂
- Sodium silicate
- Sodium hydroxide
- 85°C, 2.5 h

When compared to conventional $\text{NaClO}_2/\text{H}_2\text{O}_2$ bleaching formulations, formulations I and II produced less strength loss with comparable whiteness values. Slightly lower copper number values were obtained from KMnO_4 bleaching when compared to conventional bleaching. Bleaching by formulations I and II cost substantially less than conventional bleaching in terms of chemicals, energy comparable and time (Lokhande and Wasif, 1991b).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**Peracetic acid, H₂O₂

Cotton fabric

- Ultrasonic radiation
- Apply peracetic acid (15%) with H₂O₂ (30%)
- Adjust pH with caustic soda
- 50°C
- 1 h
- pH 1–7

Addition of peracetic acid, 1% owf at 50°C, pH 6 with ultrasound, produced fabric brightening. This brightness was not exceeded above 2% owf concentration peracetic acid. Bleaching by peracetic acid was markedly increased by ultrasound at pH 1–4. A higher degree of whiteness was achieved at pH 6. Damage to fibers within the pH range was less than damage from conventional hydrogen peroxide bleaching. Peracetic acid with concomitant ultrasound could be used at low temperature and without activators to achieve comparable whiteness, and less damage when compared to conventional peroxide bleaching (Poulakis et al., 1991).

Peracetic acid (PAA) generated from the equilibrium solution of H₂O₂, and HOAc with subsequent H₂O₂/alkaline bleaching

Cotton jersey knit fabric and yarns; linen

- Continuous bleaching
- Fabric impregnation
- Multistage
- Rope form; J-Box
- Open width, winchbeck
- pH 3–9
- 20–80°C
- 20–80 min
- [PAA] = 1.75–8.75 g/l
- With and without metal ions

High brightness for cotton was achieved with [PAA] 1.5–2.5 g/l at room temperature, followed by H₂O₂/alkaline treatment at 90°C. For linen yarns, the recommendation was scour, alkaline H₂O₂ bleaching and a PAA bleaching stage at pH 5–6, 80°C. In all cases, PAA bleaching produced less fiber damage than NaOCl bleaching in the optimum pH range 6–7, 50–80°C, 20 min. Brightness increased with [PAA] and with temperature. The PAA system

showed overall less fiber damage than NaOCl systems. Unlike H_2O_2 systems, where metal ions can catalytically degrade fibers, with PAA Fe ions have no detrimental effect and there is no loss in brightness. Continuous scour and PAA bleaching at room temperature produced whiteness values equivalent to NaOCl/ H_2O_2 bleaching with less damage to fiber (Steiner, 1993).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

NaHSO₃, Na₂S₂O₄, NaHSO₂·CH₂O, KMnO₄, Na₂O₂ (sodium peroxide), H₂O₂, NaBO₂

Silk, mulberry and Tasar varieties, degummed

- NaHSO₃: 5% owf, 1 h, 60°C
- Na₂S₂O₄: 3% owf, 2 h, 50°C
- NaHSO₂·CH₂O: 24%, 30 min, boil
- KMnO₄: 0.25% owf, 30 min, room temperature
- Na₂O₂: 0.5% owf, pH 8–8.5, 4–5 h, 65°C
- H₂O₂, EDTA: 13 ml/l, 35%, pH 8–8.5, 2–3 h, 70°C
- H₂O₂, Na₂SiO₃: 1 h, 90°C
- NaBO₂·H₂O₂: 1% owf, pH 9.2, 1 h, 80°C

Both oxidative and reductive bleachings including sodium formaldehyde sulfoxylate, HOCH₂SO₂Na or NaHSO₂·CH₂O, were necessary to whiten silk varieties. Degumming increased whiteness, decreased yellowness, and caused loss in moisture by ~5% and loss in tenacity by 7%. Highest whiteness was found by bleaching with H₂O₂·Na₂SiO₃, followed by H₂O₂, EDTA. Bleaching with H₂O₂·Na₂SiO₃ showed lowest loss in moisture regain. Average tenacity loss from all bleachings was 27%, but degradation was least by H₂O₂. Average loss in moisture regain was 16% from all bleaching. KMnO₄ and NaBO₂·H₂O₂ gave only negligible increase in whiteness. Na₂S₂O₄ and NaHSO₂·CH₂O were unstable and not recommended. The bleaching agent recommended for mulberry and Tasar silk was H₂O₂ with sodium silicate stabilizer (Shukla et al., 1993).

NaHSO₃, sodium lauryl sulfate (SLS)

Wool tops

- [NaHSO₃] = 3 g/l
- [SLS] = 5 g/l
- 50°C
- 2 h
- pH 3.0–6.5
- [SLS] = 0–10 g/l at pH 5.5

The presence of SLS imparted protection of wool's —S—S— bonds. When compared to the untreated sample, SLS contributed to increased whiteness and this increase was constant within the pH range 3.0–6.5. Best results were obtained at pH 5.5–6.5, where cysteine content was lowest and whiteness was highest. Optimal conditions: [NaHSO₃], 4.5 g/l; [SLS], 5 g/l; bleaching time, 1 h; bleaching temperature, 50°C; pH 5.5 (Gacén et al., 1993).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

Sodium hydrosulfite, sodium laurylsulphate**Wool tops**

- [Hydrosulfite], 5 g/l
- 2.5 h
- 60°C
- pH 3, 4, 5, or 6
- [SLS] = 0, 2.5, 5, or 10 g/l

Optimal conditions for hydrosulfite bleaching: [hydrosulfite], 3.5–5 g/l; [SLS], 2.5–5 g/l; pH 5–6; 1–2 h; 55–60°C. Under these conditions, the presence of SLS reduced cysteine content by 27% and increased whiteness by five units (Gacén et al., 1989).

Thiourea dioxide (TD)**Wool**

- [TD] = 1.5–3.0 g/l
- 55–85°C
- 1–4 h

Increased temperature, [TD] and bleaching time improved whiteness. Temperature increase most highly influenced cysteine content. There was a linear dependence of [TD], temperature, and treatment time on cysteine content. At higher temperatures, strength losses were greater. A maximum acceptable cysteine content of 1.5% was established at 65°C after 60 min of bleaching, or at 80°C after 30 min (Cegarra, 1988).

Thiourea dioxide (TD), sodium laurylsulfate (SLS)**Wool top**

- [TD] = 1.5 g/l
- 70°C
- 2.5 h
- [SLS] = 0.3 or 5 g/l
- Removal of SLS at pH 6.5, 8 or 9

Most efficient removal treatment for SLS after TD bleaching was at pH 9 and 45°C, which reduced SLS retention to 1.6–1.7%. SLS removal resulted in decreased whiteness but no change in yellowness. Even after SLS removal, wool bleached with SLS present was whiter than when bleached without it. The presence of SLS with or without TD increased whiteness (Gacén et al., 1992).

Bleaching system**Textile substrate****Bleaching protocol****Remarks and reference**

Photobleaching, H₂O₂, sodium formaldehyde sulphonylate, thiourea dioxide

Wool fabric

- Blue light illumination
- Dry heat photobleaching, 105°C, 1 h
- Simulated sunlight photobleaching, 40°C, 48 h

Samples, untreated and bleached by several processes (including peroxide, sulphonylate, thiourea dioxide, dry photobleaching, and catalyzed photobleaching) were evaluated for brightness after subjecting them to the following aftertreatments: boiling, Xenotest exposure, sunlamp and dry heat exposures. In each after-treatment, reversion of brightness was measured. Xenotest and catalyzed photobleaching increased brightness of all samples to the greatest extent. When compared to conventional bleaching, photobleaching did not produce a more stable brightness. When the reflectance of wool was increased by bleaching, degradative processes clearly resulted in subsequent reflectance losses (Simpson, 1990).

Visible radiation, UV radiation, H₂O₂/blue light, thiourea dioxide, sodium formaldehyde, sulphonylate, sodium dithionite

Wool fabric

- Dry photobleaching
- Wet photobleaching

Reflectance properties of photobleached and conventionally bleached fabrics were reported. Some treatments were in the presence of blue light illumination. Dry photobleaching at ambient temperature for 36 h using fluorescent tubes did not alter brightness but the presence of reducing agents increased brightness. Alkaline peroxide in the presence of blue light rapidly brightened the samples in 20 min. Maximum reflectance over the 400–650 nm range was found for fabrics bleached by peroxide-catalyzed photobleaching. Emission curves of bleached samples with excitation at 290 nm showed that conventional bleaches increased fluorescence at 340–350 nm. Photobleaching in the presence of oxidizing or reducing agents caused a 10–15 nm red shift in the wavelength of maximum absorption. Excitation with 350–360 nm radiation showed that all bleached samples except those that were dry photobleached had greater fluorescent emissions. High pH oxidative bleaching in the presence of blue light produced greater whiteness than bleaching by conventional means and this altered wool's fluorescence pattern. These studies followed the changes in tryptophan with wool degradation (Simpson, 1992b).

Bleaching system

Textile substrate

Bleaching protocol

Remarks and reference

Photobleaching: argon ion laser 480 nm and 351 nm; north light fluorescent lamps

Wool fabric; raw Merino wool; normal yellow color wool

- Wet and dry states
- Monochromatic and filtered light
- Measurements by diffuse reflectance and fluorescence spectroscopy
- Ambient temperature

UV radiation produced a rapid increase in the natural fluorescence of wool. Dirty wool showed smaller increases in fluorescence upon irradiation. Wet fabrics irradiated by filtered blue light became progressively whiter but did not increase in fluorescence intensity. The enhancement of whiteness from photobleaching was not attributed to increased fluorescence but to a possible oxidation mechanism for destroying yellow chromophores. Blue light irradiation did not result in a difference in fluorescence intensities when clean and dirty wool staples were compared. Dry and wet fabrics yellowed from UV irradiation at 351 nm and whitened from exposure to 488 nm irradiation. This effect was greater for wet fabrics (Collins and Davidson, 1993).

FWA, silicone shrink-resistant resin, acrylic resin, chlorinated organic solvent

Woolen cloth, bleached

- FWA incorporated into acrylic resin
- Sequential or consecutive application of silicone and acrylic resins with FWAs
- Padding
- FWA, 2.5% owf resin

Highest whiteness was achieved with satisfactory rate of photo-yellowing when silicone was applied before applying the acrylic emulsion that contained the suspended FWA. This result could be achieved only with high add-on levels. The improvement in whiteness was moderate when compared with conventional FWAs. Up to 5% resin application did not affect fabric hand and improved brightness by 3%. The best results for area shrinkage resulted from applying the silicone finish first. The drawback is that 10–14 days were needed for full curing of the silicone. The treatment resulted in 1% loss in brightness upon storage but the rate of photo-yellowing was significantly reduced. When silicone was applied over the acrylic resin, insufficient shrinkproofing was found. Applying silicone and acrylic resins together showed an improvement in fabric hand (Levene, 1987).

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