Chapter 11
COMBINED PRE-TREATMENT PROCESSES OF TEXTILES

11.1 Introduction

Now-a-days all efforts in the field of pre-treatment processes of textiles are directed towards shortening and simplification of the treatment. In the conventional preparation, the desizing, scouring and bleaching processes are carried out seperately at high temperatures, requiring the use of large amount of thermal energy. In order to minimise energy consumption it has become necessary to combine several pre-treatment stages by reducing number of operations or by shortening the reaction time. Although several new processes and some continuous and semi-continuous machineries have been developed, the ideal of a truely single stage process employing only one desizing cum bleaching stage suitable for all qualities of cloth and end uses, has not been developed so far. Process integration to enable integrated desizing/scouring, scouring/bleaching or desizing/scouring/bleaching continues by boosting the chemical recipe to improve the removal and decolourisation of impurities. Low energy chemical pre-treatment of textiles using higher concentrations of chemicals in order to integrate the processes can work well if the process is carefully controlled. Many methods have been reported and a number of low temperature (25-45°C) batch scouring and bleaching processes are available [1-10] combining two or all the three stages into two stage or single stage process. In all these accelerated processes, cost savings are obtained in steam, water, electricity and labour with little increase in chemical costs. The brief account given in this chapter aims at presenting a bird's eye view in the area of combined pre-treatment processes.

11.2 Combined Scouring and Desizing

Many combined scouring and desizing processes are developed but these processes are particularly useful if the sizes are not intended to be recovered [11-13]. Alkaline hydrogen peroxides and peroxy compounds such as persulphate, perphosphate, peroxydiphosphate can be used as oxidative desizing agent and free radicals are produced favouring size degradation rather than bleaching. However, some bleaching does also take place under these conditions.

A combination of peroxy compound and caustic soda at elevated temperature can effectively combine desizing and scouring conditions. In this process, the fab-

ric is treated with a solution containing 0.2% potassium persulphate and 4% sodium hydroxide and then steamed in J-Box at 95⁰C for 85 min, washed and dried. This combined process of cotton fabric is more or less adequate with a fluidity of about 1.8.

In the pad-steam process, the fabric is padded with a solution containing 70 g/l caustic soda, 3 g/l sodium persulphate and 10 g/l non-ionic detergent at 40⁰C with a wet pick-up of about 80% and then the fabric is steamed for 12 min at 102⁰C. The fabric is then washed thoroughly in an open soaper with a temperature of about 98⁰C in the first and second, 80⁰C in the third and 60 and 50⁰C in the fourth and fifth compartments respectively.

Grey fabric can be simultaneously desized and scoured by making use of a suspension of enzyme, a chlorinated solvent and surfactant solution (Markal II process, Chapter 4).

11.3 Combined Scouring and bleaching

Single stage bleaching processes using hydrogen peroxide require some additional chemicals that can act as activator, stabiliser, surfactant and scouring agent. Strongly alkaline solution of hydrogen peroxide has been advocated for such combined processes. Sodium persulphate and potassium persulphate boost the single stage operation in presence of hydrogen peroxide. Other compounds which accelerate the peroxide reactions are urea, methylcarbonate and tetra acetyl ethylenediamine. However, such chemicals increase the chemical cost. Generally, in traditional kier bleach the cost of utilities is nearly 3.5 to 4 times the chemical cost and in continuous bleach it is about twice to $2^1/_2$ times the chemical cost.

A combined process (ATIRA) can be carried out in a kier with a bleach liquor containing hydrogen peroxide (50%) 1.5%, sodium hydroxide 1.5%, sodium meta silicate 1%, sodium tetrapyrophosphate 0.5%, emulsifying agent 0.5% and wetting agent 0.1% with a liquor ratio of 2.5:1 at 60⁰C. The liquor is circulated through the material for about 12 h. A low temperature catalyst ("Urjal") developed by ATIRA avoids the use of sodium silicate in the bath and also bleaching with hydrogen peroxide may be possible even at room temperature.

In another process [14,15], the kier circulation is reduced by using emulsified solvent systems (Chapter 4). Emulsified solvent system consists of blends of emulsifier and solvents like chlorinated hydrocarbons, mineral oils etc., which stabilises

or emulsifies oils, fats and waxes from the raw cotton and enhances the action of other chemicals like hydrogen peroxide. This system may be used in kier boiling or J-Box or thermofixation chambers. In this process, the desized and washed cotton fabric is treated in open kier boiling for 4 h with a liquor containing hydrogen peroxide 1%, emulsified solvent 0.3%, caustic soda 0.3%, soda-ash 0.5%, sodium silicate 2.5%, magnesium sulphate (Mg SO_4. $7H_2O$) 2.4% and wetting agent 0.1% at 90°C. The treated fabric is then washed, soured and washed. The use of magnesium sulphate is made use for this treatment for stabilising hydrogen peroxide bath by the formation of magnesium silicate which is the actual stabiliser. This system is well suited for polyester blended fabrics because the use of caustic soda is restricted. The high concentration of caustic soda at high temperature may damage the polyester component in the blends.

In order to reduce the peroxide consumption, the fabric can be treated with sodium hypochlorite prior to peroxide treatment to increase the initial whiteness [16]. In this process, the desized fabric is first chemicked by pad-store method using sodium hypochlorite (3 g/l available Cl_2), 3 g/l soda-ash and wetting agent with pad pick-up of 100% and dwelling time of 30 min at 30°C. In the second stage, the washed and dried goods are padded with a liquor containing hydrogen peroxide (1.2%), sodium hydroxide (2.5%), potassium persulphate (50%) (0.4%) and magnesium sulphate (1.5%) at 100% pick-up. The padded fabric is then batched for 7 h followed by a hot wash at 80°C or higher for 1 min.

Sandoz has recommended two recipes (Table 11.1) for combined scouring and bleaching. The desized goods are impregnated wet-on-wet (drying after desizing and before steaming is omitted). This process demands continuous feed of a strongly reinforced feed liquor and systematic control of the concentration of H_2O_2 and caustic soda. The cloth is impregnated in a U-Box system container for 45 min at 100°C with the liquor of recipe I. In another process the cloth is padded with liquor of recipe II at room temperature (add-on 30%), batched for 40 min at 100° C and rinsed thoroughly. The result of this treatment greatly depends on the duration of reaction. The longer this is, the better the results.

In an energy saving and trouble free combined scouring and bleaching system [17], the goods are padded with a bleaching formulation containing sodium chlorite (0.85-1%), formaldehyde as catalyst (3 g/l), sodium carbonate (3 g/l) and an

TABLE 11.1

Recipes for Combined Scouring and Bleaching

Ingradients	Recipe I		Recipe II	
	Impregnation liquor (ml/l)	Feed liquor (re-inforced 3.5 times) (ml/l)	Impregnation liquor (ml/l)	Feed liquor (ml/l)
H_2O_2 (35%)	30	105	70	105
NaOH (36°Be')	20	70	22	77
Sodium silicate (38°Be')	8	28	–	–
Sandopan SF (wetting agent)	12	42	–	–
Sandopan CBN liq.	–	–	4	14
Stabiliser SIF liq.	–	–	8	28
Magnesium Chloride	0.3	0.4	0.4	0.4

emulsified solvent (pentachloroethylene) based scouring agent (2%) at 30°C and batched for 6-8 h and then washed.

11.4 Combined Desizing, Scouring and Bleaching

Many continuous processing machineries have been developed over the past few decades by which cotton and polyester/cotton blended fabrics can be desized, scoured and bleached in one single operation.

As ASISA shock system for continuous desizing, scouring and bleaching in open width gives result within few minutes without any need for previous pad-batch process. The reaction time is only 2 min.

Du Pont has developed a 2 min bleaching process for heavy fabrics using H_2O_2 at specific pH value employing a special formulation to prevent undue decomposition of peroxide and damage to the fabric under process.

ITCO process deals with a six sectioned J-Bbox system and the treatment is continuous with complete saturation and counter-current flow of water.

The Farmer-Norton steam-purge system is extremely effective in promoting a thorough saturation of the fabric with chemical pre-treatment liquors.

In the vaporloc machine full bleaching can be obtained in one passage of 90 to 120 sec duration at a temperature of 134°C (30 p.s.i.).

The ICI Markal III process combines bleaching with scouring and desizing by using an emulsion of aqueous H_2O_2 in trichloroethylene-surfactant solution, followed by steaming and washing-off.

An example of latest preparatory equipment for one step desizing, scouring and bleaching is the Reco-Yet from Ramisch Kleinewefers [18, 19]. With the Reco-Yet a heated aerosol of steam and chemicals, including a new multi-functional auxiliary agent and thermal energy, is applied to the fabric simultaneously in a reaction time of one to three minutes.

Benninger has developed "Ben-Bleach-System" for desizing, scouring and bleaching in one operation. The system comprises four models : Ben-Injecta for desizing, Benm-Impecta for impregnation, Ben-Steam and Ben-Extracta for washing. With the aid of individual dispensing system, the feed – to each module – of chemical can be controlled. In the steamer, the tight-strand fabric is plaited on a roller-bed permitting a dwell time of 1-60 min.

In the Flexnip (Kusters) cotton fabric can be processed by a single stage process and a reduction in energy and water used is claimed.

Dip-Sat Vario unit (Goller, Germany) uses a single stage process in which high degree of humidity is generated on cotton fabrics leading to efficient swelling of fats, waxes and cotton seeds, producing good whiteness with low fibre damage.

The C.R.C. process (Caustification Reductrice a chaud i.e. causticizing, Reductive, hot) from Sandoz is a simple and economical method of pre-treatment by which cotton is desized, scoured, bleached and causticized in one operation. The flow sheet diagrams of C.R.C. process equipment are shown in Fig. 11-1.

The combined desizing, scouring and bleaching is mainly achieved by the addition of a second peroxy compound to hydrogen peroxide or sodium chlorite bath when its reactivity is boosted synergistically during bleaching. In the case of H_2O_2, tetra potassium peroxydiphosphate as booster along with stabiliser and non-ionic wetting agent in the bath can act as a substitute to conventional process with savings in water and energy. The effectiveness of the system used under alkaline conditions can be interpreted in terms of free radical formation.

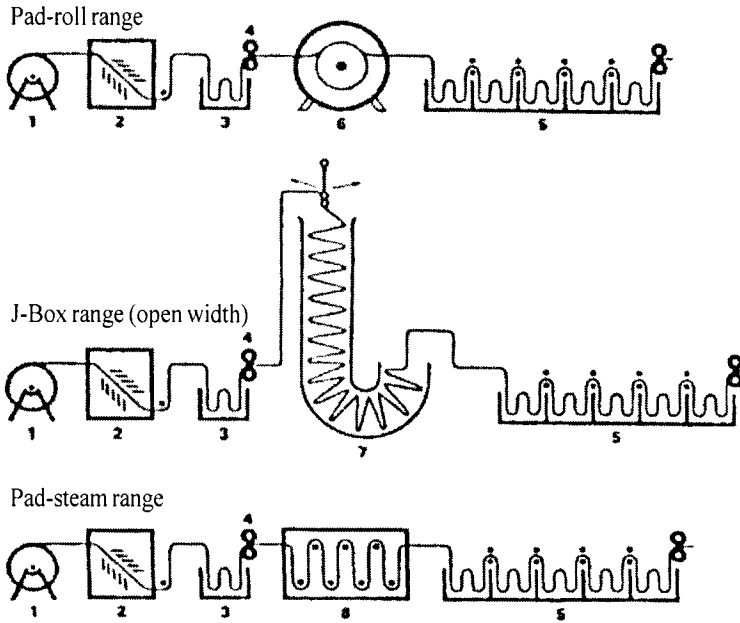A number of patents are available on the use of emulsified solvents in combined

Figure 11-1. C.R.C. (Sandoz) processs equipment.
1 Grey goods from the loom (cotton or polyester) ;
2 Singeing unit ; 3 Impregnation bath at 20-40°C ;
4 Padding mangle (80-100% pick-up) ;
5 Washing compartments (95, 95, 70, 50, 30°C) ;
6 Pad-roll chamber (60-120 min at 90-95°C) ;
7 J-Box (20-60 min at 95-100°C) ;
8 Steamer (5-20 min at 100-107°C).

desizing, scouring and bleaching. In one process, the cloth is padded with an emulsion comprising of aqueous solution of alkaline compound emulsified in chlorinated hydrocarbon with selected emulsifier at 25-60°C, dried and steamed to remove chlorinated hydrocarbons. In another process, the singed and desized cotton fabric is padded with ethylene carbonate, peracetic acid and emulsifier in trichloroethylene followed by heating at 95°C for 10 min. Solvent assisted combined desizing, scouring and bleaching process using a mixture of 4% scouring agent [a mixture of pine oil (50 parts), non-ionic emulsifier (40 parts), perchloroethylene (10 parts)], H_2O_2 (100%) 1%, sodium silicate 2% and activator 2% is reported [20]. The fabrics are padded with the mixture and batched for 12 to 24 h at 40 to 60°C.

Single stage preperatory processs for cotton using sodium hypochlorite is optimised [21, 22]. A process based on emulsified solvent system as scouring agent along with sodium hypochlorite as a bleaching cum desizing agent at pH 11 is reported [23, 24]. Around 30-35% more hypochlorite is required in the single stage process compared to conventional bleaching.

A fast desizing, scouring and bleaching system using sodium chlorite for cotton-based textile material is reported [25]. In this process, the fabrics are padded in a solution containing 20 g/l $NaClO_2$, 0.05 g/l $KMnO_4$ and 2 g/l wetting agent at pH 10 to a wet pick-up of about 80%. The treated fabrics are then exposed to 90°C for 30-60 min and washed and dried.

Another approach is the combination of an enzyme treatment with hydrogen peroxide [26]. By combining enzyme treatment (a simultaneous treatment of pectinase and cellulase), or alkaline boil-off, with an alkaline peroxide bleaching, the total degree of whiteness is reported to be higher in combination with enzyme treatment. The combined process, including an enzyme treatment, deliver results comparable with those of alkali treatment [27].

A single stage preparatory process on polyester/cotton blended fabrics can be carried out using peracetic acid as an oxidising agent. The fabric is treated with a solution containing peracetic acid 5-6 g/l, tetrasodiumpyrophosphate 1 g/l, bacterial type desizing agent 1 g/l, common salt 2 g/l and non-ionic wetting agent at pH 5 to 6 (m : l :: 1 : 3 to 1 : 5) at 75-80°C for 90 min. The treated fabric is then washed with hot water and finally with cold water.

Solar water heating system for single stage preparation in a kier and pad-batch systems with a process cost savging is possible [28, 29]. Solar heat may be utilised to the maximum extent for drying the fabric to reduce consumption of fuel.

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Chapter 12
DEGRADATION OF FIBRES ASSOCIATED WITH CHEMICAL PRE-TREATMENT PROCESSES

12.1 Introduction

Faultless pre-treatments of textiles are very essential for the quality of the final products. Faulty pre-treatments impair the reproducibility of the desired effect with an increased amount of rejects. Generally, the defects can be classified into two broad classes namely, grey mill defects and defects during chemical processing. The grey mill defects are arisen from yarn defects, warp-wise weaving defects, weft-wise defects and general defects. The defects in chemical processing may be classified as chemical damage, mechanical damage or operation faults. Chemical damages are caused by the improper application of pre-treatment processes, erroneous concept of procedure, faulty operation of machines, faulty feeding of chemicals and haphazard work. Excessive tension or stretch may often be the cause of mechanical damage.

Degradation or damage depends on chemical structure of individual fibre and pre-treatment history. Degradation also involves changes in molecular structure of the fibre. Further, the strength of cotton yarns depends not only on the strength of the fibres, but also on the twist and the lubrication of the fibres. Similarly, high and low crimp wool fibres, as a result of the influence of nutrition levels, have different levels of degradation during chemical processing [1]. Molecular orientation in a synthetic fibre, fabric thickness and spacing in a weave can also modify the way in which fabric is degraded by abrasion. Degradation may also arise as a result of storage, maintanance procedure, exposure to ultra-violet sources, weathering, fungi or other microbiological attack, heat and acid and alkaline hydrolysis of fibres.

12.2 Degradation of Cotton During Desizing

Desizing is carried out to remove the sizes and its degradation product is removed from the fabric before subsequent processing. In rot-steeping, the cloth is allowed to lie for about 24 h and the fermentation is not controlled. The degradation of cellulose may occur as a result of cross infections e.g. of mildew. The loss in weight in acid steeping is slightly higher than with water steeping. Cotton fabrics treated with dilute sulphuric acid at room temperature show little degradation, the

fluidity increases from 4 to 5.8 rhes in 4 h and about 70% of the starch is removed. Generally dilute solutions of mineral acids and acid producing salts such as $ZnCl_2$ and Al_2Cl_6 have little action on cotton fibre provided they are washed out before the fibre is dried [2-4]. If washing is not done, hydrocellulose, a break down product of cellulose, is produced with consequent tendering of the fibre [Fig. 12-1].
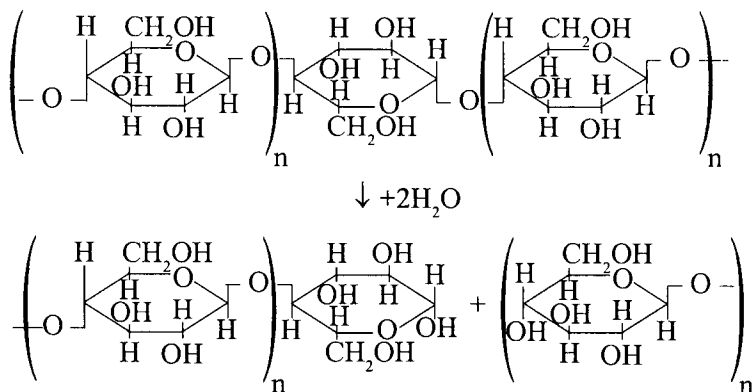

$$\downarrow +2H_2O$$

Figure 12-1. Mechanism of hydrolysis of cellulose molecule.

Due to partial hydrolysis of the cellulose molecule, the average molecular length is reduced. The appearance of additional –CHOH end groups increase the reducing power because they can undergo tautomeric change in the formation of aldehyde
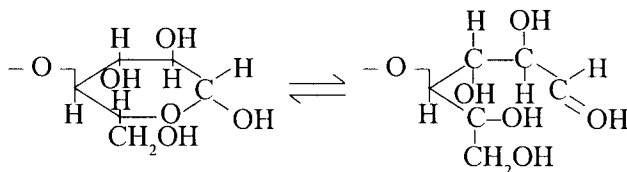
Figure 12-2. Formation of aldehyde group on hydrolysis.

[Fig. 12-2]. Most organic acids in dilute solution have little effect on cotton even if dried in, but oxalic, citric and tartaric acids are liable to cause tendering [5].

When sodium bromite is used as a desizing agent for cotton fabric by continuous and discontinuous processes, the concentration of bromite should be restricted to ensure that the oxidaiton of cellulose is kept to a negligible proportion.

In enzymatic desizing, the time, temperature and pH of the desizing bath is well controlled. Furthermore, the action of enzyme is restricted only on the sizes present on the fabric and thus degradation of the fibre due to enzymatic desizing is few and

far between. Repeated treatment of cellulase enzymes from Penicillium funiculosum [6] and trichoderma endocellulase enzymes [7] leads to extensive fragmention of cotton fibres. Repeated enzyme treated cotton shows Cellulose I pattern with the absence of 101 plane similar to that of drastically acid hydrolysed cotton [8]. This confirms that enzymatic hydrolysis of cotton fibres proceeds preferentially along the orientation, which is a cleavage phase. Morphological changes take place during the phases of degradation. Acid hydrolysis causes localised degradation whereas enzymatic hydrolysis is uniform. There are changes in moisture regain, crystallinity of the hydrolysates and weight loss due to enzyme hydrolysis.

12.3 Degradation of Cotton During Scouring

Scouring of cotton is generally carried out under mild concentration of alkali. The scouring treatment increases the wettability of the fibre, but it induces fibre degradation under severe conditions by creating crevices in fibre or dissolution of cuticle or primary wall [9, 10]. The main changes in cotton during scouring process are loss in weight (about 5-10%), loss in length due to shrinkage and alteration in count affected by both losses and changes in tensile strength (generally an increase) [11, 12]. Since the scouring treatment contributes to the dissolution of a portion of shorter cellulosic chains, it bestows on cotton an average DP higher than that of native cellulose. The alkali treatment of scouring condition does not induce pronounced changes in the fine structure of fibres and has a small effect on the degree of crystallinity [13].

The degradation of cellulose in alkali solution depends on the concentration of alkali and on the presence or absence of oxygen. In the absence of air cellulose is slowly attacked by hot alkali in a stepwise fashion at the reducing end of the cellulose chain [14] resulting in a loss of material. The entrapped air should be swept out before kier boiling under pressure. The cotton must be entirely covered by the scouring liquor as otherwise part of the fibre exposed to the air loose strength and result in unevenness in dyeing. Fig. 12-3 shows the role of pH in the endwise depolymerisation of hydrocellulose from cotton by treatment in NaOH solution (0.5 to 18.6 N) at 120°C. The curve shows a pattern similar to the degree of swelling of cellulose in alkali. The number of carboxyl groups increases with increasing [OH] ion concentration, with a rapid rate between 6 and 8.5 N, but the viscosity decreases only slightly, which implies the loss of low molecular weight compo-
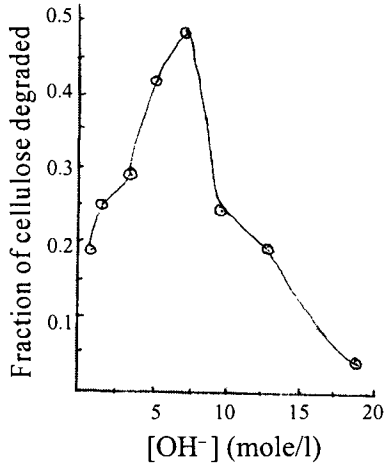
Figure 12-3. Effects of alkali concentrations on the extent
of hydrocellulose degradation at 120°C for 1 h [15].

nents. The loss in weight, however, increases with temperature of the alkaline solution [16]. The reaction scheme of this kind of degradation is represented in Fig. 12-4 by the formation of peeling-off centres on the cellulose i.e. aldehyde
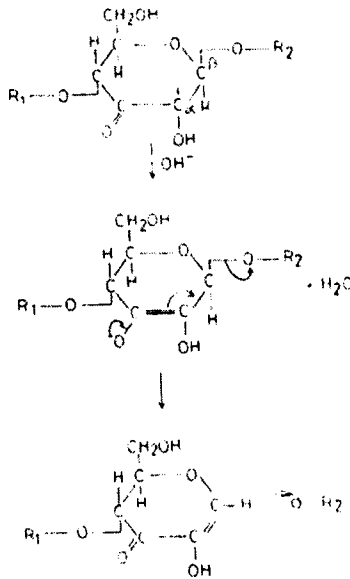

Figure 12-4. β-alkoxy elimination reaction [21].

groups, by β-alkoxy elimination reaction from the reducing ends of the chains, by the formation of carbonyl groups containing coloured products and yellowing [17] and by the formation of metasaccharinic acid at the end of the chains [18-20].

In the presence of air i.e. the reaction of oxygen with cellulose in presence of strong alkali (above 40 g/l), the degradation can be very serious and the oxidative attack may likely to follow the pattern suggested for alkali cellulose [22]. The attack of oxygen at 20°C is slow, rapid at 40-50°C and is 1000 times higher at 95°C than at 20°C [22]. A theory based on free radical intermediates i.e. the oxidative degradation which occurs with chain scission is shown in Fig. 12-5. It is shown that
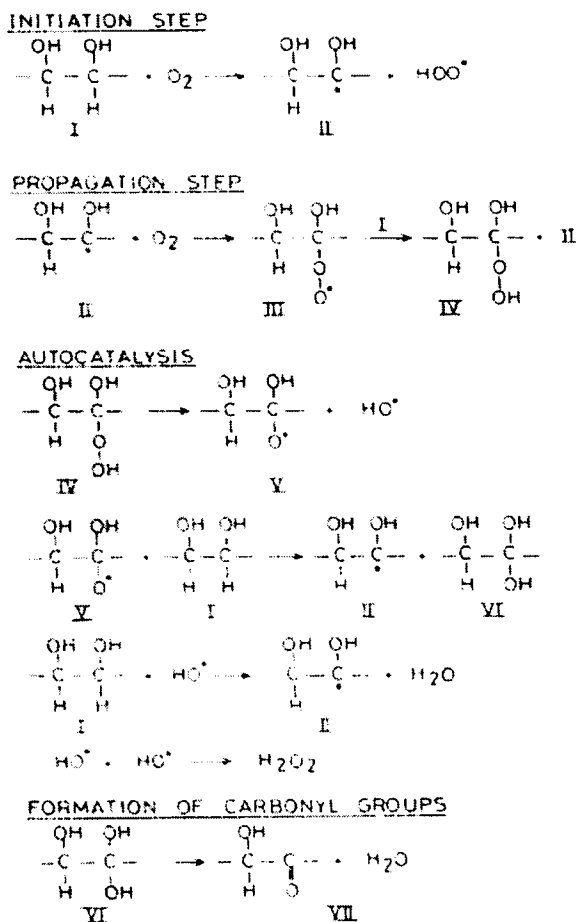

Figure 12-5. Free radical mechanism of alkali cellulose auto-oxidation [22].

hydrogen peroxide is always present during cellulose auto-oxidation. Oxygen may attack on hydrogen atom at C_2 or C_3 position to produce a radical II in the cellulose. Radical II may then rapidly take up oxygen forming a peroxide type radical III which may react with other groups in cellulose to give hydroperoxide IV and the original radical II. Thus, a chain reaction may be set up. Hydroperoxide IV gives a hydroxyl radical and a new radical V, which may abstract hydrogen from cellulose to give compound VI and the original radical II. The hydroxyl radical may attack cellulose to give new type II radicals (in autocatalysis). Hydroxyl radicals may also combine to form hydrogen peroxide. Compound VI finally loses water with the formation of carbonyl group in the cellulose chain compound (VII) and thus chain scission may occur by β-alkoxy elimination. The rate of reaction of alkali cellulose with oxygen increases with the number of reducing end groups.

An ionic mechanism (Fig. 12-6) is also proposed for the auto-oxidation of al-

CANNIZZARO REACTION
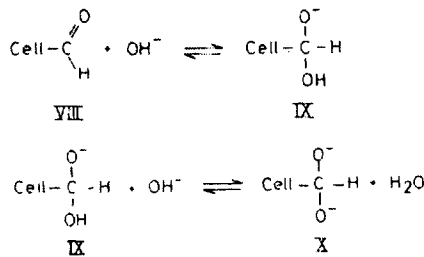
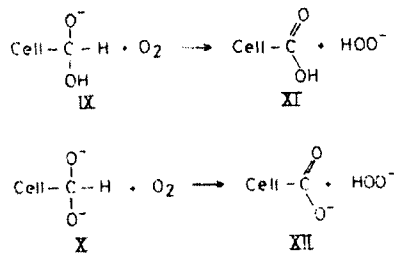FORMATION OF PERHYDROXYL ION

Figure 12-6. Ionic mechanism of alkali cellulose auto-oxidation [23].

kali cellulose [23]. The reducing aldehyde groups in cellulose under strong alkaline condition form Cannizzaro intermediates such as IX and X which is auto-oxidisable. The initiation step of auto-oxidation reaction consists of the formation

of the perhydroxyl ion. The propagation step is the attack of cellulose by the perhydroxyl ion with rupture of the cellulose chain and is similar to the degradation mechanism during bleaching with hydrogen peroxide.

12.4 Degradation of Cotton During Bleaching

Bleaching agents commonly used are mainly oxidising agents which react with cellulose forming oxycellulose with accompanying tendering of the fabric. The rate of decomposition of bleaching agent and also the rate of attack on cotton depends on concentration, pH, time and temperature of the bleaching bath and also on the soils present in the fabric. Over bleaching takes place due to lack of proper control of these parameters and oxidation proceeds at a faster rate and fabric is destroyed. Tendering takes place if bleaching is carried out in presence of metals which act as catalysts in accelerating the oxidation process. Tendering also takes place if the removal of bleaching agent during washing treatment is incomplete. Generally, bleached cloth is soured with HCl (1.5%) or H_2SO_4 (1.0%) to remove calcium carbonate or metallic composition deposited in the cloth. Tendering due to acid may also occur if the acid is not properly washed-off after the goods are soured. Hydrocellulose may form due to acid action on cellulose on storage.

Yellowing of the bleached fabric is another defect. Yellowing of the cotton fabric is caused by improper control of bleaching condition parameters, faulty working of the kier during boil-off operation, poor circulation or filtering of some cotton impurities and defective circulation of bleach liquor. The yellower the substrate, the higher is the oxycellulose present and the more susceptible the fabric to after-yellowing on storage.

12.4.1 Sodium hypochlorite bleaching and damage

Bleaching of cotton with sodium hypochlorite solution is done in alkaline condition (pH 8.5 to 10) by the the addition of sodium carbonate. Maximum damage to the fabric takes place in the neutral region of pH (Fig. 12-7). Around pH 7.0, the hypochlorous acid and hypochlorite ion are present at approximately the same concentrations and hence the rate of attack on cellulose is greatest in this region. The degree of degradation is demonstrated by increase in fluidity which also shows a maximum at approximately pH 7.0. The temperature of the liquor should be kept as low as possible and also direct sunlight should be avoided to ensure minimum oxycellulose formation. Bleaching with sodium hypochlorite can be done at 20°C
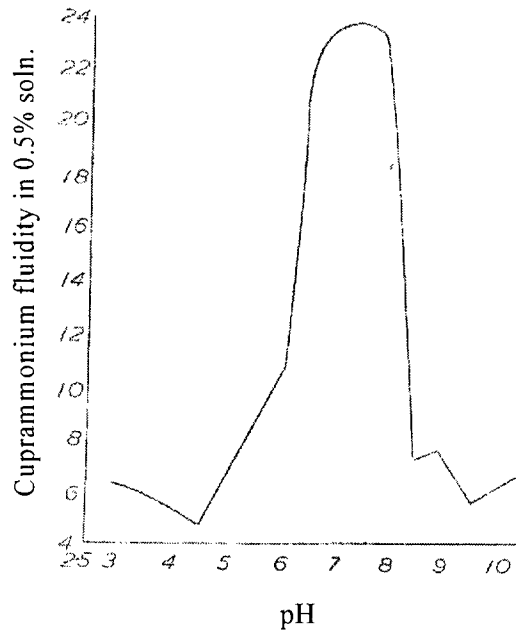
Figure 12-7. Degradation of cotton with self-buffered hypochlorite solution (3 g/l av. Cl$_2$) after 5 h treatment [24].

for a treatment time of 16 h, but the same result can be obtained for 30 min at 60°C without appreciable increase in damage to cellulose [25, 26]. The degradation of cotton at elevated temperature proceeds faster than that of impurities, but the effect is dependent only on the effective hypochlorite consumption. Certain metals such as mercury, copper, cobalt, nickel and iron should be absent in the bleach bath as the oxides and hydroxides of these metals are able to catalyse the decomposition of hypochlorite solution and the liberated oxygen converts the cellulose into oxycellulose. Certain yellow and orange vat dyes also accelerate the rate of oxidation accompanied by degradation of cellulose under combined action of hypochlorite solutions and light [27].

The reaction of hypochlorite with cellulose is non-specific i.e. not confined to a particular hydroxyl group. The degradation is located mainly on the surface of the fibre as the reaction is heterogeneous nature. Hypochlorite may attack and convert the accessible hydroxyl groups of cellulose into carbonyl groups (i.e. aldehyde and ketone groups) and carboxyl groups with subsequent chain cleavage. Strength loss,

in the early stages, is accompanied with slight weight loss but stength decreases rapidly with continued oxidation [28]. The formation and extent of carboxyl contents (determined by methylene blue absorption) and aldehyde groups (determined by Copper No.) depend on the pH of hypochlorite solution during the treatment (Fig. 12-8). Under acidic pH reducing type (aldehyde and keto groups) and under
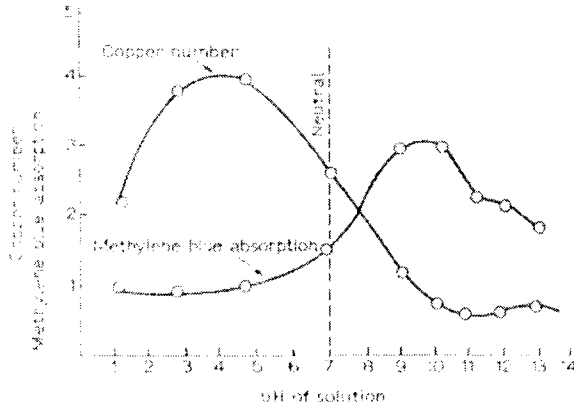

Figure 12-8. Effect of pH of hypochlorite solutions on the copper number and methylene blue absorption of oxycellulose [29].

alkaline pH acidic type (carboxyl groups) of oxycelluloses are formed. The changes in pH modify the rates of reactions but do not alter the mechanism for them [30]. The oxidation may be progressive and proceeds along a course known as β-elimination [Fig. 12-4]. Bleaching with hypochlorite is done in alkaline pH and hence oxycellulose of the acidic kind are insensative to alkali, but when in the free acid form, the hydrogen ions from the carboxyl groups catalyse hydrolysis of the adjascent glucosidic linkage. A sequence of reactions is shown in Fig. 12-9 and 12-10 [30].
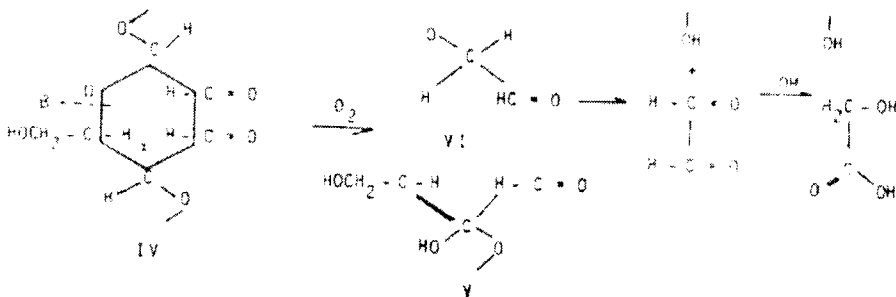

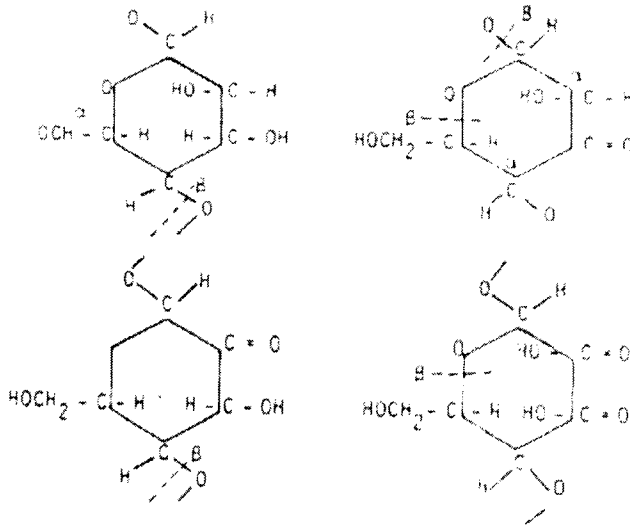Figure 12-9. Oxidation with periodate [30].

Figure 12-10. General reactions with non-specific oxidising agents [31].

Apart from degradation of fibre, the increase in the number of aldehyde and carboxyl groups also increase the dyeing and finishing problems.

12.4.2 Hydrogen peroxide bleaching and damage

Bleaching of cotton with hydrogen peroxide is carried out under alkaline condition along with sodium silicate which acts as a stabiliser. However, the use of sodium silicate is liable to cause deposition of silicon compounds on the cloth and also form hard crystalline deposits on plants and machineries which may cause abrasion damage to the fabric. This defect may be avoided if addition of alkali in the ratio of $Na_2O : SiO_2$ within the region of 2.25 : 2.75 is used. It is also recommended to use a mixture of equal proportion of NaOH and Na_2CO_3 instead of NaOH alone as only NaOH may cause initial degradation. The silicate concentration may be reduced further by the use of organic stabilisers which tend to have lubricating effect.

The damage of cotton during metal catalysed bleaching with hydrogen peroxide is a serious problem. There are various sources by which the bleaching bath can be contaminated with metal particles. The raw cotton contains high metal content because of the use of pesticides, fungicides and weed control agents in cotton-growing [32, 33]. During open end spinning, soil particles which are rich in metal containing compounds, are deposited in the rotor chamber and after temporary re-

moval get into the yarn [34]. By increasing the spinning and weaving speeds the contamination of metal particles may also increase due to friction from machinery components [35]. Metal ions present in chemicals used for bleaching can also cause problems [36].

The influence of the concentration of iron ions on decomposition of hydrogen peroxide in bleaching liquor is shown in Fig. 12-11. The influence of the concentration of complexing agent on decomposition of iron complexing peroxide bleaching liquor and cellulose is shown in Fig. 12-12. The rapid release of large amount
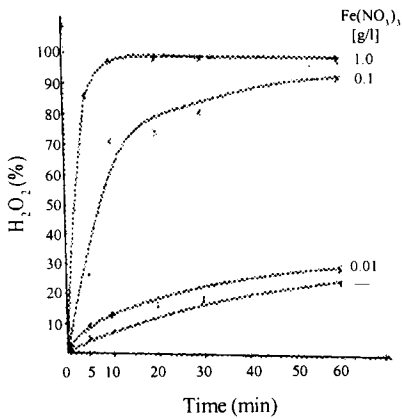

Figure 12-11. Decomposition curve of H_2O_2 in bleaching liquor at various $Fe(NO_3)_3$ concentration [37].
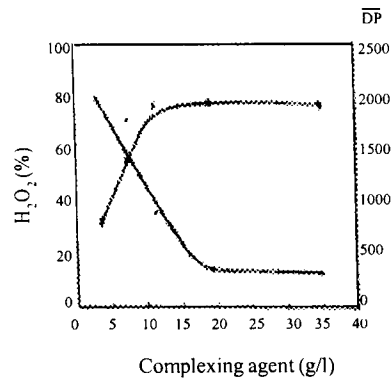
Figure 12-12. Decomposition of H_2O_2 and damage to cotton as a function of the concentration of the complexing agent, falling curve H_2O_2, rising curve $\overline{DP}$.

of oxygen species causes rapid and significant oxidative degradation of cotton cellulose in the immediate vicinity of the metallic particle. The decomposition effect of water soluble catalysts on peroxide and cellulose can be suppressed by increasing the complexing agent concentration. The catalytic damage that occurs during peroxide bleaching is due to the metallic particles trapped in the fabric and the decomposition of H_2O_2 is thought to be catalysed by metal ions present near the surfaces of the metallic particles [38]. The catalytic damage caused by metal salts is most striking in a long liquor bath and least with the pad-batch method.

12.5 Damage of Wool During Pre-treatment Processes

Boiling water can gradually break down the wool keratin and the fibre can loose

its strength. Dilute acids, however, have little effect on wool, but 20% HCl can hydrolyse wool. Cold concentrated mineral acids can dissolve wool fibre [39]. Dilute solutions of caustic alkalies rapidly disintegrate wool at a rate depending upon the temperature and concentration employed. Soda-ash and sodium carbonate have much less destructive effect and hence are used in scouring of wool fibres. Borax, soap and ammonia behave similarly.

Carbonisation of wool can cause localised damage. Wool undergoes some hydrolysis between acidising and drying steps, even at room temperature [40]. The surface acid remaining after carbonising is unevenly distributed in the wool mass and consequently localised damage is caused [41]. There is a critical point at a temperature of 70°C in the drying stage and 120°C in the baking stage above which wool hydrolysis increases significantly. Oxygen is not directly involved in hydrolysis damage to wool during carbonising. Lower drying temperatures before baking in carbonising minimise damage to wool fibres. The addition of surfactant in the carbonising bath results in the even distribution of the acid as a film over the entire surface of the fibre and can protect wool during carbonising [42].

Sometimes carbonising is done during dyeing with 1 : 1 metal complex dyes under strongly acid conditions, but this method may produce severe fibre damage and requires careful control of dyeing conditions. Fibre damages may also occur by decatising the dyed fabrics under pressure and hence decatising at atmospheric pressure is recommended [43].

Modern methods of bleaching wool is directed towards the control of chemical damages during the treatment. Chemical damage generally occurs due to excessive rapid decomposition of H_2O_2. The reaction of wool with H_2O_2 is relatively slow in acidic condition than that of alkaline condition. The presence of activating reducing agents (metal salts) can also enhance reactivity of the normal wools in presence of H_2O_2 and can lead to fibre degradation. The precautions are exactly the same as those needed in the bleaching of cotton with H_2O_2.

During oxidative damage to wool some of the cystine cross-links (the number depending on the conditions) are split and are oxidised to cysteic acid which can be regarded as a measure of the degree of damage [44, 45]. A possible mode of attack has been suggested for the reaction of persulphate ions with the peptide groups [46]. The reaction of wool with peracids and probably hydrogen peroxide is con-

sidered to yield S-monoxycystyl and S, S-dioxycystyl residues [47]. Although sulphite ions react with wool to split the disulphide linkages, dissolution does not occur. The reaction is reversible and the maximum extent of reaction takes place at pH around 3 to 4 [48]. The mechanism of reaction seems to be nucleophilic attack of the disulphide bond by either the bisulphite (HSO_3^-) or the sulphite (SO_3^{--}) ion.

12.6 Damage of Silk During Pre-treatment Processes

There may be three types of damages of silk during the pre-treatment processes. Repeated processes and improper handling may cause mechanical damages due to chafing at the silk fibre surface. Biological damages may occur on storage, especially in a non-degummed state, due to bacteria. Chemical damages may occur due to improper control of the various parameters during degumming and bleaching treatments.

The chemical behaviour of silk towards acid is somewhat like wool except that it is more readily attacked by strong acids. Silk is more resistant to all alkalies except caustic soda and caustic potash. Prolong boiling of silk fibres in water alone will produce slow degradation and hydrolysis. In acid or alkali, hydrolysis of the peptide chain occurs with loss of tensile strength of the fibres. The extent of degradation depends on the pH of the solutions and is minimal between approximately pH 4.0 and pH 8.0. Uneven degumming causes spotted batches due to uneven weft material. Lime soap residues may be present on silk due to hard water and poor rinsing showing metal spots and rust particles.

Uncontrolled oxidation of bleaching baths can attack the silk fibre. Hypochlorite, chlorine dioxide etc. can cause discolouration of the fibre probably due to the oxidation of the tyrosine residues. Hypochlorite solutions render both fibrion and sericin insoluble to an extent depending on the pH, being more effective in alkaline solution (pH 10.3), slightly less in mildly acid (pH 4.0), and not at all in strongly acid.

When silk is immersed in hydrogen peroxide solution, the latter is absorbed to an extent which is independent of pH in the range 2.5 to 9.0. This may be due to the fact that the peroxide combines with amino groups and peptide bonds of silk fibres [49]. Peroxide also causes reduction in tyrosine content presumably due to the scissioning of peptide bonds at linkages involving tyrosine [50]. Oxidation of peracetic acid causes scission at a greater rate than by hydrogen peroxide, but loss

in weight for a given rise in fluidity is greater with hydrogen peroxide than peracetic acid [51]. This is because tyrosine in silk is oxidised to acidic groups.

12.7 Damage of Polyester During Pre-treatment Processes

Polyester is highly resistant to acids but alkali can hydrolyse polyester fibres. The fibre surface is not damaged by treatment for 5 min at sodium hydroxide concentration as high as 38.9 g/l or at 5.2 g/l for 2 h, but damage does occur if fibres are treated with a 9.1 g/l sodium hydroxide for at least 2 h [52, 53]. The number of hydroxyl groups increases due to alkaline hydrolysis, but there is some damage to the fibre surface. The fibre cross-section becomes more complex and its area decreases [54]. Due to alkaline hydrolysis weight loss occurs, together with an increase in density, crystallinity, amino acid content, dye uptake and abrasion resistance, and a decrease in intrinsic viscosity, as the concentration of alkali is increased [55]. In addition, aminolysis of ethylamine proceeds by permeation of the reagent into the fibre and causes degradation, which affects the brittleness, flexural fatigue resistance, and tensile properties of the polyester [56]. These changes are explained in terms of crystallinity and crystallite size. As the treatment time increases, decrease in crystallinity and crystallite size become more pronounced. On extensive treatment, the propagation stress cracks on the fibre surface and finally results in fibre breakage [57]. The addition of cationic surfactant, dodecyldimethylbenzylammonium bromide, reduces the alkaline hydrolysis of polyester fibres subjected to NaOH treatment by reducing the concentration of alkali [58, 59, 53].

Heat-setting of polyester fibre with steam always leads to low molecular weights than occur with conventional setting. However, the cleavage of polyester fibres by hydrolytic degradation on exposure to steam occurs only after very severe exposure to steam. Generally, cleavage takes place predominantly across the fibre axis to give irregular lengths between scissions and the cleavage does not appear to be related to the significant physical phenomenon [60-62].

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