Chapter 5

SCOURING MACHINERIES

5.1 Introduction

Scouring can be carried out in batch, semicontinuous and continuous processes. The machinisation of the post-kier scouring stages had been progressively developed from the early 1930^{S}. The non-continuous process consists essentially of circulating hot alkali liquor through the cloth in a vessel called kier. The continuous scouring and bleaching in the J-Box has been established after 1960. The continuous process is based on the impregnation of the fabric in an alkali solution followed by steam ageing stage, the fabric being either in rope form or open width form. Kiers have given way to J-Boxes and J-Boxes are discarded in favour of open width scouring which requires only 2-15 min having very high production. In comparison kiers take 6-12 h depending upon the amount of impurities.

5.2 Batch Type Scouring Machines (Rope Form)

5.2.1 Low pressure kier

Various designs of kiers are available [1,2]. Low pressure or open kiers are generally made with a hinged lid, and the scouring liquors are circulated by injector system or by the provision of an external multitubular heater and pump (Fig. 5-1).

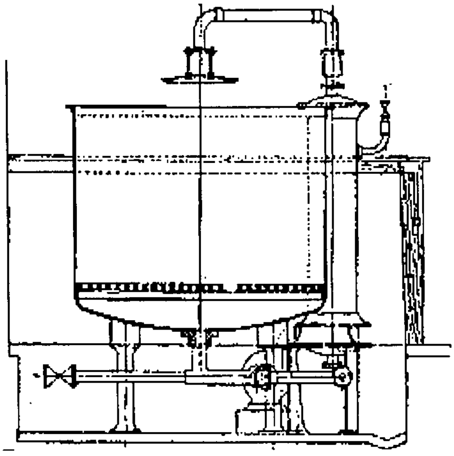


Figure 5-1. A typical low pressure kier.

The steam injector located at the centre of the kier permits the heating of the bath and the liquor is circulated from bottom to top before spraying it on the fibre. Open kiers are mainly used for linen, yarn and cloths made of loosely woven goods and knitted materials etc. which will not stand high pressure boiling in alkaline solutions. This type of kiers are also preferred for coloured woven goods which operates at atmospheric pressure below 100°C. The main disadvantage of this type of machine is the dilution of the bath by condensed steam on account of direct steam heating system.

5.2.2 High pressure kier

The prototype of modern high pressure keir (Fig. 5-2) with multitubular heater is often referred to as Walsh's kier and considered to be the best. A 2 tons capacity kier is most common which is about 9' high and 6.5' in diameter and mounted on R.C.C. columns. The kier is generally made for a maximum likely working pres-

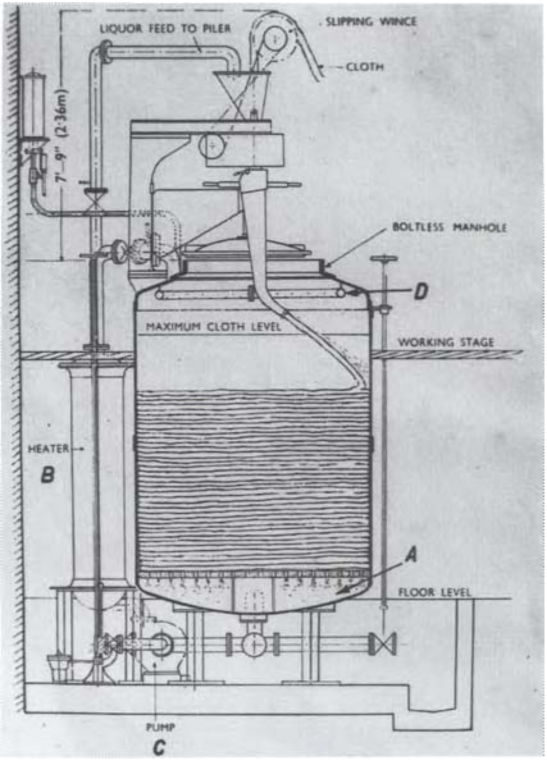


Figure 5-2. High pressure vertical kier with multitubular heater.

sure 40 lb/in^2 (2.812 kg/cm^2) at 141°C and is composed of mild steel plates with countersunk rivet heads inside to give a smooth surface. The kier is provided with various mountings and accessories such as pressure gauge, safety valve, blow off valve for air and steam, steam trap, liquor level indicator, drain cock etc.

The goods in rope form are piled either mannually or by mechanical plaiting on the perforated false bottom. The cloth can be saturated with alkaline solutions containing caustic soda (2 to 3%), sodium silicate (0.75 to 1%), sodium carbonate (0.5 to 1%) and wetting agent (0.1%) during piling. Sufficient scouring liquor is then admitted to the kier from below to sweep out entrapped air from the goods to avoid the formation of oxycellulose. The lid is then closed but the air valve is kept open. Steam is turned on and liquor is circulated by centrifugal pump (C) coupled to an electric motor. High pressure kier operates at about 130°C (2.109 kg/cm^2) for about 8 to 10 h with a liquor ratio between 5:1 to 6:1. After scouring the drain cock is opened at reduced pressure (5 to 6 lb/in^2) and equivalent amount of hot water is admitted from the top. After circulating cold water the goods are removed and washed in a rope washing machine. The liquor is withdrawn from the bottom of the kier (A) and forced through the heater (B) and spread over the top of the load by the distributor (D).

Fabrics which are to be sold in white state are given two boils and the fabric intended for printing, single boil is sufficient. Recently, the kier has been so modified as to reduce the time for pressure kiering or even peroxide bleaching. This is achieved by using saturators, autopilers and resorting to steaming as in the case of J-Box range.

5.2.3 Jafferson-Walker's kier

Kier of this type (Fig. 5-3) is also a vertical kier but utilises a vacuum system for

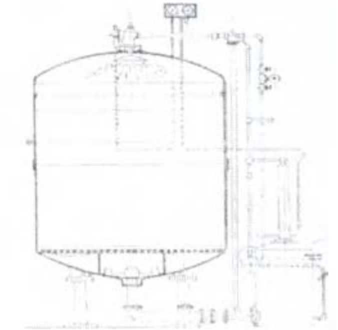


Figure 5-3. The Jefferson - Walker kier.

circulation of the kier liquor. In this system, there is a small subsidiary receiver kier between the actual kier and supply pipe. About one-fifth of the liquor in the kier is withdrawn into the receiver kier and this creates a partial vacuum, drawing fabric together. The kier liquor is periodically withdrawn, heated and then returned to the kier. The entire liquor is circulated every 10-12 min.

5.2.4 Gebauer kier

The unit (Fig. 5-4) consists of two concentric vessels one inside the other with a perforated inner jacket. The heated scouring liquor is injected at the top between the two concentric walls. In this system the flow of liquor is radial instead of vertical circulation and thus the cloth more or less floats. The pressure difference between top and bottom is eliminated.

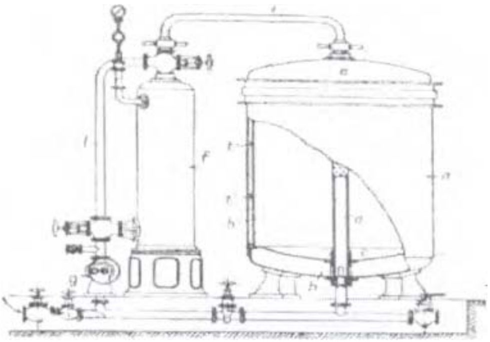


Figure 5-4. The Gebauer's kier.

5.3 Batch Type Scouring Machine (Open Width Form)

Heavy fabrics like drills, corded fabrics and other weaves show rope marks and creases if they are scoured in rope form. Such fabrics are scoured in open width form.

5.3.1 Mather and Platt's horizontal kier

Mather and Platt horizontal kier (Fig. 5-5) consists of a horizontal shell with usual mountings and accessories. Four wagons are supplied with the machine, two are filled with fabric outside the kier whilst the other two are in process in the kier. The goods saturated with scouring solution are run on the iron rails secured to the kier bottom and then the front door is closed and fastened. The hot alkaline liquor is then circulated for 6-8 h under required pressure and temperature depending on the type of goods. The bath is heated by an external multitubular heater and the

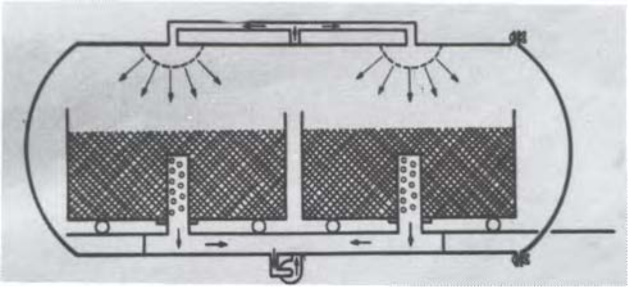


Figure 5-5. Horizontal kier (Mother & Platt).

liquor is sprayed on the fabric in the wagon by umbrella spraying device. After boiling is over the goods are washed once or twice in the kier. The direction of circulation of liquor can be reversed during the boiling or washing processes. The machine can also be used for loose cotton and yarn.

5.3.2 Jackson kier

Fabrics are secured in open width form in the Jackson kier as shown in Figs. 5-6(a) and 5-6(b). It consists of a horizontal shell and a carraige which supports three rollers. The two outer batch rollers rotate in the fixed bearings at either end of the carraige. The roller or drum is large, hollow and perforated and is carried

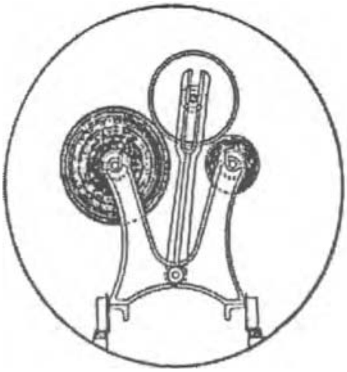


Figure 5-6(a). Jackson kier.

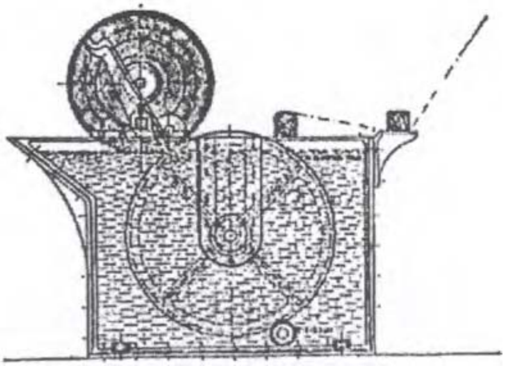


Figure 5-6(b). Impregnating device.

on oscillating arms pivoted at either end of the base of the carraige. The fabric is saturated with scouring liquor outside in an iron tank [Fig. 5-6(b)]. The batch roller is then placed on the carraige and pushed into the kier on guide rails and then door is closed. The fabric is wound from one roller to the other during the scouring process. Hot scouring liquor is circulated by the centrifugal pump and is continuously sprayed over the fabric as it passes from one roller to the other. Scouring is done under a pressure of about 30lb/in^2.

5.3.3 Jig process

Fabrics can be desized and scoured in open width form using a jigger, which is one of the oldest and most universal machine in textile finishing. A centrally controlled fully automated jigger (Fig. 5-7) to secure improved processing quality with reduced operator involvement is shown. Generally, the goods are batched onto rolls and given 6 to 15 ends on the jig through the scouring solution at boiling temperature. After scouring the goods are rinsed several ends on jig. In this process there is danger of oxycellulose formation by hot alkaline solution in presence of air. Closed jiggers are used for operation under increased pressure.

Figure 5-7. New generation of jiggers (Courtesy of Asyst S.L., Sabadell).

At the end of eighties jiggers were already controlled by microprocessor system and today microprocessor technology enables all jiggers to be connected to a personal computer. All process data, from loading the fabric, scouring, washing and unloading, is stored and can be requested any time for subsequent processing. In addition to the possibility of major automation, the machine can be supplied with batching-up facilities and such other options as automatic selvedge shifting, and a system of automatic tension regulation with floating roller in the vat designed for precise and gentle handling of elasticised or ultra-delicate fabrics.

5.4 Semi-continuous Scouring Machines

5.4.1 Pad-roll system

In this process goods are padded through the scouring solution and then batched open width onto rolls which rotate slowly for several hours ranging from 6 to 24 h depending upon the type of cloth. The goods are then washed and rinsed in open width washers.

5.4.2 Pad-steam-roll system

After impregnation with scouring liquor, the fabric is quickly pre-heated in a steam chamber or by an infra-red radiation. When it has reached a high enough temperature, the fabric is introduced into a transportable reaction chamber heated by steam injection, where it is stored in a rotating roller. The reaction time is of the order of 1-1.5 h at 100°C.

5.4.3 Pad-roll on perforated cylinder [3]

In this method the fabric after padding with scouring solution is wound on to a perforated roller. The loaded fabric is then rotated in a treatment chamber provided with a liquid reception vat and a circulation pump, The liquor is circulated from inside to outside of the loaded beam by a centrifugal pump. The main advantage of this type of machine is that the scouring, bleaching and washing operations can be carried out on the same fabric roll.

5.5 Continuous Scouring Machines

5.5.1 Saturator – J-Box-rope washer

In continuous machines, scouring can be carried out through a series of J-Boxes or range type operations for progressive desizing and scouring. The desized and washed cloth is first saturated with scouring solution at about 70-80°C in a saturator. After padding the saturated cloth, it enters into Du Pont type J-Box (Fig. 5-7) where it remains for 40-60 min in plaited form at a temperature of about 100°C. The cloth before entering J-Box is rapidly pre-heated by means of steam in a U-shaped heating tube. In case of Becco system (Fig. 5-8) there is no pre-heater and the cloth is directly heated in the J-Box which is used as a steamer. The internal surface of the entire J-Box is very smooth to avoid any friction on the moving

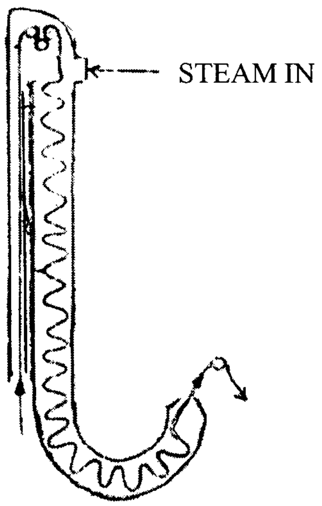


Figure 5-7. Closed-top J-Box system (Du-Pont type).

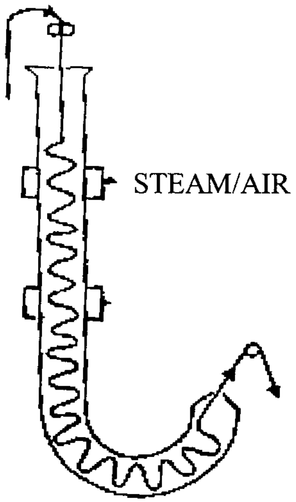


Figure 5-8. Open-top J-Box system (Becco type)

cloth. In stead of rope form a multi-stage J-Box in open width form can also be used with a dwell time of 8-10 min in J-Box. The scoured fabric is washed outside heaving a counter current arrangement at temperature of about 70-80°C.

5.5.2 Open width roller steamer

The fabric in open width form is padded (Fig. 5-9) through the scouring solution to at least 100% pick-up at 60°C with a running speed of 60 m/min and then passed through a shock steamer. The residence time in this steamer may range from 30 sec to 5 min. The usual time is 1 to 2 min exposure to wet steam at 100 to

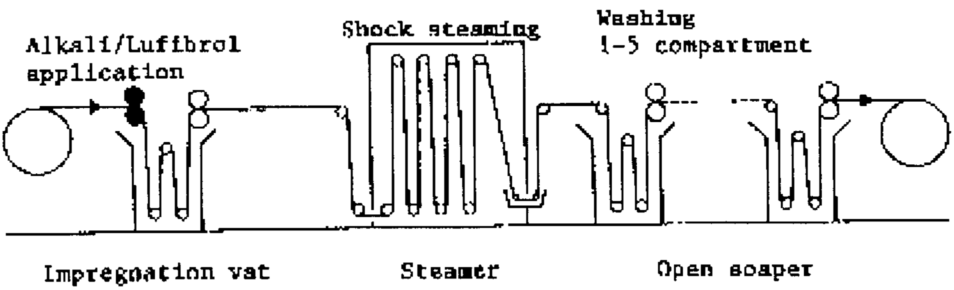


Figure 5-9. Continuous scouring of Polyester/Cotton blends [4].

110°C. The amount of fabric inside the steamer is about 60-100 yds with a production rate of about 60 m/min. The fabric is then washed in open soaper at 70-80°C with counter current flow arrangement.

5.5.3 Batch or rebatching system [5]

In this system (Fig. 5-10) there are two winding systems, one above the another.

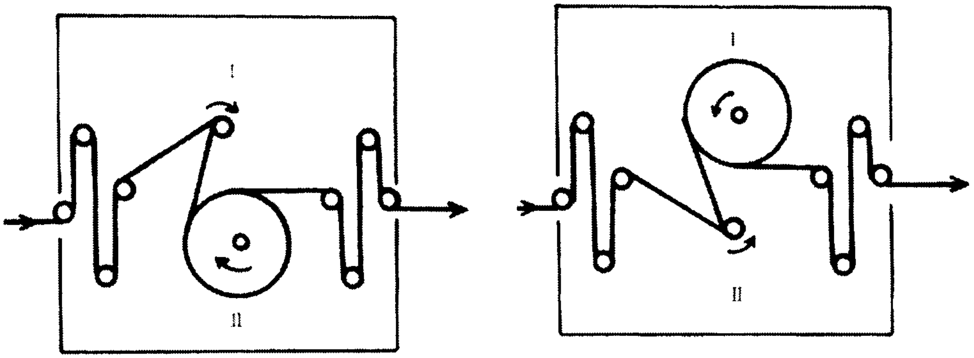


Figure 5-10. Continuous rebatching system.

The cloth is batched into two sup

layer comes from the other layer after partial ageing and the second layer comes from the impregnation device. As soon as the batch is complete on the first winder, the direction of rotation is reversed and the second layer, which comes first from the impregnation squeezer, is led to the second winder below the entering cloth, while the other layer, which has been completely aged, leaves the reaction chamber. For reaction period of about 1-2 h, the system allows fabric treatment with a production speed around 120 m/min. The main disadvantages of this system are : (i) it is suitable only for treatment of fabrics with same width and (ii) moire effect (water marks) cannot be avoided.

5.5.4 Vaporloc system

The cloth in open width form is first saturated with sodium hydroxide solution (5-9%) along with wetting agent at 70°C, padded and then entered into vaporloc reaction chamber which operates at 30 lb/in^2 (2 atm.) at a temperature of 134°C with a reaction time of 90-120 sec (Fig. 5-11). The fabric is deposited on roller-bed system and thus allows the fabric to be in a relaxed state inside the pressure chamber [6, 7]. The fabric passes in between the low friction teflon material and the centre beam special seals enables the generation of necessary pressure inside the

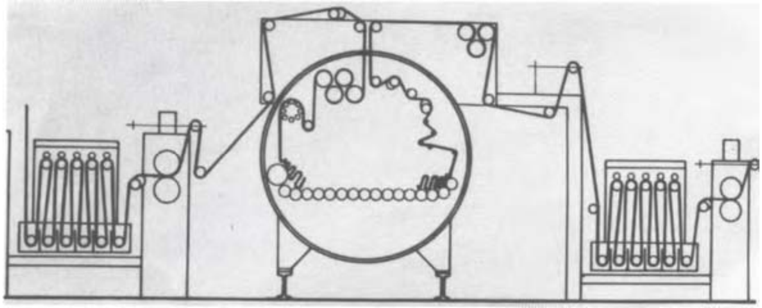


Figure 5-11. Mather & Platt continuous open-width pressure reaction chamber [8].

steamer. The cloth content inside the steamer is about 200 meters. The production speed is of the order of 120 m/min. The goods after scouring are washed off first with hot water and then with cold water.

5.5.5 High pressure Klienewefer roller steamer

Continuous processing pressure steamer of Klienewefer (Fig. 5-12) utilises roller

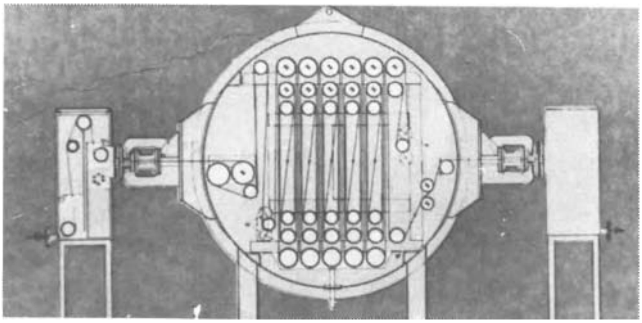


Figure 5-12. High pressure roller steamer (Courtesy of Klienewefers GmbH.).

steamer which operates at 3 atm. pressure in dwell time to 30-180 sec for a sodium hydroxide impregnation concentration equal to 60-100 g/l at 130-140°C. The production speed is of the order of 30-60 m/min depending on the capacity of the vessel. Hydraulic sealing heads are subjected to a pressure inside the vessel where the cloth is guided on rollers. The sealing heads permit continuous cloth feeding and delivery [9].

5.5.6 Conveyer storage steamer system

Another way of storing impregnated fabric consists of the use of a continuous pile storage steamer where the cloth is plaited down onto conveyer belts for necessary time [10]. In this system the accumulation of goods is such that the risks of creasing are not suppressed.

5.5.7 Roller bed steamer with pre-swelling zone

In this system the fabric in open width form is first impregnated with a scouring solution and then guided to rollers for a time sufficient for swelling (Fig. 5-13).

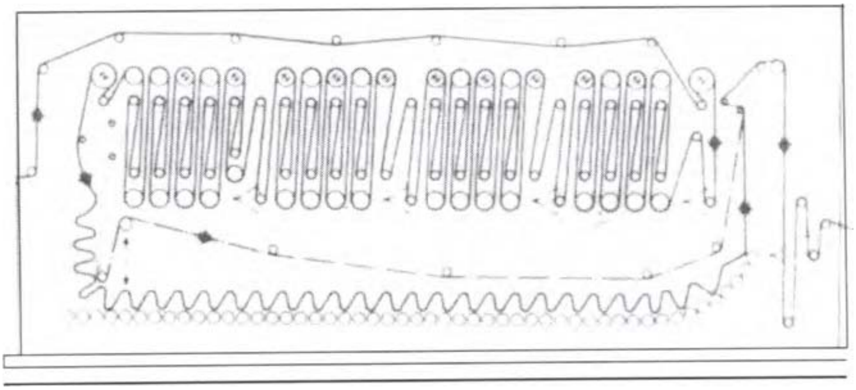


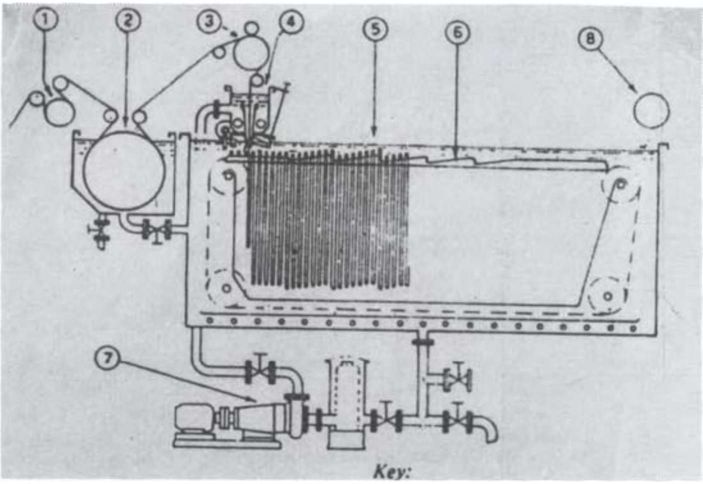
Figure 5-13. Roller bed steamer (Courtesy of Klienewefers GmbH).

The fabric is pre-swollen in the tight-strand roller section before being plaited down onto the roller bed for the required time. The roller bed conveyer can be replaced by a conveyer belt. This kind of installation permits 6-20 min dwell time at 100°C for NaOH concentration around 3-6% with a production speed of about 100 m/min. Vacuum impregnation of the fabric with the scouring solution before steaming is sometimes recommended for rapid wetting of the goods [11].

5.5.8 Continuous relaxing/scouring machine

Rotary washers (see chapter 7) have been used as an open width treating apparatus of batch type ; this has a large effect, but has such demerits as fear of relaxation specks (spot mark) and flaw (defect, spot etc.) and inefficiency. Hence continuous relaxer has been developed. The absence of tension is favourable for relaxing and each machine manufacturer has given vibration to the fabric in his own way. Mechanical impacts in the form of bending, pressing, vibrating and rubbing action are utilised for better effect during relaxing process.

In the Mezzara relaxing machine (Fig. 5-14) the fabric suspended in loops from a series of parallel rods move forward very slowly along the length of the machine. These rods are mounted in tracks on either side of the machine tank. They are located just below the surface of the liquor. The rods rise up a saw tooth ramp and then drop, say about 5 cm, thus giving an opportunity for the fabric in contact with the rod to be slightly displaced. The fabric is carefully guided into the centre of the machine and fed over a full width reel, into a V-shaped trough, with an open bottom. The trough is kept half filled with water which pulls the fabric off the reel and carries it down into the bath to form a loop, generally about 80 cm long. The maximum speed of operation is dictated by the speed of the water pouring out of the bottom of the V-trough. The bottom of the trough slowly moves forward with the advance of the rod, being loaded, and then about every 5 to 6 sec rotates back to start loading the next rod. After carrying the fabric through the machine the rods move down to the bottom of the bath and return to the feed end. The fabric being immersed in the liquor in loop form for about 20 min has a good chance to relax. The fabric is then drawn off by roller and sprayed with warm water and then cold water before being plaited down, outside the machine.



1. Draw rollers for controlling feed
2. Pre-wetting bath with driven roller
3. Draw rollers
4. Trough with V-slot
5. Main tank
6. Saw-tooth rails
7. Cemtrifugal pump with filter

Figure 5-14. Mezzera (Italy) open-width relaxing/scouring unit.

5.5.9 Solvent scouring machines

Scouring of knitted goods, wool and blended woven fabrics in discontinuous rotary-drum washing machines has been established in many countries for a number of years. Equipment for continuous preparation and dyeing from non-aqueous solvent have been developed by several companies (Table 5.1).

TABLE 5.1
Continuous Solvent Scouring Machines

Company	Unit
Bohler and Weber [12-14]	C 1600 / C 1800
ICI [15]	Markal
Bruckner [16, 17]	Solvanit
Dow [18]	Dow Scouring System
Rimmer [19]	Vibro Scour
Riggs and Lomband [20]	Scour-kleen
Neil & Spencer [21]	Libatex

In ICI's Markal process (Fig. 5-15) the dry cloth first passes through trichloroethylene (TCE) in the dewaxing vessel which is divided into number of seperate compartments. From the last compartment the cloth passes through a solvent seal and heavy mangle where much extrained solvent is removed from the cloth. The cloth then passes through a chamber into which steam is injected. Thus rapid evaporation of solvent in the cloth and the mixture of steam and TCE vapour is condensed and returned to the solvent seal where the solvent and water are seperated. In alternative method, the solvent is removed from the cloth by the use of an enclosed hot water (95°C) bath instead of steam chamber [22]. After passing through

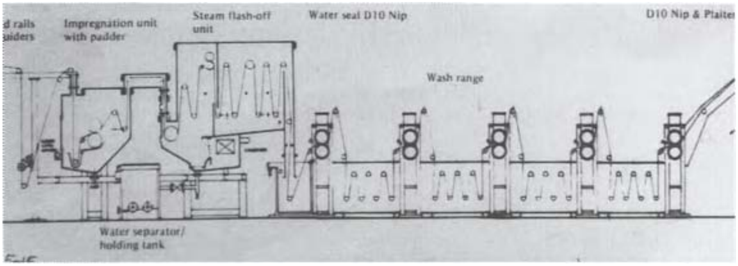


Figure 5-15. Commercial Markal (I C I) machine and combined washer.

the water wash tank, the cloth leaves the scouring machine saturated with water. The Markal II process consists of effecting simultaneous scouring and desizing by using suspension of enzyme in TCE and surfactant solution. The treated sample is then passed through steaming chamber for 10-20 sec where the solvent is flashed-off. The fabric is then given normal wash to remove the size [23, 24]. Markal III process combines bleaching with scouring and desizing by using emulsion of aqueous hydrogen peroxide in the TCE-surfactant solution, again followed by steaming and washing-off.

Another continuous solvent scouring machine for knitted and woven fabrics is shown in Fig. 5-16. The Bruckner Solvanit continuous process is used for simultaneous scouring, cleaning and for shrinking. The cloth is transported by a patented paddle wheel which ensures thorough removal of contaminants by countercurrent flow of fresh perchloroethylene. Relaxation and bulking of knitted goods occur during solvent flash-off.

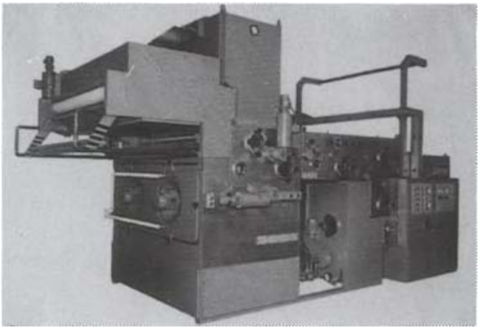


Figure 5-16. Continuous solvent scouring and finishing machine (Courtesy of Sperotto Rimar, Italy).

5.6 Wool Scouring Machines

Scouring machines of wool depend on the kind of wool to be scoured i.e. raw wool, hank form or woven fabrics. Scouring of wool can be carried out in batch or continuous process, aqueous or solvent media and rope or open width form.

5.6.1 Raw wool scouring machines

In the conventional scouring machine (Fig. 5-17), raw wool is propelled through a tank filled with warm water containing detergent, raked through the bowl, conveyed by means of a transfer mechanism to squeezing rollers and then carried into another similar tank. The bowls have false bottoms consisting of perforated plates

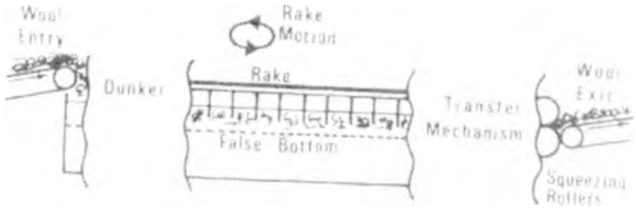


Figure 5-17. Scouring of raw wool in traditional scrouring machines.

which allow removal of dirt from the wool to fall through the perforations while preventing the fibre from passing. The wool may pass through four or more tanks in this way, until eventually it is rinsed in clean water.

The raw wool is also scoured by some unconventional machines [25]. In the Fleissner machine loose wool is conveyed through the bowl by a series of suction drums (Fig. 5-18). The flow of liquor through the wool and into the three suction drums is done by pumps through the perforated surface of the drum from outside to inside. In this type, the efficiency of removing impurities is comparatively lesser due to the gentle scouring action and are also comparatively costlier than the conventional machine.

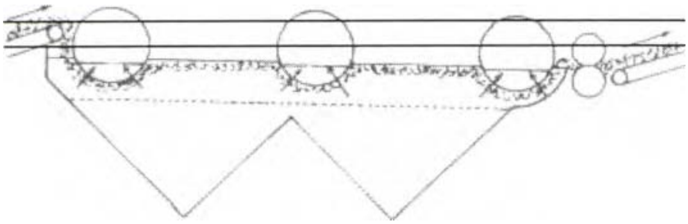


Figure 5-18. The Fleissner scouring bowl.

In the jet scouring machines (Fig. 5-19) the wool travels on a conveyer belt or a

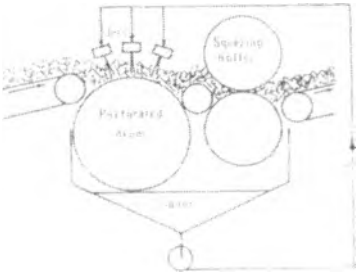


Figure 5-19. Jet scouring bowl [26, 27].

perforated drum and the scouring liquor is sprayed on the fibre through low pressure jets. Less felting takes place due to low velocity of jet and gentle movement of wool.

In the CISRO Lo-flo system [28], first one or two bowls of conventional machine are replaced and wash plate bowls (Fig. 5-20) are used instead. The wool is washed down a perforated plate into the squeezing roller by jets or sprays of scouring liquor. Liquors from Lo-flo unit and the conventional bowls are both recycled through interconnected loops incorporating heavy solids settling and centrifugal operation. This has the shortest possible bowl and has poor scouring efficiency. The process is mainly used to recover grease and for pollution control.

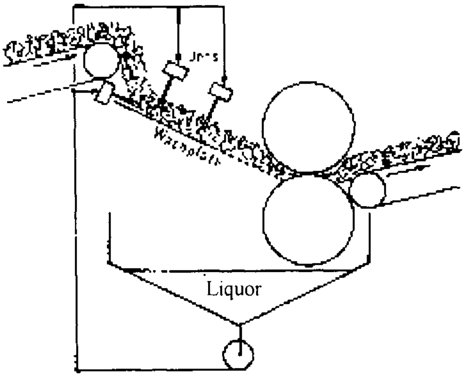


Figure 5-20. Washplate bowls used in Lo-flo process.

5.6.2 Wool hank scouring machine

Woollen and worsted yarns, unless dry spun contain significant amount of lubricating oil and are usually scoured in hank form in a continuous scouring machine. The hanks are transported through the scouring sets either by tape (Fig. 5-21) system or by battrices (Fig. 5-22). Usually, the sets have four bowls : two scour bowls, one rinse bowl and a final bowl where acidification and moth proofing is carried out. There is a pair of squeeze roller between each bowl. The top roller is usually lapped with wool or cotton sliver and the bottom roller is made of metal. Pressure is applied to have an expression of about 60%. The characteristic features of the two types of machines are summerised in Table 5.2. It is normal to scour only 1-2

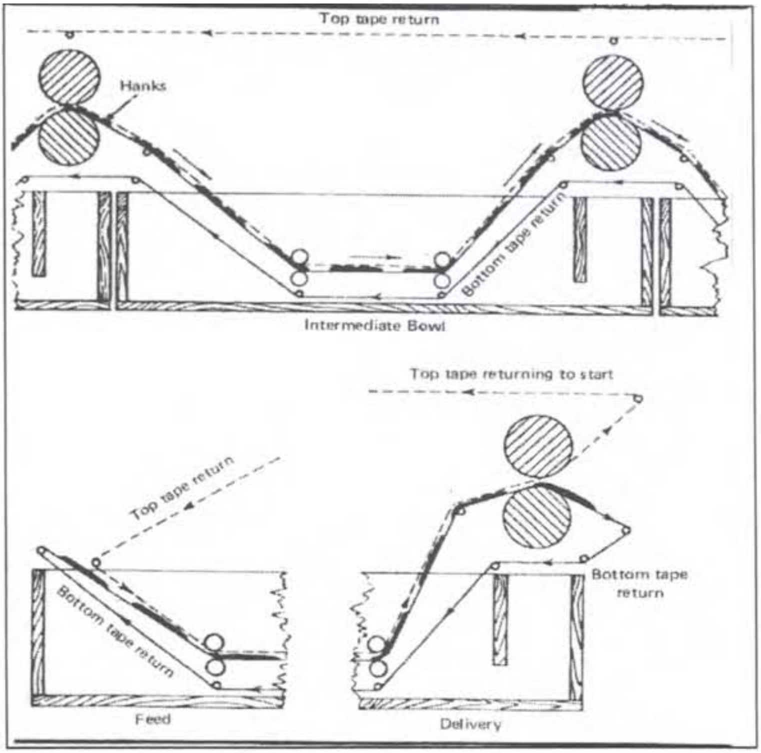


Figure 5-21. Principle of a tape scouring machine.

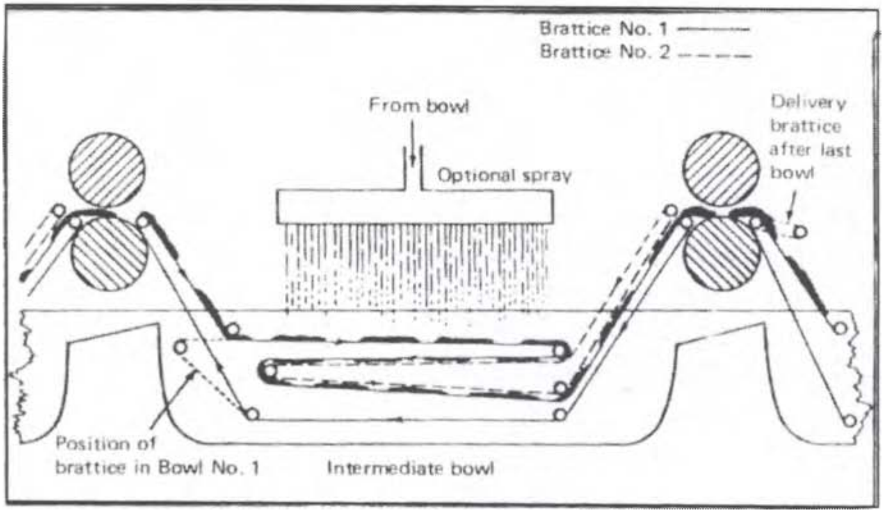


Figure 5-22. Principle of a battrice scouring machine.

TABLE 5.2
Characteristic Features of Yarn Scouring Machines [29]

	Battrice	Tape
Length of bowls (m)	2.5-4	1.5-3.5
Width of bowls (cm)	80-135	70-120
Depth of bowls (cm)	55-85	55-85
Capacity (l)	1600-2500	500-2200
Running speed (m/min)	4.5	9.0

tons of yarn in such types of machines. Due to lower running speed, battrice machines give lower immersion times compared to 6 to 12 sec given by tape machines. The bowls are usually heated by direct steam through perforated pipes or controlled steam valves.

Woollen yarns can also be scoured in packages such as in the form of cones or cheeses. Small batches may be scoured in Klauder-Weldon machine or on a Dolly washing machine.

5.6.3 Wool fabric scouring machine

Batchwise rope scouring in the Dolly [30] using soap and soda is widely practised. The Dolly consists of a wooden vessel across and over the winch vat is mounted a pair of heavy wooden squeezing rollers. Modern machines are developed (Fig. 5-23), in which the operations of washing/fulling or of high speed washing can be carried out without the need for additional machinery. Combined scouring and milling save time, man-power, water and energy. The cloth is run through the scouring liquor and the scouring is continued till the fabric is cleaned. In one system jets of scouring liquor are forced into and through the fabric ropes as they pass through a jet box immediately in front of the nip rollers. By means of two transporting and squeezing rollers (7), the fabric is compressed into the fulling tank (9), and a star cylinder (10), operating at variable speed, enables the desired packing density in the fulling tank to be achieved with the greatest accuracy and reproducibility. The setting of the pressure at the fulling flap (11) leads to a more uniform fulling effect. The material is conveyed out of the fulling tank via the cylinder (10) and after passing over another star cylinder (13), returns to the fulling liquor. In the case of high-speed washing, or after fulling, the cylinder (13) opens-out the fabric

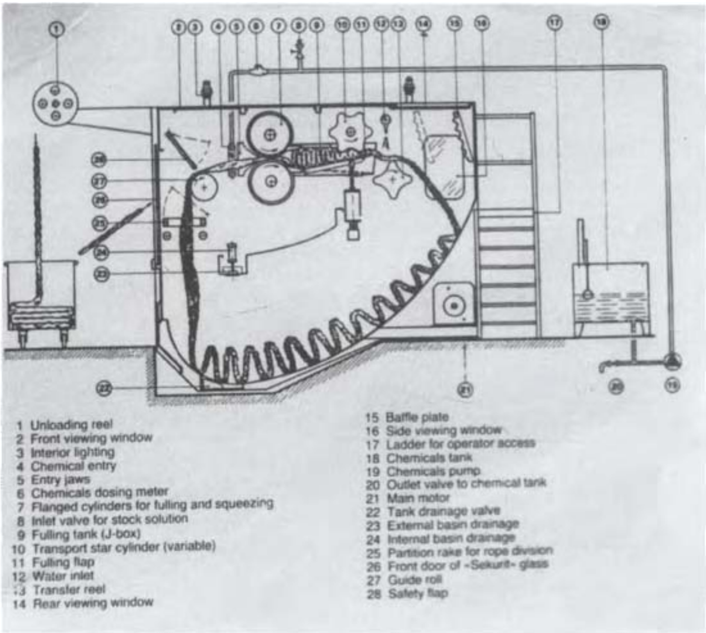


Figure 5-23. Diagram of a soft and rapid scouring and milling machine (Courtesy of CIMI Cerreto Castello, Italy).

and throws it against the baffle plate (15). The high-speed washing machine is available with 2 and 4 fulling tanks (J-Boxes), with the possibility of one or two entries per tank. The fulling tank capacity may be 50-400 kg for the machine with two tanks and 50-600 kg fabric for the machine with four tanks. The working speed can be infinitely varied between 60-400 m/min in addition to the choice of 5 preselectable speeds, which may be changed as necessary. There are some machines which can load up to 12 ropes of light fabrics. The well-known bag stitchings for all fabrics are not necessary anymore and it is guaranteed the absence of the traditional problems of creases, abrasions, tears and holes also on blends particularly sensitive to these defects. The cloth after scouring is washed-off in luke warm water.

5.6.4 Carbonising range for woollen fabrics

The carbonising process usually comprises : acidifying – drying – carbonisation – scouring. The process is same for loose stock and piece goods. The carbonising machine (Fig. 5-24) comprises : entry frame, acid bath, J-Box reaction, perforated

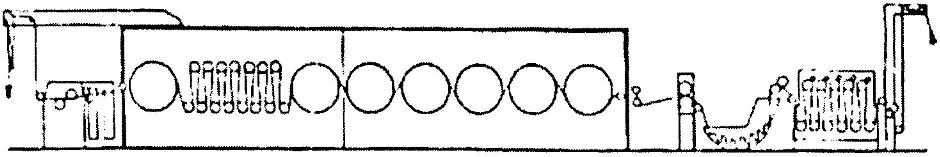


Figure 5-24. Carbonising range for woollen fabric (Courtesy of Fleissner GmbH & Co. Germany).

drum dryer with carbonising section, beating and brushing unit and plaiting or batching unit. Depending on the further process sequence, a neutralising phase (Fig. 5-25) can follow.

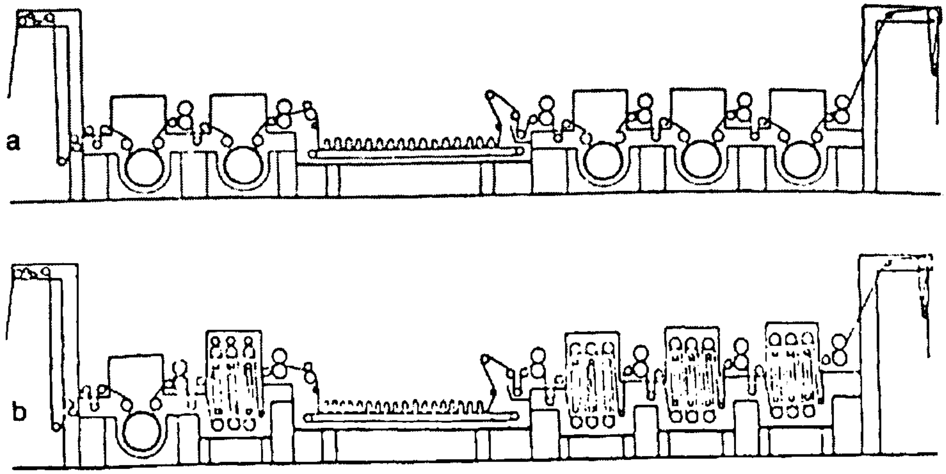


Figure 5-25. (a) Machine concept as perforated drum washing range,
(b) Roller vat range for more closely woven cloth qualities.

The acid bath is designed as a roller vat with single fabric thread-in. Rubber covered rollers press on the upper guide rollers in order to promote evacuation of the air and soaking of the fabric. Without being subjected to excessive squeezing, the fabric is deposited in J-Box reaction vessel holding about 100 m of fabric. Here the cloth, which is saturated with the liquor, has ample opportunity to absorb the acid. Following an adequate reaction period, the fabric is drawn out of the J-Box via a high expression nip. The expressed liquor is conducted back to the impregnating bath. There is also a liquor return flow connection leading from the reaction vessel. The impregnating bath is provided with a liquor circulation facility which ensure uniform concentration in the bath. The used liquor is replenished by a level controller. An automatic titration station constantly monitors the acid.

The fabric is then dried at 80°C in perforated drum dryers where the drying air is drawn through the fabric which ensures a fast, gentle and uniform drying action. Finally, the dry fabric is heated up to 120-130°C on a perforated drum in the carbonising section, and this temperature is maintained constant in the hotflue chamber, which holds approximately 30 m of cloth. The drying chamber is seperated from the carbonising section by a partition. Following carbonisation the fabric is guided through a beating and brushing unit where the combusted cellulose impurities are removed and exhausted.

A carbonising range for wool fabrics which probably applies hydrochloric acid from perchloroethylene has been developed (Fig. 5-26).

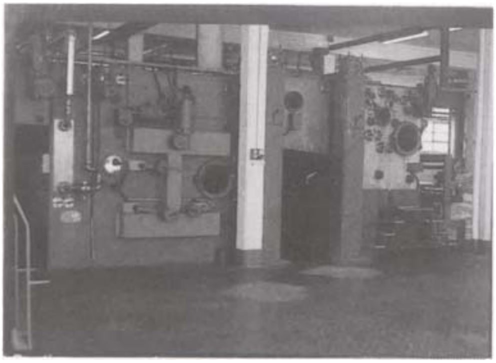


Figure 5-26. Continuous range for solvent carbonising of woollen fabrics (Courtesy of Sperotto Rimar, Italy).

5.6.5 Crabbing and decatising machines

Crabbing and decatising represent important processes in the finishing of wool goods providing wool fabrics with a top-line shrink-free finish. The continuous finishing line for worsteds are shearing – pressing – humidifying – decatising and for woollen fabrics are shearing – pressing – shrinking – humidifying – decatising.

A continuous crabbing by overheated water without rubber belt (Fig. 5-27) gives permanent effect with brighter appearance. The notable improvement of the fabric quality is due to the calendering effect in water at 110°C. There is no need for use of expensive rubber belts. Fig. 5-28 shows a continuous multiset crabbing machine.

The kier decatising (Fig. 5-29) of wool fabrics is also a process for permanently setting wool fabrics. In this way wool fabrics are given surface stability without

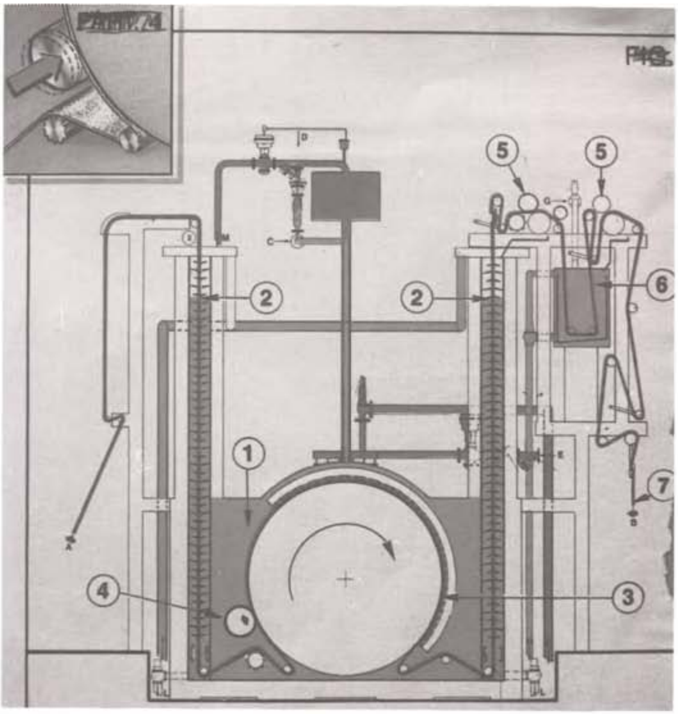


Figure 5-27. Schematic representation of Conticrabbing (Courtesy of MAT diA. Bertoldi S.p.A.).
1. Water-tight main compartment 2. Barometric columns 3. Main drum 4. Presssing roller 5. Pair of pressing roller 6. Cooling tank 7. Device to arrange fabrics in laps.

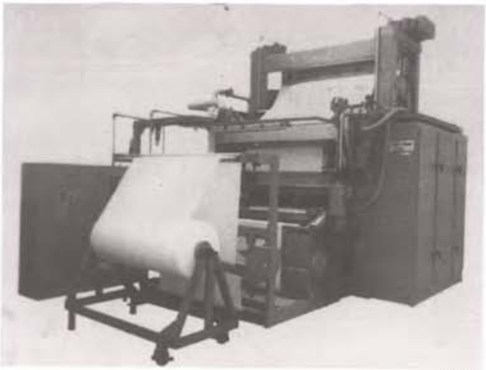


Figure 5-28. Continuous crabbing machine (Courtesy of Sperotto Rimar, Italy).

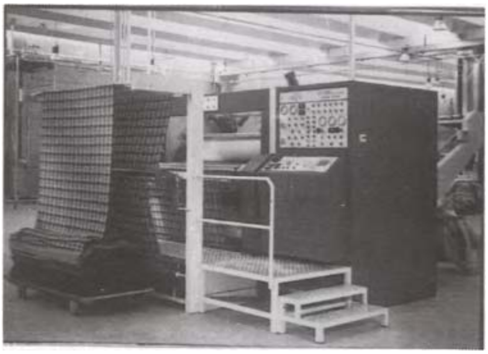


Figure 5-29. Kier decatising machine (Courtesy of Sperotto Rimar, Italy).

loosing their shaping capacity in the making up process. Temperature, pressure, moisture and time are the parameters which introduce physical and chemical processes in kier decatising. One of the disadvantage of kier decatising is its batch type method of operation. Chemical decatising of wool fabrics has long been a subject of discussion in basic research centres. The ''Menschema process'' (Kettling + Braun, Hemmer) is a low add-on applicator in combination with a Contripress® and a decatising machine. Menschner and Triatex presented it only in the form of a ''mural relief''. The new MR process (Menschner – Rotta chemical decatising) is shown in Fig. 5-30. The operational sequences of the MR process are wet finish-

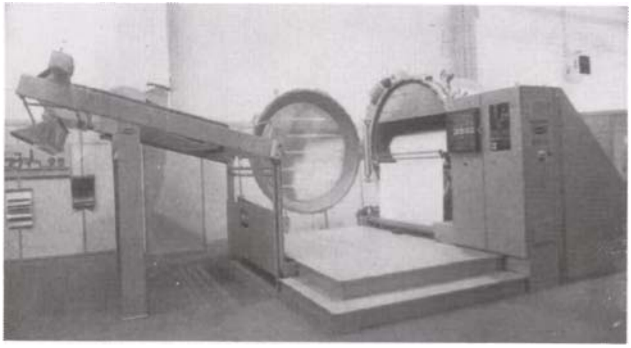


Figure 5-30. Universal permanent decatising machine
(Courtesy of Menschner – Kettling & Braun, FR of Germany).

ing, padding, depending on the effect (Rotta), drying, redamping (Weko), contripress (Menschner) and continuous decatising. Before the wool fabric is treated on the Contripress® the stabilising agents or similar products are applied in exactly the right amount by the low add-on route and then can react completely under the impermeable Contripress belt in the temperature and pressure zone. The effective range of application is freely variable. Other chemicals that set wool in the dry and wet states can also be applied. Besides greatly simplifying the finishing sequence, the process cuts costs and saves floor space.

The evaluation of the decatising effect is commonly based on subjective estimates. The handle, the glaze, the brightness of the colours, the bulkiness or hardness of the fabric are obtained from the decatising machines, the flow diagrams of which are shown in Figs. 5.31, 5.32 and 5.33. Therefore, it is required from the decatising machines that may have a wide and effective versatility.

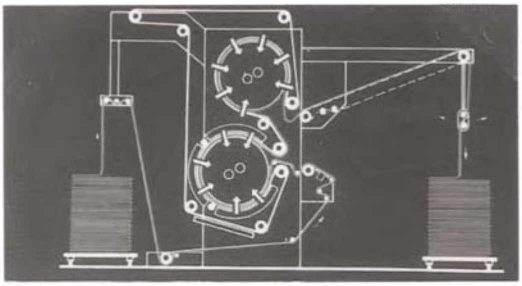


Figure 5-31. Finish decatising machine
(Courtesy of Drabert Shöne, Kettling & Braun, Germany).

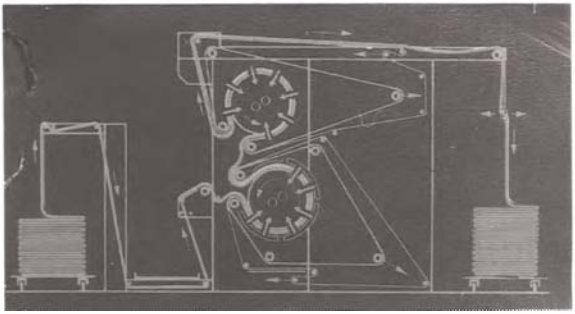


Figure 5-32. Lustre decatising machine
(Courtesy of Drabert Shöne, Germany).

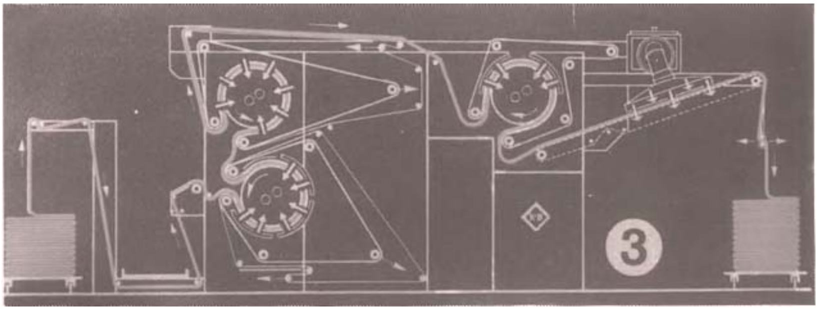


Figure 5-33. Permanent continuous decatising machine (Courtesy of Drabert Shône, Germany).

5.7 Silk Degumming Machines

Proper selection of equipment for degumming of silk is essential to prevent chafed surface, chafe marks, uneven degumming and chemical damage. However, the selection of equipment depends on the type of the article to be processed.

5.7.1 Yarn degumming machines

Silk yarn is normally degummed in the hank form. In the pack (beck), the hanks are normally hung on polished wood or metal rods which are submerged in the bath and turned by hand. Alternatively, hank and spray dyeing machines can also be used for degumming of silk in yarn form. In the foam boiling process foam produced by soap bath comes in contact with silk and thus causes degumming.

5.7.2 Piece goods degumming machines

Degumming of piece goods can be done on beck or pack system and the star machines (Fig. 5-34) are particularly suitable for delicate articles. In the beck system with strings the pieces are hung on bamboo or smooth metal rods so that the goods remain submerged in the degumming bath. The main disadvantage of this system is chafe marks (blanched places) or irregularities in the form of spots. In the well known star machines the goods may be hung from above only in the case of vertical simple star or the goods may be attached from below on hooks as well as hanging from above in the case of vertical double star or may be horizontally double star system. During degumming shrinkage takes place and hence the star machines are so designed that the hanks can be moved along the arms of the star, thus allowing for shrinkage.

In the continuous degumming machines (Fig. 5-35) the goods are hung in loops

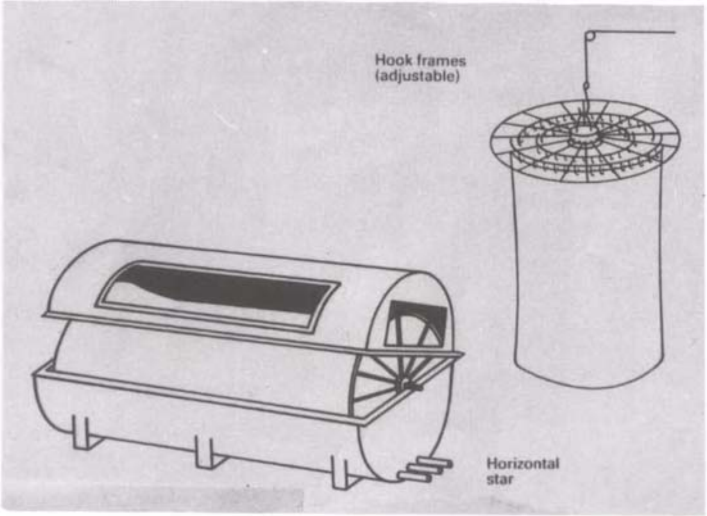


Figure 5-34. Star machines [31].

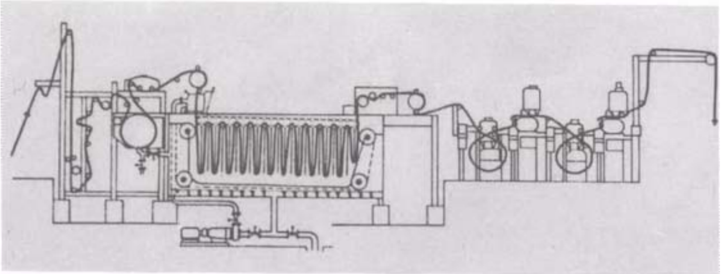


Figure 5-35. Continuous boiling off machine from Mezzera.

on rods which remain fully submerged in the bath and move continuously forward.

Articles with tight, smooth weaves may be degummed on the jig. Winches and jets are not generally recommended for complete degumming, but overflow machines can be used for knitted goods.

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Chapter 6

BLEACHING OF TEXTILES

6.1 Introduction

The natural fibre and fabrics even after scouring still contain naturally occuring colouring matter. This yellowish and brown discolouration may be related to flavone pigments of the cotton flower. The climate, soil, drought and frost can also cause various degrees of yellowness. Tips of leaves or stalks coming in contact with the moist ball after opening will cause dark spots and discolouration. Discolouration may also come from dirt, dust, insects or from harvesting or processing equipment in the form of oils and greases. The object of bleaching is to produce white fabrics by destroying the colouring matter with the help of bleaching agents with minimum degradation of the fibre. The bleaching agents either oxidise or reduce the colouring matter which is washed out and whiteness thus obtained is of permanent nature. Chemical bleaching of textile fibres is further aided by addition of optical brighteners.

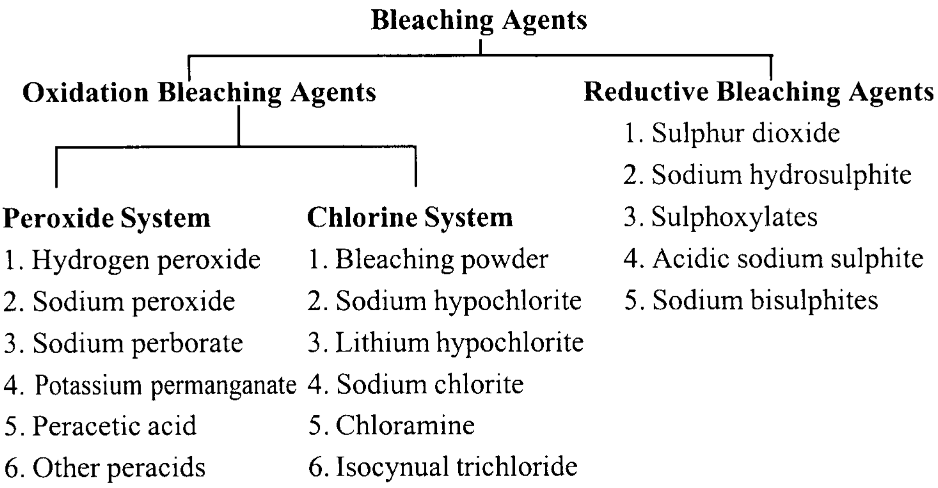
The primitive method of cloth bleaching, namely harsh scouring and exposure to the sun was also a chemical process in which light served as an oxidation catalyst. However, the processes are time consumable, labour intensive, highly variable in quality of goods produced, and tied up large amount of capital. The first major break with traditional methods of bleaching came in 1756. Nine major breakthroughs in the field of bleaching flax and cotton are shown in Table 6.1. During

TABLE 6.1
Nine Major Break-throughs in Bleaching Cellulosics

Approximate Date of Significant Usuge	
Sulphuric acid Scour	1756
Chlorine Bleach	1790
Le Blanc Process for Soda Ash	1791
High Pressure Kier	1815
Rope Washer	1830
Enzyme Desizing	1900
Peroxide Bleaching	1925
Continuous Peroxide Bleaching	1939
Fluorescent Brighteners	1950

the later stage of twenteeth century the time required for bleaching dropped steadily from months to days to hours. Now-a-days, manpower required for average plant is declined considerably and the cost of bleached finished product is also reduced. This technical break-through will continue in the future also and will reduce the cost of bleaching further.

A general classification of bleaching agents is shown in Fig. 6-1. In 1790 Bertholet developed bleaching process using water solutions of chlorine. Tennant in 1978 developed solid bleaching powder. Chlorine based materials such as sodium hypochlorite, calcium hypochlorite and sodium chlorite, predominated until the late 1920s when peroxide came into wider use with the cheaper electrolytic synthesis of hydrogen peroxide. By 1940, about 65% and to-day about 90% of all cotton is bleached with hydrogen peroxide.



Bleaching Agents

Oxidation Bleaching Agents

Peroxide System
1. Hydrogen peroxide
2. Sodium peroxide
3. Sodium perborate
4. Potassium permanganate
5. Peracetic acid
6. Other peracids

Chlorine System
1. Bleaching powder
2. Sodium hypochlorite
3. Lithium hypochlorite
4. Sodium chlorite
5. Chloramine
6. Isocynual trichloride

Reductive Bleaching Agents
1. Sulphur dioxide
2. Sodium hydrosulphite
3. Sulphoxylates
4. Acidic sodium sulphite
5. Sodium bisulphites

Figure 6-1. Classification of bleaching agents.

6.2 Bleaching with Hypochlorites

Hypochlorites as bleaching agents are still popular despite the anti-chlorine lobby and environmental pressures. Some of these salts which are used for the bleaching of textiles are briefly described.

6.2.1 Calcium hypochlorite (Bleaching powder)

A solution of bleaching powder contains calcium hypochlorite [$Ca(OCl)_2.4H_2O$], calcium chloride [$CaCl_2$, $Ca(OH)_2.H_2O$], lime hypochlorous acid formed by the hydrolysis of hypochlorite, possibly free chlorine and other soluble impurities like calcium chlorate, calcium permanganate etc. Calcium hypochlorite is generally prepared from bleaching powder or from liquid chlorine and slaked lime suspension. It is also possible to make solutions of hypochlorite by passing chlorine into milk of lime. Solid bleaching powder may be obtained by passing chlorine over hydrated lime [1]. In this process care must be taken not to increase the temperature above 55°C, since at higher temperatures, chlorate and chloride are formed.

Bleaching powder is partially soluble in water. A smooth paste with water is first prepared and then diluted with water. This is then allowed to stand until whole of the suspended matter has settled to bottom. The clear supernatent liquid is then drained-off for use which is about 12°Tw and contains about 3.9% available chlorine. This is then diluted to the required strength.

Calcium hypochlorite undergoes rapid exothermic decomposition on heating above 175°C. Bleaching powder solution reacts with acids with the evoluation of chlorine.

$$Ca(OCl)_2 + HCl = CaCl_2 + 2HOCl$$
$$Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HOCl$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$
$$2HOCl + 2HCl = 2H_2O + 2Cl_2$$

Certain metals or their oxides bring about catalytic decomposition of bleaching powder. Similar reaction can also occur with other metals such as iron or copper.

$$Ca(OCl)_2 + 4CoO = 2CoO_3 + CaCl_2$$
$$2CoO_3 = 4CoO + O_2$$

The oxidising action of calcium hypochlorite is due to hypochlorous acid. The conditions (pH) which favour the formation of hypochlorous acid increase the oxidising power of bleaching powder. Freshly prepared calcium hypochlorite solution has a pH of about 11.05 which on standing or agitation reduces the alkalinity by precipitating insoluble carbonate and thus increasing the concentration of hypochlorous acid. This acidic hypochlorous acid is more powerful bleaching agent than the alkaline hypochlorite and are not safe as this causes degradation of the cellulosic material due to the formation of oxycellulose.

6.2.2 Sodium hypochlorite

Sodium hypochlorite is a sodium salt of hypochlorous acid (HOCl). Sodium hypochlorite can be prepared by passing chlorine gas into a tank containing prepared solution of caustic soda, sodium carbonate or mixture of the two (about 4% by weight) at about 27°C.

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O + 25 \text{ Cal}$$
$$6NaOH + 3Cl_2 = NaCl + NaClO_3 + 3H_2O$$

Another way of preparing sodium hypochlorite solution is by the electrolysis of a solution of sodium chloride. In this method sodium hydroxide is formed at the cathode and chlorine at the anode on passing electric current through this solution. The sodium ion reacts with water to form sodium hydroxide and the liberated chlorine reacts with sodium hydroxide forming sodium hypochlorite.

$$Na + e \rightarrow Na$$
$$2Na + 2H_2O \rightarrow 2NaOH + H_2O$$
$$2Cl \rightarrow Cl_2 + 2e$$
$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

Sodium hypochlorite solution is strongly alkaline ($pH \simeq 11.55$) and the free caustic present in the solution acts as a stabiliser. Soda-ash scavanges free hydrochloric acid forming a non-volatile salt and maintain its alkalinity. Stability of sodium hypochlorite solution is also improved by storing it in a dark room below 30°C and free from contaminations of any heavy metal salts. The decomposition of sodium hypochlorite can be represented by the following reactions :

$$2NaOCl \rightarrow NaCl + NaClO_2$$
$$\text{or } 2NaOCl \rightarrow 2NaCl + O_2 \uparrow$$
$$\text{or } 3NaOCl \rightarrow 2NaCl + NaClO_3$$

The bleaching mechanism of sodium hypochlorite consists of the following reaction [2] :

$$NaOCl \rightarrow NaCl + (O)$$

The above reaction is accompanied by severance of glucose linkage in cotton, resulting in loss of tensile strength.

6.2.3 Lithium hypochlorite and chlorinated trisodium phosphate

Lithium hypochlorite can be obtained by mixing strong solutions of sodium hypochlorite with lithium chloride. This results in partial precipitation of sodium chloride. The product obtained by evaporation of supernatent solution typically contains 30% lithium hypochlorite (LiOCl), 34% sodium chloride and other salts. Chlorinated trisodium phosphate is a hydrated complex having chemical formula $(Na_3 PO_4 . H_2O) NaOCl$ and contains approximately 4% available chlorine. Generally, they are mainly used as laundry detergents, because sodium and lithium do not precipitate anionic surfactants as the calcium salts.

6.2.4 Factors effecting in hypochlorite bleaching operations

Cotton can be bleached with hypochlorite solution at room temperature containing 1-3 g available chlorine per litre at pH range of 9.5 to 11. The pH is maintained by adding 5 g/l sodium carbonate in the bleach bath. After bleaching the cloth is treated with dilute hydrochloric acid to neutralise any alkali (souring) present in the cloth. An antichlor treatment with sodium thiosulphate or bisulphite is also recommended to remove any residual chlorine from the cloth. Finally, the cloth is washed with water to rinse out acid from the cloth.

$$2NaOCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HOCl$$

$$2HOCl \rightarrow 2HCl + 2O$$

$$HOCl + HCl \rightleftharpoons Cl_2 + 2H_2O$$

6.2.4.1 Effect of pH

Hypochlorite ionises differently under different pH conditions and active component can be effective in three different states (Fig. 6-2). In the region of pH 7, when hypochlorous acid and hypochlorite ion are present approximate the same

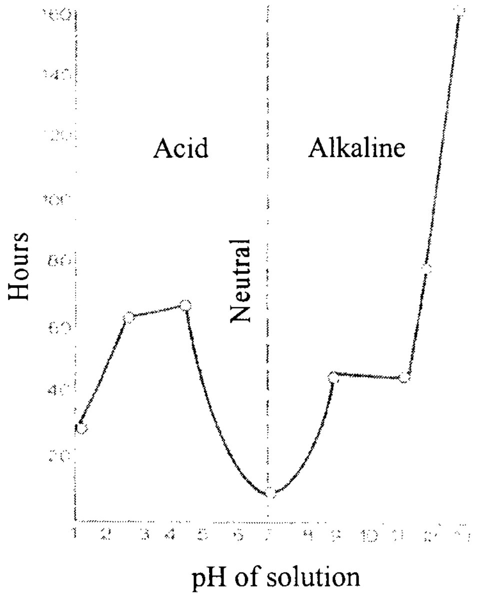


Figure 6-2. Rate of oxidation of cellulose in terms of the consumption of half the total available chlorine.

concentrations, the rate of attack on cellulose is greatly enhanced. In the case of bleaching powder the pH has fallen to within the danger zone after 15 min and after 1h when sodium hypochlorite is used. As the pH falls below 5, the liberation of chlorine begins to take place and pH below 1.5, the whole of hypochlorous acid is converted into chlorine. In the pH range 9 to 11, a plateu occurs at which little change occurs and is the normal use range for bleaching with hypochlorite solution. The active species [4] appear to be OCl^- ion, or a complex of HOCl and OCl^-. The pH (8.5-11.0) is stabilised by the addition of buffers (5 g/l Na_2CO_3).

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$$

6.2.4.2 Effect of temperature

Generally bleaching of cotton is carried out with 1.5 g/l of hypochlorite solution at about 40°C for 1 h. Higher temperature increases the rate of bleaching but at the same time degradation of cotton is also increased. Hypochlorite solutions by themselves are quite stable at the boil at pH values 11 or higher, but decomposes at lower pH values [5]. During the decomposition of hypochlorite solutions, chlorate formation predominates in the absence of cotton, while in the presence of cotton, it is practically absent under alkaline condition [6]. Hypochlorite solutions if buffered to pH 11, the rate of bleaching is increased by a factor of 2.3 times for every 10°C rise in temperature. It is thus, possible to bleach at 60°C in 7 min, but is difficult to control the degradation of cotton in such short period of bleaching.

6.2.4.3 Effect of concentration

The commercial solution of sodium hypochlorite contains 14-15% available chlorine, compared to 35-36% in bleaching powder. The concentration of hypochlorite in the bleaching bath generally varies from 1 to 3 g/l available chlorine. The optimum bleaching conditions, however, depend on the degree of discolouration of the cloth and thus the temperature and time of reaction should be adjusted according to the requirement. The concentration of hypochlorite solution is normally estimated by means of standard thiosulphate or arsenite titration.

6.2.4.4 Effect of electrolyte

The addition of salt in the hypochlorite bleaching bath increases the activity in the initial period due to the production of nascent chlorine. The addition of chloride moves the equilibrium to the left-hand side, but after, say 15 min, when the new equilibrium is reached, the sudden stimulated effect is ceased and bleaching resumes its normal course and hence action of salt is only temporary and confined to the first stage of bleaching.

$$2Ca(OH)_2 + 2Cl_2 \rightleftharpoons Ca(OCl)_2 + CaCl_2 + 2H_2O$$

$$HOCl + NaCl = 2Cl + NaOH$$

6.2.5 Accelerated hypochlorite bleaching

The aim of accelerated bleaching is to adopt a continuous bleaching by reducing the bleaching time and chlorine consumption with the help of more reactive bleach liquor. However, the accelerated bleaching may lead to degradation and yellowing of the cotton fabric.

6.2.5.1 Accelerated bleaching in the danger zone

Bleaching with hypochlorite solution containing 1 g/l of available chlorine with the addition of 5 g/l sodium carbonate at pH close to 7 can be done in just 10 min. The system is more reactive in the danger zone and thus bleaching can be done in a shorter time.

6.2.5.2 Accelerated bleaching in conjunction with H_2O_2

Hypochlorite bleaching can be accelerated by the addition of hydrogen peroxide, ammonia, chloramine etc. [7, 8]. Hydrogen peroxide reacts with hypochlorite forming hydroxyl and $HO_2^{\bullet}$ radicals. The hydroxyl radical may react as before or

$$H_2O_2 + \bar{C}l\,O \rightarrow H\,O_2^{\bullet} + \bar{C}l^{\bullet} + OH$$

$$HO_2^{\bullet} + \dot{O}\,H \rightarrow H_2O + O_2$$

terminate by reaction with $HO_2^{\bullet}$. In actual practice fabric is first treated with cold alkaline hypochorite solution as a pre-bleaching agent and then an after bleach is carried out (without rinsing) in conjunction with hydrogen peroxide or sodium chlorite [9]. The cold hypochlorite treatment can be carried out in a J-Box type cold reaction chamber of 7 min reaction time. The cloth then passes in another hot reaction J-Box in open width form and plaited into a bigger pile without any serious risk of creasing and possible crease marking. The advantages of this process are that the total reaction time of the bleaching process can be reduced, H_2O_2 acts as an antichlor and fabrics containing cotton/rayon mixture as well as colour-woven goods can be bleached due to milder conditions employed in the hypochlorite stage.

6.2.5.3 Accelerated bleaching at elevated temperature

Another possible way to reduce the bleaching time is to work at elevated temperature [5, 10]. Rapid bleaching may be done at 60-80°C containing 0.9-1.6% of active chlorine (o.w.f.) in the pH range of 8.6 to 12.8.

6.2.5.4 Accelerated bleaching in presence of additives

Sometimes bromides or related compounds are added to the hypochlorite liquor to accelerate the bleaching action. It is likely that sodium hypobromite is formed which is a stronger oxidising agent than hypochlorite.

Methods of bleaching at high temperature and pH close to 7 in presence of sulfamic acid in hypochlorite bleaching of cotton has been suggested [11]. It has a stabilising effect, slowing the rate of decomposition of hypochlorite and reducing the damage to the fibre, without having any adverse effect on the final whiteness.

6.2.5.5 Accelerated bleaching by steaming

An accelerated method for bleaching polyester/cotton blended fabric is described [12]. The process consists of steaming at 100 ±15°C for 60 min followed by washing and padding through a solution containing 10-12 g/l active chlorine at 25°C. The fabric is then aged in a series of chambers for 60 min and then led through an acidifying bath with 2-2.5 g/l sulphuric acid at 20°C. The accelerated effect is achieved by changing the order of the operations.

6.2.6 Advantages of sodium hypochlorite bleaching over bleaching powder

Sodium hypochlorite has practically replaced bleaching powder due to its various advantages although solutions of hypochlorite are more expensive than calcium hypochlorite.

(i) Bleaching powder is a mixture of calcium hypochlorite with lime. Thus, calcium carbonate settles on the fibre during bleaching process. On the contrary, sodium hypochlorite is free from any such danger of specks of lime being deposited on the cloth.

(ii) Bleaching powder is partially soluble in water and exists in a solid form. However, sodium hypochlorite, being a sodium salt of hypochlorous acid, does not require any dissolving arrangement and are ready for immediate use. Hypochlorites are easy to handle.

(iii) Chlorinated lime requires higher alkalinity than that of sodium hypochlorite solutions for active bleaching conditions.

(iv) Sodium hypochlorite solutions have less tendency for the pH value to fall during bleaching. Caustic soda is liberated by the hydrolysis of sodium hypochlorite form sodium carbonate under the action of carbon dioxide from atmosphere. Sodium carbonate thus formed can be easily washed away with water and reduces acid requirement for souring. In such case, sulphuric acid may be used as souring agent in place of the more costly hydrochloric acid.

(v) Sodium hypochlorite can penetrate into the fabric more thoroughly than in the case of bleaching powder and therefore shorter time of bleaching is possible in the case of sodium hypochlorite.

6.2.7 Disadvantages of sodium hypochlorite

(i) Sodium hypochlorite does not produce completely satisfactory whites inspite of many advantages.

(ii) Bleaching with sodium hypochlorite produces slight damage to cellulosic fibres.

(iii) Sodium hypochlorite cannot be used for the bleaching of synthetic fibres as it produces greater damage to such fibres.

(iv) Bleaching with sodium hypochlorite solution requires corrosion resistant equipment.

(v) Sodium hypochlorite produces unpleasent odours in working environment.

(vi) Sodium hypochlorite solution is harmful to skin in concentrated form.

(vii) It produces harsh handle on fabric. Furthermore, it cannot be used on natural animal fibres.

(viii) Stabilisation of sodium hypochlorite is difficult to achieve where pH varies.

(ix) The formation of highly toxic chlorinated organic biproducts (AOX) during the bleaching process has limited its use because these compounds are a potential hazard to the drinking water resources when discharged [13, 14].

6.3 Bleaching with Peroxide

Hydrogen peroxide was discovered in 1818 and its use in bleaching textiles was first suggested in 1866. However, its high cost limited its use in cotton bleaching until 1935. The problem was partially solved by the process using barium peroxide and phosphoric acid. In 1926 hydrogen peroxide was manufactured by an electrolytic process based on the decomposition of persulphuric acid (H_2SO_5) [15].

Sulphuric acid is first ionised into hydrogen and bisulphate ions which is discharged on the anode and then form persulphuric acid, which on vacuum distillation reacts with water to form hydrogen peroxide. Hydrogen peroxide can also be obtained by dissolving sodium peroxide in water. Instead of dissolving the peroxide and then neutralising the liberated alkali, the peroxide can slowly be stirred into slight excess of sulphuric acid. The reaction is carefully controlled as a large amount of heat is evolved. For every 100 lb of H_2O_2 (40% by volume) 95 lb of Na_2O_2 is to be used.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$2HSO_2^- - 2e \rightarrow 2HSO_4$$
$$2HSO_4 \rightarrow H_2S_2O_8$$
$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$$
$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$
$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

Pure hydrogen peroxide is fairly stable in presence of sulphuric acid and phosphoric acid if stored away from sunlight in a perfectly smooth bottle. In alkaline medium it is less stable and even traces of alkali (NaOH, Na_2CO_3) decompose aqueous solution of hydrogen peroxide. The addition of alcohol, glycerine or berbituric acid also stabilise hydrogen peroxide. Hydrogen peroxide also decomposes in the presence of finely divided heavy metals such as copper, iron, manganese, nickel, chromium etc. or their oxides with liberation of oxygen.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The volume strength of hydrogen peroxide is expressed as the volume of liberated oxygen at N.T.P. on heating one volume of hydrogen peroxide sample. Hydrogen peroxide is generally made of 10, 12, 20, 100 and 130 volume strength. A 10 volume peroxide solution is one which will liberate 10 times its own volume of oxygen. The percentage concentration is expressed as the quantity of pure hydrogen peroxide in 100 parts of sample and is expressed as x%, y% etc. The commercial supply of hydrogen peroxide are generally 35% and 50%. A 10 volume hydrogen peroxide contains 3% hydrogen peroxide and thus, 1% H_2O_2 = 3.3 volume concentration. The strength of the available oxygen can be estimated by titrating the peroxide using standardised potassium permanganate ($KMnO_4$) until or faint permanent pink colour appears. However, iodine method is preferred to permanganate method.

6.3.1 Mechanism of peroxide bleaching

Though hydrogen peroxide is stable in acidic medium, but bleaching occurs by the addition of alkali or by increased temperature. Hydrogen peroxide liberates perhydroxyl ion (HO_2^-) in aqueous medium and chemically behaves like a weak dibasic acid. The perhydroxyl is highly unstable and in the presence of oxidisable substance (coloured impurities in cotton), it is decomposed and thus bleaching action takes place. Sodium hydroxide activates hydrogen peroxide because H^+ ion is neutralised by alkali which is favourable for liberation of HO_2^-.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$H_2O_2 \rightarrow H^+ + HO_2^- \xrightarrow{OH^-} HO_2^- + H_2O$$

However, at higher pH (above 10.8) the liberation of HO_2^- ion is so rapid that it becomes unstable with the formation of oxygen gas which has no bleaching property. If the rate of decomposition is very high, the unutilised HO_2^- may damage the fibre. A safe and optimum pH for cotton bleaching lies between 10.5 to 10.8 where the rate of evolution of perhydroxyl ion is equal to the rate of consumption (for bleaching). At higher pH, hydrogen peroxide is not stable and hence a stabiliser is frequently added in the bleaching bath.

6.3.2 Stabilisers for peroxide bleaching

The process of regulation or control of perhydroxyl ion to prevent rapid decomposition of bleach and to minimise fibre degradation is described as stabilisation. Stabilisers for peroxide normally function by controlling the formation of free radicals. These are complex blends of a selection of materials serving a number of functions. They could include any of the following :

- Alkali, e.g. caustic soda/carbonate/silicate.
- Dispersant, e.g. acrylates/phosphonates.
- Sequestrants, e.g. EDTA/DTPA/heptonates/gluconates.
- Inorganics, e.g. magnesium salts.
- Colloid stabilisers, e.g. acrylic polymers.

The selection of alkali to be used in peroxide bleaching is dependent on the fibres or blends being bleached. Sodium hydroxide, sodium carbonate are generally used on cellulosic fibres whilst ammonia and various phosphates are used when bleaching protein fibres. Of the various phosphates only tetrasodium pyrophosphate, $Na_4P_2O_7$ and hexametaphosphates are of interest as stabilisers in alkaline bleach bath.

Sodium silicate is the most conventional, easily available and widely used stabiliser. Sodium silicate [16] is mildly alkaline in nature and the commercial grade consists of polysilic acid and having a Na_2O : SiO_2 ratio 1 : 3.3. The most preferred ratio for bleaching is 1 : 1, however, the final ratio will depend on the bleach bath and alkali used. Sodium silicate forms a complex compound with perhydroxyl ions which are liberated slowly at higher temperature during bleaching process. Metallic silicates are also oxidation and thermal resistant, offer a buffering effect, are colloidal in nature and are not greatly effected by the presence of ionic iron. Sodium silicate, however, has a greater stabilising action in the presence of calcium and magnesium salts so that water with hardness between 2° and 5° is recommended or, if water of zero hardness be used, 0.06 g/l magnesium sulphate may be added. The effect of magnesium ions in the form of $MgSO_4.7H_2O$ for stabilising peroxide bleaching bath is recommended [17]. Colloidal magnesium silicates and hydrated silicas must be kept in colloidal form during their formation and during bleaching. Since this is seldom fulfilled completely under plant conditions, some deposition of silicate onto fibre produces harsh feel and silicate scale on J-Box surface which abrades the goods producing defects. It is advisable to rinse very thoroughly after bleaching to avoid harshness on the fabric. Alternative way to avoid precipitation, an additional alkali may be added to bring the ratio of Na_2O : SiO_2 to within the region of 2.25 : 2.75. Calcium phosphate, produced by the addition of disodium phosphate brought to pH about 9.6 with caustic and buffered with borax, substitutes satisfactorily for silicate and no scale is formed.

Sequestering agents for heavy metals should theoretically make the best stabilisers. In effect, stabilisation may be effected by elimination of heavy metal ions that are responsible for free radical formation. This appears to be an anticatalytic reaction. Many types of sequestering agents are used in textile processing. The main types are :

- polyphosphonates,
- polyhydroxy-carboxylic acids,
- aminopolycarboxylic acids,
- phosphonic acids,
- polyacrylic acids.

Organic stabilisers are often commercially blended products which may or may not contain magnesium salts, the three main types being the aminopolycarboxylate, protein degradation products and selected surfactants. The preferred sequestering agents in terms of both sequesteribility and stability to oxidation are diethylene triamine pentaacetic acid (DTPA), either as sodium or magnesium salt, and its hydroxy derivatives. Aminopolycarboxylic acids used in the form of their magnesium and calcium salts have the advantage over conventional amino polycarboxylic acids in that they are not reduced to amino oxides at high temperature and thus do not loose their sequestering power. Polycarboxylic acids act mainly as dispersing ion-exchangers. Phosphonates have limited application and since recently, due to their eutrification nature, are not preferred. Phosphonates are active as complex formers with good dispersing properties.

In recent years acrylates have been used in preference to phosphonates and whilst heptonates and gluconates have replaced EDTA and DTPA. Acrylic acid copolymers are normally not biodegradable. A method has been patented to introduce sugar molecules directly in the polymer chain of polycarboxylic acid [18]. The sugar molecule in the tautomeric endiol form has C=C double bond which is necessary for copolymerisation with acrylic acid. Sugar polyacrylates, however, due to the hydroxyl groups of sugar, have a binding capacity for ferric ion. Other biodegradable compounds (stabilisers) are prepared by graft copolymerisation of available unsaturated monomers such as maleic acid, vinyl acetate, methallyl sulphonates, methoxy PEG, methacrylate and saccharose and have a molecular weight range of 3-20 thousand. They can be used in the form of free acid or their salts. The binding power of calcium and magnesium salt is 3-5 times that of homopolyacrylates, particularly for hydroxides of iron, calcium and magnesium at room temperature as well as at boil. They have high dispersing power for iron oxides, of the level of phosphonates.

6.3.3 Parameters in peroxide bleaching operations

It is very difficult to specify strict guidelines for optimum bleaching conditions for hydrogen peroxide as the operation is normally affected by the nature and quality of the goods to be bleached, the amount of bleaching required and on the equipment available. However, the following general variables are considered to be important :

6.3.3.1 Effect of pH

The stability of hydrogen peroxide depends on pH. At pH 1 to 3 it is stable ; but at highly alkaline pH 11.5 to 13 it has least stability. The bleaching takes place around 10.5 due to accumulation of perhydroxyl ions in the bleaching bath. At neutral or weak alkaline media, hydrogen peroxide does not produce any whitening effect and may cause degradation of cellulose.

6.3.3.2 Effect of temperature

In practice cotton bleaching with hydrogen peroxide is carried out at 90-100°C, but the temperature may be increased to 120°C in the case of pressurised equipment with a corresponding reduction in process time. The rate of bleaching increases with the increase in temperature, but at the same time solution becomes unstable and degradation of cotton increases. Below 80°C, the evolution of perhydroxyl ion is very slow so also the rate of bleaching.

6.3.3.3 Effect of concentration of liquor

The optimum concentration of hydrogen peroxide depends on number of factors namely liquor ratio, temperature and class of fibre. In the batch process using kiers about 2-4% (o.w.f.) hydrogen peroxide is sufficient for cotton fabrics with a liquor ratio of 10:1 to 20:1. In the continuous process, the cotton fabrics are saturated with bleach bath containing 1-2% (o.w.f.) hydrogen peroxide. Very high concentration may damage the fibre.

6.3.3.4 Effect of time

The time required to bleach with hydrogen peroxide depends on temperature, class of fibre and equipment used for bleaching. In general, the time of bleaching is inversely proportional to the temperature of the bleaching bath. Cotton may be bleached in open kiers by circulating heated hydrogen peroxide solution (88-95°C) for 6 to 10 hours.

6.4 Bleaching of Wool with Hydrogen Peroxide

The natural colour of animal fibre is closely related to the character of environment in which the animal lives [19]. Wool lots completely free of dark fibres do not exist [20]. In animal (and human) hair two kinds of pigments occur, namely eumelanin (responsible for black, dark brown and grey colours and commonly referred to as melanin) and pheomelanin (present in yellow, reddish-brown and red hair). Both are thought to be formed by different mechanisms and chemically differed [21]. Eumelanin is formed by enzymatic (tyrosinase) oxidation of tyrosine and polymerisation of several oxidation product [22]. Pheomelanin occurs in form of discrete grannules. Melanin grannules can occur in the cortex or in the cuticle.

Scoured wool varies in shade from the light cream of wools considered to have good colour to discoloured, urine-stained wools and the near black of heavily pigmented wool. Bleaching is common with all these wools which has been well reviewed [23-25]. The main problem is that the whiteness of wool attained during bleaching is not permanent. Wool tends to yellow over a period of atmospheric exposure of approximately six months. Blueing or optical whiteners may be added either to bleach liquor or to final rinse bath. The main bleaching agents for wool are oxidising and reducing agents. Amongst the oxidising agents hydrogen peroxide is most commonly used because sodium hypochlorite gives a deep rust colour and sodium chlorite develops pink colouration on wool. Traditionally wool is bleached by oxidative processes either in the presence of alkaline stabiliser or under acidic condition of hydrogen peroxide [27, 28].

6.4.1 Bleaching of wool in alkaline hydrogen peroxide solution

In the alkaline condition, wool is treated at pH 8-10 with a 1.5-3 vol. solution of hydrogen peroxide containing 2-3 g/l stabiliser, which may be sodium silicate or sodium pyrophosphate. A mixture of sodium pyrophosphate and ammonium oxalate is also useful for use as a stabiliser in bleaching of wool with hydrogen peroxide [28]. Bleaching may be carried out at 50°C for 3 to 5 h and then rinsed, treated with dilute acetic acid and rinsed again. The level of whiteness can be controlled by concentration of hydrogen peroxide, length of treatment time, pH and temperature of treatment bath.

6.4.2 Bleaching of wool in acidic hydrogen peroxide solution

In the acid process wool is treated with a solution of hydrogen peroxide containing formic acid (2.5 g/l) at pH around 4 to 4.5 at room temperature. The treated wool is then squeezed to remove excess liquor and passed into a drier where bleaching takes place. Ageing is preferable because the colour of the wool continues to improve for 24-48 h after drying. Citric acid activates peroxide bleaching of wool between 80 and 60°C [29]. Activated hydrogen peroxide bleaching of wool with reduced bleaching time and damage is reported by treatment in a bath consisting a mixture of organic salts that form carboxylic acids [30, 31]. Further, bleaching with alkaline and acidic hydrogen peroxide at 60°C can be improved by adding 100 to 200 g/l of urea [32]. The precautions during bleaching are exactly the same as those needed in the bleaching of cotton with hydrogen peroxide. The advantages of acid process are lower chemical degradation of wool, rinsing after bleaching is not required and no tendency for bleeding of coloured threadings.

6.4.3 Alkaline peroxide bleaching followed by hydrosulphite treatment of wool

Where an excellent stable bleach is required, especially if it is to be followed by the application of a fluorescent brighteners, then an alkaline peroxide bleach followed by stabilised hydrosulphite treatment is necessary. Bleaching is carried out for 3-5 h at 50°C with alkaline hydrogen peroxide followed by a second treatment with 2 g/l of hydrosulphite solution to raise the whiteness further.

6.4.4 Mordanting and peroxide bleaching of wool

The best chance for an efficient bleaching of highly pigmented wool with minimum fibre damage is provided by the use of metal catalysts in a mordanting step preceeding peroxide bleaching.

Mordanting is done in presence of hypophosphorous acid and it is an excellent stabiliser for iron (II) ions under mordanting conditions (Table 6.2). More importantly, cystine suffers hardly any attack from hypophosphorous acid under conditions that favour disulphide scission induced by sulphur containing reducing agents [34-36]. It is possible to avoid the use of formaldehyde in pigment bleaching when a mild reducing agent such as hypophosphorous acid is present. However, with hydrosulphite, ferrous sulphate and ammonium sulphate mordanting, addition of 4% of 40% formaldehyde as a cross-linking agent to prevent fibre degradation is suggested [37, 38]. Rinsing following the mordanting step proved to be critical with regard to selectivity and consequently to fibre damage. A normal cold rinse would remove virtually no iron from the fibre.

TABLE 6.2

Mordanting and Rinsing Conditions for Pigmented Wool [33].

	Mordanting	Rinsing
Iron (II) sulphate heptahydrate	10 g/l	–
Hypophosphorous acid (50%) (reducing agent)	3-4 g/l	–
Formic acid	To pH 3 to 3.5	–
Temperature (°C)	80	80
Time (min)	60	20

In the second stage, bleaching is carried out in alkaline condition of hydrogen peroxide. Iron that settles on the surface and inside the fibre acts as a catalyser and brings about enhanced bleaching action by extremely reactive radicals ($HO\cdot$ and $HO_2\cdot$) that are produced from oxidising agent. The bleaching conditions are summerised in Table 6.3. Tetrasodium pyrophosphate (diphosphate) (10 g/l) is a good stabilising agent in peroxide bath having liquor ratio of 15:1. After bleaching the wool is thoroughly rinsed with water. The retention of non-selective ferrous ions on wool following rinsing and subsequent bleaching with hydrogen peroxide leads to an undesirable light brown discolouration from ferric species. Selectively bleached fibre may be given a second step reductive or oxidative bleaching to yield whiter material for customer requirement.

TABLE 6.3

Bleaching Conditions for Wool Pigmented in the Bulk

Fibre type	H_2O_2 (35%) (ml/l)	pH (adjusted with amm. hydroxide)	Temp. (°C)	Time (min)
Karakul Wool, Cashmere, Alpaca, Camel, Yak.	25-45	8-8.5	50-60	45-180
Rabbit, Chicken feather.	20-40	8-8.5	50-60	45-120
Goat, Human hair.	30-50	8.5	60-70	60-180

6.4.5 Sequential oxidative and reductive bleaching of wool

There are two approaches for sequential oxidative/reductive bleaching of wool in a single bath. In the first approach, following the oxidative bleaching of wool using hydrogen peroxide, the peroxide bath is converted to reductive bath by addition of thiourea and bleaching continues without the need for a fresh bath for the reductive steps. In the second approach after bleaching of wool with oxidative hydrogen peroxide (alkaline or acidic), the remaining active hydrogen peroxide is decomposed by the use of an organic catalyst, and finally a reductive bleaching agent is added to the bath with necessary pH adjustment.

Regarding the first approach vast amount of information is available on thiourea [39-43] and the reaction mechanism can be represented as :

$$\underset{\text{thiourea}}{H_2N-C(=NH)-SH} + 2H_2O_2 \xrightarrow{pH\,4.5-5.5} \underset{\text{thioureadioxide}}{H_2N-C(=NH)-SO_2H} + 2H_2O$$

$$H_2N-C(=NH)-SO_2H+2OH^- \xrightarrow{pH\,7-8} \underset{\text{urea}}{H_2N-C(=NH)-OH}+\underset{\text{sulphinate ion}}{SO_2^-}$$

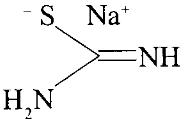
$$SO_2^- + [\text{chromophore}] \rightarrow SO_4^{2-} + [\text{reduced chromophore}]$$

The reaction route and the final products of the reaction of thiourea with hydrogen peroxide are very much dependent on the molar ratio of reactants and the pH of the reaction. Thiourea dioxide is produced in situ and reductive bleaching occurs. The bleaching conditions developed are, alkaline hydrogen peroxide bleaching at 60°C for 60 min followed by an addition of thiourea, pH adjustment, and subsequent reductive bleaching at 60°C for 25 min followed by washing and rinsing. There are number of patents on these new bleaching process [44, 45].

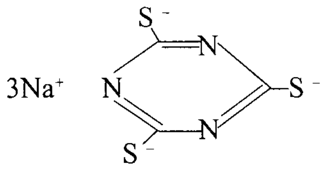
In the second approach, the addition of thiourea directly to hydrogen peroxide bath is avoided because it wastes considerable reductive agent due to large excess of hydrogen peroxide usually left in the bleach bath. To avoid this problem, organic catalysts that decompose hydrogen peroxide are added and finally thiourea dioxide or methane sulphinate is added directly to the bath with necessary pH adjustment. There are many inorganic catalysts that readily decompose hydrogen peroxide, but some (Fe^{3+}, Fe^{2+}, Cu^{2+}, Mn^{2+}) tend to cause excessive damage as well as discolouration of wool. Co^{2+} is the only metal cation reported to cause no damage or discolouration [46].

Despite the advantages of using thiourea to induce in situ reductive bleaching, some potential users of single bath processes hesitate to use it due to the toxic nature of thiourea. Furthermore, thiourea though easily handled and thoroughly consumed, is classified as carcinogen unlike its oxidised counterpart, thiourea dioxide (formamidinesulphinic acid).

Trithiocyanuric acid (TTCA; s-triazine-2, 4, 6-trithiol) is a cyclic analog of thiourea. Na_3TTCA is not classified as a carcinogen and thiourea may be replaced by it. Na_3TTCA is most effective at 90% of the stoichiometric weight to peroxide, as



Thiourea



Sodium salt trithiocyanuric acid (Na_3TTCA)

opposed to 70% for thiourea. The Na_3TTCA is more sensitive to the pH of the rinse bath than the thiourea process and is more expensive than thiourea. Nevertheless, the attractiveness of using Na_3TTCA is the avoidance of a potential carcinogen and achievement of exceptional whiteness over conventional peroxide bleaching [47, 48].

6.4.6 Bleaching of wool with emulsion of hydrogen peroxide

Wool has been successfully bleached with a stable emulsion of hydrogen peroxide [49] or permonosulphuric acid [50] in perchloroethylene. By this means it appears to be possible to obtain the same degree of whiteness as that attainable in a standard aqueous bleach, but more rapidly and with the use of less peroxide. No stabilising or activating agents are needed, but the bleaching of wool in perchloroethylene seems to be more deleterious to mechanical properties of bleached wool than equivalent aqueous procedure.

6.5 Bleaching of Silk with Hydrogen Peroxide

The natural colour of silk thread differs depending upon the type of silkworm and its feeding habit. Although the bulk of the natural dyestuff such as chlorophil, xanthophil and carotin are to be found in the silk gum, the degummed mulbery silk also has strong yellowish inherent colour. Since some of the sericin is tenaciously held by fibrion, complete elimination of colour by degumming is not achieved. Thus, the fabrics manufactured from yellow raw silk retain a yellowish tint after boiling-off. This natural yellowish tint on silk is desired by some fashion designers as a 'soft white' or natural shade. The desired degree of whiteness can be relatively easily achieved with Bombyx mori silk on bleaching. With tussah silk the yellowish colouring of the fibrion is considerably more intensive. One reason for this is that with the tussah silk the sericin also penetrates the actual silk fibre, so that the natural dyestuffs lend the tussah fibrion a typical brownish yellow to greenish yellow colour. The natural colouring matter is the tannin of the oak tree leaves on which tussah silkworm is fed. The bleaching process for tussah silk to get white fabric is thus usually very difficult, which makes such silks unsuitable for white fabrics or for certain pastel tones. The silk may be bleached by oxidative as well as reduction methods. If a very high degree of whiteness is required, a combination of both methods in the form of double bleach is applied.

The best method of bleaching silk is the use of hydrogen peroxide in a seperate bath. The perhydroxyl ion or even atomic oxygen is responsible for the oxidation effect on the organic colouring matter present in silk and thus for bleaching effect. The recipes for bleaching two varieties of silk with hydrogen peroxide are given in Table 6.4. The material after degumming is entered into the prepared bleaching bath at 40°C. With these fibres, which are sensitive to alkali, the alkali necessary for activation of hydrogen peroxide must be added to the bleaching bath should be ammonia or tetrasodium pyrophosphate. The pH value of the bleaching liquors should lie between pH 8.5-9. Stabilisers are added to the bath to achieve a slow seperation of the oxygen needed for the bleaching effect. Water glass, which is often used as a stabiliser, should not be used for bleaching silk, because owing to the precipitation of silicic acid the silk can get a hard, brittle handle [51]. In this case, tetrasodium pyrophosphate and fatty protein condensates are the ideal choice. The mixtures of sodium silicate and trisodium phosphate or organophosphates exert a great stabilising effect on peroxide and help to control bleaching action. Generally, one should consider whether instead of the seemingly contradictory method of using activators on the one hand and stabilisers on the other hand, it would be better to have exact metering of the hydrogen peroxide solution. The dispensing systems that most dyehouses are now using make this feasible. Hard water with metallic salts or impurities is avoided as the metals act as catalyst and weaken the silk. It is advisable to use stainless steel or aluminium vessel and rods. Bleaching above the specified temperatures lower the tensile strength of silk and becomes yellow. The bath is gradually raised to required temperature in 1 h and bleaching is done at this temperature for specified time. Whereas bleaching of mulbery silk is

TABLE 6.4
Recipe for Bleaching Silk with Hydrogen Peroxide

Chemicals	Mulbery silk	Wild silk (tussah, muga, eri)
Hydrogen peroxide (35% by wt.)	15-20 ml/l	20-30 ml/l
Stabiliser	2 g/l	4 g/l
M : L ratio	1 : 20	1 : 30
Temperature (°C)	75-80	80-90
Time (h)	1-2	3-4

complete after about 2 hours, the time required for bleaching tussah silk can be a lot longer depending on the origin and inherent colour. The silk after bleaching is thoroughly rinsed first with warm water and then with cold water, hydroextracted and dried. Standing baths of peroxide can be used by replenishing the bath with 1/3rd the quantity of hydrogen peroxide and 1/4th the quantity of stabiliser originally taken for bleaching.

Silk goods to be sold as white require a treatment with 0.08 to 0.5% optical whitening agent along with 0.5% glauber's salt at 45°C for 20 min at pH 4 to 5 with the addition of acetic acid. Ultramarine Blue is also recommended in the optical brightening bath to obtain a bluish tinge to the white silk goods.

6.6 Bleaching of Synthetic Fibres with Hydrogen Peroxide

6.6.1 Bleaching of regenerated cellulose

Filament viscose rayon may not require bleaching since this is normally carried out during manufacture. However, viscose in staple form requires bleaching as it may not necessarily include a bleaching treatment during its manufacture. The same reagents as those used for bleaching linen and cotton fabrics are useful for these fibres. For very good whiteness, rayon may be bleached on a jigger with alkaline hypochlorite or combined scour and bleach using hydrogen peroxide (up to 1 vol. strength) containing sodium silicate and alkaline detergents at a temperature of about 70°C. The presence of heavy metals (from Xanthate hydrolysis stage) makes the use of peroxide a hazardous process. It is also possible to use peracetic acid with viscose rayon.

6.6.2 Bleaching of acetate fibres

The whiteness of the fabric made of acetate may be improved by treatment with hydrogen peroxide (30%), 1-3 g/l in presence of sodium silicate, 0.3 g/l. During this treatment the alkalinity of the bath and the required temperature should be carefully maintained. The pH of the bleach bath should not be greater than 9 and treatment for 1 h at 45°C gives combined scour and bleaching with the addition of non-ionic detergent.

6.6.3 Bleaching of acrylic fibres

Certain acrylic fibres should not be chlorite bleached because of their tendency to yellow/or loose stability to light. Many fluorescent brighteners added to the chlorite bath are also not stable and such materials may exhibit an accelerated fade when exposed to sunlight in wet alkaline condition. Such fibres can be bleached with hydrogen peroxide or hydrosulphites. However, the need for bleaching varies with different acrylic fibres. Acrilan 16 is sufficiently white for most purposes, but Acrilan 1656 has a more yellowish brown natural colour. Orlon 42 has a colour which is intermediate between natural and bleached cotton.

6.7 Advantages and Disadvantages of Peroxide over Hypochlorite Bleaching

Advantages :

(i) Peroxide is an universal bleaching agent and can be employed for wool, silk as well as cotton. It is specially suited to the bleaching of union fabrics containing both cotton and wool or silk.

(ii) Hydrogen peroxide is a milder reagent than hypochlorite and the degrading effect of peroxide bleaching on cellulose is less influenced than is the case with hypochlorite.

(iii) Peroxide is capable of continuing the scouring action simultaneously with the bleaching action, thus a single stage combined scour and bleach or a continuous method is possible using hydrogen peroxide.

(iv) Peroxide bleaching is in general less liable to have adverse effect on dyed threads. The white effect is good and permanent and there is less risk of yellowing at a later stage.

(v) Thorough rinsing followed by scouring or antichlor treatment is required with hypochlorite bleaching, whereas with peroxide a comparatively short rinsing suffices.

(vi) With hydrogen peroxide, there is no danger of equipment corrosion, no unpleasent odours and no limitations as to processing techniques.

(vii) Increasing strict control over the discharge of AOX from chlorine bleaching liquors has led to a greater advantage of peroxide processes for bleaching cellulosic fibres [52-54].

Disadvantages :

(i) Bleaching with peroxide is costlier than that of hypochlorite or bleaching powder.

(ii) Hydrogen peroxide bleaching requires stabilisation usually with silicates which brings the risk of forming resist stains in subsequent dyeing, and causes a build-up of hard crystalline deposits on plant and machinery causing abrasion damage to the fabric during passage.

(iii) 'Catalytic damage' occurs during hydrogen peroxide bleaching of cotton fabrics and results in small spots of unevenly dyed fabric or even, in severe cases, the formation of small holes.

(iv) There is limitation in white obtained on acrylic fibres. It also causes deleterious effect on skin when used in a concentrated form.

6.8 Bleaching with Sodium Chlorite

Commercial manufacture of sodium chlorite under the trade name of 'textone' began in 1930s and by 1939 it was being promoted for continuous bleaching of cellulosic textiles for which purpose US manufacturers, Mathieson Alkali Co. designed a large conveyer system. Sodium chlorite ($NaClO_2$) in its white crystalline form is highly hygroscopic in nature. Solid sodium chlorite is stable at room temperature for a longer time when it is mixed with small quantity of alkali (Na_2CO_3). Now-a-days chlorile bleaching is increasingly being used for polyester, because the chemistry is better understood [55].

6.8.1 Mechanism of chlorite bleaching

Sodium chlorite on decomposition produces a strong oxidising gas known as chlorine dioxide. The lower the pH values and higher the temperature (above 70°C) of bleach bath, the greater is the speed of decomposition [56]. The rate of chlorine dioxide formation is proportional to the concentration of sodium chlorite in the solution. Chlorous acid ($HClO_2$) that is formed is unstable and decomposes to chlorine dioxide (ClO_2) which is the acitve species so far as bleaching is concerned. Maximum chlorine dioxide is formed between pH 2.5 and 3.0. In the absence of metal ions and textiles, the rate of formation of chlorine dioxide approximately doubles for each 0.4-pH drop, in the 3.0-5.0 range, at 85°C. Addition of an acid such as formic, acetic or phosphoric acid is recommended so that pH lies between 3 to 5. If the pH drops below 3.0, cotton fibre is severely damaged because weak acid ($HClO_2$) and strong acids (HCl and $HClO_3$) are formed which hydrolyse the cellulose. On the other hand, the loss of oxygen evolution from hot chlorite solution when cotton is added also suggests that chlorite ion rather than chlorous acid is responsible for bleaching [57].

$$2NaClO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HClO_2$$

$$HClO_2 \rightarrow ClO_2 + H^+$$

$$HClO_2 \rightarrow HCl + 2O$$

Aqueous sodium chlorite solutions, which are stable under alkaline conditions are to be activated by acidification. Activation with strong acid produces a toxic corrosive chlorine dioxide gas. It is thus necessary to control its rate of evolution. Technical developments have been linked mainly to control the chlorine dioxide evolution [58-60]. In practice this is generally achieved by controlling the temperature and pH by addition of buffers in the bleach bath. This can be avoided by addition of weak acid (which forms a buffer with the alkali in the chlorite) or a mixture of weak acid and its salt wtih a strong base [61]. Some auxiliary products function by giving a slow development of acidity on heating or long stroage at ambient temperatures. Special brands of sodium chlorite are available which contain acid generating materials and thus attain the required pH, without further addition on reacting at bleaching temperature. Activation with persulphates above pH 7 [62], aldehyde at pH 3-7 [63], bromides [64], salts with cobalt, nickel and manganese at pH 5-8.5 [65], sulphur, selenium or finely divided carbon [66] and chlorinated hydrocarbon [67] have been proposed and also acitvation by organic acid esters such as ethyl lactate (1-3 g/l) with addition of sodium nitrate (1-3 g/l) to inhibit corrosion [68] is possible. Sodium hydrogen orthophosphate (NaH_2PO_4), sodium formate which produce acid when the liquor is heated are also suggested as buffers. Organic esters such as diethyl tartarate which hydrolyses to give tartaric acid, or sodium chloroacetate which liberates hydrochloric acid and glycollic acids during steaming, have also been suggested as buffers [55]. Other alternatives are the use of either special auxiliary products which limit chlorine dioxide evolution, for example, foam formation on the bleach liquor surface or other chemicals capable of trapping chlorine dioxide chemically.

6.8.2 Bleaching of cotton with sodium chlorite

Cotton can be effectively bleached with sodium chlorite (1-2%) at a pH 4.0 ± 2 containing sodium dihydrogen phosphate (0.2-0.5%), stable foaming and wetting agent (0.1-0.25%), nitrogenous chlorine absorber and formic acid to maintain the pH. The temperature of the bleach bath is raised to 82-90°C and maintained at this temperature for 1-3 h depending upon the machines (batchwise) employed for bleaching. Chemicals should be added in the following order : water, previously dissolved sodium nitrate, buffer salts or other chlorite stabiliser, surfactants, sodium chlorite (pre-dissolved, if solid product) and lastly the diluted acid. The addition of acidic materials to concentrated sodium chlorite solutions must be avoided. Sodium nitrate is used as a corrosion inhibitor. It is not essential to use acid chlorite solutions in the semi-continuous processes (pad-roll or pad-stack) where effective liquor ratio is low and neutral chlorite solutions (10 g/l) are recommended. When long batching time are used, soda-ash (1 g/l) is added to maintain stability of the bath.

Cotton goods that have been prepared in kiers are advantageously bleached by an alkaline sodium chlorite activated by hypochlorite. In this method, cotton goods

$$2NaClO_2 + NaOCl + H_2O \rightarrow 2ClO_2 + NaOH + NaCl$$

passes through a saturator containing (1-3 g/l available chlorine) mixture of sodium chlorite and sodium hypochlorite and a buffer mixture of bicarbonate of soda and soda-ash. An available chlorine pick-up of 0.3% (o.w.f.) is typical. In actual practice, the hypochlorite : sodium chlorite ratio can vary between 3 : 2 and 3 : 1, on an available chlorine basis. The acceptable pH varies from 8.8 to 9.7 maintained by buffer. After leaving the saturator, the goods remains in J-Boxes or bins for the time necessary for bleaching, usually 1-2 hours. At the end of the bleaching cycle the goods are washed, antichlored, and washed again.

The third method of activating sodium chlorite involves the reaction of sodium chlorite with chlorine. The reaction goes to completion very rapidly. However, this

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

method has not yet found an application in the industry.

6.8.3 Bleaching of polyester with sodium chlorite

Synthetic polyester fibres are normally supplied in an off-white state. Sometimes high degree of whiteness is required for white goods. The polyester is generally bleached with sodium chlorite in a bath containing sodium chlorite (50%), 3-5 g/l, formic acid to get pH 3.0 for 1-2 h at a temperature of 95°C. A small quantity of wetting agent can be added in the bleaching bath. Bleaching is followed by anti-chlorination with thiosulphate (2-3 g/l) at 60°C for 20 min. Finally, warm (60°C) and cold rinses are given for 10 minutes.

6.8.4 Bleaching of nylon with sodium chlorite

Nylon is also supplied in quite white state. Bleaching of nylon is normally carried out where the nylon has been discoloured by heat-setting treatment. The problem of discolouration is comparatively less in the case of nylon 6 than that of nylon

6,6 due to the lower temperature required in the spinning process and lower softening point of nylon 6,6.

Neither sodium hypochlorite nor hydrogen peroxide is recommended for bleaching of nylon. When hypochlorite is used, there is a tendency for chlorine to combine with secondary amino groups, causing decrease in tensile strength. Nylon can be bleached in a bath containing sodium chlorite (80%), 1-2 g/l, sodium nitrate, 1-3 g/l, formic acid (85%), 2 ml/l for 1 h at 80-85°C. Acetic acid is preferred to formic acid for adjusting the pH (3.5 to 4) because it has a buffering action on sodium chlorite solution in the required region. A small amount of acid stable detergent (0.2 g/l) may be added to the bleach bath to have a combined effect of scouring and bleaching as well as reduction in the loss of chlorine dioxide to the atmosphere due to the formation of surface froth. An activator for bleaching with sodium chlorite is also recommended so that bleaching can be carried out in near neutral pH. Acid donors organic esters e.g. ethyl lactate are readily hydrolysed in bleach bath and split into alcohol and organic acid. As the hydrolysis progresses

$$\text{R-COOR}' + H_2O \rightarrow \text{RCOOH} + \text{R}'\text{OH}$$

the organic acid which is slowly liberated regulates the the decomposition of chlorite. The pH of the bath. is maintained within 6.6 to 6.0 during the period of bleaching. The amount of ethyl lactate added to the bath depends on the liquor ratio. For short liquor ratio 2-3 ml/l and for long liquor 1 ml /l of ethyl lactate is sufficient. Sometimes ammonium chloride is also used as an activator for bleaching with chlorite. Bleaching of differential dyeing nylon is not normally recommended since this tends to limit the contrast effects during subsequent dyeing. However, when bleaching is essential a mild chlorite bleach [69] can be employed.

6.8.5 Bleaching of acetate fibres with sodium chlorite

It is more safe to carry out bleaching of acetate fibres with sodium chlorite than with hydrogen peroxide. Bleaching can be carried out with sodium chlorite (0.5-2 g/l) in presence of mono substituted ammonium phosphate (0.5-2 g/l) and non-ionic detergent at 70-80°C for 60-100 min.

6.8.6 Bleaching of polyacrylonitrile with sodium chlorite

Fabrics made from polyacrylonitrile in grey condition have a yellowish or cream tint. Polymer textile finishing agents containing polyacrylonitrile and nitrile groups tend to yellow during fibre processing and requires bleaching [70].

6.8.7 Bleaching of polyvinylalcohol with sodium chlorite

After boiling with 1-2 g/l of non-ionic or anionic detergent for 45-60 min at 85-90°C, the fabrics requrie bleaching if they are delivered undyed. The bleaching can be carried out with a solution containing sodium chlorite, 0.4-0.7% (o.w.f.), pH 3-4, at 70-80°C for 30-45 min.

6.8.8 Problem of corrosion and its prevention in chlorite bleaching

Most of the materials used in the construction for bleaching equipment, are corroded due to free chlorine dioxide gas evolved during bleaching process. Various approaches have been suggested to minimise the evolution of chlorine dioxide gas and corrosion problem.

(i) Stainless steel containing 2.5% molybdenum makes the bleaching equipment quite resistant to chlorine dioxide. Titanium also does not corrode in presence of chlorite [71], but its use is limited due to its high cost. Vessels lined with titanium, glass or ceramics can be used. Fibre-glass J-Boxes are sufficiently smooth, resist reactions with chlorite. Cross-linked polyester and resins [72] used in surface coatings are sufficiently resistant to chlorine dioxide.

(ii) Corrosion can be suppressed virtually completely by adding selected assistants which tend to harness the free evolution of chlorine dioxide [73]. These assistants are those products which contain nitrogen and have the ability to scavange chlorine and its products. These assistants range from products such as ammonium dihydrogen phosphate, sodium and ammonium nitrate (NH_4NO_3), nitric acid to nitrogenous resins such as melamine, urea and others.

(iii) The problems of corrosion hazard, fuming and formation of chlorate are all minimised without loss of bleaching efficiency by raising the pH from 3 to 5 by means of magnesium dihydrogen phosphate activator [74].

(iv) It is claimed [75] that the salts of mono –, di – or triethanolamine will maintain a pH of 7.0-8.5 at 20-50°C and yet bring about quantitative decomposition of chlorites at temperatures above 70°C.

(v) To eliminate the corrosion of the exposed parts by chlorine dioxide vapour, the machine should be designed in such a manner that condensation is prevented [76] or by means of gas washeries which are installed within the ventilation duct with water or an alkaline hydrogen peroxide solution [77].

(vi) Corrosion can be well controlled by the use of ammonium salts, which reacts with commercial alkaline chlorite in the following manner,

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$$

The ammonium salts appear to act by neutralising chlorite solutions. Moreover, they appear to improve bleaching at 100°C.

(vii) The suppression of chlorine dioxide by addition of hydrogen peroxide has been suggested [78], but, although this is effective at pH 4.0-7.0, there is some deterioration in bleaching efficiency.

(viii) Sometimes surfactants which are stable in acid chlorite bath of producing minute foam cells are added. The foam bubble can trap the gas formed before it is emitted to the atmosphere.

(ix) It has been stated that corrosion difficulty may be partly circumvented by pad application of cold chlorite solution followed by steaming.

(x) Use of a discontinuous process i.e. closed jigger, the closed package bleaching methods have also been successfully employed to minimise the problem.

6.8.9 Merits and demerits of chlorite bleaching

Sodium chlorite as a bleaching agent has got the following technical merits :

(i) Sodium chlorite is a versatile bleaching agent. It can be used for cotton and synthetic fibres and their mixtures. Man-made fibres which are sensitive to alkali can be safely bleached with sodium chlorite.

(ii) Sodium chlorite bleaching will give permanent white coupled with excellent mote removal on cotton which has not been kier boiled. There is little or no tendency to degrade cellulose.

(iii) The vigorous alkaline treatments employed in kier boiling are not necessary in using sodium chlorite for bleaching. Cotton waxes are very easily freed from bleached cloth by hot-alkaline after-treatment.

(iv) Under the acid conditions of chlorite bleaching, hardness of water has little harmful effect and therefore low ash content is obtained on bleached cotton.

(v) Sodium chlorite is rather insensitive to the presence of metal ions as iron with peroxide.

(vi) Sodium chlorite is ideally suitable for bleaching of cotton/polyester blended fabrics since both fibre components respond to acidic chlorite bleaching. However, hydrogen peroxide is also found equally satisfactory for this fibre blend.

The chlorite bleaching process suffers from certain drawbacks as follows :

(i) Sodium chlorite is more expensive than hydrogen peroxide. It is not useful for the bleaching of silk and wool, since it gives pink colouration which, however, can be removed with treatment of soidum bisulphite solution.

(ii) Even at pH 4-5 certain amount of chlorine dioxide is evolved, and the bleaching action is extremely corrosive to metals including stainless steel. Neutral and alkaline pH may tender the cotton.

(iii) Chlorine dioxide is a very toxic gas because it can decompose into both hydrochloric acid and chlorine gases. The gas mixture is a skin irritant, attacks mucous membranes and can cause fatal pulmonary edema. The TLV of this compound is 0.1 p.p.m. and shows the necessity for adequate care and ventilation during usuage.

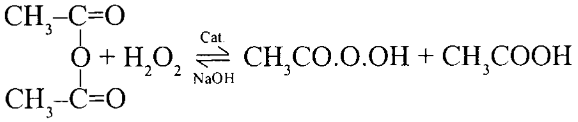
(iv) Explosions are fostered when gaseous chlorine dioxide and $HClO_2$ is exposed to uv light.

6.9 Bleaching with Peracetic Acid

Peracetic acid is an equilibrium solution consisiting of hydrogen peroxide, acetic acid and peracetic acid. It can be used for bleaching of nylon, viscose rayon, cellulose acetate and even cotton [79, 80]. Peracetic acid is commercially available for textile bleaching in 5, 15 and 40% solutions as what is known as ''equilibrium peracid''. Peracetic acid can be prepared by the interaction of concentrated hydrogen peroxide and acetic acid in the presence of strong mineral acid such as sulphuric acid [81, 82]. Alternatively, it can be prepared by mixing hydrogen peroxide with acetic anhydride at room temperature in presence of suitable catalyst like caustic soda or EDTA [83]. The optimum reaction takes place with 1 part of hydrogen peroxide and 6 parts of acetic anhydride after about 4 h at room temperature to give a yield of about 80%. The excess acetic anhydride may, however, cause an undesirable side reaction to yield highly explosive diacetyl peroxide.

$$H_2O_2 + CH_3COOH \xrightarrow{H^+} CH_3.CO.O.OH + H_2O$$

peracetic acid



$$\begin{array}{l} CH_3-C=O \\ \quad\; | \\ \quad\; O + H_2O_2 \underset{NaOH}{\overset{Cat.}{\rightleftharpoons}} CH_3CO.O.OH + CH_3COOH \\ \quad\; | \\ CH_3-C=O \end{array}$$

acetic anhydride

The physical and chemical properties of peracetic acid is summerised in Table 6.5. The concentrated solution of peracetic acid is volatile and has a pungent smell and strongly irritates the mucous membrane. The stability of peracetic acid is not quite high as that of stabilised hydrogen peroxide. Free radicals may be produced in the presence of ions such as copper, iron etc.

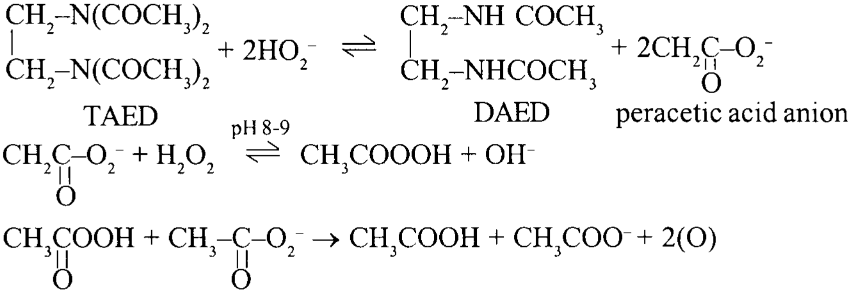
TABLE 6.5
Properties of Peracetic Acid

Properties	Concentration of peracetic acid	
	5%	15%
Physical properties		
Appearance	–	colourless liquid
odour	–	pungent
pH	2.0	2.0
Density (g/mL, 20°C)	1.120	1.480
Chemical properties		
H_2O_2	27.0	22.0
Acetic acid	6.3	16.6

Peracetic acid has proven to be effective bleaching agent in the household detergents and also found wide application in the laundry industry. To reduce the danger in the on-site production of peracetic acid from acetic anhydride/hydrogen peroxide, activators can be used in household detergents to generate peracetic acid in situ. The commonly used activators are sodium perborate and acetylated 0 or N-compounds such as tetraacetylethylenediamine (TAED) [84, 85]. The perborate activators are assumed to act via the stages of peracetic acids [86]. Perborate hydrolyses in aqueous solution and hydrogen peroxide is produced. Reactive peroxide anion is produced from hydrogen peroxide under weakly alkaline medium and then the activator reacts [87].

$$Na_4(H_4B_2O_8) + 4H_2O \rightarrow 2Na_2[B(OH)_4] + 2H_2O_2$$
$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$
$$X\text{-}Ac + HO_2^- \rightarrow X^- + AcOOH$$

The chemistry of TAED/H_2O_2 bleaching is based on the following mechanism :



$$\begin{array}{l}CH_2{-}N(COCH_3)_2\\ |\\ CH_2{-}N(COCH_3)_2\end{array} + 2HO_2^- \rightleftharpoons \begin{array}{l}CH_2{-}NH\ COCH_3\\ |\\ CH_2{-}NHCOCH_3\end{array} + 2CH_2\underset{\overset{||}{O}}{C}{-}O_2^-$$

TAED DAED peracetic acid anion

$$CH_2\underset{\overset{||}{O}}{C}{-}O_2^- + H_2O_2 \overset{pH\ 8\text{-}9}{\rightleftharpoons} CH_3COOOH + OH^-$$

$$CH_3\underset{\overset{||}{O}}{C}OOH + CH_3{-}\underset{\overset{||}{O}}{C}{-}O_2^- \rightarrow CH_3COOH + CH_3COO^- + 2(O)$$

The peroxide anion reacts with TAED to form DAED (diacetylethylenediamine) and peracetic acid anions. At pH 8-9 the peracetic acid anion is in equilibrium with the free peracetic acid. This equilibrium peracetic acid oxidises its own per anion to form active oxygen, which acts as a bleaching agent [88].

6.9.1 Bleaching of cotton with peracetic acid

Though the use of peracetic acid has been suggested for bleaching of cotton but has never reached the commercial success like hypochlorite, chlorite and peroxide [89]. The mechanism of reaction is somewhat similar to that of hydrogen peroxide.

$$CH_3COOOH \rightarrow CH_3COOH + (O)$$

Recently, peracetic acid is used as a replacement of hypochlorite in multi-stage bleaching process of cotton and linen [90, 91]. Peracetic acid is most effective as a bleaching agent of cotton in the pH range of 6 to 7. The preferable bleaching temperature range is between 50-80°C and bleaching time of 20- 60 min depending on the temperature. The degree of brightness increases proportionately with the concentration of bleaching agent. To avoid the damage of cloth, a sequestering agent may be added to remove to those catalytically active ions such as Cu, Fe etc. which can be absorbed by fibre.

Bleaching of 100% cotton in rope form in a J-Box with peracetic acid (1.5-2.5 g/l) at room temperature, followed by an alkaline hydrogen peroxide treatment at 90°C yield a good whiteness.

Linen can be successfully bleached using a process consisting of scouring, alkaline hydrogen peroxide bleach and a peracetic acid bleaching stage.

6.9.2 Bleaching of nylon with peracetic acid

Peracetic acid is particularly suitable for bleaching of nylon because this can be applied in a liquor which pH is virtually neutral and hence there is no danger of loss of strength of nylon fibre. The bath is set with pre-dissolved chemicals containing sequestering agent(0.75%), sodium bicarbonate (0.75%), caustic soda (flake) (2.00%) and peracetic acid (5.0%) on the weight of the fabric. Seperate container is used for peracetic acid and concentrated alkali is not mixed. Bleaching may be carried out at a pH between 6.0 and 7.5 for about an hour at 80°C. After bleaching the material is rinsed thoroughly in cold water. The bleaching equipment should not contain copper, brass or iron and preferably it should be made of ceramic or stainless steel.

6.9.3 Bleaching of cellulose acetate with peracetic acid

Peracetic acid is very suitable for bleaching of cellulose acetate fibres. The liquor should be made-up in the following manner :

Peracetic acid (36 - 40%)	0.3 kg
Sodium hexametaphosphate	0.05 kg
Wetting agent	0.1 kg
Water	99 litres

The solution is adjusted to pH 5-6 by the addition of well diluted sodium hydroxide and bleaching is carried out in 1 h at 66°C. It is desirable that pH should be checked at intervals. The bleached goods is then rinsed in hot and then in cold water.

6.9.4 Bleaching of acrylics with peracetic acid

The bleaching bath is set with predissolved (all o.w.f.) sodium hydroxide (50%), 1%, sodium bicarbonate, 1%, sequestering agent, 1% , and prediluted peracetic acid, 5% in the given order. The goods are run cold for 10-15 min and then the bath is heated slowly to 75°C and bleaching is continued at this temperature for 20 min. The bath is then cooled, dropped and the goods are rinsed well. For white goods, an optical brightener may be added.

6.9.5 Merits and demerits of bleaching with peracetic acid

The advantages of peracetic acid as a bleaching agent are :

(i) Peracetic acid is environmentally safe since it decomposes to acetic acid and oxygen and do not form any toxic product [81].

(ii) Peracetic acid as an industrial chemical is easily available and can be safely introduced to an existing process design [82].

(iii) Peracetic acid is very suitable for bleaching of nylon and it can be used successfully for the bleaching of cotton dyed with indanthrene colours.

(iv) Peracetic acid bleached goods show comparable or even higher brightness with less fibre damage.

(v) In the household powder detergent, peracetic acid is generated in situ from activators.

The disadvantages of peracetic acid as a bleaching agent are :

(i) Concentrated solution of peracetic acid (35-40%) is dangerously explosive and cannot be handled. The concentrated solution has a pungent odour, is caustic and burns the skin. It needs to be carried in specially protected tanker wagons when transported by rail.

(ii) It is expensive for bleaching of cotton and rayon and is used only as a last resort.

(iii) The stability of peracetic acid is not quite high as that of stabilised hydrogen peroxide. Free radicals may be produced in the presence of Cu and Fe ions.

6.10 Reductive Bleaching of Wool

Reductive bleaching treatments are normally employed for the bleaching of wool, silk and nylon fibres. Now-a-days, the main form of reductive bleaching employs hydrosulphite compounds. The treatments using sulphur dioxide or sodium bisulphite are now only of historical value as the process has many practical disadvantages. Sodium hydrosulphite may be used alone, provided the temperature of the bleach bath is kept low to prevent rapid decomposition. However, a stabilised form of sodium hydrosulphite is more commonly used, in which the inclusion of sodium pyrophosphate (or other non-phosphate buffers) controls the pH close to neutral to inhibit the too rapid decomposition of the hydrosulphite. By the use of such stabilised hydrosulphite compound a much higher temperature can be employed. Thioureadioxide is sometimes employed as a reducing agent for the bleaching of wool [93-95]. The decomposition rate of thioureadioxide increases with increasing pH and temperature and decreases with increasing concentration [96].

6.10.1 Bleaching of wool with sulphur dioxide (stoving process)

In this method moist woollen yarn in the hank form is exposed to the action of sulphur dioxide produced by burning sulphur (3 to 6% o.w.f.) placed in an iron or earthenware pot inside the chamber. Sulphur is converted to sulphur dioxide and sulphurous acid gas in the presence of moisture. Sulphurous acid is a strong reducing agent which reduces the organic colouring matter into colourless substances. The material is exposed to sulphur dioxide for 6 to 8 h or over-night and then rinsed for 15 min in H_2O_2 (0.1%) solution at 35°C which oxidises retained sulphur dioxide (present as sulphurous acid) to sulphuric acid and finally neutralised with dilute sulphuric acid and blued. Piece goods in moist condition can also be stoved in a similar manner by passing them into the stove through a narrow slit in the stove and suspending on wooden rollers arranged in two tires.

The disadvantages of this method are :

(i) Bleaching effect is not permanent, the natural colour of wool returns gradually.

(ii) The sulphurous acid gas may be formed by the reaction of SO_2 and water, which can cause permanent damage to eyes and respiratory system.

(iii) Even after thorough washing wool retains sulphur dioxide and hence treatment with oxidising agent like NaOCl or H_2O_2 is necessary.

(iv) The process requires longer time for bleaching.

(v) If wool is too dry, the bleaching effect is poor.

6.10.2 Bleaching of wool with sodium bisulphite

In the sodium bisulphite method [97], wool is impregnated with a solution containing 2°Tw sodium bisulphite and 1°Tw H_2SO_4 for 2 h. Alternatively, wool can be treated with a solution of sodium bisulphite (2°Tw) for 6 to 10 h, squeezed, and is then followed by second impregnation in H_2SO_4 (1°Tw) and washed thoroughly.

6.10.3 Bleaching of wool with sodium hydrosulphite

Reductive bleaching with non-stabilised sodium hydrosulphite [98], sodium hydrosulphite-based sulphoxylate formaldehyde [99] and sodium and zinc hydroxymethanesulphinate [100] have been shown to provide wool excellent whiteness, with a lower cystine content than in the case of bleaching wool with other reducing agents. The result obtained is permanent, in contrast to the unstable peroxide white.

The goods are treated with a solution containing sodium hydrosulphite (4-8 g/l) or stabilised sodium hydrosulphite (5-10 g/l) and pyrophosphate or buffer (3-4 g/l) at 50-55°C for 1-2 h. Sodium hydrosulphite in aqueous solution is converted into sodium bisulphite when applied at 50°C at pH around 7.0. After bleaching the goods are rinsed in warm water and then in cold. The presence of sodium laurylsulphate (SLS) in the bleaching bath improves the whiteness and mechanical properties of the bleached goods without affecting the cystine content [101]. The protection is the outcome of sulphitolysis inhibition derived from the ionic or non-ionic interaction of SLS in the positive sites of keratine ($-NH_3^+$) or in the paraffinic side chains of same amino acid residues. The interaction or combination of SLS with protein increases its net negative charge and hinders the access of the reducing agent to the disulphide linkage [102]. Iron and copper in the hydrosulphite bleach bath can cause a greyish discolouration due to the formation of their respective sulphides which are difficult to remove during washing.

6.10.4 Bleaching of wool with thio-urea dioxide

The optimum bleaching value of wool can be achieved at thio-urea dioxide 1.5 g/l, time 30 min and temperature 80°C. The cost of bleaching with thio-urea dioxide is claimed to be three times lesser than that of bleaching carried out with sodium hydrosulphite. Also, its lack of mutagen activity and its low COD and BOD values recommended it as a non-toxic product giving a low concentration of effluents.

6.10.5 Photobleaching of wool

The novel method of bleaching wool by exposure to intense light are attractive because of the dry and pollution-free nature of the process. Photobleaching can be rapid and the resulting colour and brightness are similar to those of peroxide bleached wool [103]. Though photochemical bleaching is industrially possible, but not economically attractive yet. Wool can be photochemically bleached [104] by exposure to u.v. light below 360 nm. When wool is treated with a zinc complex of thioglycollic acid to minimise yellowing and then exposed to sunlight, undergoes photochemical bleaching which effectively destroys the impurities caused by photo-degradation.

6.11 Bleaching of Silk with Reducing Agents

Silk fibrion is highly sensitive to oxidising agents like hypochlorite and chlorite solutions. Oxidation and substitution in the benzene ring of tyrosine is responsible for degradation of silk with the formation of chloro-amino acids, ketonic acids and chloramine in several stages [105].

Reduction bleaching of silk is generally carried out with sodium hydrosulphite or appropriate stabilised commercial products on this basis. The silk fibrion is resistant to the reducing agents. Since the bleaching effect is poorer than with peroxide bleach, the term "half bleach" is sometimes used. A brief resume of the bleaching operations is highlighted in Table 6.6.

TABLE 6.6
Bleaching of Silk with Reducing Agents

Reducing agent	Condition
Sulphur dioxide or Sulphurous acid.	4 to 6 h at an atmosphere of SO_2, yellowish tint obtained.
Sodium hydrosulphite. $Na_2S_2O_4 + 4H_2O_2 \rightarrow 2NaHSO_4 + 3H_2$	4 to 6h at temperature around 50°C, pH 7, concentration around 45 g/l.
Stabilised hydrosulphite.	30 to 90 min at temperature of 60-90°C, pH 5 to 7, concentration around 10 g/l.
Sodium sulphoxylates. $NaHSO_2.CH_2O + H_2O \rightarrow NaHSO_3 + H_2$	Concentration 4 to 6 g/l, temperature 60-95°C, pH 4 to 5.5, time 20-30 min.

Sometimes silk is still bleached with sulphur dioxide in gas form. To do this the damped fabric is subjected to the sulphur dioxide gas for several hours in an enclosed chamber. Through the formation of sulphur dioxide some natural dyestuffs are reductively destroyed, whereas others are only converted to water soluble leuco compounds, which then have to be washed out, so as not to risk reoxidation and thus yellowing during storage. The frequently noticed unpleasant odour of the remaining sulphur dioxide on the fabric can be eliminated by a rinsing process with hydrogen peroxide of 35% strength (1 mg/l).

If a very high degree of whiteness is required, a double bleach process is recommended. Here bleaching is carried out on two seperate stages, first the silk is treated with 3 to 5 g/l stabilised sodium hydrosulphite at 60°C for 1 h, followed by oxidative bleaching using H_2O_2, 10-20 ml/l (35% strength), 2-3% sodium silicate, the pH of the bath being maintained at 8.5-9.0 at 90°C for 1 h. With this process, as a rule, an excellent full white is achieved, which will endure storage and is lightproof. Certain tussah silks cannot, however, be bleached to a full white, even applying this process [106].

6.12 Reductive Bleaching of Nylon

Reductive bleaching of nylon is normally employed under acidic conditions.

Virtually no fibre degradation occurs and the resistance of the fibre to photo-degradation is not impaired. The liquor is set with 2-4% (o.w.f.) stabilised hydrosulphite, 2% (o.w.f.) sequestering agent, 0.2-1% (o.w.f.) selected fluorescent brightener and acetic acid to pH 4.5. The goods are entered into the bath and the temperature is raised slowly (1°C/min) to 85-100°C. Treatment is continued until the desired colour is achieved. The goods are then cooled and rinsed thoroughly.

6.13 Peroxygen Bleaching Compunds

There are several peroxygen derivatives that occasionally find use in textile industry. These are potassium peroxymonosulphate (monopersulphate), potassium perphosphate and urea peroxide. These compounds are rarely used by themselves, but are used primarily as bleach boosters. They are all powders and are usually compounded where a strong colourless oxidising agent is indicated. The mechanism of potassium peroxydisulphateperoxide is represented by the following reactions ;

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}\bullet$$
$$SO_4^{-}\bullet + H_2O \rightarrow H^+ + SO_4^{2-} + OH\bullet$$
$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$$
$$HO_2\bullet + S_2O_8^{2-} \rightarrow O_2 + HSO_4^{-} + SO_4^{-}\bullet$$
$$HO_2\bullet + H_2O_2 \rightarrow O_2 + H_2O + OH\bullet$$

to give a net reaction

$$S_2O_8^{2-} + H_2O_2 \rightarrow O_2 + HSO_4^{-}$$

Above pH 5.0, the addition steps are written :

$$HO_2\bullet \rightleftharpoons O_2^{-} + H^+$$
$$O_2^{-} + S_2O_8 \rightarrow O_2 + SO_4^{2-} + SO_4^{-}$$
$$O_2^{-} + H_2O_2 \rightarrow O_2 + OH^{-} + OH\bullet$$

Under the name of ''Oxone'' Du Pont has put on the market a bleaching agent for polyamide fibres. Its active bleaching component is potassium persulphate ($KHSO_5$, pH of a 1.0% solution is 2 to 3). Oxone is used for the bleaching of nylon, together with NaCl and a mixed buffer K_2CO_3 and $NaH_2PO_4.2H_2O$ at pH between 7.5 and 8.0 at 80°C. This bleaching auxiliary is used more for domestic bleaching than for bleaching finish works.

6.14 Bleaching of Jute

The art of bleaching jute has received fresh attention as diversified jute products like decoratives, soft luggage, and upholstry material are in great demand now-a-days. Raw Indian jute is brown in colour and requires bleaching. Scoruing of jute fabric before bleaching has no beneficial effect, rather it deteriorates whiteness index. The grey jute fabric attains reddish tone after scouring in alkali. However, scouring of jute fabric before sodium chlorite bleaching enhances the whiteness index. A damage to the jute fibre occurs at concentrations of caustic soda higher than 9.0% [107]. Bleaching renders jute near white resulting in better lustre and appeal to the fabric. Bleaching of jute is also required for good colouration background.

Bleaching of jute can be affected by all bleaching agents, but bleaching powder and hydrogen peroxide [108,109] find commercial application. Owing to the presence of non-cellulosic constituents, particularly lignin, the actions of conventional bleaching agents such as H_2O_2, $NaClO_2$, peracetic acid and NaOCl are somewhat different as compared to their action on cotton [110,111]. The bleaching effect of H_2O_2 and peracetic acid on lignin is almost nil. The use of sodium hydrosulphite, sodium bisulphite, sodium borohydride have also been recommended for bleaching of jute [112]. Jute bleached with reducing agents is not all stable and develops reddish or brown tinge on storage.

6.14.1 Bleaching of jute with sodium hypochlorite

Jute piece goods are bleached in open width e.g. on jigs and jute carpet yarn is bleached in hank form or in the form of cross-wound cheeses in an open machine. Jute can be bleached with alkaline hypochlorite using 5-7 g/l available chlorine. Afterwards the goods are usually given an antichlor with sodium bisulphite, but it is not soured because of the difficulty of removing the traces of acid. However, the sodium hypochlorite bleaching produces poor whiteness which is not acceptable for subsequent dyeing and printing.

6.14.2 Bleaching of jute with hydrogen peroxide

Hydrogen peroxide bleaching process is most suitable for bleaching jute fabrics and the bleached goods are suitable for making diversified jute products.

Bleaching exclusively with hydrogen peroxide in the presence of silicate generally necessitates high peroxide consumption level and rigorous conditions and hence substantial fibre damage can result. Bleaching of grey jute can be carried out with H_2O_2 (2 vol.), sodium silicate (10 g/l), sodium hydroxide (1 g/l), trisodium phosphate (5 g/l), pH around 11 at 80°C for about 1 h. After bleaching the fabric is thoroughly washed, neutralised with 2 ml/l acetic acid and then usual washing and drying is carried out. Alkaline hydrogen peroxide gives a good white colour and less marked yellowing than that of hypochlorite bleach. The losses in strength and weight due to bleaching treatment are also less in case of peroxide bleaching process, compared to hypochlorite bleach.

Process involving only use of H_2O_2 is not very suitable as above certain percentage of H_2O_2 (6% of 50% H_2O_2) concentration, there is no appreciable increase in brightness value. Modified bleaching recipes for jute are now being reported [113, 114]. Jute with high lignin content compared with other cellulosic fibres, can be bleached in a sequential process using sodium chlorite or hypochlorite followed by hydrogen peroxide-sodium silicate bleach to produce the best fibre whiteness without appreciable strength loss. Lignin present in jute is chlorinated to convert into chlorolignin which are further extracted during alkaline extraction. This is then followed by peroxide bleaching. The whiteness can further be raised by the application of a suitable fluorescent brightening agent to the bleach bath or seperately.

6.14.3 Bleaching of jute with sodium chlorite

Scouring and bleaching of jute with sodium chlorite with an acceptable whiteness can be achieved, but the process is a time consuming two step process. Moreover, sodium chlorite is metal corrosive and health hazardous.

A single stage process containing 5% sodium chlorite solution at 65-70°C with a liquor ratio of 10:1 can produce pale yellow colour, with moderately good wet strength, but the fabric is turned yellow on exposure to light [115]. In another attempt, treatment of jute with 3 g/l sodium chlorite at boil for 90 min at pH 4 and then followed by treatment with H_2O_2 (0.5 vol.) solution buffered to pH 10 at 80°C for 30 min, gives a product with comparatively improved whiteness and resistance to yellowing on exosure to light [116]. A direct bleaching process [117] by the use of a solution containing sodium chlorite, hydrogen peroxide as a stabiliser for the chlorite, and buffer salts such as mono-and di-sodium phosphate (50-250% based on chlorite content) at pH 4.5-7 is also reported. The fabrics are wrung out to remove excess liquid, are heated by means of a superheated steam and are kept at a temperature of 90°C for 3 h. The whiteness of the fibre is uniform and of a high standard. A minimum change in the DP occurs when the jute is bleached with 0.7% sodium chlorite at pH 4 and 65-70°C for 80 min. The rate of bleaching can be increased by increasing the temperature [118].

6.14.4 Bleaching of jute with peracetic acid

The use of peracetic acid as a bleaching agent for jute fabrics is reported [119]. The optimum bleaching results are obtained at 70°C around pH 6.5. The mild acidic condition is most suitable because of the fact that neither hydrocellulose nor oxycellulose is produced at this pH. Peracetic acid bleaching is more effective in reducing losses in weight and tensile strength than hydrogen peroxide bleaching. The improvement in handles/feel and low ash content of peracetic acid bleached jute fabrics is attributed to silicate free bleaching. Jute can also be effectively bleached with peracetic acid in the presence of selected buffering and stabilising agents [120]. A superior bleaching effect can be achieved by using tetrasodium pyrophosphate (TSPP) as a stabiliser under mildly alkaline conditions (pH 8.0-8.5) and excellent fibre brightness can occur at temperatures as low as 40-60°C. This process offers a more energy efficient option for bleaching 100% jute fabric. This process can also be extended to bleaching of jute/cotton blends.

6.14.5 Drawbacks in bleaching of jute

There are some serious drawbacks with reference to the bleaching of jute. They are :

(i) Jute fabric bleached with alkaline hypochlorites or hydrogen peroxide undergoes marked losses in weight and strength and also shows decrease in width. These are mainly attributed to the action of bleaching agent or alkali or alkaline reagents on the non-cellulosic constituents of jute i.e., hemi-cellulose and lignin [121, 122].

(ii) The heavy deposits of calcium or magnesium silicate on the surface of the fabric, resulting from peroxide bleaching with silicate, produce harsh feel and present difficulties in subsequent processing.

(iii) The main drawback of hypochlorite or peroxide bleached jute is photoyellowing. The reason for yellowing is environmental effects like heat, air, uv radiation in sunlight etc. On exposure to light, the shade of bleached jute turns to brownish yellow, which ruins the decorative look. This yellow-brown colour can be removed by second bleaching treatment, but it appears on further exposure to light. The on-set of yellowing varies considerably with the bleaching agent used.

6.14.6 Causes of yellowing and improvement of photostability of bleached jute

Jute has three main components α-cellulose (60%), hemi-cellulose (24%) and lignin (13%). The first two components do not absorb uv-radiation present in the sun-light (300-400 nm), lignin however does. The reaction is believed to be oxidative in nature and heat and oxygen in the air cause photo-sensitization of lignin. This discolouration is also associated with loss of strength. The degradation of lignin may be associated with the production of simpler aromatic compounds having two phenolic functional groups, or a phenolic and an aldehyde functional group attached to the nucleus. The compounds then appear to undergo condensation reactions involving a free radical mechanism. In this process, chromophore groups are formed with quinone-methide types of structures, and these are responsible for yellowing.

The improvement of photostability of jute fabric itself is an important matter to be given priority. Various processes have been developed in which bleached jute does not revert to its natural colour on exposure to light. The blocking of reactive phenolic groups by etherification or esterification is expected to arrest the yellowing process. The presence of some chromophore in dyes can cause absorption of near uv-radiation of sunlight and prevent discolouration. Bleached jute goods treated with copper-potassium dichromate (0.25% o.w.f.) improve photostability over conventional bleached fabric [123].

Bleaching of jute with H_2O_2 followed by treatment with an aqueous solution of potassium permanganate (8-12% o.w.f.) and a mineral acid, H_2SO_4 (8-12% o.w.f.) is recommended [124]. Subsequently, the reduced permanganate is cleared by rinsing the fabric in an aqueous solution of sodium bisulphite or sodium sulphoxylate formaldehyde at pH 3.0-3.5. Another process [125] consists in bleaching of jute fabric at a pH below 3.0 and a temperature in the range 15-43°C in an aqueous solution of potassium permanganate and phosphoric acid in amounts such that the ratio of potassium permanganate to phosphoric acid ranges between 1 : 0.7 and 1 : 1.1. The bleached fabric is then scavanged with an aqueous solution of an organic reducing agent, such as sodium bisulphite, at a pH below 4.0. The fabric is then scoured with hot water or steam.

A continuous or semi-continuous process for bleaching of jute fabric with chlorinated derivatives of cyanuric acid is developed [126]. The process comprises a preliminary treatment with boiling water, followed by impregnation of the materials with 0.4-0.6% aqueous alkaline solution, and then subjection of the material to steam treatment. Thereafter, the material is treated at 20-50°C with a mixture of trichlorocyanuric acid and cyanuric acid (with available chlorine content 7-15 g/l), containing sodium carbonate or bicarbonate. The pH of the solution is finally adjusted to 4-5 with acetic acid or phosphoric acid. The treated material is then bleached with H_2O_2. The time of treatment is usually 40-60 min, but can be extended to 2 h in the case of a heavy fabric with high lignin content.

A two step process [127] based on the preferential removal of lignin from the surface of jute fibres has been developed. In the first step the fabric is treated with either moist chlorine gas and aqueous chlorine solution or with an aqueous solution of hypochlorous acid at pH 6 and containing available chlorine equivalent to 5-10% (o.w.f.). In the second step, the treated fabric is extracted with an aqueous solution of at least one compound selected from : sodium hydroxide, phosphates, and sulphites ; an equivalent to 5-10% (o.w.f.). Finally, the fabric is washed, and is bleached by the conventional H_2O_2 and/or hypochlorite method.

Biological bleaching techniques using direct growth of lignin degrading fungi [128-130] or pre-treatment with hemi-cellulase enzymes [131] have been reported in the delignification of kraft pulp. A brief pre-treatment of lignocellulose jute with mixed enzyme preparation containing cellulase and xylanase enhances the brightness of fibres after bleaching with alkaline hydrogen peroxide [132].

Surface fuzziness and yellowing on exposure to light can be overcome and the cloth may be made more dyeable with improved light-fastness by judicious use of sodium hydroxide on the bleached fabric or enzymatic treatment of the grey state material. The effects of progressive delignification and various bleaching processes on jute fibres show that surface features progressively changes with gradual removal of lignin and lead to the ''cottonization'' of jute fibre at 93% delignification [133, 134].

6.15 Bleaching of Linen

The morphology of linen and the nature and amount of impurities is related to the scouring and bleaching method. The recipes for scouring and bleaching linen by conventional process are already discussed in Chapter 4. There is an interaction between scouring and bleaching that can cause a wide spectrum of cottonization effect. Green scutched flax generally bleached more easily than retted flax, but the bleaching of green flax, even after boiling with alkali, gives a higher loss in weight than of retted flax. The loss in weight is generally 18% by the older method of bleaching. This is due to the removal of hemi-celluloses, which are low molecular weight polysaccharides and polyuronides. These are sensitive to alkaline treatments and are present in linen fibre to the extent of about 18%. The optimum results are generally obtained with a mixture of (3:1) soda-ash and causitc soda followed by chlorite and peroxide bleaching sequence [135-138]. The lignin content of flax is much lower than that of jute. The lignin is difficult to remove in the wet processing of flax, and incomplete removal is responsible for yellowing of the fibre after bleaching.

Bleaching of linen can be carried out by either sodium hypochlorite or sodium chlorite. Linen can be bleached white from the grey state without any prior boiling treatment by using higher concentration of sodium chlorite (20-30 g/l at 80°C and pH 3.5-4), the impurities in grey flax activate sodium chlorite. However, bleaching by chlorine containing compounds gives organohelogen compounds AOX. This is caused by reaction with chlorine containing bleaching agents with lignin [139]. This problem is eliminated by replacing it with another bleaching agent that also lignify fully.

A technique for removal of flax rust (Melampsoza lini) from flax fabrics is established [140] by using bleaching mixture (NaOCl – H_2O_2). The fabric made from rusted flax yarns is treated with an aqueous solution of NaOCl (2.5 g/l of active chlorine) at pH 9 and ambient temperature. This is followed by treatment with 30% H_2O_2 (3.5 g/l) at pH 9 and at a temperature of 85-95°C. For good white, optical brightening agent may be finally applied. The exhaustion of the oxidant is slow and the degree of whiteness can be improved, if the moderate scouring is done before bleaching [141]. The main disadvantage by using sodium chlorite or peroxide bleaching of linen is that of presence of ''sprit' (remmnants of woody core of flax stem). The dyeing properties of sprit may differ from those of the linen fibre. The only effective way to remove it is by treatment with hypochlorite.

Peracetic acid/peroxide combinations can replace hypochlorite/peroxide and similar whiteness can be obtained as the chlorine route [142]. The results are summerised in Table 6.7. Peroxide itself is a good delignification agent, and in

TABLE 6.7

Reflectance Value of Bleached Linen

State	Reflectance (%)
Grey linen	20
Ash scoured	30
Peroxide bleached	65
Peracetic acid process	77
Hypo/peroxide bleach	67

fact, better than peracetic acid [143]. It is likely that peracetic acid will be able to replace these agents both as bleaching and delignification agents. The water insoluble products of peracetic acid on lignin is almost nil. On chemical analysis of the water insoluble product after treatment for 1 h, the proportion of functional groups are also reduced by different degrees (Table 6.8). The high chlorine content in lignin treated with hypochlorite indicates that in this chlorination is more vigorous, whereas with sodium chlorite oxidation processes are dominant and the chlorination reaction is almost absent.

TABLE 6.8
The Effect of Oxidising Agent in the Functional Groups of Lignin Extracted from Flax [144]

Functional group	Percentage of functional groups in				
	Original lignin	Lignin treated with			
		Hypochlorite	H_2O_2	PAA	$NaClO_2$
Methoxyl	4.47	2.23	1.55	2.91	1.62
Hydroxyl	6.50	0.83	4.15	3.76	2.41
Carboxyl	1.23	0.23	0.34	1.03	0.76
Aldehyde	6.50	7.50	4.30	5.80	4.55
Elemental Analysis	%	%	%	%	%
Carbon	58.39	39.86	51.03	51.23	49.27
Hydrogen	6.40	5.96	7.45	7.48	7.68
Chlorine	–	12.90	–	–	0.30

6.16 Bleaching of Blended Fibre Fabrics

In tropical countries like India synthetic fibres blended with cellulosic fibres fabrics are very popular due to their excellent combination of aesthetic properties and easy care properties. Thus, bleaching of blended fibre fabrics before further processing is an important step. Many of the preparatory processes used for natural and synthetic fibres have little or no application in preparation of blended fibre fabircs.

6.16.1 Bleaching polyester/cotton blends

Polyester fibre in blends with cellulosic fibres in the ratios of 65/35 and 50/50 are common construction. When cellulose portion is rayon, the blends rarely require bleaching, but when cotton is present bleaching is usually necessary. Bleaching treatments of such blends are normally required to remove the natural colours of cotton, sighting colours and if the polyester portion is turned yellow at the time of heat-setting operation. Chlorine bleaching, peroxide bleaching and chlorite bleaching are employed widely. If the polyester portion requires bleaching, then chlorite bleaching is used, as this bleaching agent bleaches both polyester and cellulose. If the polyester portion does not need bleaching, then a peroxide bleaching is more convenient. However, in case of hypochlorite bleaching, if chlorine remains in fibre degradation can occur. Peracetic acid bleaching causes no undue degradation of the fibre.

Chlorine bleaching can be done at 1-2°Tw bleaching powder solution for 2-3 h, which is followed by dechlorinating treatment. Sodium thiosulphate, acidic sodium sulphate, ammonia, H_2O_2 etc. can be used as dechlorinating agents.

Alkaline hydrogen peroxide bleaching is the most preferred system for polyester/cotton blends and bleaching can be carried out on various equipment using batchwise, semi-continuous and continuous method. Table 6.9 shows conditions for bleaching with hydrogen peroxide in HT/HP equipment by batchwise system. However, the use of continuous open width bleaching with short reaction time has led to considerable and dramatic advances in the bleaching of polyester/cotton blended fabrics. It enables the complete pre-treatment to be accomplished in 12 min instead of 24 h required for pad-roll system. In this system the desized fabric after impregnation with a liquor containing H_2O_2 (above recipe) solution at 35°C is

TABLE 6.9
Bleaching of Polyester/Cotton at HT/HP Condition with H_2O_2

Chemical	Concentration
Hydrogen peroxide (35%)	30-40 ml/l
Sodium silicate (38°Be')	10-12 ml/l
Sodium hydroxide (solid)	2-4 g/l
Sodium tripolyphosphate	some quantity
Surfactant	some quantity
Temperature	130-140°C
Time	60-120 sec

steamed (heated to 95-96°C) and stored in the J-Box for 75 min. The fabric is then washed at 65°C and dried. Blended fabrics containing coloured threads can be bleached at 80°C instead of 95-96°C without danger of bleeding.

The most effective method of bleaching polyester/cotton is sodium chlorite, which may be followed by peroxide bleaching. Chlorite bleaches the husk, but does not destroy them completely. Polyester/cotton blends may be bleached with sodium chlorite in long liquors and also by pad-steam process [Table 6.10]. The amount of various chemicals required for bleaching depend on the liquor ratio. The fabric after bleaching is rinsed as hot as possible and an antichlorination treatment is given with sodium bisulphite. In another method, the cloth is steeped in the liquor at pH 3 to 3.5, squeezed at 100% pick-up, put in a reaction tower made of titan, passed through a heating duct so that the cloth temperature is raised to proper temperature, put in a staying chamber where the cloth is steamed and bleached.

TABLE 6.10

Recipe for Bleaching Polyester/Cotton Blends with $NaClO_2$

Condition	Jig	Winch beck	Pad-steam (Dry-in-wet)
Liquor ratio	7:1-3:1	50:1-20:1	70% pick-up
$NaClO_2$ (80%), g/l	5-7	1-2	10-20
Stabiliser, (g/l)	2-4	0.5-1	–
Sodium nitrate, (g/l)	2-3	1-2	10-15
Formic acid to maintain pH to	3.5-4	3.5-4	5.5-6
Reaction temp., (°C)	80-90	80-90	85-90
Reaction time, (h)	1-3	1	2-4

Peracetic acid can also be used for bleaching polyester/cotton blended fabrics with a solution containing 4 g/l peracetic acid, 1 g/l tetrasodium pyrophosphate (stabiliser) and 1 g/l wetting agent with a liquor ratio of 5 : 1. Peracetic acid has a pH of about 1.5 and the bleaching bath solution is adjusted to pH 5.5 with the help of dilute alkali. The material is entered cold and run for 10 min. Then the temperature is raised to 65-70°C in 15 min and bleaching is continued at this temperature till the concentration of peracetic acid drops to 0.09 g/l. The fabric is then washed thoroughly with hot and cold water. The bleaching can be performed in the kier or in the jigger.

A single stage combined scouring and bleaching of polyester/cotton blended fabric can also be done for economy. There are various approaches which include : alkali treatment with detergent and peroxide hot bleach ; alkali treatment with detergent and sodium chlorite bleach ; sodium chlorite and peroxide bleach ; and peroxide cold and peroxide hot bleach.

6.16.2 Bleaching of polyester/wool blends

The wool portion contained in the blend show reversion to a creamy colour and yellowing of the fabric. In general, blends containing wool and polyester fibres can be bleached with hydrogen peorxide either in acid or alkaline medium without risk of damage.

In acid medium, the fabric is treated with a solution containing 30-40 ml/l H_2O_2 (35%), 2-4 g/l organic stabiliser, 0.25 g/l wetting agent and 0.25 g/l detergent at pH 5.5-6 (acetic acid) for 40-60 min at 80°C or 2-2.5 h at 65°C. The treated fabrics are then given warm and cold rinse.

In alkaline medium, the bath comprises of H_2O_2 (35%), 30-40 ml/l ; sodium pyrophosphate, 2-4 g/l ; ammonia to maintain the pH between 8.5-9.0. The bath is set at 40°C and the goods are treated for 2-4 h, and rinsed well in warm and cold water.

As peroxide-bleached goods tend to show reversion to a creamy colour, it is usual to follow with a treatment in reducing agent to stabilise the bleach in a bath containing 3-4 g/l stabilised hydrosulphite and 1 g/l synthetic detergent at 50°C for 30-40 min, rinsed and dried.

Polyester/silk blends can be bleached by a similar manner to that of polyester/ wool blends.

6.16.3 Bleaching of nylon/cellulose blends

Blends of nylon and cellulosic fibres may be bleached with either H_2O_2 or $NaClO_2$, using batchwise or continuous method [145, 146].

H_2O_2 does not bleach nylon and normal methods of bleaching degrade nylon and cause yellowing. Blends containing 30% or less of nylon may be bleached by the continuous H_2O_2 method, and in such cases cotton will absorb the peroxide preferentially and so protect the nylon from damage. The use of protective agents which prevent undue damage to the nylon poriton of the blend is reported [147].

The goods are entered into a bath containing 2-3 volume H_2O_2, 1 g/l sodium hydroxide flake, 0.2 g/l peroxide stabiliser, 0.25 g/l sequestering agent and 0.002 to 0.05 g/l free radical suppressor at 40°C, the temperature is raised to 85°C and then the treatment continued for 1 h. The treated goods are then cooled and rinsed thoroughly. When appropriate, selected optical brighteners may be incorporated in the peroxide bleach bath.

Hypochlorite does not damage nylon but it has got no bleaching action on it. Sodium chlorite causes no degradation of either cellulosic or polyamide and is a better bleaching agent than peracetic acid for cotton. For batchwise bleaching the fabric is treated with a solution containing sodium chlorite (2-5 g/l) at pH 3 to 4 at 90°C for $1^1/_2$ to 2 h. This is followed by a treatment in a 2 g/l solution of sodium carbonate at 40-50°C and finally hot and cold rinses are given in water. Pad-roll and continuous processes are also used for bleaching polyamide /cellulose mixture.

6.16.4 Bleaching of nylon/wool blends

It is difficult to bleach this blends since the method normally used for nylon degrade wool. The usual method is either to bleach the wool portion with H_2O_2 at low temperature [148] or to carry out reduction bleaching process [149]. Alkaline H_2O_2 bleaching always damage the polyamide fibres to some extent. Normal alkaline H_2O_2 bleaching process may be used with safety on blends containing up to 25% polyamide, but an acid bleach must be used when proportion exceeds this figure. The fabric can be bleached with a solution containing 12-15 ml/l H_2O_2 (35%), 2 g/l tetrasodium pyrophosphate, 1 g/l EDTA (30%) and 0.25 g/l protective agent at 60-65°C for 45-60 min and then rinsed well in water.

6.16.5 Bleaching of acrylic/cellulosic blends

If the cellulosic portion is cotton, bleaching is invariably required for this fibre. If the acrylic portion does not require bleaching, then a peroxide treatment can be done at pH 9.5. The alkaline condition should not be high as otherwise it would cause degradation of the fibre. The fabric is treated with a solution containing 7.5-10.0 g/l H_2O_2 (35%), 3 g/l sodium silicate (79°Tw) and 1 g/l sodium carbonate at 90°C for 45-60 min. After bleaching the bath is cooled slowly to 50°C, rinsed and neutralised.

When acrylic fibre also requires bleaching, then mild chlorite treatment will act on both the fibres in the blend. The bath is prepared at 35°C with 1.5 g/l sodium chlorite, 2 g/l oxalic acid, 1 g/l tetrasodium phosphate and 1 g/l corrosion inhibitor. The bleach bath should give a pH of about 3.5 to 4.0. The temperature of the bath is raised to 90°C over 30 min and processing continued for 30-45 min at this temperature. The bath is cooled slowly to 50°C and then rinsed thoroughly. An antichlor treatment is given in a bath containing sodium bisulphite (1.5 g/l) and tetrasodium phosphate (1.5 g/l) at 60°C for 20-30 min, cooled the bath and rinsed well. The temperature of drying should not exceed 80°C.

6.16.6 Bleaching of acrylic/wool blends

Hydrogen peroxide is not suitable for acrylic fibre at highly alkaline condition and moreover acrylic fibre turns yellowish on alkaline peroxide treatment. The discolouration can be improved by after-treatment with formic acid in presence of detergent. Acrylic/wool blends can also be bleached by a reduction bleach or by combination of peroxide and reduction bleaching process.

6.16.7 Bleaching of acetate/cellulosic blends

Diacetate/viscose blends have been used in dresswear, shirting and under-wear. These blends may be bleached with hydrogen peroxide or sodium hypochlorite, preferably the latter.

The goods may be treated with a solution containing 5 g/l H_2O_2 (100 vol.), 2 g/l sodium silicate and 1 g/l soap at 70-75°C for a minimum time of 30 min.

Bleaching can be done by treatment with a solution containing sodium hypochlorite (2-3 g/l available chlorine) adjusted to pH 10 at room temperature for 30 min, and then the fabric is given cold treatment with 1 ml/l HCl and thorough rinsing. Alternatively, an acid solution is prepared with 10 ml/l sodium hypochlorite (50°Tw) and 2 ml/l hydrochloric acid adjusted to pH 3. The treatment is carried out cold for 40 min, goods are well rinsed and then treated in a second bath with 3 g/l sodium bisulphite at 40°C for 20 min.

6.16.8 Bleaching of polyester/linen blends

Polyester/long-staple fibres are used in the linen industry, where yarns may be of either the ''stretch broken'' or ''unbroken'' type, but more commonly of the latter. The linen component of the blend may be of bleached or unbleached fibre and yarns spun from unbleached fibre may be bleached before weaving. Most fabrics in this blend are woven on sized (singles) warps. Unmodified warp sizes are removed by enzyme treatment and non-cellulosic matter is removed by an alkaline scour.

Goods made from bleached yarns or fibres require only a light scour with 2 g/l soda-ash along with 1 g/l detergent. Goods prepared from unbleached yarns or fibre are padded with dilute caustic soda solution at 70 to 80°C, batched on a roll and allowed to rotate at this temperature for 24 h. The goods are then rinsed, scoured and bleached with hydrogen peroxide or with sodium hypochlorite. Sodium chlorite is not normally used for bleaching this blend.

6.16.9 Bleaching of wool/viscose blends

Bleaching is usually carried out by immersion of the material in a liquor containing 1-2 vol. H_2O_2 and 5 g/l sodium silicate or sodium pyrophosphate at 30°C overnight or at 40-50°C for 4 h. The bath is adjusted to pH 8 and it is advisable to add 0.25-0.5 g/l of a suitable sequestering agent. For treatment by the shorter time, the concentration of H_2O_2 may be increased to 3 to 3.5 vols. The amount of H_2O_2, however, depends on the quality of wool or proportion of viscose in the blends.

6.16.10 Bleaching of viscose/cotton blends

Viscose/cotton blends can be bleached either by batch method on jig and winch or by a continuous process using J-Box [150]. Bleaching is done on a winch with sodium hypochlorite (2 g/l available chlorine) adjusted to pH 10-11 with sodium carbonate, for 1 h at 25°C, or alternatively, with 5 g/l sodium chlorite adjusted to pH 4 with acetic acid for 30 min at 80°C. Alternatively, the bleaching treatment may follow with alkaline hydrogen peroxide at 85°C.

In the continuous method the fabric is saturated with bleach liquor consisting of H_2O_2 and potassium persulphate, passed through a J-Box, followed by short boil-off, rinsing and drying over cans with a total processing time of 15 min. The temperature in the J-Box approximates 70°C and that of wash liquor 80°C.

6.17 Bleaching of Cotton Weft Knitted Fabrics

Knitted fabrics can be produced from a wide range of fibres and blends, either as flat fabric or garments. Garments, ranging from outerwear (including sport and leisure wear) to hosiery, are generally weft knitted. Warp knits usually require filament yarns which are 100% synthetic and do not normally require bleaching. The weft knitted fabrics produced from 100% cotton and synthetic fibre/cotton blends may be called jersey, rib or fleece depending on how the loop lie. While weft knitted fabrics are comfortable to wear, since they are light and pleasing to the skin, they do have disadvantages in that they are easily deformed by mechanical stresses and wet creased than woven fabrics.

Since knitting yarns are unsized and usually combed to reduce seed and 'trash content', there is normally any need for treatment prior to bleaching. The knitting lubricants which replace the size on woven fabrics are usually self scouring, but sometimes from their very volume may create problems with foam and stains in wet processing or in the knitting machine which need to be treated with solvent containing auxiliaries.

The bleaching of knitted fabrics-like that of woven fabrics-should result in high whiteness, low chemical or abrasion damage, low crease formation and high absorbancy to water. Sodium hypochlorite is generally not suitable for bleaching of knitted fabrics on account of alkaline nature of the bleach process and recent restriction on adsorbable organo-helogen compound (AOX) generation. However, hypochlorite may be used at pH 11 and at temperature not exceeding 30-35°C in presence of effective wetting agent [151]. Then the fabric is given an antichlor treatment, the whole process taking 3-4 h.

The acidic nature of sodium chlorite bleaching process make it ideal for knitted fabrics, as the natural fats and waxes of the fibre were not scoured out, enhancing the soft, voluminous handle of the goods. Alternatively, a single-stage combined scouring and bleaching can be operated using a peroxide solution containing mild alkali, a detergent and sodium silicate as stabiliser. The alkalinity of peroxide bleaching conditions may scour out the natural fats and waxes from knitted fabrics and results in harsher handle and poorer sewability. A soft fabric can be produced by treating with softener after peroxide bleaching. The combined hypo/peroxide process generally provides the highest whiteness on knitted cotton fabrics. Cotton hosiery made from dark coloured mercerized yarn can be rapidly bleached by hypochlorite followed by peroxide without preliminary scour. Cotton in knitted fabrics is usually less seedy than for woven fabrics making one step scour/bleach with peroxide more readily applicable. Low tension machineries are generally suitable.

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