

MERCERIZATION

9.1 Introduction

Mercerization was discovered by John Mercer in England and the process is named after him : mercerizing. The process of alkaline treatment of cotton was patented in 1850. Later Horace Lowe in England found that the glazing effect became even more pronounced when cold caustic soda acted on cotton under tension. He discovered the actual mercerizing process and applied for its patent in 1890.

Mercerization gives cotton woven cloth a silky lustre, and is the foundation of many improved and beautiful finishes. Sewing and embroidery cotton yarns are mercerized with tension in the form of hank. Stretched yarn can be made by mercerizing without tension [1, 2]. The stretched materials are used for bandages, casual wear (originally garments for skiing), skirts, boat covers etc. The increasing cost of chemicals, machinery, labour, effluent control and recovery of caustic soda make the process of mercerization less attractive now-a-days.

9.2 Conditions for Mercerization

Mercerization is defined as the treatment of cotton textiles with a concentrated solution of alkali consisting the following conditions:

- (a) Application of caustic soda solution around 55-60° Tw (\approx 31 to 35%) at a temperature of 15 to 18°C.
- (b) A dwell period of 55 sec on an average, so as to permit diffusion of alkali into the fibre.
- (c) Warp tension during alkali treatment and stretching the weft (width) of the fabric during washing are necessary to prevent shrinkage.
- (d) Finally, washing-off of the traces of alkali from the treated fibres.

Mercerization may be carried out on grey fibres or after scouring/bleaching. The cloth should be singed before mercerizing to give a smooth surface. If mercerization is carried out in the grey state, complete removal of alkali is not necessary during washing treatment as the residual alkali in the cloth is used for the kier process. However, mercerization is commonly carried out after scouring, but it is preferable to mercerize after bleaching if continuous bleaching plant is available.

Another necessary condition for successful mercerization is the rapid and uniform wetting of the grey cloth. Penetration of alkali is hindered by the high viscosity of the strong caustic soda solution at lower temperature on the one hand and the hydrophobic nature of the fatty matter present in the size coating as well as natural fats and waxes present in the fibre on the other. To obviate these problems a small amount of penetrating and wetting agent is added to the caustic bath, . The wetting agents should be selected so that it should have good solubility and high wetting ability in the alkaline bath, should have no affinity to fibre, low foaming power , good efficiency at low concentration and stability under conditions of sodium hydroxide recovery by centrifuge or vacuum evaporation technique etc. [3]. It is obvious that a single wetting agent does not show all these properties and, therefore, blends of wetting agents are needed to get the optimum effect during mercerization process. Generally, two types of wetting agents are commonly used in mercerizing liquors e.g. cryslic acid derivatives coupled with selected solvents such as triethyl or tributyl phosphate and the other type is non-cryslic type. Mixtures of ortho, meta and para cresols (also called cryslic acid), $\text{CH}_3\text{-C}_6\text{H}_4\text{-OH}$, are not soluble in water, but dissolve in strong caustic soda solutions . Their wetting power is also found to be improved considerably by incorporating methylated spirit, polyhydric alcohols having C_{18} chains , butanol , polyethylene glycol etc, by diminishing the viscosity of mercerizing liquor. Non-cryslic wetting agents include sulphated lower fatty alcohols such as hexyl or octyl alcohol and the addition of polyhydric alcohols, enable the stabilisation of wetting agents while avoiding their precipitation during the process of recovery of sodium hydroxide. A product obtained by the distillation of pine oil as a fraction between turpentine and rosin, has excellent wetting, penetrating and emulsifying properties in mercerizing liquor. Wetting efficiency of non-cryslic type is generally higher than that of cryslic type. In case of mercerization of knit goods which contain paraffin products, the wetting agents used must also possess dispersing power towards these products [4].

9.3 Changes in the Properties of Cellulose Due to Mercerization

Cellulose undergoes chemical, physico-chemical and structural modifications on treatment with caustic soda solution of mercerizing strength [5]. Chemical reactions lead to the formation of alkali cellulose, physical reactions, to a change in arrangement of units of cellulose. The optimum modifications in the properties of

cellulose can be manipulated with the selection of proper concentration of alkali, time, tension and temperature during the mercerizing process.

9.3.1 Swelling and shrinkage of cellulose

When cellulose is immersed in a solution of caustic soda of mercerizing strength, water and alkali diffuses in and the material swells. The fibre hair quickly commences to untwist from its twisted ribbon like form and tends to become cylindrical rod-like surface due to deconvolution. The cross -section of the fibre diminishes, the diameter of the fibre becomes more round. The surface of the nearly cylindrical cotton fibre after mercerizing reflects light more evenly to all sides than the kidney-shaped cotton fibre and the fibre surface becomes more lustrous [6]. As the fibre swells, the fibre shrinks in length [7, 8]. Swelling and shrinkage are more when there is no tension in the fibre, but the alteration in cross-section caused by swelling is more when mercerization is carried out under tension . Under optimum conditions each cotton fibre may contract nearly 9% in length and swell nearly 150% . Swelling of the cotton fibre also has a disadvantage . The fibre becomes more compact in its swollen condition. This compacting diminishes the further penetration of caustic soda into the fibre i.e. penetration slows down and mercerization in the fiber's core is lower than on its surface.

Maximum swelling concentrations of different alkalies depend on the degree of hydration of the alkali ion [9, 10]. Table 9.1 contains data of different kinds of

TABLE 9.1

Effect of Alkali Metal Hydroxides on the Swelling of Cotton Fibre [11]

Reagent	Concentration of alkali at which maximum swelling is obtained		Increase in fibre diameter (%)
	g/100 g of solution	mole/l	
LiOH	9.5	4.0	97
NaOH	18.0	4.5	78
KOH	32.0	5.8	64
RbOH	38.0	3.8	53
CsOH	40.0	2.7	47

alkali metal hydroxides on the swelling of cotton fibre. For small concentration of alkali, the diameter of the hydrated ions is too large to penetrate into the

macromolecular structure of cotton , but as the concentration increases , the number of water molecules available for the formation of hydrates decreases and thus hydrated ion pairs, dipole hydrates (solvated or not) are formed with the decreasing hydrodynamic diameter, are capable of penetrating into the fibre structure of cellulose forming hydrogen bonds with the molecular chains of cellulose . Thus mercerization induces important structural modification of cellulose when interfibrillary swelling takes place. With further increase in concentration of alkali-metal hydroxides in the solution, fibre swelling is reduced due to decrease in hydration of alkali metal ions.

The influence of alkali concentration and temperature of treatment on swelling

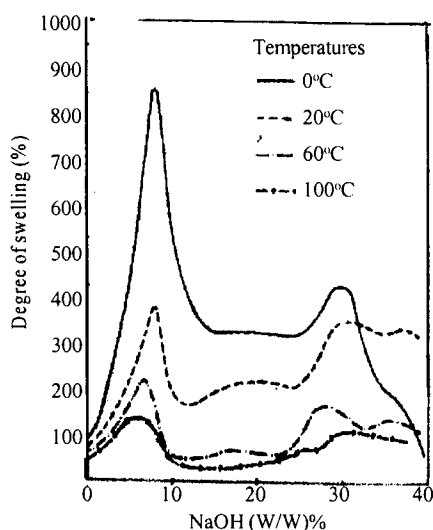


Figure 9-1. Dependence of swelling on temperature and concentration of alkali [12].

of cellulose are represented in Fig 9.1. The extent of swelling depends on the concentration of alkali. In solution with an increasing concentration of NaOH at 20°C, the swelling of cellulose (cotton linters) increases to a maximum value for a concentration equal to 8 to 9% by weight of NaOH ; next it decreases to a minimum (12 - 13% NaOH by wt.) and then slowly increases in higher concentration ranges.

Though 8% NaOH (by wt.) solutions give maximum swelling, commercially mercerization is done at higher concentration of about 31 to 35% which indicates that swelling is not the only determining factor. This is because of preferential

absorption of NaOH during mercerization process. This preferential absorption is associated with the question of compound formation to form soda-cellulose. The amount of alkali adsorbed is very much greater than that of preferentially adsorbed (Fig. 9-2) as a result of very large swelling and adsorption of water in the cellulose. The adsorption of NaOH is found to be constant between certain concentrations of

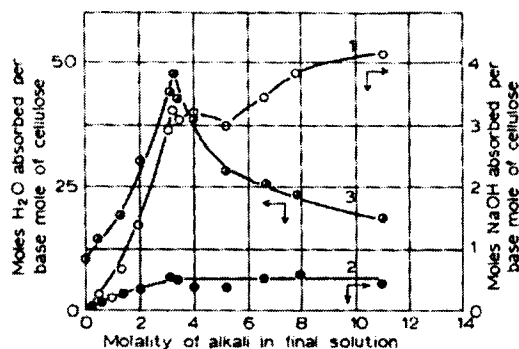
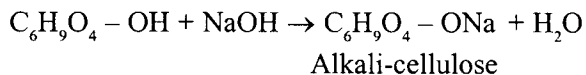


Figure 9-2. NaOH and water absorbed by cellulose sheet at 25°C [13, 14]. 1-total alkali absorbed, 2-preferentially absorbed alkali, 3-water absorbed.

alkali, it is thus assumed that a definite compound is formed with the cellulose molecule. Further water absorption plays a large part and this water absorption fall rapidly after reaching a maximum, thus causing alkali absorption to appear constant.

Two broad explanations are possible for the interaction of cellulose and caustic soda. For the first one, it is assumed that cellulose combines with caustic soda to form alkali-cellulose and swelling is due to the molecular attraction with associated



hydration. The extent of this combination is governed by the concentration of alkali. It is assumed that alkali-cellulose is more hydrated than the native cellulose. Maximum swelling in particular range of alkali concentration is the result of the attraction of alkali-cellulose on the one hand and the remaining free alkali on the other. The hydration of the cellulose increases with the increased fixation of alkali in solutions of rising concentrations up to a certain limit, after which free alkali exerts a dehydrating effect on the alkali-cellulose to a great extent. The second theory is based on osmotic phenomena. It is assumed that cellulose behaves as a very monobasic acid due to the hydroxyl groups in it and forms an alkali-cellulose

during mercerization with alkali. The excess alkali diffuses into the cellulose according to Donan's theory of membrane equilibrium. The presence of ions in cellulose result in unequal distribution and thus brings about an osmotic pressure. This causes water to enter the fibre until such time as the osmotic pressure is in balance with the restraining or elastic forces of the swollen fibre. When the alkali solution is replaced by a large excess of water, the sodium cellulosate is hydrolysed, osmotic pressure falls, undissociated hydroxyl groups are reformed and the cellulose is recovered chemically unchanged, but permanently distorted if the osmotic pressure is high enough. Another term is transient swelling. When alkali impregnated material is washed with water, increased swelling is observed whilst the alkali is being removed (Fig. 9-3). Water diffuses into the cellulose more rapidly than the alkali ions can diffuse out, and hence, since the activity of the water in the aqueous phase

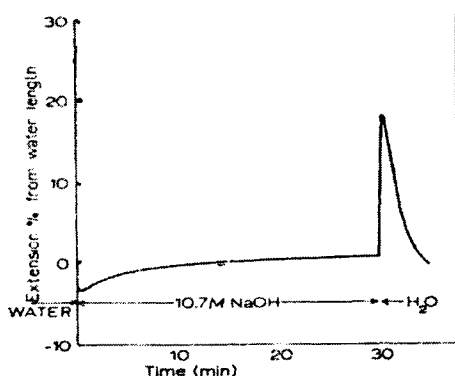


Figure 9-3. Transient swelling of cellulose [15].

is increased, the osmotic pressure is transiently larger. This greater momentary swelling which occurs for a short period of time decreases as the ions diffuse out of the fibre. If the activity of water in the wash liquor is reduced by the addition of salt, the swelling effects are reduced and the alkali may be removed without undue swelling of the fiber [16].

Swelling of cellulose fibres in alkali increases with a decrease in temperature [17] as the formation of alkali-cellulose compounds is an exothermic process. At 0°C the swelling of cellulose in alkali (8-9% by weight) is about 800% (Fig. 9-1) and swelling decreases rapidly at higher concentration of alkali due to the decrystallisation of NaOH hydrates. The extent of swelling also decreases as the

treatment temperature increases (60°C or 100°C) and maximum swelling is observed at 7-8% NaOH by weight.

Shrinkage of cotton is greatest on swelling in alkali at 15-18°C and the value decreases with increase in temperature. The use of cold (2°C) concentrated solutions of alkali reduce the shrinkage as the solutions become too viscous to impregnate fibres significantly in a short time. The shrinkage of raw cotton fibre is lower than that of scoured cotton [18]. Volume changes are significant ranging from 62cc to $177 \pm 8\text{cc}$ in the alkali concentrations ranging from 14.3 to 48.8% (w/w) [7]. The increase is, however, small if treatment is carried out under tension.

9.3.2 Structural modification

Due to swelling of cellulose in caustic soda solution of mercerization strength, many hydrogen bonds are broken, the plane of molecular chains have been moved apart, molecular structure tends to become decrystallised, the chains or spaces within the cellulose structure become more uniform and the chains of glucose residues have been given a slight twist. Because of the distortion of polymer network and changes in crystalline structure, the process of mercerization is irreversible [19-23]. Mercerization also affects the size of the crystallites [24] and orientation of the crystalline region [25, 26] and the extent of orientation depends on the tension during mercerization. The influence of alkali concentration on changes in the crystalline structure of cotton yarns mercerized for 60 secs at 20°C with constant length (0% stretch) is illustrated in Fig. 9-4. Soda-Cellulose I is formed with sodium

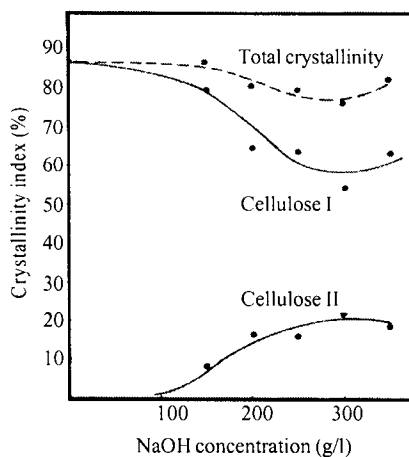


Figure 9-4. Influence of NaOH concentration on the crystalline structure of cellulose fibres [27].

hydroxide at concentrations of 12-19% (by wt.) [28-30], Soda-Cellulose II at concentrations between 20 and 45% by weight. Cellulose I exists in a parallel chain conformation while Cellulose II exists in an antiparallel chain conformation [31]. Soda-Cellulose III is obtained by drying Soda-Cellulose I [32, 33]. For temperature higher than 30°C and in solution 20-25% NaOH (by wt.), the formation of Soda-Cellulose III and II is obtained [34]. Soda-Cellulose IV is obtained by washing Soda-Cellulose I and II in water or in dilute solution of NaOH [35]. Soda-Cellulose V appears between -10 and +20°C in a wide range of NaOH concentrations of about 40-45% (by wt.) [36-38]. However, concerning the formation of Soda-Cellulose compounds there is some approximation the manner in which they form with respect to the nature of NaOH hydrates present in concentrated solutions. Cellulose I content and total crystallinity index decreases as the temperature of mercerization increases, whereas Cellulose II follows an opposite course due to the better penetration of NaOH hydrates. Mercerization without tension allows total conversion of Cellulose I to Cellulose II to take place, whereas when mercerizing with tension, mixtures of the two are formed [39, 40]. Cellulose III, IV and X can also be obtained by treatment of cotton with ammonia at -35°C, hot glycerine and phosphoric acid respectively. The shape of native cellulose crystal (Cellulose I) is monoclinic and the dimensions of monoclinic unit cells of various crystalline forms (Cell I to Cell X) are shown in Table 9.2. Out of various Celluloses, Cellulose II is most stable and the other Celluloses may be reconverted into each other [41, 42].

TABLE 9.2

Dimensions of Unit Cell of Different Celluloses on Structural Modification

Dimensions	Cellulose I	Cellulose II	Cellulose III	Cellulose IV	Cellulose X
a (Å)	8.35	8.14	7.74	8.11	8.10
b (Å)	10.30	10.30	10.30	10.30	10.30
(fibre axis)					
c (Å)	7.9	9.14	9.9	7.9	8.16
β (degrees)	84	62	58	90	75.36

9.3.3 Increased lustre

Unmercerized cotton has a general appearance of a flat ribbon with spiral twists, its surface is rough and non-uniform, its cross-section is irregular and ear-shaped

while the lumen, the central canal, is broad, irregular and resembles a collapsed tube. All these factors result in less lustre. When a cotton hair is brought into an aqueous solution of sodium hydroxide of 18% (40° Tw), cellulose begins to swell immediately, the hair is elliptical in section in a few seconds, and on further swelling becomes circular and the lumen is practically eliminated. The untwisting of the fibre takes place under effect of swelling and increased alignment and packing of the fibres in the yarn also take place. The changes that take place in the cross-sectional shape of cotton fibre during mercerization are shown in Fig. 9.5. Stages 1

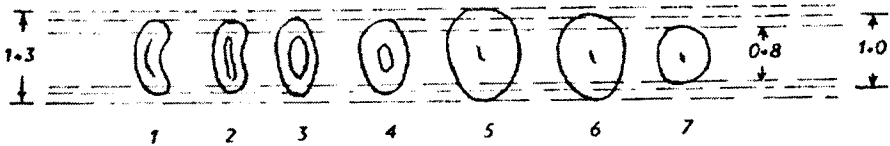


Figure 9-5. Seven successive stages of change in the cross-sectional shape of a cotton fibre as produced during mercerization.

to 5 show the change for a twisted ribbon like fibre to one which is uniformly cylindrical and in its most swollen form at 5. Stages 6 and 7 show some contraction but without losing its cylindrical form when the fibre is washed with water (6) and then dried (7). During the last three stages, the hair retains the same form of section, but shrinkage proceeds uniformly towards the centre and lumen does not recover its original size. But to secure an increase in lustre the cotton material must be prevented from shrinkage by stretching the yarn lengthwise and the fabric both lengthwise and widthwise during the treatment and washing out of the alkali by water. When cotton is mercerized without tension, the fibre while much smoother and rounder with little or no twist, still show residual creases and wrinkles and there is no appreciable increase in lustre as the cross-section is oval and lumen is contracted but not collapsed. Lustre increases as the tension applied to the fibre during mercerization is increased [43, 44].

Lustre also depends on other factors. Mercerization reduces the axial ratio and increase the light scattering within the fibre (transparency) and thus increases the lustre. The presence of short fibre on the surface decreases lustre and is removed during singeing. Lustre increases from 180 g/l of NaOH solution to a maximum at 260-300 g/l, then decreases slightly [45]. Theoretically lustre increases with an increase in swelling and therefore with a decrease in the temperature of merceriza-

tion [46]. However, if the temperature is decreased, there will be surface dissolution of the fibre which may result in a decrease in lustre [44]. On the contrary, lustre increases with increase in temperature of mercerization [47, 48] inspite of lower swelling value. This may be due to the faster and uniform penetration of NaOH at higher temperature. The staple length of the cotton is also significant since the long staple fibre has the best shape of cross-section. Twisted double yarn is more lustrous after mercerization than non-twisted loose yarn. A face cloth such as sateen will show the greatest increase in lustre and is caused by the long floats lending themselves to the effective tension more readily than shorter crossings of the yarn.

9.3.4 Gain in strength

Mercerization, both slack and with tension, increases the strength uniformity along the fibre length [49], but mercerized fibre with tension shows greater gain in strength than that of without tension. In practice, the improvements in strength are noticed mostly upon yarn treatments, with fabric the major effect is on the surface only. Mercerization increases the tensile strength of cotton fibres by eliminating the weakest points in the fibre [50, 51]. Mercerization increases the cohesion between individual cotton hairs and this closer embedding of the hairs in the yarn not only increases the strength but makes it more uniform in strength and less in diameter.

The physical properties of mercerized fibres are related to the orientation factor; the Young's modulus increases with increase in orientation. The elongation acts in reverse, decreasing as the orientation increases [52, 53]. The increase in orientation of the crystallites with respect to fibre axis can be attributed to such factors as the reduction in crystallinity of the fibre, the decrease in lengths of crystallites and fibre deconvolution [54, 56]. In case of slack mercerized cotton increased strength is accompanied by an increase in extensibility, thus deconvolution is not the only factor influencing the changes in mechanical properties on mercerization apart from decrystallisation and length of crystallites [57].

The twist of yarn plays an important role and low twist appears to be essential for maximum increase in strength. Grey yarn with soft doubling twist gives stronger yarn.

9.3.5 Increased moisture absorption

Mercerized celluloses absorb more water, have higher regains and more easily wet out than unmercerized fibres. Due to caustic soda penetration, many hydrogen

bonds are broken and it is estimated that the number of available, hydroxyl groups are increased by about 25%. Mercerization, thus decreases the amount of crystalline part or increases the amorphous content of the fibre. This increase in the proportion of amorphous part is directly related to the moisture sorption. Moisture is assumed to be absorbed by suitable groups in the amorphous region and on the surface of the crystallites. When mercerization is carried out under tension, the changes in crystalline portion is comparatively lower than that without tension and hence also the moisture sorption. Standard cotton has moisture content of about 7%, mercerized cotton with tension has about 9% and that of without tension about 11%.

9.3.6 Increased dye adsorption

Mercerized cotton shows increased depth of shade, increased rate of dyeing and the irregularities due to neps and unripe cotton are less prominent. Generally immature cotton with large lumen responds particularly well to increased light scattering and hence decreased dye uptake. The greater colour yield on mercerized cotton takes place to different degrees at different depth of colours [58] and the magnitude of increased depth of shade varies for different dyestuffs [59]. The increased depth of shade of mercerized cotton has been attributed to optical effects arising from the modifications of fibre size and shape [60, 61] and to changes in internal light scattering [62], as well as to actual increases in dye content due to increased amorphous part of the fibre. About half the total dye savings is attributed to optical effects. The change in pore volume and reduction in lumen diameter are primary causes of consequent improvement in colour yield and reduced light scattering within the fibre. Mercerization thus lowers the dye costs, savings at 2% depth averaged 40%, while at 6% with the same dyes the average saving is about 60%.

Cotton can be causticized or half-mercerized to increase the dye uptake and economics up to 25% may be realised. Semi-mercerization or causticization is carried out in caustic soda solution between 25 and 30°Tw at a temperature of 20-25°C, sometimes without stretching the cloth to restore original dimensions. Sodium hydroxide solution above 30°Tw the rate of colour absorption decreases. Semi-mercerization is also an important step where heavy shades are required with the expensive vat colours. Better results are also observed with aniline black on goods which have received a semi-mercerization treatment.

9.3.7 Increased reactivity

The reactivity of mercerized cotton is increased by about $1\frac{1}{2}$ times at lower temperature in comparison to that of unmercerized cotton. The increased reactivity is not so marked when mercerization is carried out under tension. The reactivity ratio is generally referred to as the ratio of copper number of the mercerized to unmercerized samples. The increased reactivity increases dye absorption, moisture sorption and chemical reaction, but at the same time it also accelerates the reaction with acids and oxidising agents and is susceptible to degradation.

9.3.8 Removal of immature cotton

Mercerization has been recognised as a method for removing immature (dead) fibres to obtain level dyeing effect on cotton fabrics. The dead fibres are underdeveloped and appear as flat or slightly twisted tapes. They are non-crystalline, convolutions are sometimes absent, cell walls are extremely thin and the lumen is collapsed and hence do not contain dye to same extent as matured fibres.

9.3.9 Physical compactness

Mercerization improves dimensional stability of cotton woven fabrics [63]. When knitted fabrics are compared with respect to their relative openness, temperature increases can be said to improve mercerization because when the goods are bleached and then mercerized, the fabric becomes more dense. However, when unbleached fabrics are mercerized, the fabrics become more open [64]. Mercerization also gives moderate improvement in crease recovery of cotton fabrics [65] as well as some protection against the decrease in tensile strength caused by easy-care finishing.

9.4 Mercerization of Ramie and Flax Fibres

Ramie and flax are often used in the same fabrications and are often blended with cotton to improve its performance. Informations as a result of common conditions of mercerization are of great interest to minimise the variation in dyeing behaviour for the three natural cellulosic fibres. Flax fibres generally possess a high degree of lustre and mercerization is generally done to improve the affinity of dyestuffs, assist in the crease-resisting process, improve abrasion resistance and cover the reediness in cloth associated with yarn unevenness.

The effects of slack and tension mercerization on the morphology and accessibility characteristics of ramie, flax and cotton fibres are compared [66]. Mercer-

ized remie increases in size but not in circularity; mercerized flax fibres do not increase in size or shape; mercerized cotton fibres increase in area and in circularity as a result of swelling in caustic soda. The changes occurring in linen [67, 68] and flax [69, 70] fibres have been reported. Slack mercerizations of remie and flax result in considerable losses in yarn strength, while tension mercerizations result in increased strength. Increased yarn strength is seen in both slack and tension mercerization of cotton yarn. Increases in fibre accessibility are obtained in all mercerized fibres, but the magnitude of change in flax is approximately half of that in remie and cotton. Changes in fibre shape and accessibility characteristics are lower when cellulose yarns are held under constant tension than when they are allowed to shrink freely during mercerizing treatment. Mercerization of remie results in a complete conversion of Cellulose I to Cellulose II and a decrease in the degree of crystallinity to 50% [71]. The orientation of the crystallites in cotton is increased and that of remie is decreased due to intra-crystalline lateral swelling unrestrained by a restrictive primary wall [72]. Structural realignment of cellulose crystals does take place during the NaOH treatment of flax fibre [73].

With the same dyes and conditions of dyeing used for remie, flax and cotton, variations exist in the shade produced. All three fibres can be successfully mercerized to improve dye exhaustion and colour yield, but the extent of increased depth of shade produced on each treated fibre will vary with the specific dye used.

9.5 Mercerization of Blended Fibre Fabrics

Mercerization of blended fabrics containing polyester and cotton is done to improve the low lustre of cotton as compared to polyester and also to secure a more solid dyeing. For such blends the mercerization process is generally carried out in the same way as 100% cotton, but using caustic soda of lesser concentration i.e. 42° Tw along with penetrating agent. Hot mercerization has been found to give more uniform results. Under the mercerizing conditions cotton component in the blend undergoes physical and chemical changes, whereas polyester component undergoes a topochemical changes, resulting in surface hydrolysis. This leads to a reduction in strength proportional to the weight loss of the polyester component. The fabric after mercerizing is neutralised and made slightly acidic (pH 6) with acetic acid.

Generally, the blends containing polyester/viscose or polyester/polynosic com-

ponents are not mercerized. Fabrics containing mixtures of cotton and rayon require special precautions as the regenerated fibres, and in particular the viscose fibres show a higher alkali solubility than cotton fibres. Maximum swelling and solubility of viscose fibres occur at room temperature for NaOH concentration on the order of 9-10% by weight (100 - 110 g/l). Actually, viscose rayon withstands the action of alkali of mercerizing strength, but during washing with water, the alkali becomes diluted and at a concentration of about 9-10% (by wt.), the hydrated ion pairs, $20\text{H}_2\text{O}$ can penetrate the amorphous as well as crystalline regions, causing an unlimited swelling and the fibres are degraded. The loss in strength of viscose fibre, thus, is not during mercerization step, but during the washing-out process. The following approaches can be adopted to minimise the degradation of viscose in the blends:

- (i) Alkali should be quickly removed from the fabric after mercerization with a good flow of water at 100°C . The solubility of viscose is less marked at higher temperature.
- (ii) If possible, hot mercerization can also be adopted to minimise degradation.
- (iii) Addition of electrolyte (e.g. NaCl) in the rinsing bath diminishes the proportion of dissolved viscose. Other protective agents such as sucrose, glycerine etc. are also recommended.
- (iv) Additions of electrolyte into the mercerizing liquor are also possible.
- (v) Use of KOH or mixture of KOH and NaOH in the similar proportion (ratio) to that of blended fibres in the fabrics is useful. Mercerizing with KOH alone can be done in a solution of 55-60° Tw at $15-18^\circ\text{C}$ with dwell time of 90 sec but is expensive.

Polynosic fibres are more stable than the ordinary viscose fibres in alkaline medium and thus cotton/polynosic blended fabrics can be mercerized without taking any special precautions. However, rinsing process with hot water is also advisable. High wet-modulus (HWM) fibre induces a higher strength loss and thus mechanical degradation can be minimised by applying sufficient tension.

9.6 Mercerizing Machineries

Mercerization with alkali can be carried out in the cloth (woven and knitted) form and in the yarn (hank) form. Mainly two systems i.e. chain and roller mercer-

izing machines are developed for mercerizing cloth in open-width form. There has been a long standing supremacy contest between chain type and chainless mercerizer. One particularly tricky problem is reconciling the need for tension during mercerizing with the undesirability of tension in knit goods. Yarn mercerizing has, of course, been commercially established for many years in the manufacture of sewing threads, embroidery cottons, and lace goods. Farmer Norton, Benninger, Mather and Platt, Machinen, Bobcock, Bruckner, Brugman (Netherlands), Co. Pro. Tex S.r.l. (Italy), Menzel, Kusters, Goller, Dornier, Cibitex, S.r.l., Kleinewefers, Jaeggli and other makers have developed new types of machines with the aim of low mercerizing liquor pick-up, good degree of mercerization, better final width control, increased output and cost reduction. Now-a-days mercerizing units are equipped with liquor concentration regulator, measuring unit, cooling unit, lye recovery unit, purification unit, reciprocating metering pump and unit to dissolve caustic soda. Generally a mercerizing machine consists of four sections which will have different tasks according to the process technique :

- i) mercerizing section : impregnation with caustic soda;
- ii) intermediary squeezing aggregate : dividing off the mercerizing section against the stabilizing section;
- iii) stabilizing section : water treatment and thinning down concentration of the lye;
- iv) intermediary squeezing aggregate : dividing off the stabilizing section against the washing section;
- v) washing section : washing-off the alkali and neutralisation (if necessary).

9.6.1 Cloth (woven) mercerizing machines

A typical clip chain mercerizing machine for woven cloth is shown in Fig. 9-6. In this type of mercerizing machine shrinkage is allowed in the primary stage of the

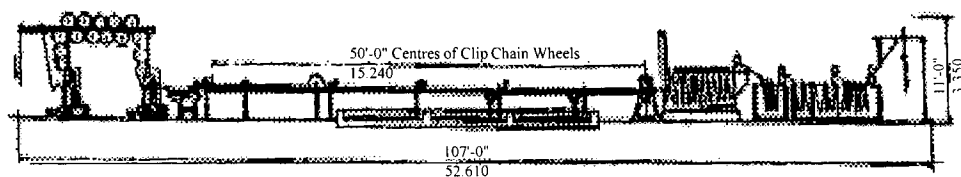


Figure 9-6. Clip chain mercerizing machine (Courtesy of Mather & Platt).

process and tension is applied in the later stage to bring the material to the original dimensions. The cloth is impregnated with cold concentrated caustic soda solution by passing through two 3- bowl padding mangles. Pressure of 10 to 25 tons is applied and more pressure is applied to the second mangle. In between the padding mangles the cloth is passed over timing drums to allow thorough action of alkali on the cloth. Due to higher speed of the second mangle only warp tension can be applied to the fabric and a warp tension indicator is fitted on the drums. On leaving the second mangle, the cloth is led to an open stenter frame for applying tension both the filling and warp direction. After the cloth has travelled about 20 ft in a stretched condition alkali is rinsed from the fabric by overflowing water from a series of cascades. Beneath each of the cascades, vacuum extraction slots are mounted so that as the rinse water overflows it is immediately vacuumed from the underside of the fabric. The washing on the stenter can be carried out in a counter current system. The residual alkali concentration should not be more than 8% on the cloth. After leaving the stenter the cloth passes over compensating rollers which regulate the tension. The cloth then enters the recuperator or the steaming box divided into series of compartments. The residual caustic in the cloth is dissolved under the action of steam and caustic is collected at the bottom of each compartment. On emerging from the steaming chamber, the cloth is squeezed and washed. These washing units are the final portion of the mercerizing range and may be a series of 7 to 8 washers followed by neutralising washer using either sodium bicarbonate or acetic acid. The whole range is about 107 ft long with a standard chain length of 50 ft. The width of the range is 14 ft. Production of this machine is about 55 m/min.

The chain mercerizing machine has one inherent disadvantage. As the force for keeping the material under tension acts mainly on the outer edges and the line of force diminishes towards the middle, a greater elongation takes place at the edges than in the middle of the fabric (Fig. 9-7). Prior to needling up on the chains the warp density, threads per cm over the whole width of the fabric is constant, after stentering it is less at the edges than in the middle. Different measures were tried to avoid this considerable disadvantage but none were really successful. Therefore development took place from chain mercerizing machines to chainless mercerizing or roller mercerizing machines.

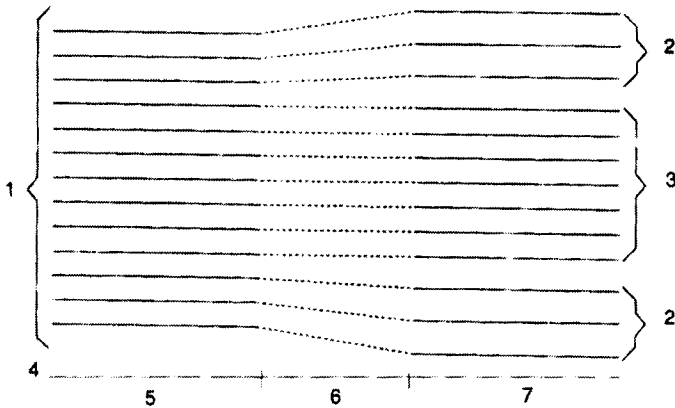


Figure 9-7. Disadvantages of chain mercerizing.

1. normal warp density ; 2. reduced density ; 3. normal density ;
4. difference in warp density ; 5. in front of chain expanding unit ;
6. in the chain expanding unit ; 7. after the chain expanding unit.

The line diagram of a Benninger chainless mercerizing machine is shown in Fig. 9-8. Fig. 9-9 shows a traditional chainless mercerizing machine with the roller

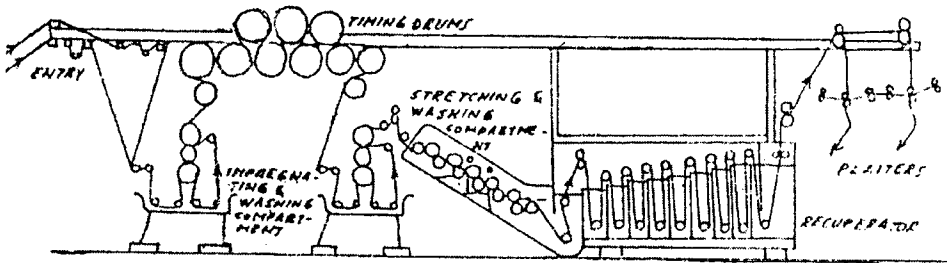


Fig. 9-8. Chainless mercerizing machine (Courtesy of Benninger AG).

arrangement. In this system the fabric is pre-stretched, tension is maintained till the mercerizing process and after-washing are completed. The cloth enters the padding set-up exactly in a similar manner to that of chain type. The cloth after padding with mercerizing liquor is passed through specially curved and specifically dimensioned expander rollers which make possible an even expanding effect over the whole width. The expansion depends on the diameter of the roller, the curvature of the roller as well as the angle of warp. Fig. 9-10 shows the expanding zone

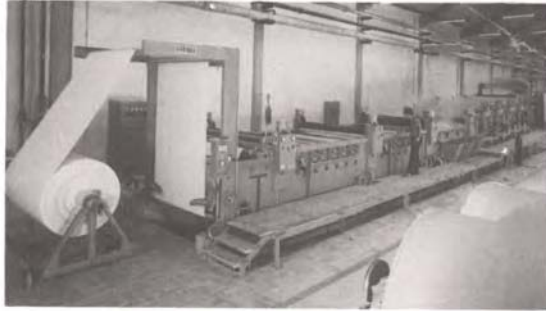


Figure 9-9. Chainless mercerizing machine (Courtesy of Swiss Association of Machinery Manufacturers, VSM).

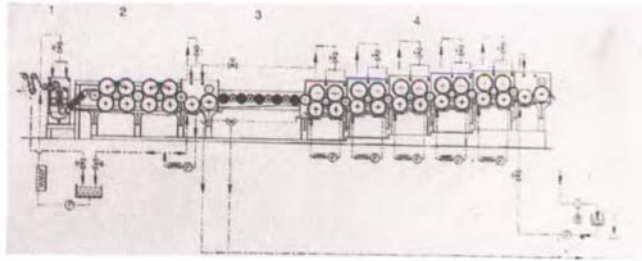


Figure 9-10. Expender zone in the "Ecommerce" (Courtesy of Kústers).

1. "Flexnip"; 2. Diffusion zone; 3. Expanding zone; 4. Stabilizing zone.

incorporated in the "Ecommerce" mercerizing installation and Fig. 9-11 its drive

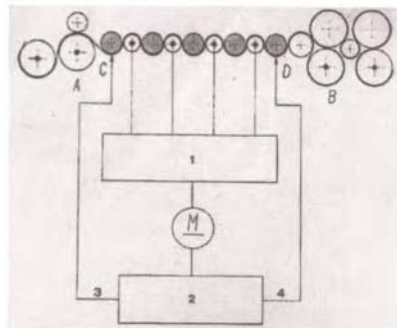


Figure 9-11. Driven system of the expanding zone.

1. Differential gear unit; 2. Cloth tension control;
3. Actual value; 4. Nominal value.

arrangement. The expanding zone consists of a combination of 5 curved expander rollers and 4 driven cylindrical rollers. The drive system is driven by one motor which drives the 4 driven rollers via differential gear unit.

Washing takes place only after the cloth has passed over first few rollers. Normal shrinkage takes place in the washing compartment. The material - at the entry into the mercerizing section - is expanded to its original width at the entry into the washing section by the "mycock" roller arrangement. Fig. 9-12 shows the arrange-

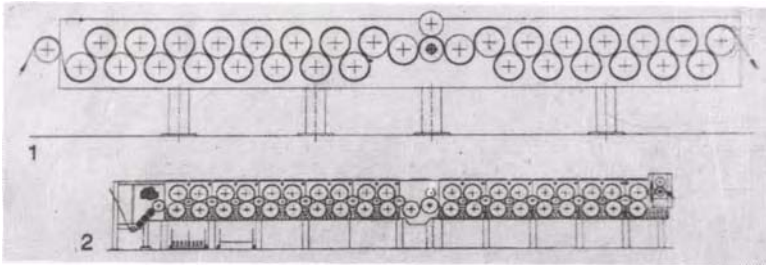


Figure 9-12. Different types of chainless mercerizing installations.
 1. traditional roller arrangement ;
 2. new roller arrangement of the Zittauer Maschinenfabrik.

ment of the rollers in a traditional chainless mercerizing machine as well as the improved arrangement found in the mercerizing machine of the Zittauer Maschinenfabrick. In this the rollers are not situated obliquely to one another but directly one above the other in pairs. The material in this arrangement has a longer contact with each other. The cloth content in the mercerizing compartment is larger, or alternatively, for the same cloth content as in a traditional compartment, this arrangement permits a far more space-saving installation.

Generally, hot water is used for washing. The steaming (recuperator), washing and neutralising steps are carried out in a similar manner mentioned in the chain type of machine. Development of new high efficiency washing units in the mercerizing machines have minimised the amount of water required to adequately remove alkali from the processed fibres [75, 76]. Open-width washing sections with vertical or horizontal cloth run with 15-25 m fabric holding capacity, drum washing section with squeezing units and "Extracta" with efficient predetermined washing effect with low water and steam consumption are some of the washing units frequently used with mercerizing machines. The advantages of chainless mercerizing

system over chain type are less floor space requirement and more production. It is possible to process two, or three cloths superimposed in chainless machine to increase the output.

Mercerizing and causticizing of cotton woven fabrics can also be carried out in batch system for small and medium lots [77]. Figs. 9-13 and 9-14 show the line

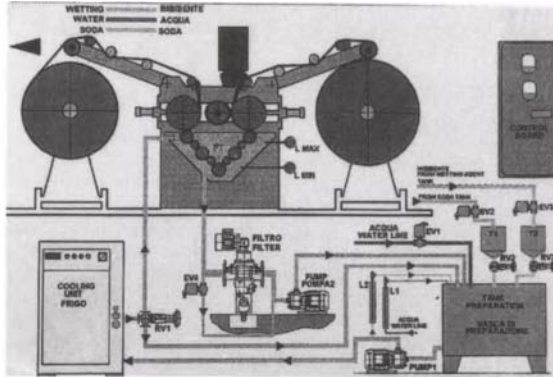


Figure 9-13. Cibitex model C.B. causticizing and mercerizing machine.

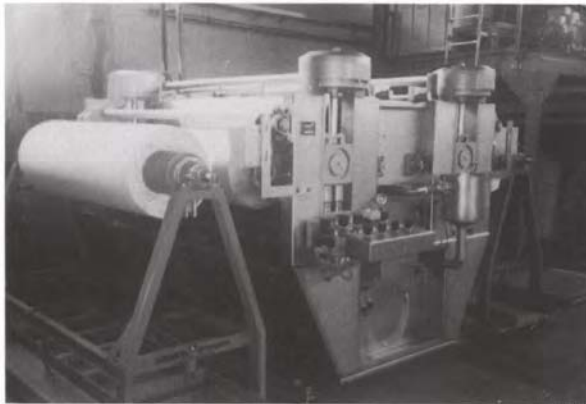


Figure 9-14. Menzel "minimerce" range for mercerizing-caustic treatment.

diagrams of "Sodatrice" (Cibitex S.r.l.) and "Minimerce" (Menzel) mercerizing and causticizing machines. In these systems the fabric after impregnation in alkali and extension is wound onto a roll. The caustic soda supply tank is mounted overhead, providing gravity feed to fill the impregnation tank. After the trough has been filled

it is lifted by hydraulic pistons. At the same time the rubber and steel rollers, which are arranged in a V-formation, are pressed from below against the two squeeze rollers (Fig. 9-13). The guide rollers squeeze the goods repeatedly (7 times) below the liquor surface. The high liquor fabric interchange ("sponge impregnation") thus set-up promotes extremely uniform penetration of the textile by the mercerizing liquor. Continuous contact with the guide rollers prevents widthwise shrinkage. The squeeze rollers above the impregnation trough work with a fixed, driven centre roller and two horizontally movable squeeze rollers. The goods are squeezed off to liquor uptake of about 80%. After the impregnation and batching the goods are ready for washing-off and neutralisation, washing-off is a high-temperature operation. Water is continuously sprayed on the fabric during unwinding and stabilisation occurs. The repeated immersion squeeze off promotes rapid removal of the caustic soda solution during washing. The advantages of this system are space saving, best economic efficiency, complete process control, tight-strand fabric guidance with tension control and reduced pollution of environment. The productivity of this type of machine is about 3000 m/h with more uniform mercerization than on continuous ranges and a favourable cost/performance ratio.

Among the various other developments Küster's Ecommerce is a new system utilising the Flex Nip impregnation unit in which the treatment liquor is metered through twin banks of pipes which feed a V-shaped treatment bath (Figs. 9.15 and 9.16). Fabric passes vertically downwards at open-width through the liquor and

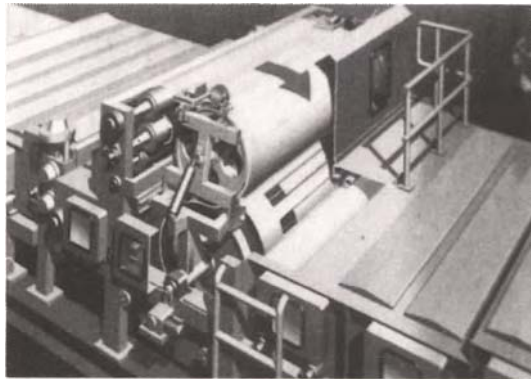


Figure 9-15. Ecommerce Mercerizing machine (Courtesy of Küsters).

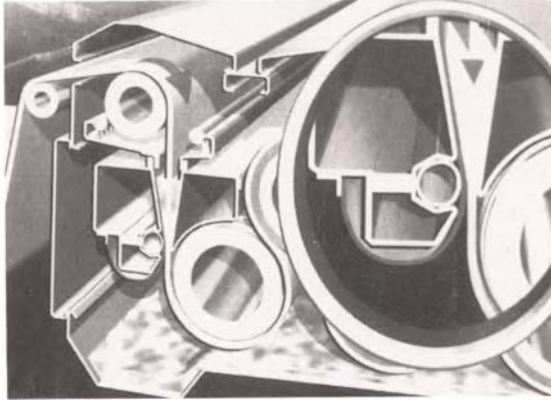


Figure 9-16. Flex-Nip impregnation unit (Courtesy of Küsters).

the fabric is squeezed on exit from the bottom of the V-shaped low liquor capacity bath. "Ecommerce" is designed for hot mercerization in accordance with the wet-on-wet process. The great ecological and economic advantage of the "Ecommerce" process is that the lye circulation contains only approximately 10-20 litre of lye. This chainless mercerizing system maintains a constant fabric tension in both warp and weft directions by the use of differentially controlled stretching zone.

Kleinewefers has promoted the application of reduced pressure to the fabric immediately prior to impregnation using "vacuum cap" unit [78] to facilitate fast, more rapid and complete swelling. In core mercerizing (Fig. 9-17) the impregna-

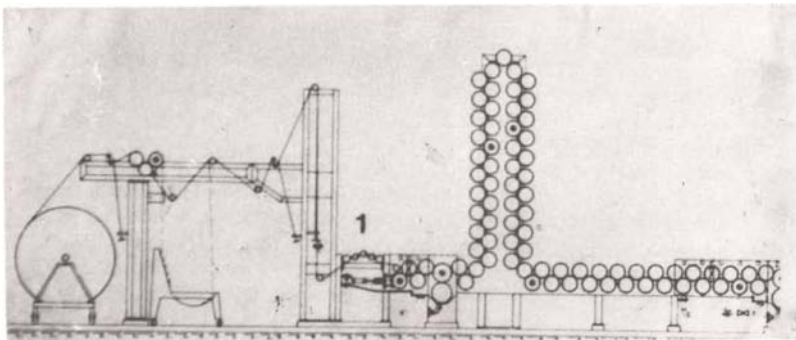


Figure 9-17. Core mercerizing system with vertical reaction section, 1 Vacuum hood (Courtesy of Kleinewefers).

tion and reaction sections constitute the mercerizing compartment. The fabric is impregnated with caustic soda solution in the impregnating section with vacuum hood. At the exit squeeze rollers remove excess liquor from the fabric. Moving on, the fabric runs through the reaction section under positive guidance in the same way as in a conventional mercerizing machine.

The Farmer Norton dual purpose chain mercerizing machine can be used for conventional cold lye impregnation or for hot impregnation. Higher impregnation temperatures are always followed by cooling section to ensure maximum fibre swelling. Farmer Norton (U.K.) has also developed a "Baby Mercerizer" where the fabric passes both direction through the machine. Apart from the low level investment character, this machine is useful for small scale processors.

The Gollar Perfecta chain mercerizer uses two low volume impregnation units with low tension fabric guiding. The Gollar Optima Model MM chainless mercerizing range for single run treatment of woven and knitted fabrics, from pile or large-diameters batch, may be optionally used for impregnation with caustic soda dry-on-wet or wet-on-wet.

Benninger's Dimensa mercerization range (Fig. 9-18) is a combination of

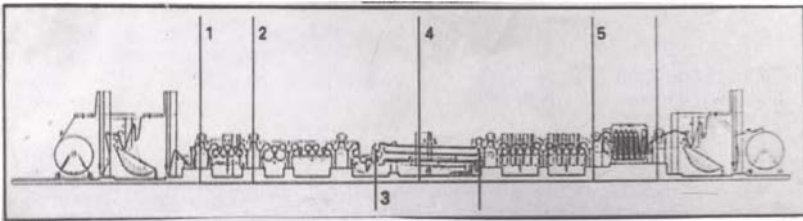


Figure 9-18. Dimensa mercerizing machine : cloth run diagram. 1. impregnating zone; 2. cooling and reaction zone; 3. stenter frame; 4. stabilizing zone; 5. washing and neutralising zone.

chainless and chain type mercerizing machine. The fabric is first impregnated with hot mercerizing lye in a very short intensive impregnation compartment followed by a cooling and reaction zone. In this area fabric guidance is on the chainless principle. This is followed by a pin stenter section or stabilising zone in which hot weak lye is introduced into the fabric using the chain principle. Ultimate stabilisation is obtained using a conventional, highly effective stabilising compartment with chainless guidance. The final section comprises a high efficiency washing and

neutralising zone consisting of Extracta compartments. Saving on strong lye, water and steam of around 30% and shorter down times are claimed.

Application of foamed alkali liquor on the cloth can produce one sided mercerization and differential dyeing [79].

Some innovative open width washing units are developed in which steam, water and air are projected onto both sides of fabric in any desired combination to generate turbulence and intensive washing of the mercerized fabrics.

9.6.2 Yarn mercerizing machines

Many machines for mercerizing of cotton yarn in the form of hank are developed. The yarn mercerizing machine usually available may be single sided or double sided with about 5 to 10 kg per batch per pair of rollers. Almost all the yarn mercerizing machines have similarity in design. Mather & Platt, Bertshinger, Kleinewefer, Noubold, Jaeggli and others are well known makers of yarn mercerizing machines. Useful summaries of the state of the art of yarn mercerizing have been presented [80-82]. A typical two sided yarn mercerizing machine (double arm type) is shown in Figs. 9-19 and 9-20. The machine is provided with pairs of

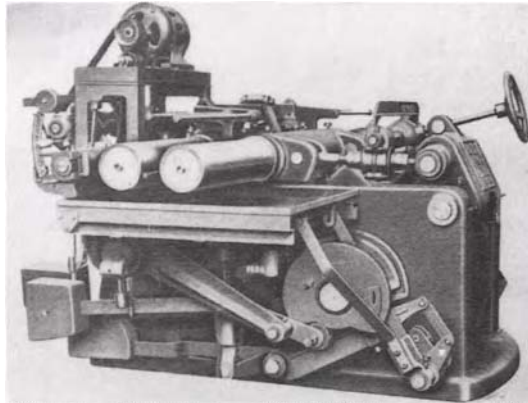


Figure 9-19. Yarn mercerizing machine (Courtesy of Mather & Platt).

rollers and one roller is fixed and the other is movable (B) (Fig. 9-20). Yarn is laid on the rollers and then caustic soda solution of 25% strength at 20°C is applied by raising the trough, F. The rollers are caused to rotate and the yarn is allowed to shrink during impregnation process to ensure penetration of alkali. It is arranged to bring the rollers somewhat closer together while they still continue rotating. Squeez-

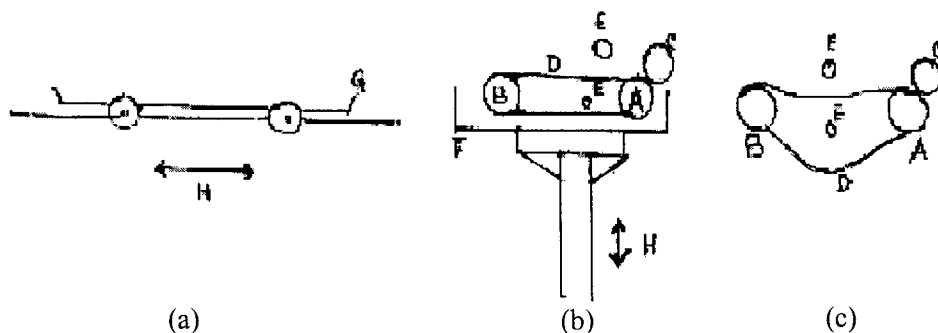


Figure 9-20. Line diagram of yarn on rollers (a) water trough on trolley ; (b) in stretched state ; (c) in slack state.

- | | |
|-----------------------|-----------------------------|
| A – Stationary roller | E – Spurt pipe |
| B – Movable roller | F – Caustic soda trough |
| C – Squeezing roller | G – Water trough on trolley |
| D – Yarn in hank form | H – Rail |

ing roller (C) above the fixed roller also assists penetration of alkali. The yarn is then stretched during which the rollers are made to move away from each other steadily thus extending the length of the skien and stretching the yarn to about its original length. The excess alkali is squeezed out. The alkali trough (F) then goes down and the water trough (G) is brought into position. The yarn is washed by spraying hot and cold water through spurt pipe and the yarn is still under tension and is squeezed. During mercerizing and washing the direction of the rotation of rollers and thus the skien are periodically reversed which ensures even penetration. Finally, the supporting arms go down, tension is released, rollers come closer together, squeezing rollers are lifted up, hanks are removed from the rollers and then neutralised with acid and again washed in other apparatus. The complete cycle takes 5 min out of which alkali treatment lasts for 2.5 min. The whole cycle occurs in one complete revolution of the cam shaft. Machinery developments of interest include the cone-to-cone continuous yarn mercerizing machine from Jaeggli with highly developed automatic control [83]. Various studies have been carried out to examine the potential for mercerized rotor yarns [84, 85].

9.6.3 Knit goods mercerizing machines

The traditional machines used for mercerizing woven fabrics are inadequate to treat circular knit fabrics. Owing to knit structure, such fabrics are easily deformed, distorted and extended on stretching during mercerization and washing. These dis-

tortions become permanent and have adverse effect on the elastic properties of the fabric structure [86, 87]. The existing chainless mercerizing machines can be modified to suit the knit goods either by installing tension controlling device [88, 89] or by processing between conveyer belts [90, 91]. However, the main disadvantages of open width knit goods mercerizing are edge creases of the flattened tube and variation in several characteristics from edge to centre. To eliminate edge creasing problem air is introduced into the fabric by means of jets to balloon the tube [92] and several manufacturers have produced machines for knit goods mercerization.

A typical Dornier continuous mercerizing range for tubular knit goods is shown in Fig. 9-21. Fig. 9-22 shows the line diagram of similar Sperotto Rimar Knit goods mercerizing range.

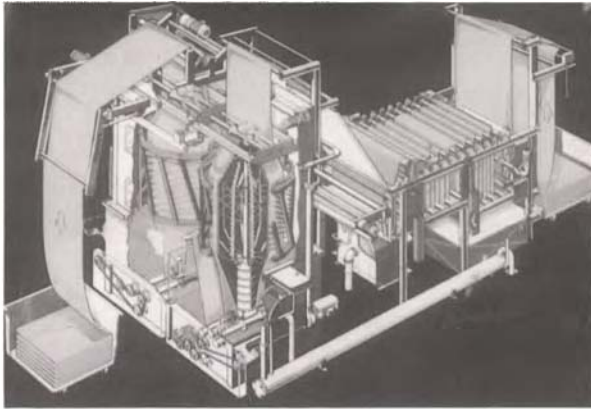


Figure 9-21. Knit goods mercerizer (Courtesy of Dornier, GmbH).

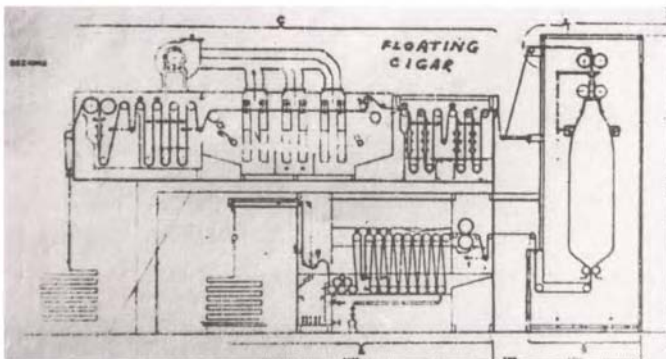


Figure 9-22. Sperotto Rimar Knit goods mercerizing range.

mercerizing range. Other machinery manufacturers offering equipment for tubular fabric mercerizing include Jaeggli [93], Caber [94], Pegg-Whiteby [95,96] etc. Dornier's tubular mercerizing range consists of a flat tubular impregnation zone followed by opening of the fabric using a circular expander with rolling friction and pressure compensation. Thus a higher spreading tension can be achieved with almost constant traction force, i.e. longitudinal tension. Motorised adjustment of circular and flat tube expanders drastically decrease the setting up times, and the water used in rinsing is recycled and passed through a heat recovery system.

The sperotto Rimar MT-15 tubular cotton knitted fabric mercerizer consists of three units, an impregnation/reaction tank, a stabilisation and reduction tower and a washing and rinsing tower. To achieve tension in the width steel spreaders (called cigars) are necessary, these being placed inside the circular knit fabric enabling stretching during passage of the fabric both in the first phases of hot washing and in the following cooling phases. In case of MCS machine this frame is flat and horizontal, but the other manufacturers produce vertical frames of tubular design.

Knit goods mercerization can also be done in batches by rinsing the knitted fabrics after impregnation and winding onto a perforated beam [97] or by carrying out the stabilisation by water spraying during batching after impregnation [98, 99].

Based on the tubular fabric mercerizing machine, Dornier, GmbH, has developed a combinable mercerizing and bleaching concept for tubular warp knitted fabrics. The combined mercerizing/bleaching machine (Fig. 9-23) comprises im-

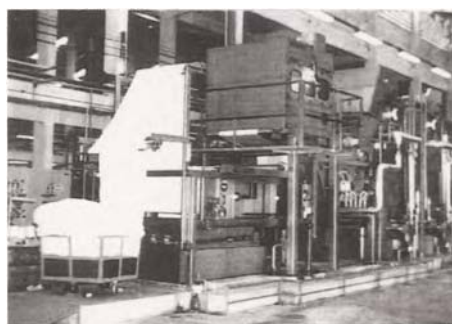


Figure 9-23. Combined mercerizing/bleaching machine for tubular warp knitted fabrics (Courtesy of Dornier, GmbH).

pregnating, reaction and scouring sections in the mercerizing unit, and is comple-

mented by a heating and dwell zone for peroxide bleaching. A combined after-washing section can be integrated, enabling fluorescent brighteners to be applied, including a neutralising bath and treatment trough located after the scouring unit. The metering cycles are controlled, automatically regulated and partially monitored.

9.7 Hot Mercerization

Since the beginning of the sixties, mercerization with hot caustic soda at a temperature between 60-70°C has become known as hot mercerization. In classical cold mercerizing, processing takes place at temperatures of 15 to 18°C with 31 to 35% caustic soda solution with a dwelling period of about 50 seconds. At that range cotton swells best but also fastest. The fast swelling increases the outer edge density of the fibre also rather swiftly. The viscosity of the caustic solution is also such that the penetration into the grey fabric becomes even more difficult. These result in poor mercerizing of the core and lack of uniformity as the reaction is restricted mainly to the surface of the yarn or fabric. To increase the penetration into the fibre alkali stable wetting agents are necessary and are expensive. In addition, the effluent load is considerable and ecologically critical.

In hot mercerization process, with caustic soda at 60-70°C the cotton swells more slowly. The outer edge density of the cotton fibre is not increased as fast as in cold mercerizing. At 60-70°C, the viscosity is considerably low. Thus the penetration of alkali is extremely rapid with improved core mercerization and consequently results in better uniformity of alkali treatment. Due to higher temperature and higher diffusion into the core the dwell time of the material in the mercerizing section can be reduced from 50 sec (cold) to 20 sec (hot). In other words, the mercerizing installation for the same production speed is shorter than the one based on cold mercerizing. Fig. 9-24 shows the interrelations between the necessary dwell time and the temperature of the lye. Cold mercerizing requires about 55 sec to reach a nominal concentration of 300 g/l on the material. Hot mercerizing at 60-70°C achieves the same possible effect already in 20 seconds.

In hot mercerization fabric is either padded through hot caustic solution or at ambient temperature and then passed through steamer where the fabric is steamed. The process sequence of two step hot mercerization is as follows :

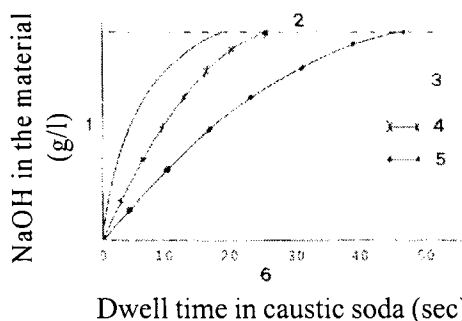


Figure 9-24. NaOH concentration in the textile fabric in relation to dwell time in the lye and lye temperature. 1 NaOH in material (g/l) ; 2 nominal concentration (approx. 300 g/l NaOH) ; 3 ‘Flexnip’ addition mercerizing 60 70°C ; 4 hot mercerizing 60 70°C ; 5 cold mercerizing 10 15°C ; 6 dwell time in NaOH.

- i) Saturation of cotton material with sodium hydroxide solution of mercerizing strength preferably under relaxed condition at temperature between 60°C and boiling point with an impregnation time ranging from 4 to 60 sec.
- ii) Controlled hot stretching following the saturation. The material being stretched 2-20% of its original dimensions.
- iii) Cooling the stretched material to a temperature less than 25°C which completes the swelling effect.
- iv) Tension controlled washing to NaOH solution of 6% (stabilisation).
- v) Final washing or neutralisation under normal condition without tension being applied to the fabric.

Another possible method of hot mercerization consists of wet-in-wet impregnation of fabric immediately after washing at 95°C and a subsequent hot squeezing with high speed steam injected. The heated fabric is then impregnated with caustic solution at 30°C in the first step and 20°C in the second step. These offer the stabilisation. Sequence is normally carried out under tension controlled condition.

The various factors changing the properties of cotton due to hot mercerization are slightly different from that of conventional mercerization. The degree of swelling of individual fibre is lower at higher temperatures [100] as the process is an

exothermic one. The conversion of the crystalline structure from Cellulose I to Cellulose II is retarded at higher temperature and reveals a skin-core appearance [101]. Mercerizing at elevated temperatures can lead to improvements in lustre and shrinkage, has no adverse effect on strength, and under certain recommended conditions, can result in a softer handle [102-105]. However, the improvement in lustre is contradictory which may be due to the fact that the double treatment during hot mercerization produces a different response compared with that of the single stage process in cold mercerization. Temperatures upto 45°C can be used without any deterioration of lustre [106], but on the other hand no substantial improvement in lustre is found as a result of double mercerization [107].

The following advantages can be detailed for the hot mercerizing process :

- i) Due to higher and rapid penetration of alkali, level and uniform mercerization can be obtained with lesser contact time resulting in greater productivity with more compact unit.
- ii) At higher temperature (about 100°C) the shrinkage is nearly half as compared to conventional mercerization and the shrinkage does not vary with dwell time.
- iii) The necessary and expensive alkali resistant wetting agents needed in cold mercerization are not necessary for the hot mercerizing process. Production costs are reduced and the environment load is lowered.
- iv) In hot mercerization the freed reactive heat is used to raise the temperature of the lye to about 40°C. The further increase in heat to about 60-70°C is done in a moderately priced heat exchanger.
- v) The fibre and fabric structure become more pliable and less elastic.
- vi) Higher tensile strengths are obtained due to greater degree of stretch and modification of cellulose while saturated with hot caustic soda solution. These lead to a greater orientation of molecular structure and increased cohesion between fibres.
- vii) Hot mercerized fabrics have better wet crease recovery than conventionally mercerized fabrics. It induces easy care finishing characteristics. Hot mercerized fabrics are flatter and less crumpled when drip dried.
- viii) Hot mercerized cotton fabric gives uniform application of dyes. Though the total uptake is better, but the colour yield is less pronounced than con-

ventional mercerized cotton. The colour yield decreases as the temperature of mercerizing treatment increases [108].

- ix) The combined mercerizing and desizing, and mercerizing and scouring processes minimise the energy conservation and can lead to cost saving. In combined processes a steaming step is inserted between hot alkali saturation and stabilisation [109]. The steaming time is about 10 min at atmospheric pressure and about 5 sec under pressure at 130 - 140°C.
- x) Hot mercerizing technique also reduces the inventory and pollution problem.

9.8 Liquid Ammonia Mercerization

Some twenty years ago it was found in systematic research work that a treatment of cotton fibre with liquid ammonia produces effect similar to that obtained with caustic soda. Liquid ammonia treatment was first developed by the English firm Coats in the mid-1960s. Coats developed a process with which it was possible to treat cotton yarn in a continuous manner and the firm Platt Saco Lowell Ltd., Accrington, England acquired the world wide licence for this process called ‘‘Prograde’’. The firm Cluett, Peabody & Co., known for its process of compressive shrinking (Sanforising), has in 1973 registered two trade marks : ‘‘Duralized’’, name for a material treated with liquid ammonia and ‘‘Sanfor-Set’’, name for a material treated with liquid ammonia as well as by compressive shrinkage, system Cluett. The liquid ammonia treatment is widely accepted for yarns used in sewing threads and for special fabrics such as denims, corduroys, chambays, pillow material, materials made of cellulose, linen, jute and mixtures of cellulose with polyester or nylon.

Among various amines, the liquid ammonia appears to be unique in its swelling action on cellulose and its effect on crystal structure. Anhydrous liquid ammonia, being smaller molecule, penetrates cellulose very rapidly and complexes with hydroxyl groups of cellulose after breaking hydrogen bonds in crystalline regions and increases distance between cellulose chain in crystallites [109-115].

The ‘‘Prograde’’ process requires the addition of selected amines to improve the original ammonia system. In this process (Fig. 9-25) yarn is treated in liquid ammonia at its boiling point (–33°C or –28°F) for less than a second, then subsequent immersion of yarn under tension in hot water for about 0.1 sec to produce a 40%

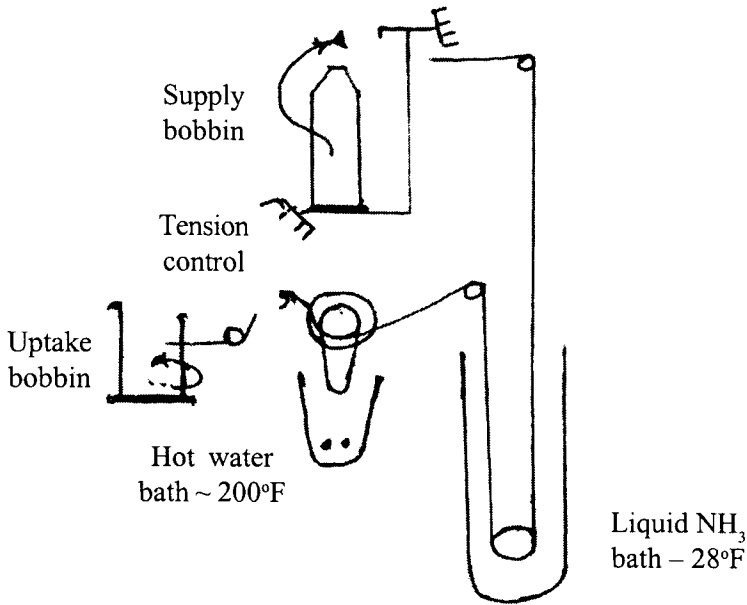


Figure 9-25. Diagram of the "Prograde" process [116].

increase in tensile strength, improved lustre etc. In this process the yarn after ammonia treatment is stretched and subsequently ammonia is removed by hot water washing.

"Sanforset" represents a combination of exclusive liquid ammonia processing and controlled compressive shrinkage to provide no iron characteristics without strength loss on cotton denims, plus an unusually soft and supple handle. The installation for ammonia treatment on woven and knitted fabric is shown in Fig. 9-26. Fig. 9-27 shows the fundamental construction of such an installation for the ammonia process. After the entering process (1) the material passes over five pre-drying cylinders (2) and then through a cooling station (3). The drying cylinders reduce the moisture content of the material to below the normal humidity, whilst the cooling station it is being cooled. The material then passes through a lock (4) into the actual treatment chamber (5) where it is impregnated with liquid ammonia in a trough (6). Finally it is squeezed off in a padder which can be determined by looping (7). The ammonia is driven off in two felt calenders. In this heat treatment some 90-95% of the ammonia is removed. The rest, which is chemically bound to

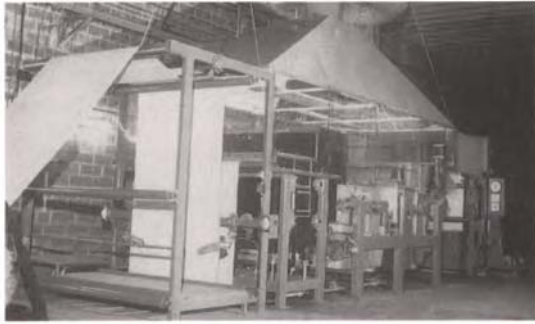


Figure 9-26. Installation for ammonia treatment on woven and knitted goods (Courtesy of Veramtex S.A/N.V.).

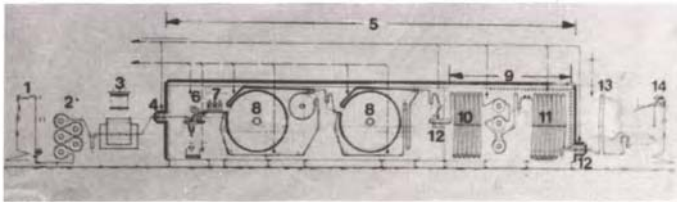


Figure 9-27. Sanfor-set treatment range (Courtesy of Monforts, Germany).

the cellulose is removed in a steaming compartment (9) consisting of a pre-dwelling zone (10) and a steaming zone (11). The entering and exit ends of the steaming compartment are again sealed by locks (12). An after dwelling zone (13) and the take-off device (14) complete the installation. The treatment chamber is kept under slight vacuum to prevent ammonia gas from escaping. The evaporated ammonia is led to a recovery unit where it is compressed, cooled and liquidized, to be led to a storage tank for later perusal. The chemically bound ammonia is removed from the material separately. It is possible to dissolve it in water and reuse it as a chemical or as manure. It can also be heated until it escapes and is oxidised. In all cases care is taken that no pollution occurs.

The properties and swelling processes of cotton fibres after treatment with liquid ammonia are compared with conventional and hot mercerized cotton in Table 9.3. The nature of the improvement in properties resulting from the treatment of cotton with liquid ammonia depends on the conditions of its removal from the fibre. Dry removal of ammonia after treatment converts Cellulose I to Cellulose III,

TABLE 9.3
Comparison of Various Swelling Processes [117]

	Mercerization		Liquid ammonia treatment	
	Conventional	Hot	NH ₃ /H ₂ O	NH ₃ /dry-steam
<u>Characteristics of swelling processes</u>				
Speed	Relatively low	Relatively fast	Very fast	Very fast
Degree	High	Decreases with temperature	Somewhat less than hot caustic	
Evenness	Uneven in tightly constructed fabrics	Good	Good	Good
Shrinkage forces	Relatively small shrinkage forces and exhibit good extensibility in swollen condition.		High shrinkage forces, may lead to difficulties in maintaining exact dimensions.	
<u>Properties</u>				
Lustre	Large increase	Improved	Improved but not quite as high as mercerization.	Only slightly increased.
Dye take-up	Strongly increased	Not quite as high	80-90 % compared to conventional mercerization.	Slightly or no improvement.
Strength	Improvement in the treatment of yarn or knit goods, none in the treatment of fabric. Similar effect for all methods.			
Dimensional stability	Similar effect by all methods. On heavy and tight fabrics, NH ₃ treatments have the advantage.			
Resistance to deformation	Relatively stiffer and harshes	Somewhat softer hand	Similar to hot mercerization	Softer and more resilient.
	Dry crease recovery angle (C.R.A.) is scarcely altered.			Distinctly increase dry C.R.A.

and there is hardly any increase in dye diffusion. The ammonia-water system gives an improvement in colour yield in subsequent dyeing which is only slightly less than that obtained by mercerizing [118]. This has been attributed to the changes in internal volume after ammonia treatment [49]. The moisture regain and water absorbancy of fibres treated with liquid ammonia are increased compared with values of untreated fibres, whereas both these parameters and dyeing properties of mercerized cotton are adversely effected by liquid ammonia treatment. "Sanforest" process produces a shrinkproof material which does not only shrink in domestic washing (as is the case with Sanforised material) but also not during drying in tumbler dryers. The treatment with liquid ammonia produces non-iron properties without loss of strength, such as one must put up with in the so-called non-iron finishing processes. At the same time the wearing properties of the material are improved ; it acquires a smoother surface, better uncreasing angles and soft and pliable handle (Table 9.4). The stretching of the fabric with 60-80% ammonia not only avoids shrinkage during the treatment but also compensates for shrinkage during scouring and bleaching. The ashing shrinkage potential is greatly reduced and fabrics treated in this manner are more resistant to shrinkage through repeated washings (Fig. 9-28). Liquid ammonia treatment prior to resin application will improve the relationship between strength and crease recovery and increase resistance in most cases to tensile, tear strength and abrasion (Table 9.5). Liquid ammonia is found to reduce fibrillation in the laundering of resin-finished goods. A combination of slack mercerization and liquid ammonia treatment for the production of cotton stretch fabrics have been reported [124]. It is also possible to combine liquid ammonia treatment with dyeing into a single operation as in the case of "Rapid anhydrous method". Liquid ammonia treatment is found to have less pollution problem but comparatively an expensive process. The most important cost element is the recovery of ammonia which involves refrigeration. The liquid ammonia treatment can also be applied in the pre-and after-treatments with organic solvents, since no water is used and the liquid ammonia can be largely recovered. There is no danger of the personnel being troubled by smell, etc., since the machines are hermetically sealed and the process is carried out in a closed system which is under slight vacuum.

TABLE 9.4
Mechanical Properties of a 100% Linen Fabric for Garments

Properties	Conventional finishing	Finishing with dry condensation		Finishing with damp reticulation	
		Without NH ₃	With NH ₃	Without NH ₃	With NH ₃
Shrinkage after 5 washings at 40°C					
Warp	- 8%	- 3.50%	- 1.10%	- 4.20%	- 1.20%
Weft	- 8%	- 3.50%	- 2.00%	- 4.00%	- 1.50%
Creasing angle (Warp + Weft)					
Dry	127°	170°	250°	145°	240°
Wet	124°	165°	235°	170°	265°
Wash-and-Wear behaviour (Monsanto)					
	1.5	3	4.3	3.5	4.5
Abrasion resistance (Accelerator 3'000 rpm/120') - 10%					
		- 32%	- 16%	- 26%	- 10.50%

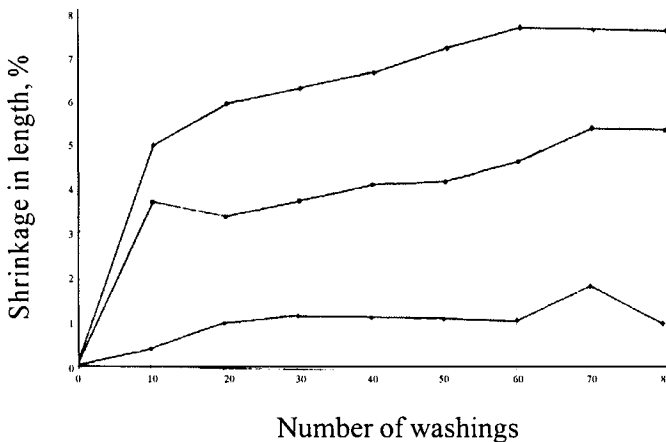


Figure 9-28. Shrinkage after multiple washings ; cotton fabric for professional clothings, 290 g/m².
1 Bleached ; 2 Bleached + NH₃ ; 3 Bleached + NH₃ + Resin.

TABLE 9.5
Results of the Ammonia Treatment on Cotton Fabric [120-123]

	Grey fabric	Bleached sample	Bleached + NH ₃	Bleached + NH ₃ + resin
Tensile strength				
Warp	1191.9 N	1267.5 N	1393 N	896.6 N
Weft	890.7 N	864.3 N	879 N	662.2 N
Elasticity				
Warp	16.30%	10.20%	11.20%	12.40%
Weft	11.10%	15.60%	20.80%	13.80%
Tear strength				
Warp	50.2 N	29.3 N	30.8 N	48.3 N
Weft	48.1 N	24.0 N	28.2 N	40.2 N
Creasing angle				
Dry		183.6°	193.2°	220°
Wet		128.8°	143°	235°
Creasing angle (3'000 rpm/90s)		4.40%	3.60%	3.90%

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OPTICAL BRIGHTENING AGENTS

10.1 Introduction

Textile fibres do not appear perfectly white due to the presence of certain coloured impurities. During chemical bleaching, coloured impurities are either destroyed or decoloured by oxidation or reduction. Over-bleaching may reduce the fibre strength. Even well bleached fabrics possess a slight yellowish appearance. This yellowish hue of the materials can be eliminated by whitening with optical brighteners or fluorescent brightening agents (OBA or FBA). Sometimes blueing agents are also used. In 'blueing' the initial yellowish shade of the textiles is covered by the blue dye and a bluish white results. However, the corresponding blue dye itself absorbs in visible light and thus the total amount of reflected light is smaller than in the case of unblued material, so that the blued material is less bright i.e., it is dull, or greyish.

The optical brighteners counteract the yellowness of the fabric by increasing the reflection of blue light rays. They convert invisible short-wave ultraviolet rays of sunlight into visible blue light and has a degree of whiteness which is comparatively more intense. Fig. 10-1 illustrates a comparison of the possible spectral

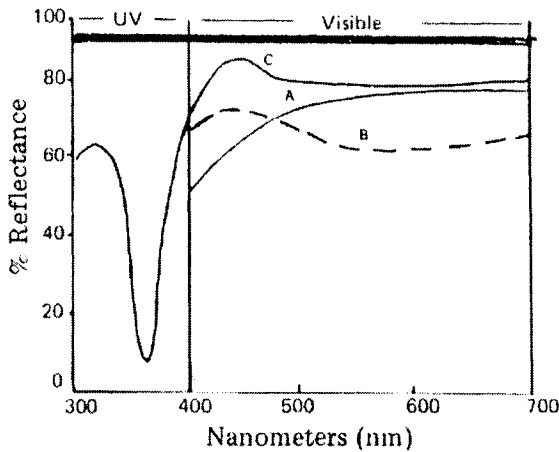


Figure 10-1. Reflectance of a bleached cotton fabric (A), after adding a blue tint (B) and after adding a fluorescent brightener (C) [1].

reflectances of a fabric after bluing and optical whitening. The 100% reflectance

which represents a pure white light is shown as a straight line parallel with the horizontal co-ordinate. Curve A which represents the bleached cotton deviates from the ideal, while the fabric with blue tint (Curve B) is apparently whiter although there is some loss of intensity and less reflectance. The fabric treated with whitening agent (Curve C) improves the distribution over the spectral reflectances and also add to the total amount of light reflected, thus giving whiteness of outstanding brightness. One possible reason for high reflectance in the visible region is that the fluorescing material does not absorb light in the 400-500 nm region and exhibits the effects of emission. The whitening effect given by the optical brightener is thus an additive effect, while that produced by 'bluing' is a subtractive effect.

10.2 Chemical Constitution of Optical Brighteners

The production and consumption of optical brighteners are constantly increasing and the annual increase is amounted to about 10-12%. In addition to textile, detergent and paper industries (Table 10.1), optical brightening agents are also used

TABLE 10.1
Consumption of Optical Brightening Agents

Branch	Consumption (%)
Detergent mixture	40
Paper	30
Textiles	25
Synthetic fibres & plastics	5

for the brightening of feather, fats, gelatine, wood shavings and sand dust, for the brightening of paints, leather, furs, straw and in the photographic industries.

Fluorescent brightening agents are organic compounds, which when present on textile fibres, exhibit fluorescence. FBAs resemble dyes in all respects except that they have no visible colour and are thus called colourless dye. They are substances normally having a system of conjugated double bonds [2] and must be essentially planer and should contain electron donating groups such as OH, NH₂ etc. and be from electron accepting groups such as NO₂, -N=N- etc. Table 10.2 contains a selection of important basic structures with reference to the main field of their derivatives. The majority of the compounds are built up from aromatic and heteroaromatic structural elements which are reconnected together either by direct

TABLE 10.2
Chemical Constitution of Some Important Optical Whiteners [3, 4]

Fields of application and substrates	General basic structures	Substituents
Textiles, detergents Polyamide (T,W).	<p>4, 4'-bis-(γ-triceol-zoyl) stilbene-2-2' disulphonic acids</p>	$-R=H, -\text{alkyl}, -\text{SO}_3\text{H}$
Textiles, detergents, Spinning solutions/melts, plastics Polyamide (T,W), Polyester (T,W,S), Polyvinyl chloride (K), Polystyrene (K), Polypropylene (K), Triacetate (T,S).	<p>bis-(benzoxazolyl)-derivatives</p>	$-R=H, -\text{C}(\text{CH}_3)_2,$ $-R_1=H, \text{CH}_3, \text{CH}_2\text{COOH}$
Textiles, detergents, Spinning solutions/melts, plastics Polyamide (T,W), Polyester (S), Polyacrylonitrile (T), PVC (K).	<p>Coumarins</p>	$-R_2=-\text{N}(\text{C}_6\text{H}_5), -\text{N}(\text{CH}_2\text{CH}_2\text{COOH})$ $-R_3=-\text{N}(\text{C}_6\text{H}_5), -\text{N}(\text{C}_6\text{H}_5)$
Textile, detergents Wool (T), Silk (T), Triacetate (T), Polyacrylonitrile (T), Polyamide (T,W).	<p>Pyrazolins</p>	$-R_1=-\text{N}, -\text{Cl}$ $-R_2=\text{Cl}, -\text{SO}_3\text{H}, -\text{SO}_2\text{NH}_2,$ $-\text{SO}_2\text{NH}, \text{SO}_2\text{CH}_3$ $-R_3, -R_4=H, \text{Alkyl}-\text{C}_6\text{H}_5$ $-R_5=H, -\text{Cl}$
Textiles Polyester (T), Polyacrylonitrile (T), Sec. acetate (T), Triacetate (T).	<p>Naphthalimides</p>	$-R_1=\text{alkyl}, -(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$ $-R_2=-\text{O alkyl}, -\text{SO}_3\text{H}, -\text{NHCOCH}_3$
Textiles, detergents Polyamide (T,W), Polyester (T,W).	<p>2-styryl-benzoxazoles and naphthoxazoles</p>	$-R_1=\text{CN}, -\text{COO alkyl}, -\text{Cl}$ $-R_2+R_3=\text{C}_6\text{H}_5$ $-R_3, -R_5=H, -\text{alkyl}$ $-R_4=H, -\text{alkyl}-\text{C}_6\text{H}_5$
Textiles, Spinning solutions/melts Polyester (T), Polyamides (S).	<p>4-phenyl-4'-benzoxazolyl stilbene</p>	$-R=-H, -\text{Cl}, \text{alkyl}-\text{SO}_2\text{CH}_3$

T = Textiles, W = Detergents, P = Paper, S = Spinning solutions, K = Plastic.

bonds or by ethylene bridges. These latter serve as π -electron bridges and connect the resonance systems without interrupting the continuous conjugation essential to the whitener molecule (Table 10.2). By far the greater number of compounds are derivatives of stilbene, benzidine, benzthiozole, benzaminazole, benzoxazole, coumarin, pyrazolines etc. [3]. About 80% of all optical brightening agents produced are derived from stilbene. The world market now carries more than 2500 trade marks, representing 200 various products belonging to more than 15 structural types [4].

10.3 Mechanism of Fluorescent Whitening

When a specimen transforms a part of the absorbed light into light of another wavelength instead of into heat (as is the case with normal dyed specimens), it is called fluorescent specimen. FBAs absorb ultraviolet light in 300-400 nm region from day light and emit it in the visible region (400-460 nm) at the blue-violet of the spectrum. The emitted blue light compensates for yellow tints of fibres and at the same time they also increase the luminosity of the goods. The emission spectrum is characteristics of a particular agent on a given substrate. Depending on the energy distribution of the spectrum, the fluorescent light emitted is blue-violet, blue, blue-green [5]. According to Stoke's law the shape of the fluorescense band can be predicted from the shape and the position of the absorption band, and the colour of the fluorescence can thus be determined. The relative distribution of the emitted light within the emission band is also important.

The mechanism of optical brightening is also explained on the basis of quantum theory of light and electronic structure of atoms and molecules [6, 7]. In the fluorescent substance molecules which have absorbed radiation (light) of short wavelength can pass into an excited state of higher energy. These excited molecules then return to the ground state of lower energy with re-emission of light quanta only slightly smaller than those absorbed i.e., of lower energy and longer wavelength (visible light). The average mean life of excited molecules is 10^{-8} to 10^{-9} sec and in general the shorter this life the less difference will be there between the wavelength of fluorescence and emitted light and greater will be the fluorescence as there will be less time for dissipation of energy as heat.

10.4 Factors Influencing the Functions of Optical Whiteners

Optical brighteners are applied to substrate as a seperate after-treatment process

or are incorporated into bleaching and finishing baths. Since the fluorescent brightening agents behave like dyestuffs, their efficiency and effectiveness are influenced by various factors that are important in application.

10.4.1 Substrate

The brightening effect is dependent on the nature of the substrate. For example, a very strong reflectance is observed with whitened cotton, but it is weaker in viscose and wool. All synthetic fibres absorb strongly in the near ultraviolet region. Since the fluorescence produced by optical brightening agent is added to reflectance of the substrate, the maximum fluorescence effect is achieved on those substrate whose ability to absorb the ultraviolet region is suppressed by chemical brightening. In the absence of sufficient affinity of brighteners, the application results in yellow to green colour yield.

10.4.2 Saturation

There is a saturation limit for each optical whitening agent. Above certain concentration on the fibre a yellow colour is superimposed on the fluorescence resulting in decrease in whiteness. This is because at higher concentration of brighteners a protective optical layer (filter) is formed on the surface of the substrate which prevents the extinction of the molecules of the brightening agent in deeper layers (so called self-quenching, concentration quenching of fluorescence or filter effect).

10.4.3 Method of application

The saturation limit of an optical brightening agent, however, is also dependent on the method of application to the substrate. Usually exhaust application process gives higher whiteness value than it does when applied by padding technique for a given amount of whitener.

10.4.4 Time

Generally optical brightening agents have high rate of exhaustion on the substrate and therefore great care is to be taken to avoid unlevel application. Slow exhaustion rate and increased migration time is necessary to produce level whiteness on the fabric.

10.4.5 Temperature

The optimum temperatures of optical brightening agents on cellulosic fibres are usually between 40 and 60°C and further rise in temperature tend to lower the exhaustion. However, for synthetic fibres higher temperature is needed for good penetration of the brighteners.

10.4.6 pH

The chemical stability, solubility and affinity of optical brightening agents depend on effective pH value in solution. For example, for wool and polyamide fibres, optimum pH is on the acidic side for better exhaustion.

10.4.7 Salt

Generally salt is added in the application bath to promote and also to control the rate of exhaustion of the brighteners on cellulosic fibres.

10.5 Application of Optical Brighteners

The application of fluorescent brightening agent depends on the kinds of fibres on which it is applied and accordingly can be classified as direct (or substantative), disperse and cationic types. The direct brightening agents are mostly derivative of 4, 4'-diaminostilbene-2, 2'-disulphonic acid and are used mainly for the brightening of cotton, paper, viscose, linen and polyamides. Acid optical brightening agents contain free sulpho groups and serve mainly for the brightening of silk and wool. Basic optical brighteners contain amino groups and include mainly coumarin and pyrazoline types. They are used primarily for the brightening of natural and synthetic polyamides. Disperse optical brightening agents are water insoluble compounds of various structures and are used mainly for the polyester, cellulose acetate and polyacrylonitrile. They are mainly triazolyl stilbenes, bis (benzoxazolyl), ethylene coumarins etc. Often mixtures of optical brightening agents with violet and blue/green type are used to get a natural white fluorescent effect [8]. Cation-active optical brighteners are compounds mainly of the methane ethanine type, which are used mainly for the brightening of polyacrylonitrile fibres.

Optical brightening agents may be obtained as powders, pastes, liquid water-insoluble forms or stable dispersion. The stabilised dispersions are suitable only for insoluble disperse optical brighteners. Generally the liquors of the brightening agents are not stable to light and should not be stored for a long time or exposed to light. They undergo cis-trans isomerisation in addition on exposure to light resulting in a compound which has practically no fluorescent effect. They also accelerate the photodegradation of textile materials on exposure to sunlight. An optical brightener should not be used on dyed materials because it flattens the shade.

Optical brightening agents are applied to textiles at the time of scouring, bleaching or finishing. When chlorite bleaches are used anti-chlorinating measures must

be taken. The fluorescent brighteners should be stable in the bleaching bath and also should be stable on the fibre at the thermosoling temperature in the case of polyester. In continuous processing when sodium chlorite is the bleaching agent, then fluorescent brighteners must be applied after bleaching in the wash-off, but with hydrogen peroxide bleaching it can be included in the peroxide bleach liquor. Fluorescent brighteners can be applied to cotton materials prior to resin treatment or it can be added to the resin formulation bath. However, proper selection of catalyst is needed since certain catalysts impair the light fastness of the treated fabric. Sometimes optical brightening agents are added during polymerisation of synthetic fibres to impart a reddish to neutral bluish tinge to fibre [9, 10]. Mass brightened material gives equal fluorescence intensity throughout the fibre, while the textile brightening effects have a ring of bright fluorescence with little intensity in the centre of the cross-section. For blended fabrics, a mixture of two whiteners that are suitable for both the component fibres is used.

10.5.1 Cellulosic fabrics

Optical brightening agents when applied to cellulosic fibres behave like direct cotton dyes and their uptake is influenced by temperature, electrolyte concentration and liquor ratio etc. The links between fibre and brightener involve hydrogen bonds, Van der Waal's forces and interactions of the dipoles of the brightener. The brightener penetrates the fibre in a monomolecular form, and having expelled a part of water in it, aggregates there, and takes on a greater volume, where it can no longer so easily leave the interior of the fibre.

Optical brighteners can be applied on cellulosic fibres either by exhaust or padding methods. In the exhaust method, goods are entered into the cold liquor containing optical brightener (0.5-0.6%, o.w.f.) and electrolyte (5 g/l) and then the temperature of the bath is raised to optimum slowly over a period of 15 min. When required temperature (depending upon the brighteners used) is reached, a further 30 min of running is sufficient for complete exhaustion.

When padding methods are used, the fabric is padded with a solution containing 0.05 to 4 g/l brightening agent in a two-bowl mangle at room temperature keeping 80-100% expression. The material is dried and stored in dark. To achieve good diffusion, full fluorescence and complete development of the brightener, a subsequent heat treatment on stenter or in curing unit may be given.

The light fastness properties of the direct optical brighteners used for cellulosic materials are medium i.e. of the order of 2-3. Other fastness properties are good to water and washing at 40°C, medium to good to washing at 95°C and medium to heat treatment at temperatures above 150°C and to sanforising.

10.5.2 Woollen fabric

Wool fibres have amphoteric properties rendering them capable of combining with both acidic and basic substances. However, wool contains more number of basic side groups which enable them to combine with acid type optical brighteners containing sulphonic or carboxylic groups. The most common brighteners for application to wool are a selected range of diazotriazine derivatives with certain pyrazoline derivatives. The mechanism involves salt formation with amino groups of the polypeptide chains in the wool structure. In addition to this hydrogen bonds are also formed depending on the structure of the brighteners.

The goods are treated with a solution containing 0.02 to 0.2% fluorescent brightening agent and 2-4% acetic acid (40%) or 1-2% formic acid (85%) to maintain the pH of the exhaust bath 3 to 5. The treatment time is about 20 min at 40°C. A final rinsing with water completes the process.

Optical brighteners are often applied to wool with a reductive bleacher under acid or alkaline conditions. Wool after peroxide bleaching, a reductive bleaching is carried out for 1-3 h at 50-55°C, during which optical brightening agent may be added. It is usually added into the neutral reducing bath after 75% of the reduction time. When all the dithionite has been consumed, a 2% formic or acetic acid is added to complete the exhaustion of the whitening agent. Brightening in an acid bath alone does not give much good results.

The main problem of wool is its creamy colour and yellowing on exposure to sunlight. Both the bleaching and fluorescent brightening of wool accelerate the photo-yellowing and also photo-tendering [11]. These yellowing and tendering of wool have been shown to depend on the spectral distribution of light (affected by glass etc.), the pH [12], the moisture content of wool, the temperature [13] and the nature of chemical pre-treatment [14]. Photo-tendering is caused by oxidative and hydrolytic cleavage of the protein chains and the disulphide bonds [15]. The anionic degradation of protein fibres has been associated with photochemical reactions of the tryptophan, histidine and tyrosine residues [16, 17]. The fluorescent

brightening agents present on the fibre absorb uv light and thus accelerates the yellowing. The chemical structures of chromophores found during photo-yellowing have been reported, with amino acid dityrosine being identified on irradiated wool [18, 19].

A number of chemical treatments have been suggested to reduce the photo-yellowing of bleached and whitened wool. Tetrakis(hydroxymethyl) phosphonium chloride, thiourea (alone or as a formaldehyde condensate) and some mercaptans and reducing agents [20, 21] and the reaction of wool with sulfamic acid [22] have been shown to offer some protection against photo-yellowing, particularly on wet wool.

10.5.3 Silk fabric

In contrast to wool, in silk the acid nature of the proteinic substance (fibrion) predominates, which can permit whitening with acid and basic type of brightening agents. However, for silk direct brightening agents are preferred.

After degumming of silk, a peroxide bleaching is given and the brightener is added in the subsequent reductive bleaching bath containing 0.5 to 4% optical brightener and 2-5 g/l reducing agent and treated for 45 min at 70°C. Then the pH of the bath is adjusted to 3.5 with formic acid and the treatment is continued for about 15 min, rinsed warm and cold.

Silk is generally brightened by exhaust method because higher degree of whiteness can be obtained in this case than by padding method. In the padding method, fabric is padded with a solution of 5 to 20 g/l of optical brightening agent along with 1 g/l wetting agent at room temperature, squeezed to approximately 100% pick-up and then dried at 100 to 120°C.

Like wool, yellowing is also a problem with silk. Fluorescent brightening agent accelerates the photo-degradation of silk, resulting in greater yellowing and losses in strength, especially in the presence of moisture [23-25].

10.5.4 Polyester fabric

Polyester fibres have no affinity for the water soluble optical brightening agents and thus water insoluble compounds are applied to polyester from dispersion in the same manner as disperse dyes by the formation of a solid solution in the fibre. These brightener particles penetrate into the fibre in a state of molecular dispersion and they are held in the fibre by Van der Waal's forces. A part of the finely dis-

persed particle forms a molecular solution in the bath. Only this proportion which has dissolved in the bath penetrates into the outer layer of the polyester, from where it diffuses slowly into the interior of the fibre. Diffusion within the interior of the fibre is essentially a function of the temperature and the concentration of the brightener in the interfacial zone.

In carrier method of application by exhaust process the polyester fabric is entered into a bath containing 0.5 to 2.0% optical brightening agent, 1 g/l dispersing agent, 2-4 g/l suitable carrier and acetic acid to maintain the pH around 5 to 6. The goods are run through the solution at 40°C for 15 to 30 min, the temperature of the bath is then raised to boiling in 30 min, and the treatment is continued for at least 90-120 min at the boil. Compounds such as diphenyl and chlorinated hydrocarbons are suitable carriers. The goods are then rinsed with hot water and dried.

In the thermofixation process the fabric is padded with 5-25 g/l dilute suspension of optical brightening agent at room temperature with a liquor pick-up of approximately 50%, dried at about 120°C in an open stenter and then heated for 30-60 sec at 190-200°C. Finally, the goods are washed and dried. This process makes possible higher throughput of material with superior dimensional stability.

In the pad-steam process the goods after padding with a liquor pick-up of about 80% are steamed at 100-101°C for 2-3 h or under pressure (1-1.5 kg/cm²) for 25-30 min. Alternatively, the goods may be thermofixed by superheated steam at 150-170°C for 3-5 min.

10.5.5 Nylon fabric

Optical brightening agents of acid dyeing type are applied to nylon from an acid bath. Direct cotton dyeing type of brighteners vary in their affinity for polyamides. Cationic optical brighteners show affinity at low temperature, but maximum yield and fastness is not developed below 70°C [26]. The disperse optical brighteners are applied to nylon at boil in presence of dispersing agent (0.5-1%) at pH 5 to 6. They exhibit better light fastness (3-4) and washfastness (4-5 at 60°C) than acid dye type of brighteners.

With acid dyeing type, the goods are treated on jiggers or winch beck with a solution containing high affinity type brighteners (0.05 to 0.5%) and acetic or formic acid (pH 3.8 to 4.5) at 40°C for 10 min and then the temperature is raised to boil in 15 min and the treatment is continued for 30 min. The goods are rinsed and

dried. The light fastness of the anionic product is of the order of 1-2 but yellowing does not occur as in wool fibre. Nylon can be brightened by the hydrosetting process in HT equipment. The bath is set with 0.2-2% optical brightening agent, 0.5% sodium hydrosulphite, 0.1-0.5 g/l sequestering agent and 0.5 g/l surface active agent. The bleached goods are treated at 40°C for 10 min and hydrosetting is carried out for 15-20 min at 120-130°C (120°C for nylon 6, 130°C for nylon 6, 6). The treatment liquor is cooled to 80-85°C and then the goods are rinsed and dried. The improved light (≈ 3) and wash (≈ 5) fastness can be obtained.

Selected acid and disperse type of optical whitening agents can be applied to nylon by continuous or semi-continuous process. In the pad-roll process, fabric is padded with 10-20 g/l optical brightening agents at 50-70°C with padding mangle expression at 60-70% and then kept in a chamber for 1-2 h at 90°C. Acid conditions are maintained by adding ammonium chloride in the pad-bath solution. In the pad-steam process, the padded goods are steamed for about 3 min at a steaming temperature of 105°C. In the acid-shock process, the fabric after padding with cold solution containing brighteners are then treated in a boiling bath containing formic acid in an open width soaper, washed and dried. Certain acid type brighteners (pyrazolines and 1 : 2 : 3 triazoles) can be applied to polyamide by the thermosol process at 170-190°C. Heat fastness during heat treatment and fixation, however, is medium.

10.5.6 Polyacrylonitrile fabric

The acrylic fibres are normally white, but variations in degree of yellowness and stability to thermal degradation with fibres from different sources can be minimised by application of whitening agents [27, 28]. The Neochrome process involves applying brightener during the gel stage of fibre production. Though chlorite bleaching removes yellowness but certain fibres such as Courtelle cannot be bleached with chlorite because of subsequent degradation of the fibre. Furthermore, the nature of copolymer also determines the affinity of fibre for various optical brighteners. Mostly, polyacrylonitrile containing anionic groups confers an affinity for cationic type optical brighteners. These types of brighteners have either a heterocyclic nitrogen or external amino group with cationic character.

In the exhaust method, the fibre material is introduced into a bath containing cationic brightening agent and 3-5% formic acid (85%) to maintain the pH 3 to 4 at

about 70°C. The liquor is then brought to the boil in 30 min and held at that temperature for a further period of 30 min. The bath is finally cooled and the material is washed or rinsed.

The one bath two stage bleaching and brightening of acrylic fibres is quite popular. In this procedure, the material is boiled with chlorite, using oxalic acid as an accelerator for about 30 min, the bath is cooled to 80°C and excess chlorine is eliminated with sodium hydrosulphite. In the second phase, the optical brightening agent is added and the bath is again heated to the boil in 30 min and the material is treated at this temperature for further 30 min. The material is then worked up in the usual manner.

Non-ionic brightening agent can also be taken up by the fibre from suspensions. The fibre material is treated with a solution containing disperse type brighteners and 2% formic acid (85%) (pH 3 to 4) at 100°C for 30 to 40 min. Exhaustion can be accelerated by raising the temperature of the bath to 110°C.

There are certain type of acrylic fibres that can be whitened by padding techniques. The three methods of padding are pad-roll, pad-steam and acid-shock process. In the pad-roll process, the fabric is padded with a solution containing optical brightening agent, formic acid, dispersing agent and thickening agent, at room temperature to a mangle pick-up of 80-85%, batched, stored on roll in a chamber set at 100-105°C for 2 h. In the pad-steam process, the padded fabric is steamed in a saturated steam for 5 min at 105°C. In the acid shock process, the fluorescent brightening agents are applied to the material by mechanical pick-up and white is developed by acid treatment in a separate bath.

10.5.7 Cationic dyeable polyester fabric

Cationic dyeable polyester possesses anionic group and hence cationic brighteners can be applied as in the case of acrylic fibres. However, the effect of cationic brighteners on acrylic fibres cannot be reproduced on anionically modified polyester [29]. This proves the fibre-brightener inter-relationship. Disperse brightener can also be applied to cationic dyeable polyester. The optical brightening agent can be applied to cationic dyeable polyester in a chlorite bath. The brighteners are applied at 98°C in presence of carrier based on dichlorophenyl or biphenyl. Suitable brighteners are chlorite resistant types based on benzofuranyl and benzoxazolyl – benzimidazole. Certain brighteners can be applied by thermosol method at 200°C.

Soft disperse brighteners can be applied at 160°C. The light fastness ratings of cationic brighteners on cationic dyeable polyester are higher than on acrylic. Non-ionic brighteners give poor ratings than on normal polyester.

10.5.8 Polyvinyl chloride fabric

The low melting types of PVC permit a maximum temperature of 60°C during optical brightening and thus carrier must be used in the application bath. The heat resistant types of PVC can be brightened either in presence of carrier at 65 to 75°C or without carrier in a boiling bath. Brightening is generally done during bleaching with sodium chlorite and optical brighteners, carrier, dispersing agent and cross-linking agents are added in the bleach bath. The bleaching bath is heated to 55°C and worked at this temperature for about 45 minutes. The material is then washed with cold water.

10.5.9 Other synthetic polymers and plastics

The use of fluorescent brighteners in whitening of polyolefins, polycarbonates and poly (methyl methacrylate) are reported [30]. The increasing demand for many new applications for plastics and trends for recycling have created a demand for the use of special optical brightening agent. Long life expectations for children's playing things, refrigerators and rainwear need a long life of optical brightening agents. New stilbene derivatives and addition of stabilisers improve the brilliance and high long life. These compounds also prevent yellowing of plastics during thermosol processing, giving a better white based material.

10.5.10 Blended fibre fabrics

The polyester/cotton blended fabrics can be optically brightened to the same degree of intensity and brilliance as pure cotton fabric. Normally, after application of disperse type optical brighteners for polyester fibre, either by exhaustion or padding method, the usual direct optical brighteners are applied to cotton by exhaust method. An intermediate treatment with hydrosulphite is necessary to remove polyester brightener deposited mechanically on cotton portion during padding operation. Optical brightening of polyester/cotton blends can be combined with bleaching. In the combined process, the goods are treated in a bath containing 1-5 g/l sodium chlorite along with 0.5-1.5% fluorescent brightener (o.w.f.) and acetic acid (pH = 4) at boil about an hour. The bath is then drained and the goods are given treatment with an optical brightening agent for cotton. In the continuous process of

application, the blended fabrics are padded with a solution containing disperse and cellulose brighteners along with dispersing agent. After padding and drying, the white is developed by baking for 20-30 sec at 150-200°C. The fabrics are then washed-off with detergent (2 g/l) and soda ash (1 g/l) at 50-60°C for 15 min, rinsed and dried. Pad-steam process can be applied to polyester/cotton blends in the same way as for 100% polyester by the inclusion of the pad bath of a suitable concentration of a cellulose brightener. In another method, the optical brighteners for polyester/cotton blends may be added in the resin finishing bath. In this method, the goods are padded with a solution containing cross-linking agent, catalyst, softener, fluorescent brightener for both polyester and cotton and wetting agent, dried and cured at 140-150°C for 4-5 min. A final scouring followed by washing process completes the process. Although the process is economical, the brightening effects obtained are not very intense.

The most efficient process for optical brightening of polyester/wool blended fabrics is to brighten polyester content first and then bleach wool portion with peroxide and brighten the wool in a reducing bleach following peroxide bath. However, the two bath process is time consuming. In one bath process, the goods are treated with a bath containing the optical brighteners for wool and polyester, carrier, dispersing agent, a protective agent for wool and acetic acid (pH \approx 5) at 95-100°C for 20-30 min, cooled the bath, rinsed and washed with non-ionic detergent (2-3 g/l) at 40-45°C for 15 to 20 min. However, the one bath process suffers from the disadvantage of possible staining of the wool by the carrier and polyester brightener not being removed by a simple scour.

The blends containing polyamide/cellulose can be optically brightened with a solution containing selected cellulose brighteners by adjusting the temperature and pH of the application bath. The brighteners which show little change in uptake on nylon by change in pH should be selected. Likewise, raising the temperature increases the uptake on the nylon relative to cellulose. The temperature of the bath is raised to 95-100°C over 30 min and the fabric is treated for 30-40 min and then rinsed well and dried.

For polyamide/wool blended fabrics fluorescent brightening agents (1-2%) are applied following hydrogen peroxide bleaching in presence of stabiliser (3-5 g/l). The treatment is carried out at 70-75°C for 45-60 min and then rinsed and dried.

For brightening of acrylic/cellulose fibre blended fabrics the compatibility of the brighteners for each fibre is most important. If the two classes of brighteners are not compatible, then a two-bath process is necessary, first applying the acrylic brightener and, then in a fresh bath the cellulose brightener. Peroxide/hypochlorite bleaching of acrylic/cotton or combined bleaching techniques can be used. Chlorite stable products should be applied from the bleach bath. Another requirement is wet light fastness in presence of perborate containing washing agents. Garments made from PAN or their blends on drying in sun, after washing with washing powders containing perborate, are observed to show yellowing.

For acrylic/wool blends, the acrylic portion is brightened in the normal way and then the wool is bleached with hydrogen peroxide and subsequent reduction bleaching is done in a bath containing suitable brightener (1-2%) and stabilised sodium hydrosulphite (3-5 g/l) at 85°C for 30 min. The fabric is then rinsed and dried.

For polyamide/acrylic blends, both the fibres can be brightened by using suitable disperse type brighteners at 95-98°C for 30-60 min, cooled, rinsed well and dried. Where bleaching is necessary, a suitable brightener stable to chlorite may be included in the bleach bath.

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