Chapter 15

APPLICATION OF BIOTECHNOLOGY IN THE PRE-TREATMENT PROCESSES OF TEXTILES

15.1 Introduction

Biotechnology can be defined as the ''application of scientific and engineering principles to the processing of materials by biological agents to provide goods and services''. The earliest evidence of biotechnology include baking of bread using yeast by the ancient Egyptians and brewing [1]. Early methods of producing coloured pigments from natural viable sources may also be cited as primitive technology [2-6]. Today enzymes have been used on a large scale in medicine, food analysis, genetically modified food, transgenic animals and plants and also in the domestic detergent fields. The discovery of chemical structure of DNA has led to genetic engineering, DNA finger-printing, rapid gene sequencing and host of related technologies such as process engineering, fermentation, enzymology, downstream processing, microbiology, biochemistry, process control, reactor design, immobilised cells and enzymes, biosensors, biopolymers and biotransformation [7]. Modern genetic technology is constantly producing new types of application potential which will continue in the future. Biotechnology is also increasingly gaining importance in bioremediation and in the clean up of polluted environments.

15.2 Enzymes for Textile Application

In textile application, the knowledge of specific action of enzymes-amylases for starch splitting began around 1857, when malt extract was used to remove size from fabrics before printing [8]. The use of enzyme in pre-treatment processes of textiles has found much broader acceptence. At present the priority areas are scouring and bleaching of cellulosic fibres and carbonising, bleaching and shrink-resist treatment of wool. Enzymes have traditionally been used for stone washing and bio-polishing of cotton fabrics and garments. Also enzymes have been incorporated in detergents to remove fibre fuzz and brighten the colour of the fabric. In contrast to cellulose and woollen fabrics, the other market segments includes a spectrum of fibres from linen to lyocell (Tencel), rayon (viscose) and cellulose acetate and a multitude of blends, weights and fabric constructions. With the apparel industry trend towards increasing use of cotton knits for achieving novelty finishes is observed.

15.2.1 The chemistry of enzymes

Enzymes are naturally-occuring proteins capable of catalysing specific chemical reactions and being catalysts, facilitate the reaction without being consumed. After catalysing the chemical reaction, therefore the enzyme is released and is able to catalyse another reaction-and so on.

Enzymes have a protein like structure with primary, secondary, tertiary and quaternary structures and are susceptible to denaturing (degradation due to temperature, ionising radiation, light, acids, alkalies and biological effect factors). The textile and clothing sector is now a major user of enzymes during manufacturing and after-care. Table 15.1 summerises some of the already important established en-

TABLE 15.1
Important Enzymes for Textile Application [9]

Enzymes	Origin	Effect
Amylase	Bacillius Subtilis Bacillius lickerinforms	Desizing of starches. Desizing of jeans. (AQUAZYM) makes denim streak-free, softer and more uniformly faded.
Cellulases and Hemicellulases	Trichoderma raesci Aspergillus niger	Desizing of CMC, stylish effects on cellulosic fibres, Non-stone treatment for jeans.
Pectinase	Aspergillus niger	Scouring of vegetable or bast fibres like jute, hemp, flax, remie etc.
Proteases	Bacillius subtilis B. Licheniformis B. Oryzaeof	Scouring of animal fibres, or degumming of silk, modification of wool properties.
Lipases	Aspergillus niger Muco javanicus	Elimination of fats and waxes.

zymes. Cellulases are widely used in textile application. Cellulases are high mo-

lecular colloidal protein catalysts in metabolic form and are commonly produced by soil-dwelling fungi and bacteria [10]. Industrial cellulases are complexes of a number of cellulases, cellobiase and related enzymes in non-uniform composition, with molecular weight ranging from 10,000 to 4,00,000 [11]. Cellulases comprise a multicomponent enzyme system, including endoglucalases (EGs) that hydrolyse cellulose chains randomly, cellobiohydrolases (CBHS) that split cellobiose from cellulose ends, and cellobiases that hydrolyse cellobiose to glucose. EG or EG-rich preparations are best for aging and defibrillation of fibre surfaces, while complete cellulase systems are best for cleaning and depilling effects [12, 13]. In general, there are two major commercial classifications of cellulase enzymes based on optimum ranges : 'acid cellulases' exhibit the most activity within the pH range 4.5-5.5, at a temperature of 45-55°C ; while 'neutral cellulases'', are more effective in the 5.5-8.0 pH range at 50-60°C. Currently, acid cellulases and neutral cellulases are more commonly used. With alkaline cellulases, there is a possibility of applying the enzymes in combination with reactive dyes from a dyebath.

15.2.2 Mechanism of enzyme action on cotton textiles

Enzyme's effect mechanism, i.e. enzyme catalysis, operates first of all to form an enzyme substrate complex [14]. Direct physical contact of enzyme and substrate is required to obtain the complex. The current proposed mechanism of cellulase action is illustrated in Fig. 15-1. However, the mechanism of enzymatic hy-

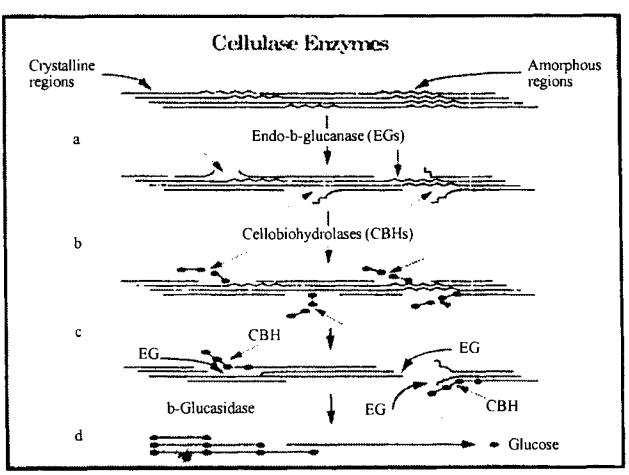

Figure 15-1. Schematic representation of synergistic action of enzymes on cellulosics [15].

drolysis of cellulosic materials is complicated and not yet fully understood [16-18]. Enzymes contain true activity centre in the form of three dimensional structures like fissures, holes, pockets, cavities or hollows. Endoglucanases or endo-cellulases hydrolyse cellulose polymers randomly along the chains, preferably attacking non-crystalline region [19]. Cellobiohydrolases or exo-cellulases, attack the polymer chain ends and produce cellobiose [20]. Coupled with the binding domains associated with the enzyme, exo-cellulases may assist in degradation of cellulose by disrupting the local crystalline cellulose structure, which makes the region more susceptible to subsequent hydrolysis by endo-cellulases [21]. Fig. 15-2 shows the reducing and non-reducing end groups by the action of cellu-

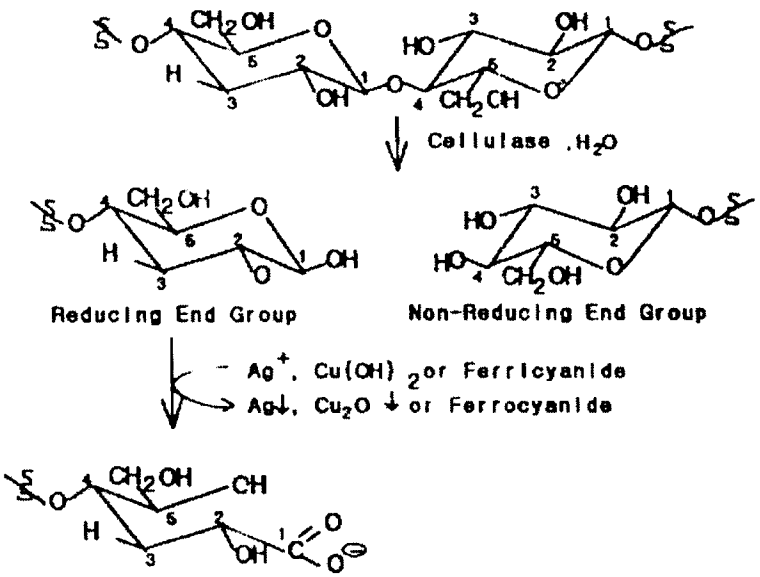

Figure 15-2. Enzymatic hydrolysis of cotton cellulose [22].

lase on 1, 4-β-glycoside bond of the cellulose molecule. β-glucosidases hydrolyse small chain oligomers, such as cellobiose into glucose. The three types of cellulase component act synergistically in degrading cellulose to glucose. Synergism of different components in the cellulase complex and inhibition mechanisms further complicate the reaction [23, 24]. Enzyme diffusion plays a much more decisive role in the heterogeneous system of soluble enzyme and solid substrate. The kinetics of reaction therefore depend on the diffusion of enzyme to and into the solid phase of

the substrate and the diffusion of the reaction products out of the solid phase into the liquor. For cotton, the restriction of the enzyme to the fibre surface is easily achieved because cellulose is a highly crystalline material and possesses only small amorphous areas, making the diffusion of enzymes into the interior of the fibre nearly impossible. Thus, by regulating enzyme dosage and choosing the right type of enzyme, the catalytic action of the enzyme can be confined to the surface of cotton and to the amorphous regions, leaving the fibres, as a whole, intact [25].

15.2.3 Parameters governing the cellulase treatments

The cellulase multi-enzyme complex is completely non-uniform. Added to that is substrate specificity in the form of a selective suitability for enzymatic degradation, due to non-uniform structure of collulose. Yarn type, structure and textile substrate also influence the break-down effect. Fine yarns and open material constructions, particularly any freely accessible projecting fibres, are specifically susceptible to degradation. Prior to enzymatic treatment any impurities or additive present have to be removed first. In particular, the substrate must be free from any enzyme toxins. Some of the enzyme toxins recognised are formaldehyde containing finishing agents, tannic acids like natural tannin or polyphenolic fastness after-treatment agents, proteases, specific surfactants and microbiocides. Denaturing can occur through specific storage effects. In general buffered granulates are more stable for storage. The presence of chemical substances such as organic salts, iron, magnesium and zinc ions etc. can either enhance or inhibit enzyme activity [26].

Both pH and temperature are critical factors affecting cellulase treatment (Fig. 15-3 and Fig. 15-4). A particular type of cellulase will only operate under a specific pH and temperature optima and its activity will decrease sharply on both

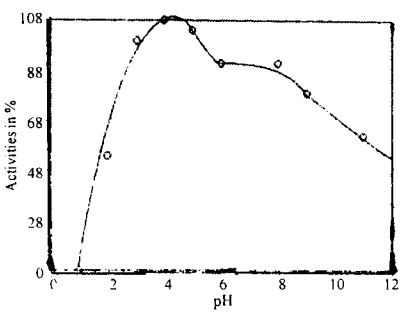

Figure 15-3. pH dependency of cellulase activity.

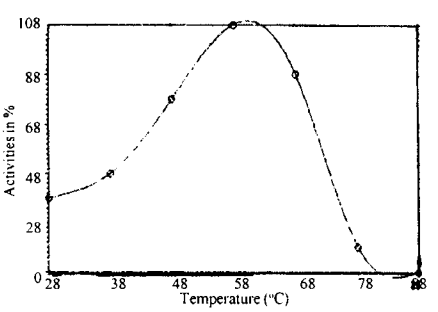

Figure 15-4. Effect of temperature on cellulase activity.

sides of the optimum range. Neutral cellulase is advantageous as it is stable over a broader range. Generally, a treatment time of 45-120 min is appropriate as prolonged treatment time may increase the fibre loss significantly. Similarly, excessive cellulase dosage may also increase the weight loss %. The degree of agitation also considerably increases the weight loss. Machines with vigorous action such as a launderometer cause a much greater weight loss than does hand stirring. The decrease in bursting strength is roughly proportional to the weight loss of the fabric. The decrease in drape co-efficient and the flexural rigidity are apparent and hence leads to the improvement in the handle of the cotton knits after cellulase treatment.

15.2.4 Changes of structures and morphology of fibres by enzymatic hydrolysis

The cellulase complex diffuses through the pore system to the microfibrils, attacks the cellulose chains and hydrolyses each chain to the end. The differences in the efficacy of cellulases on various fibres are dependent on number of factors such as the amounts of non-cellulosic wood pulp-derived matter, the degree of polymerisation, the type and degree of crystallinity, and the type and number of chemical substitutions to the cellulose [27-30]. Key features for the cellulose substrate are crystallinity, accessible surface area and pore dimensions [31]. Variation of any of these factors, e.g., structural changes of cellulose substrate by pre-treatments, will influence the course of the entire degradation process [32, 33].

Viscose rayon is inherently a weak fibre, particularly when wet, therefore it is highly susceptible to damage if enzymatic hydrolysis is not controlled. The enzymatic hydrolysis of viscose fibres causes a decrease of the intrinsic viscosity from 250 to 140 ml/g and an increase in crystallinity from 29 to 39% after 44 h [34]. Strong changes of the structure, however, are not typical for the enzymatic hydrolysis of cellulosic materials. Neither cotton nor wood pulp show an essential decrease of the DP during enzymatic hydrolysis [35-37]. The kinetics of the enzymatic hydrolysis of regenerated cellulose fibres before and after acid prehydrolysis changes the kinetics from a monophasic to a biphasic first order reaction [38].

Bast fibres like linen and remie are multiple cellular systems, in contrast to cotton, which consists only of a single cell. Multicellular fibres contain natural gums and resins that keep the cell together. Crystallinity indices of cotton, linen, remie and viscose fibres do not change after the enzymatic hydrolysis, nor does accessibility to moisture [39]. Consequently, neither the ratio of crystalline to amorphous material nor the DP of the residue changes significantly [40].

15.2.5 The uses and advantages of enzymatic processing

Recently enzymes are used in textile application. The use of enzyme in degrading starch has been known. Enzyme technology is of great interest in the chemically demanding pre-treatment of cotton, wool and silk fibres. Cellulases can be used to finish treatments of cotton pertaining to fabric softness, good performance and fashionable looks as well as the potential to simplify and cheapen manufacturing processes. Popular uses perhaps are stone-washing of denim jeans and bio-polishing. Enzymes are also used for degumming of silk and bast fibres, removal of skin residues and vegetable matter from wool and anti-felting and surface modification of wool. Cellulases show great promise in terms of effectiveness and the entire pre-treatment processes do not appear to be beyond the bounds of possibility in the future. In some of the processes the enzyme treatment is combined with mechanical action to enhance the accessibility of cotton substances. Another approach is the combination of plasma treatment with enzyme treatment [41].

The following points are achieved in practice :

i) The enzymatic process removes the small fibre ends found in yarn surface which eventually lead to pilling on the fabric surface.

ii) Knitted fabrics treated with cellulases are free from surface hairiness, neps, fluff and knops with much improved handle and flexibility.

iii) The material sticking (the burr effect) is prevented particularly with mercerized knitted fabric. Material texture relaxation takes place and improve sewability.

iv) The effect of treatemnt is long lasting. The colour of the dyed goods become brighter with a visual improved colour yield.

v) The process is particularly suitable for the pre-treatment of napped, knoppy goods when there are no suitable cleaning, beating, brushing and shearing machines available.

vi) Complete or partial replacement of pumice stones by cellulase enzymes for the effect of 'stone-washing' on denim is well established and the concept of 'bio-polishing', which originateed in Japan has been extended to knitted structures and blended fabrics.

vii) Cellulases have been incorporated in detergents to remove the fibre fuzz and this means brighten the colours of the fabrics.

viii) Another advantage of enzymatic processes is that they can be adopted to run on equipment already existing in textile plants.

ix) The method is of interest from the view point of energy savings, pollution control and safety. Because the cellulase enzyme, being a biocatalyst, offers advantages such as energy savings through lower treatment temperatures of 40-50°C. The enzymatic pre-treatments of textiles are not so aggrasive to fibres and environment. The 'clean chemistry' aproaches is an advantage in comparison to the powerful alkalies, acids, oxidisers and reducers needed in traditional processes, tending to attack the textile material as well as causing considerable contamination in the environment. After the enzyme stops, residues are present only in the primary strucutre, while there is no chemical residues likely to affect the skin. Besides, they will not leave chemical residues on the processed materials and the colour change on the dyed goods is minimal.

The disadvantages still unsolved in the practical application of the cellulase treatment are that the cellulase catalytic reaction rate is affected appreciably not only by pH and temperarture, but also by coexisting chemicals such as dyes or surfactants in the treatment solution or on the substrate.

15.3 Treatment of Cotton with Enzymes

The cotton fibre has a single biological cell. The layers in the cell structures are from the outside of the fibre to the inside, cuticle, primary wall, secondary wall, and lumen. These layers are different structurally and chemically. The primary and secondary walls have different degrees of crystallinity as well as different molecular chain orientation. The cuticle, composed of wax, proteins and pectins, is 2.5% of the fibre weight and is amorphous. The primary wall is 2.5% of the fibre weight, has a crystallinity index of about 30%, and is composed of cellulose. The lumen is composed of protoplasmic residues. Additionally, sizes and soilings are added to cotton fibres. The total material added to the fibre is up to 20% of the fibre weight. Traditionally, the absorbancy of cotton is improved by alkaline scouring and whiteness is improved by oxidative bleaching. The intensive basic research currently being conducted opens up interesting possibilities for the use of enzymes for gentle removal of cotton's attendent material without the hitherto necessary use of alkalies and other dubious effluent content.

15.3.1 Enzymatic desizing of cotton and silk fabrics

Malt extract was used originally for the desizing of amylaceous sizes from the fabric. Later, around 1900, Diastafor was found more efficient for starch desizing. Rapidases were introduced in 1919 and cause the liquefaction of starch in compounds soluble in water. At present a variety of these products are available commercially. They are mainly based on amylopectic enzymes. These enzymes do not damage the cellulose. These enzymes are effective at various temperatures ranging from 20 to 115°C covering all means of applications [42]. Now-a-days special attention is paid towards the development of simultaneous desizing and scouring in an alkaline medium replacing two-stage process.

Degumming of silk to remove the sericin is an important step. Soda-ash and sulphides used in conventional degumming process not only reduces the fabric strength but also causes pollution problem. Enzymatic degumming on the other hand, offers a very safe and simple method of degumming. Apart from sericin the silk fabric also contain about 2% oil to facilitate weaving. Enzymes not only dissolve the gummy portion but also dissolve the oil at the same time. The method of application is either cold water soaking for 12 to 16 h or warm water (50-55°C) soaking for 3 to 4 h with appropriate enzyme solution. The application of serine protease (Bactosol SI) combined with hydrogen peroxide bleaching in the presence of detergent provides efficient desizing of sericin in 1 hour [43].

15.3.2 The use of enzymes in mercerization

The effect and action of enzymes seems to be very limited because of the stronger conditions of alkali of mercerizing strength. Enzymatic hydrolysis is accelerated when mercerization is carried out without tension [44]. The greater accessibility and lower crystallinity of cellulose mercerized without tension is a decisive factor in the enzymatic hydrolysis process. Mercerized cotton is generally more prone to enzymatic modification than untreated cotton.

15.3.3 Application of enzymes in scouring and bleaching of cotton

To achieve good absorbancy of cotton, dirt, sizes and natural impurities are usually removed by alkaline scouring. If these impurities are not removed, can lead to the formation of AOX in the effluent when NaOCl is used as a bleaching agent [45].

Enzymatic treatment of unscoured cotton fabric can be done with pectinase,

cellulase, protease, lipase and other enzymes [46]. Cellulases are especially suited to scouring of cotton fabrics [47]. The degree of whiteness of a cotton sample treated with cellulases only is lower by 8-10% than the degree of whiteness of alkaline boiled-off treatment. Pectinolytic enzymes can be used for enzymatic degradation of pectin adhering to cotton [48]. Cotton fibres or their blends with other fibres can be treated with aqueous solutions containing protopectinases for 18 h at 40°C to give scoured yarns with good tensile strength retention [49]. Pectinases and cellulases are very effective compared to the proteases and lipases [50]. The most significant results of various enzymes are listed in Table 15.2. The change in the water absorbancy of cotton is rapidly catalysed by pectinases, cellulases or their

TABLE 15.2
Summary of Results and Conditions of Enzymatic Treatments for Adequate Absorbency of Cotton [50].

Fibre/Fabric	C_1	C_2	C_3	P_1	P_2	P_3
Fibre						
Cotton weight, g	0.2	0.2	0.2	0.2	0.2	0.2
Enzyme units	–	40	30		4	4
Concentration, %	0.1	0.44	0.023	0.025	0.0067	0.0017
Treatment time	10 min	10 min	10 min	2 hr	10 min	10 min
Weight loss, %	3.900	2.266	3.044	2.571	1.642	1.898
Fabric						
Fabric weight, g	0.4-0.5	0.5	0.5	0.4-0.5	0.5	0.5
Enzyme units	–	<60	<45	–	<16	<16
Concentration, %	0.15-0.2	<0.66	<0.0345	0.1	<0.0268	<0.0068
Treatment time	20 min	20 min	20 min	3 hr	20 min	20 min

Note : C_1, C_2 and C_3 are cellulases, P_1, P_2 and P_3 are pectinases.

mixtures. Pectinases can destroy the cuticle structure by digesting the inner layer of pectins in the cuticle of cotton. Cellulases can destroy the cuticle structure by digesting the primary wall cellulose immediately under the cuticle of cotton. By combining the enzyme treatment (a simultaneous treatment of pectinase and cellulase), or the alkaline boiled-off, with an alkaline peroxide bleaching, the total degree of whiteness is higher in combination with enzyme treatment. Cellulases break the

linkage from the cellulose side and the pectinases break the linkage from the cuticle side. The result of the synergism is a more effective scouring in both the speed and the evenness of the treatment.

Natural pigments present in cotton are responsible for greyness of the substrate before bleaching. Motes are swollen in alkaline scouring and removed or rendered colourless in oxidative bleaching. In the Synbleach project [51] natural fibres are bleached with hydrogen peroxide followed by enzymes, photosensitisers and UV light. Methods of bleaching of paper pulp and deinking printing paper using enzymes have been reported [52]. A friction treatment is suggested before the enzymatic treatment to remove the pigment more easily and ensure that cellulase and hemi-cellulase are effective [53].

The cellulase, xylanase and pectinase enzymes have tremendous effect on processing of jute. The treatment of enzyme before bleaching of jute improve whiteness whereas due to backstaining at optimum pH, there is decrease in whiteness and increase in yellowness index, if treatment is carried out after bleaching. The enzyme action is more on 4% NaOH scroured fabric. Scouring causes higher hemicellulose loss producing open structure and thus larger surface area of lignin is accessible to hydrogen peroxide resulting in higher whiteness [54].

15.3.4 Bio-polishing

Surface modification of cellulosic fabrics to improve their cleaner surface conferring cooler feel, brighter luminosity of colours, softer feel and more resistance to pilling using cellulases is often known as bio-polishing [55, 56]. This treatment can be applied to knit and woven cellulosic fabrics such as cotton, viscose and linen and their blends [57-60]. The elimination of superficial microfibrils of the cotton fibre through the action of cellulase enzymes is obtained by the controlled hydrolysis of cellulose leaving the surface of the fibres free and conferring a more even look [61-63]. The effect of cellulase enzymes on fabric hairiness is shown in Fig. 15-5. The picture on the left shows an untreated woven 100% cotton fabric, while on the right the same fabric appears after enzyme treatment. These improvement in fabric softness and smoothness are permanent in contrast to the softeners applied to the fibre surface. Further the water regain is not decreased by the enzymatic treatment [64, 65].

A number of patents are obtained to obtain softening effect by enzymatic treat-

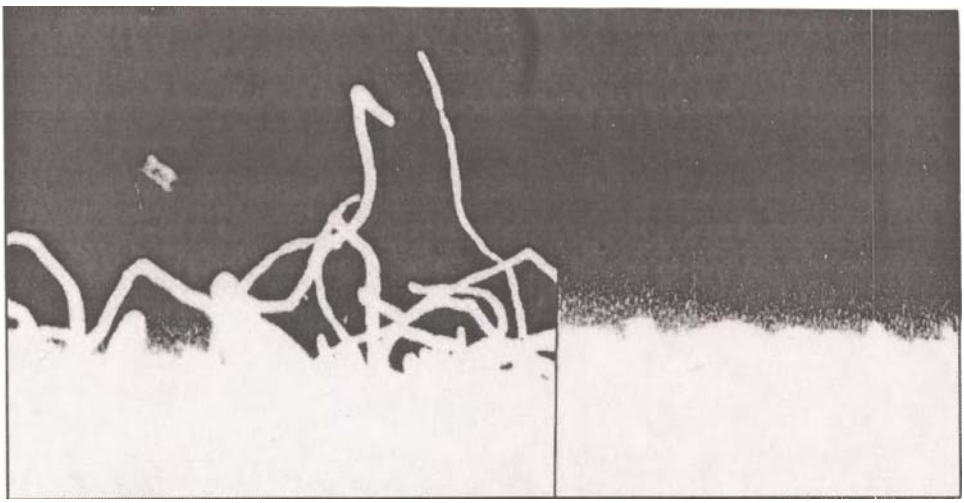

Figure 15-5. The effect of cellulase on fabric hairiness.

ment of cotton textiles [66-71]. Although bio-polishing may be carried out at any time during wet processing, it is most conveniently performed after bleaching. Fabrics may be treated in either piece or garment form and the treatment can be combined with another process or kept as a single operation. Batch processing, using washers, jets, becks and winches is extremely suitable as pH and temperature can be controlled easily.

Controlled finishing with cellulase enzymes optimises the surface properties of the fabric, but decrease in tensile strength [72]. Commercial processes aim for 3-6% weight loss after hydrolysis and a maximum of 10% loss in strength is considered acceptable [73, 70]. The strength/weight loss relations of remie and linen differ from those of cotton and viscose rayon [39]. The mechanical properties before and after enzymatic hydrolysis of different fibres are compared in Table 15.3. For all the fibres after 6 hours' treatment there is significant reductions in tensile energy (WT) and tensile linearity (LT), while tensile resilience (RT) is increased, indicating that the fabrics become less stiff, easier to stretch and looser in structure. However, after 48 hours' treatment, shear hysteresis (2 HG) values are markedly lower than those of controlls, indicating yarns have become more mobile in the fabrics.

Anionic dyes such as direct and reactive dyes and cationic and anionic surfactants inhibit cellulase catalytic reaction appreciably resulting in decreased weight loss, whereas non-ionic dyes such as vat dyes and non-ionic surfactants do not

TABLE 15.3
Comparison of Mechanical Properties of Cotton After Enzyme Treatment [39].

	Enzyme treatment for			
Fabric	0 hours	6 hours	24 hours	48 hours
Cotton				
WT, cm^2	4.86	3.47	3.11	2.13
LT	0.87	0.77	0.83	0.78
RT, %	41.85	48.61	46.29	49.09
2HG, g/cm	7.04	7.29	5.12	3.36
Linen				
WT, cm^2	5.65	3.00	3.93	4.07
LT	0.72	0.66	0.71	0.69
RT, %	42.14	48.93	42.00	44.05
2HG, g/cm	0.83	1.02	0.56	0.29
Remie				
WT, cm^2	5.45	2.45	2.40	2.30
LT	0.85	0.63	0.69	0.73
RT, %	52.70	65.69	67.87	68.76
2HG, g/cm	4.59	4.16	3.84	3.36
Cotton/linen (warp)				
WT, cm^2	1.61	1.02	1.25	0.84
LT	0.81	0.69	0.72	0.75
RT, %	44.87	50.27	57.82	46.73
2HG, g/cm	1.08	0.94	1.14	0.97
Cotton/linen (filling)				
WT, cm^2	2.22	1.96	1.84	1.51
LT	0.85	0.84	0.86	0.81
RT, %	56.39	51.24	58.72	57.98
2HG, g/cm	1.08	0.94	1.14	0.97

show remarkable inhibition [74-76]. The planner structure of vat dyes with larger molecular sizes than indigo dye play an important role in their inhibitory effect [77]. DMDHEU treated fabric shows a slower progress of enzymatic cleavage on

cross-linked cellulose. The degree of inhibition depends on class of dye and dye concentration. The inhibitory effect may be due to the ionic interaction between cellulase and anionic dyes with sulphonate groups, the cross-linking ability of bi-functional dyes or the large planner structure of vat dyes.

15.3.5 Effect of cellulase treatment in washing processes

There are three methods to remove surface fibres from 100% cotton woven and knit goods, namely singeing in the greige state and bio-polishing. The third method is home laundering the fabrics using detergent that contains a cellulase enzyme.

Laundering of knit fabrics with detergent containing cellulase enzymes help to maintain a clean surface appearance and the appearance of the fabric look better even after multiple launderings [78]. Today's detergents contain a sophisticated cocktail of enzymes designed to breakdown stains and assist the cleaning process at low wash temperature. Proteases, lipases and amylases are generally used to increase the efficacy of removal of stains. Cellulases assist in the removal of particulate soils by removing microfibril from the cotton fibres, which initially form the pills and which scatter incident light [79, 80]. Generally the detergents for this purpose rely on a mixture of enzymes, strong sequestrants and soil-release polymers to provide satisfactory stain removal and soft finish.

The short fibre ends emerging from the fabric surface is enzymatically hydrolysed, but an additional mechanical treatment is necessary to complete the process, to remove the fibres normally leading to pilling for example, rotating drum washers and jets [81, 82, 10, 12]. Increasing the degree of mechanical agitation increases the extent of the hydrolysis [83]. Prior mechanical agitation makes cellulosic chains more accessible for cellulase hydrolysis [84]. The cellulase treatment and the further washing process show similar effects to that of one step process, but with smaller changes, which confirms the role of simultaneous mechanical agitation in cellulase textile process [85]. The cellobiohydrolase rich enzyme mixtures produce more soluble reducing sugars, which can also reduce the indigo dye and increase backstaining. In the two-step process of washing, the total loss of colour is about 20%, while the one step washing process yields a loss of colour of about 40%, under the same conditions [10].

15.3.6 Stone washing

Stone and denim washed garments, generally cotton, show a characteristics well-

worn look and are very popular with young people. In the stone washing process, the finished garments, whose fabric had been dyed with sulphur, or reactive dyes or indigo are subject to the eroding action of pumice stone in a washing machine in the presence of an oxidiser, usually potassium permanganate. The treatment results in uneven decolourisation, without excessive loss of fabric strength. The blue denim is faded by the abrasion action of pumice stones.

Cationisation of the cotton surface by a treatment with 1, 1-dimethyl-3-hydroxy-azetidinium chloride (DMA-AC) followed by dyeing with reactive dyes can develop the appearance of a denim type effect on specially constructed fabric [86].

In the same way, wash-out and stone-wash effects can be produced on dyed jeans by subjecting piece goods to a bio-finish process with suitable cellulase complexes without pumice stone and bleaching agents [72, 87]. Complete or partial replacement of pumice stones by cellulase enzymes for the effect of stone-washing on denim is well established and hundreds of looks can be generated from any piece of standard denim fabric [87-90]. The enzymes or combination of enzymes eliminate partially projecting dyed fibres, exposing the undyed material underneath. This forms the uneven, colour-flecked surface of wash-out article, but with no material surface damage and with an elegent fabric appearance. The surface frictions play an important role in the enzymatic decolourisation of cellulosic fabrics [84]. The mechanical action opens the outermost layers of the cellulosic crystal, thus increasing the part of the cellulose accessible to enzymes, and allowing the enzymatic removal of the dye.

The use of acid cellulases are recommended for fast treatments and neutral cellulases for more severe treatments when marked effects are required [56, 91]. Endo-enriched acid cellulase is found to be best for easily weekened fabrics such as linen and viscose rayon. Standard whole acid cellulases are best for sturdy fabrics such as lyocell, modal rayon and heavy weight cotton [92].

15.4 Treatment of Protein Fibres with Enzyme

Enzymatic pre-treatments to protein fibres are generally concentrated on wool and silk. It is possible to remove skin residues, skin grease and vegetable matter of wool by enzymatic degradation method. Furthermore, the wool surface can be modified, and felt free finishing with simultaneous improvement of lustre and handle of woollen fabric is possible by enzyme treatment.

The two major morphological parts in the structure of wool are cuticle and cortex. The epi-cuticle of wool fibres surrounds each cuticle, it consists of approximately one-quarter fatty acid and three-quarters protein by mass. The hydrophobic epicuticle acts as a barrier to dyes which enter the wool fibre between cuticle cells through the highly cross-linked cell membrane complex (CMC). Enzyme from the liquor can diffuse into the interior of the fibre and hydrolyse parts of the endocuticle and proteins in the cell membrane complex, completely damaging the fibre if not controlled. In contrast, the catalytic action of enzyme on cotton is confined to the surface and the amorphous region only.

Enzymes such as proteases, lipases, lipoprotein lipases and proteolytic enzyme derived from the bacterium Streptomyces fradie (known as SFP) is capable of attacking natural keratin hydrolysing some peptide linkages. However, proteases are most widely used.

15.4.1 Wool carbonising

Vegetable matters of wool are normally removed by a process known as carbonising. Carbonisation of wool with inorganic acid may cause some degradation of the fibre. The replacement of carbonisation by the use of enzymes, such as cellulases, ligninases, hydrolases, lyases and oxidoreductases are reported [93]. A biochemical alternative using complex combination of enzymes to the chemical process of carbonising with sulphuric acid is also reported [94]. The amount of sulphuric acid required for carbonisation can be reduced by the action of cellulolytic and pectinolytic enzymes [95].

Natural soilings on wool such as vegetable matter and skin flakes can also be enzymatically modified [96]. Burr removal becomes easier after lubricating wool with cellulases due to weakening of the cohesion between burr and wool [97]. Lignin of the burrs in wool can be degraded by the use of lignin peroxidases [98].

15.4.2 Wool bleaching

Bleaching of wool is necessary for the enhancement of whiteness and lustre. Using proteolytic enzymes alone [99] or in combination with peroxide [100], the degree of whiteness and hydrophilicity of the fibres are increased, compared with the oxidative treatment alone [99]. Serine protease stable to hydrogen peroxide is active in an alkaline medium and its activity increases with increasing peroxide level [94]. Higher whiteness index is caused by the decolourising action of the enzyme on natural colorants present in the wool fibre [100].

15.4.3 Shrinkproofing and hand modification of wool

Wool fibres have a tendency to felt and shrink due to its scaly structure. The differential frictional effect (DFE) causes the fibre to move towards their root end when mechanical action is applied in the wet state. Generally shrinking of wool is done either by oxidative or reductive methods and/or by application of resin. The most frequently used commercial process consists of chlorination, followed by dechlorination and polymer application. Among the various processes, nickel-catalysed surface degradation by hypochlorite [101-103] and the use of 'second generation' chlorination equipment [104] are commercialised. Though such descaling is expected to improve the handle of the wool fibres by making them smoother, the handle is actually made harsher, perhaps because the fibres become sized by degraded protein. However, the softness of the fabric can be improved as a final application of a silicone microemulsion [105], but expensive equipment are needed.

It is possible to limit chlorination and other oxidations to the cuticle layer to remove the fibre from the surface of the fabric without damaging the fibre and thus increases its softness too. Consequently, in addition to the antifelting effect achieved by the pretreatment and processing of wool fibres, a soft handle is also obtained. Of all the enzyme processes available for wool, only a few are 'pure' enzymatic processes. The majority of enzymatic processes published are combined processes. In most of the treatments for improving the handle of wool, reduction of the fibre diamerter is done by complete descaling which produce a non-tolerable weight loss of the fibres. Descaling is generally performed by pretreating the fibres with potassium permanganate as a preoxidising agent [106] or by gas chlorination (the Chlorzym process [107]) or by hydrogen peroxide (the Perzym process [108]) and subsequent treatment with a proteolytic enzyme [109]. Thus it is possible to remove the scales by using much less than 5% chlorine if the process is followed by an enzyme.

Protease, trypsin or papain are commonly used as enzymes for wool fibres. Protease is quite unreactive unless acted upon by a mild reducing agent, i.e. bisulphite or cysteine, so as to split disulphide to sulphydryl groups [110-113]. Other enzymes have been proposed [114, 115], including bacterial alkaline proteases of the type used in washing powders. In some processes proteases are used to cut-off damaged fibres [116] or to achieve certain texturising effects [117, 118].

Descaling is also achieved by the applicaiton of heat-resistant neutral protease, resulting in cashmere-like feel [119]. The combined use of the chlorinating agent, dichloroisocyanurate and proteolytic enzyme can improve handle properties [120, 121].

Physical, as well as chemical, pretreatment processes have been combined with the enzyme treatment of wool. A low-temperature plasma is applied to the fibres prior to treatment with polymeric shrinkproofing agent [122]. Combined protease and heat treatment with a saturated steam [123] and the use of high frequency radiation on enzyme treated materials are reported.

15.5 Bio-technology and Effluent Treatment

Environment friendly pre-treatment processes of textiles are the need of the day due to tremendous awareness of chemical pollution and mounting legislation to limit the chemical burden of the factory effluent. Biotechnology can be used for the treatment of wastes which can solve the problem either partially or totally. The applicaiton of biotechnology is mainly attributed to the removal of colour from the dyehouse effluents. Living organisms is used to bind and degrade colour (e.g. artificial reed beds) or dead organisms (e.g. straw, chitin/chitosan, microfungal hyphae etc.). Selected microbes or isolated enzyme may be used to assist specific areas. The discharge of dyestuffs into the environment is not solely an aesthetic matter and many dyestuffs are identified to be mutagenic [123]. Biosorption has the potential to remove metal ions such as chromium [124], which are used in the manufacture and application of mordant dyes. The enzymatic bleaching of released dye reduces process time and the amount of energy and water needed to achieve a satisfactory textile quality [125]. However, the type and the concentration of dyes as well as the amount and type of substrate used are found to play a major role in dye adsorption [126, 127]. Chitosan is found to be most efficient in absorbing dyes of small molecular size [128].

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Chapter 16

ANALYSIS AND TESTING IN PREPARATORY PROCESSES

16.1 Introduction

The objective of chemical pre-treatment of textiles is to obtain uniform effects as regards to size removal, absorbancy, whiteness, absence of husks, dye affinity ; high dependency of results ; minimum fibre damage and favourable cost performance relationship. The factors which affect the pre-treatment are goods (printed or dyed), machinery, dispensing system, dependability of results, end use, customer requirements, economical and ecological aspects etc. The potential defects during pre-treatment processes are inadequate or uneven desizing, incomplete removal of greases and wax, poor or uneven absorbancy, unlevel mercerization, inadequate or unstable ground white, poor mechanical strength, low DP value, catalytic damage and creases etc. In the case of synthetics that are heavily oiled prior to or during knitting, dye spots and speckiness later attribute to poor dyeing practices. Improper size removal is the major cause of unlevelness encountered in thermosol or range-dyed goods.

It is thus necessary to optimise the effects of various pre-treatment chemicals, focusing on fabric physical properties such as tensile strength, weight loss, fuzzing, hand, copper number, moisture regain and colour change (in the case of dyed fabrics).

This chapter is devoted to evaluate the usefulness of measurement of different physical and chemical properties of textile fibres before and after chemcial pretreatment to provide a direct assessment of effects of different chemicals. Such information about a property that is immediately and directly affected by chemical reaction will help to optimise the process conditions, whereby the desired effects can be achieved while minimising the undesired effects such as excessive strength loss etc.

16.2 Analysis of Water

To calculate the hardness of a particular water the concentration of actual magnesium or calcium salt is converted to an equivalent weight of calcium carbonate. Hardness is generally expressed as equivalent parts per million (p.p.m.) of calcium carbonate irrespective of the actual salt present. By defination, 1° English hardness

is 10 mg of $CaCO_3$ in 0.71 and 17 mg per 0.71 = $\frac{17}{10}$ = 1.7° English hardness. Similarly 1° US hardness is 1 mg/l of $CaCO_3$ and so 24 mg/l = $\frac{24}{1}$ = 24° US hardness.

16.2.1 Suspended matter

2 litres of water are filtered through previously weighed filter paper. The residue is dried and weighed (x g). The results are expressed as

$$\text{p.p.m.} = \frac{x \times 10^6}{10^3}$$

16.2.2 Total soluble salts

First of all the dirt and suspended materials are removed from the sample water as described above. 250 ml of this water is put on dried platinum dish and heated on iron plate. The dish is then transferred on a hot water bath when some quantity of water remains in the dish. Finally, the content is dried to constant weight in the oven, cooled in a desciccator and wighed (x g). The results are expressed as

$$\text{p.p.m.} = \frac{x \times 10^6 \times 4}{10^3 \times 1}$$

16.2.3 Total hardness

The total hardness of water can be determined either by using standard soap solution or by using EDTA reagent.

In the first method, 100 ml of water is placed in a 200 ml stoppered flask. 1 ml of standard Wanklyn's soap solution is added at a time until a lather is obtained on shaking which persists for one minute. If the titre on 100 ml of water is T ml, since 1.0 ml of standard soap solution ≡ 1.0 g $CaCO_3$.

$\therefore$ 100 parts of water contain 0.001 T parts of $CaCO_3$

and 1,000,000 parts of water contain 10T parts of $CaCO_3$.

$\therefore$ Total hardness = 10 T p.p.m. as $CaCO_3$.

In the second method, 100 ml of sample water is pipetted into a 250 ml conical flask. 2.0 ml of ''balanced'' buffer [50 ml HCl (Sp. gr. = 1.18) is added to 400 ml distilled water. 310 ml ethanolamine is slowly added with constant stirring, followed by 5.0 g of magnesium disodium EDTA. The content is diluted to 1 litre] is added, mixed and then added one or two drops of indicator solution [5.0 g

Solochrome Black WDFA (C. I. Mordant Black 11) is dissolved in a mixture of 75 ml triethanol amine and 25 ml alcohol]. The content is titrated with EDTA solution (0.02 N) until last reddish tinge disappears. Let the titre obtained be T ml. Since 1.0 ml of 0.02 N EDTA solution $\equiv$ 1.0 mg $CaCO_3$,

$\therefore$ Total hardness = 10T p.p.m. as $CaCO_3$.

16.2.4 Calcium hardness

100 ml of the water sample is pipetted into a flask and 1 ml of 4N-sodium hydroxide and one tablet of calcium hardness indicator (BDH) is added. The content is titrated with 0.02 N-EDTA solution until the solution becomes violet (0.1 ml causes no further colour change).

$\therefore$ Calcium hardness = 10T p.p.m. as $CaCO_3$.

16.2.5 Magnesium hardness

This is obtained by difference as follows :

Magnesium hardness = Total hardness – Calcium hardness

(all values expressed as p.p.m. $CaCO_3$)

Magnesium hardness (p.p.m. $MgCO_3$) = 0.84 × magnesium hardness (p.p.m. $CaCO_3$).

16.2.6 Temporary and permanent hardness

100 ml of water is titrated with 0.02 N-EDTA solution as described above.

Another 100 ml of water is boiled gently for 10 min in a 250 ml flask. This will decompose bicarbonates. The content is cooled, filtered and the filtrate is diluted with distilled water to make up the volume to 100 ml and then titrated with 0.02 N – EDTA solution to obtain permanent hardness.

Temporary hardness = Total hardness – Permanent hardness

(all values expressed as p.p.m. $CaCO_3$).

16.3 Analysis of Non-Cellulosic Residues

Such analysis is useful as a diagnostic aid in finding the cause of poor preparation or may be required for specific end uses, e.g. surgical cottons.

16.3.1 Ash content (mineral matter)

The ashing of a yarn or fabric can be used to determine inorganic residues like silicate, phosphate, calcium, copper and iron contents on the fabric.

Approximately 5 g of dried samples are placed in a weighed crucible. The material is slowly ignited over a Bunsen flame and then the crucible is placed in a

muffle furnace maintained at a temperature of 750°C for 1 h or until constant weight is obtained.

$$\text{Ash content (\%)} = \frac{100 \times b}{a}$$

where a = dry weight of the sample,

and b = weight of ash.

Typical values for grey cotton are 0.5-1.0%, which drops to 0.2-0.5% after scouring and bleaching.

16.3.2 Silicate and phosphate

Approximately 5 g sample is ashed as above and cooled. The content is then mixed with 5-6 times the amount of sodium-potassium carbonate (made by mixing equal weights) and then heated until a clear melt is obtained. On cooling, the solidified melt is then dissolved in distilled water and granular ammonium molybdate is added to it. Then the content is acidified with nitric acid (20%). In the presence of silicate an intense yellow colour or a yellow, crystalline precipitate is produced.

For testing phosphate contents in the sample, the ash is dissolved in 10 ml nitric acid (20%), filtered and the residue is mixed with 5-6 times the amount of sodium-potassium carbonate and then continue as above.

16.3.3 Calcium and magnesium

5 g sample is ashed and the ash is mixed with hydrochloric acid (10%) and ammonium chloride. Ammonia (Sp. gr. 0.88) is added until the solution is alkaline. The ammonical filtrate is acidified with acetic acid and calcium is precipitated with oxalic acid as calcium oxalate. The presence of calcium is indicated by a characteristic red flame colour placed in a bunsen flame.

For quantitative analysis of calcium, the filtered calcium oxalate is washed with little distilled water and then taken up in warm sulphuric acid (20%) and titrated against 0.1N $KMnO_4$ solution.

The concentration of calcium and magnesium, expressed as a percentage on weight of raw cotton is usually in the following ranges :

Calcium 0.43 – 0.15%

Magnesium 0.046 – 0.11%

Calcium and magnesium may be taken up by the fibre during growth or from the liquor during wet processing, where they are present as hardness formers.

16.3.4 Iron and copper

The presence of compounds of iron and copper can cause fibre damage during bleaching, by so-called ''catalytic tendering''. It is important to know if such contaminants are present and remove them prior to bleaching.

0.5 – 1.0 g fibre is spotted with 1-2 drops of nitric acid (5%) and allowed to stand for 2-3 min so that any iron present is oxidised to ferric ions. Then 2-4 drops of potassium thiocyanate solution (10%) are added and a red colour indicates ferric ions. The intensity of colour indicates the amount. The test can be carried out on an ashed sample.

In another method, the fibre is spotted with hydrochloric acid (10%) and the acidified area is spotted with 1% potassium ferrocyanide. A dark blue colour indicates the presence of iron.

For testing of copper, the ash is spotted with 5-10 drops of nitric acid (10%) and then dilute ammonia (1:1) is added until the ash is alkaline. A blue colour shows the presence of copper. For fabric, the sample is first spotted with dilute nitric acid and then after neutralisation with ammonia, 1-2 drops of diethyldithiocarbamate solution (0.1%) are spotted on to the same area. A yellow colour shows the presence of copper.

Metal contents may also be determined on the ash by emission spectroscopy or atomic absorption spectroscopy.

16.4 Evaluation of Wax Content on Cotton

Soxhlet extraction is the usual procedure for seperation of the wax from the cotton, with percentage composition being obtained by gravimetric means after the evaporation of solvent. Different values are sometimes encountered for the same source of cotton when different solvents are used. Solvents commonly used are ethanol, ether, benzene, benzene-methylene chloride, chloroform, carbon tetrachloride and acetone. The results of the cotton wax extracted by the above process are reported in Table 16.1. Modern analytical techniques such as gas chromatography, mass spectrometry and X-ray defraction can be used for detection of the individual wax components. It is confirmed that a waxy substance is present within the crystalline cellulose chain. Cuxam is used to dissolve the cotton fibre, the wax portion is separated through the use of organic solvents, and greige cotton is found to contain approximately 2% wax. By continuing the extraction process, an additional

TABLE 16.1
Composition of Cotton Wax [1]

Wax	Percentage
Wax ester	22
Phytosterols	12-14
Polyterpenes	1-4
Hydrocarbons	7-8
Free-wax alcohols	42-46

1% wax is detected, even though normal extraction processes had suggested that this batch of cotton contained only 0.6 - 0.7% wax.

16.5 Evaluation of Lubricants

Sizing materials for both filament and spun yarn usually contain additional film modifiers to produce a product with improved sizing qualities. One such compound is lubricants. Lubricants can be divided into two basic groupings, saponifiable and unsaponifiable. The saponifiables are easily removed and can, in fact act as emulsifiers for the unsaponifiables [2]. The unsaponifiables, such as paraffin waxes, are considered to be the best friction reducers. Tallow, bleached tallow, hydrogenated tallow glycerides, and fatty esters are used as fats and fatty components. Crude-scale paraffin wax, slack paraffin wax, refined paraffin wax and some polyethylenes are used as unsaponifiable materials. In general practice, there are three general categories of lubricants, or kettle waxes : water soluble, water dispersible, and size dispersible. Wax concentrations on cotton yarn increase weave efficiency when used at a concentration of up to 5%. Above 10-15%, no increase in efficiency is achieved and desize problem can occur.

16.5.1 Total fatty matter

8-10 g of sample is weighed in a dry conical flask and about 50 ml of 2N sulphuric acid is added. The contents are refluxed for 2 h using a water condenser. After cooling the fatty matter is extracted with 50 ml of ether twice in a seperating funnel. The combined ether extracts are washed with water till free from acid. The ether extract is transferred to a weighing beaker, the ether evaporated using a water bath and the residue dried in an oven at 110°C and weighed after cooling.

$$\text{Total fatty matter (\%)} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

16.5.2 Saponification value of an oil

0.5 g of the sample is weighed into a conical flask and 50 ml of 0.5N alcoholic potassium hydroxide solution is added to it. The contents are boiled under reflux for 2 h. After cooling the excess alkali is back-titrated against 0.5N HCl using Methyl Orange as an indicator. A blank is also run (without tallow sample).

1.0 ml of 0.5 N HCl solution = 28.05 mg KOH

x ml of 0.5 N HCl solution = 28.05 x mg KOH

W g of sample requires 28.05 x mg KOH

$$\therefore \quad \text{Saponification value} = \frac{28.05\ x}{W}$$

where, x = (blank reading – sample reading)

16.5.3 Unsaponified matter

The solution preserved after the determination of saponification value is extracted with petroleum ether, evaporated and dried in an oven. After cooling the residue is weighed.

$$\text{Unsaponified matter (\%)} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

16.6 Determination of Moisture Content [3]

The amount of moisture in a textile material can be determined directly or indirectly and may be expressed either as ''moisture content'' or as ''moisture regain''. In the direct method the amount of moisture in a definite weight of material is driven out, usually by heating in an oven at 105 - 110°C (for cotton) for a period of 4 h, at the end of which the sample is cooled in a desciccator and the loss in weight is determined. In the indirect method, a property of the material, usually its electrical conductivity or resistance, which is dependent on the moisture content of the material, is made use of. The moisture content, is defined as the moisture present in the sample and is expressed as percentage of the original weight of the sample in the condition in which it is received for test, whereas moisture regain is expressed as a percentage of the oven-dry weight of the sample. The two quantities can be expressed as follows :

$$\text{Moisture content (M.C.)} = \frac{a-b}{a} \times 100$$

$$\text{Moisture regain (M.R.)} = \frac{a-b}{b} \times 100$$

where 'a' and 'b' represent original weight and the oven-dry weight of the sample.

16.7 Tests and Analyses of Sizes

The warp size, once applied to the yarn and dried, increases the tensile strength and abrasion resistance of the yarn. This minimises down time or ''breakouts''. The sizing formulations may consist of natural and synthetic polymers, gums, starches, metal-to-fibre lubricants, preservatives, and defoamers. The solution, after impregnation into the warp yarns at a level of 10-15% (o.w.f.) for cotton [4] and cotton blends, and at a level of 3-5% on filament synthetics, is dried in continuous form over drying cylinders and then wound onto large goods called beams. The compounds commonly used for filament sizing and spun yarn sizing are shown in Table 16.2 and 16.3 respectively. In desizing operation the size is removed and the effectiveness of the removal of size can be tested depending on the kind of size used.

TABLE 16.2
Filament Sizing Materials

Fibre	Basic size
Nylon	Polyacrylic acid
	Polyvinyl alcohol
Polyester	Acrylic copolymers
	Alkali soluble polyvinyl acetate
	Linear polyester
	Stymer (styrene – maleic anhydride coplymer)
	Gelatin
Viscose rayon	Polyvinyl alcohol
	Amylose derivatives
	Carboxymethylcellulose
	Blends
Glass	Polyvinyl alcohol
	Dextrins
	Amylose derivatives
	Blends

TABLE 16.3
Spun Yarn Sizing Materials

Fibre (100 % or blends)	Basic size
Cotton	Starches : corn, potato, tapioca
Rayon	Unmodified – pearl
Nylon	Acid modified, 20-60 fluidity
Polyester	Oxidised, several fluidities
Acetate	Dextrinized – British gum
Acrylic	Derivatized
Wool	Acetate, Hydroxyethyl ether, Acrylate, Styrene, Cross-linked, Cationic, High amylose, Polyvinyl alcohol, CMC, Blends and other polymers

16.7.1 Identification of sizes

Starches are hydrolysed by acids, alkalies or by enzymes during desizing process. Acid hydrolysis of starches yield mixtures of saccharides or glucose. Enzymatic (β-amylase) hydrolysis of starches yield maltose and amyloglucosidase yields D-glucose. All these products give different coloured residues on treatment with iodine. Because of the hydroxyl content of the cellulose, reaction can occur with many different compounds. The identification of different sizes with the help of different reagents are summerised in Table 16.4. Starch apparently contains two fractions, a soluble amylose (10-20%) and an insoluble residue, amylopectin (80-90%), account for the violet colour and blue colour that are yielded on treatment with iodine. Amylose gives the blue colour and amylopectin gives the violet to red-violet colour. In enzyme hydrolysis of starch, amylose is completely hydrolysed to amylase [4], whereas only 60% of amylopectin can be hydrolysed. Table 16.5 shows the assessment of pre-treatment effects on desizing starch size from cotton fabrics. Poor removal of size during desizing may effect in warp stripeness, stains during dyeing and printing, uneven mercerization and uneven absorbancy.

Normally extraction techniques are useful for assessing the rinsing effectiveness and size residue. Sequential extraction technique with solvent and enzyme [5] or water, enzyme and solvent [6] or solvent, water and enzyme [7] is used.

TABLE 16.4
Identification of Sizes

Sizes	Reagents	Procedure	Reaction	Notes
Starch	iodine/potassium iodide solution.	1. apply solution dropwise, 2. rub in gently, 3. assess colour reaction.	colourless = no starch size present, blue violet = starch present, brown = modified starch or mixture with PVA present.	cool material and test ; neutralise alkaline goods with acetic acid.
Polyvinyl alcohol (PVA)	iodine/potassium iodide solution, boric acid soln.	1. apply iodine/potassium iodide solution dropwise 2. apply boric acid solution dropwise to the same spot as the I_2 / KI soln.	colourless = no PVA present, blue = PVA present.	colour intensity depends on amount of size.
Polyvinyl acetate	iodine/KI solution.	1. spot with I_2 / KI solution.	deep reddish brown = polyvinyl acetate present.	colour intensity increases on hot washing.
Starch + PVA	I_2 / KI solution, borax.	1. Treated with warm (70°C) water, 2. aqueous extract is tested with I_2/borax.	blue solution or precipitate = PVA.	colour intensity depends on PVA.
CMC + Acrylate	copper-II-sulphate solution.	1. cut up the sample, 2. add water at ratio 40:1, 3. boil up for 10 min, 4. filter off liquor and cool, 5. add 5 drops solution to the liquor, 6. assess reaction.	clear liquor = no CMC or Acrylate present, white turbidity/ precipitation = CMC or Acrylate present.	distinguish between CMC and Acrylate by adding 2-3 drops acetic acid 80% to the liquor, Reaction : ppt. dissolves = CMC, ppt. undissolved = Acrylate.

TABLE 16.5
Assessment of Starch Size on Desizing

	Extraction content (water extract)	TEGEWA violet scale
Grey-state fabric	6-10%	1
Pre-treatment, good	0.1-0.4%	6-9
Pre-treatment, poor	more than 0.5%	2-5

16.7.2 Percentage size by ordinary method

The weighed cloth is first washed in water and then boiled in caustic soda solution (2%) for about 30 to 40 min. The sample is washed again in water and boiled for 60 min in a solution of hydrochloric acid (1%), adding water as it evaporates. The sample is washed, dried slowly and weighed. The difference in weight indicates the loss of sizing material. In normal practice allowance of 1 to 2% for weight loss by removing natural impurities is allowed during the boiling.

16.7.3 Estimation of total size by Soxhlet method

5 g of accurately weighed sample is extracted with chloroform in a Soxhlet extractor for about 1 h at a minimum rate of 100 drops per min. The sample is then dried in air and washed in hot water several times and then rinsed by hand 12 times. The material is then treated in 0.5% diastase solution (20 to 30 times the weight of cotton) at 70°C for 1h and then washed in hot running water, dried at 110°C and weighed. Side by side a sample is also tested for moisture determination.

$$\text{Apparent size (\%)} = \frac{100 - (a - 1.03b)}{a} - k$$

where, a = dry weight of sample,
b = weight of desized sample, and
k = desizing blank.

In the absence of unsized control, k may be taken as 3% of the desized and dried sample. No correction is required for bleached and dyed cloth. For total size content the ash content (%) of the desized sample is to be added.

16.7.4 Total size by enzyme method

The material is desized by using 5 g/l diastase and 10 g/l NaCl at 70°C (pH 6.5 to 8.5) for 1 h, liquor ratio 40 : 1. The sample is washed thoroughly in hot and cold

water and dried. Either the loss in weight is determined or the carbohydrates in the extract is estimated by oxidation with potassium dichromate under acid conditions.

16.8 Determination of the Efficiency of Scouring

Immediately following the desizing, the yarns and fabrics are washed with detergents and alkalies by a process known as scouring. The efficiency of scouring are assessed by the removal of various types of impurities from the cotton material, e.g. loss in weight, changes in protein content (determined by nitrogen analysis), residual wax content, absorbance etc. Apart from these the decrease in Methylene Blue absorption is indicative of the removal of pectic substance and that of copper number of the removal of hemicelluloses and sugars.

16.8.1 Measurement of weight loss

5 g of dried sample is treated with 200 ml of 1% NaOH for 1h at 80°C, after which the sample is well rinsed and run out in hot water. It is then treated in 200 ml of 0.5% HCl at 80°C for 1h, after which the sample is once again rinsed, boiled for $^1/_2$ h in distilled water, dried and weighed. Weight loss on scouring is normally 6-9%.

16.8.2 Measurement of residual wax content [8]

A known weight of oven dried sample is placed in the Soxhlet extractor and refluxed for 3 h in chloroform (solvent) for cellulose and petroleum ether for polyester blends. The solvent is distilled-off and the flask containing the sample is reweighed. The difference in weight will give the fat and wax contents. For well bleached cotton, the fats and waxes should be below 0.2%. Knit goods should have an acceptable value higher than 2% as processing is designed to aid sewability.

16.8.3 Practical test of absorbancy

Fig. 16-1 shows the technique for evaluating wetting speed by the standard Draves wetting test [9]. Wetting and scouring are normally associated as being

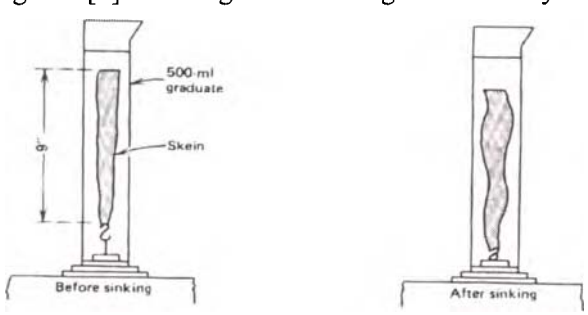


Figure 16-1. Apparatus for running Draves wetting test (Courtesy of Union Carbide).

synonymous, however, this unfortunately is not true. Experimental data indicate that the best wetting agents are usually non-ionics with low ethylene oxide content, whereas the best scouring compounds generally have a long chain hydrophile and hydrophobe.

However, the absorbancy of fabrics can be estimated by a test in which a drop of distilled water is allowed to remain in contact with the scoured cloth for 30 sec. If the drop is absorbed in this time, the material is judged to be absorbant and suitable for bleaching and dyeing. In the case of printing cloth, the time of absorption of the drop of water must be lower than 1 sec. The assessment of pre-treatment effects by absorbancy test is given in Table 16.6. Poorly pre-treated goods will have increased amount of dye on the fibre surface as a result of inadequate

TABLE 16.6
Assessment of Pre-treatment by Absorbancy Test

	Spot	Wicking test		Wicking rate		
	test	5 min	10 min	1 cm	2 cm	3 cm
Pre-treatment Good	1-5"	30-50 mm	50-90 mm	3-5"	10-30"	40-70"
Pre-treatment Poor	more than 10"	< 30 mm	< 50 mm	> 10"	> 30"	> 100"

penetration, poor fastness properties and unlevel dyeing.

16.8.4 Removal of motes (kitties)

This is done visually by observing the kitties present on the prepared samples, and the ratings on an arbitrary scale of 1-5 are given. A rating of 5 may be given to the sample with no kitties present on the fabric.

16.9 Testing and Evaluation of Bleaching Agents

Although it is generally accepted that an improvement in whiteness is one of the basic requirements in bleaching it is by no means the sole objective. Now-a-days with the increased production of polyester/cotton blended fabrics, polyvinyl alcohol, CMC and starch or their blends are used as sizing agents. During enzymatic desizing starch sizes are being solubilised, but the PVA and other polymers will be ineffective. Therefore, one of the major purposes of bleaching is the removal of these polymers apart from the degradation of the naturally occurring pigments in

the fibre. Also extremely high whiteness is not worthwhile if it is obtained at the expense of degrading the material being bleached. It is impossible to give strict guidelines for the optimum bleach bath because of the nature and quality of the goods to be bleached, the amount of bleaching required and the availability of equipment in which bleaching is to take place. The evaluation of effective bleaching can be done by measuring the absorbancy, fluidity, whiteness and analysis of impurities which should be 2-3% or less with an ash content of 0.20-0.25%. However exact control on the concentration of bleaching agents is most important along with the treatment time, temperature, pH and stabilisation of the bleach bath. The processed fabric should be absorbant, clean, white, uniform bottom for dyeing and printing.

In the textile industry, it is quite common to check the strengths of solutions by means of normality, molarity, specific gravity, density, percentage and g/l of available chlorine. Bleach liquors, mercerizing liquids and resin solutions are checked with hydrometer for determining specific gravity and strength is expressed in terms of degrees Twaddell (°Tw). Sometime Baume (°Be') is also used to express the strength in solution. The relations among the three common methods for expressing the density of solutions can be simplified by arithmetical expression for quick routine checking.

$$\text{specific gravity} = \frac{145}{145 - {}^{\circ}\text{Be'}}$$

$${}^{\circ}\text{Be'} = 145 - \frac{145}{\text{specific gravity}}$$

$$\text{specific gravity} = 0.005\ ({}^{\circ}\text{Tw}) + 1$$

$${}^{\circ}\text{Tw} = 200\ (\text{specific gravity} - 1)$$

$$\text{precent by weight} = \frac{\text{g/l}}{10\,(\text{specific gravity})}$$

$$\text{pounds per gallon} = \text{g/l} \times 0.008345$$

The relationship between °Tw and strength of bleaching powder solution is shown in Table 16.7. These methods of expressing strengths of solutions, however are far from accurate and hence quantitative estimation by titration for practical control of bleaching operation is preferable.

TABLE 16.7
Fresh Bleaching Powder Solutions [10]

°Tw	Available chlorine, g/l
0.5	1.40
1	2.71
2	5.58
3	8.41
4	11.41
5	14.47
6	17.36
7	20.44
8	23.75
9	26.62
10	29.50
15	45.70
20	61.50

16.9.1 Analysis of bleaching powder

5 g sample is made up to 500 ml in a volumetric flask. 50 ml of this solution is pipetted out to a 250 ml conical flask and 25 ml of distilled water is added followed by 20 ml of KI solution (10%) and 10 ml of glacial acetic acid. The liberated iodine is titrated against N/10 sodium thiosulphate solution using starch solution as indicator towards the end point when the blue colour will be discharged.

$$Ca(OCl)_2 + 4KI + 4CH_3COOH \rightarrow CaCl_2 + 4CH_3COOK + 2I_2 + 2H_2O$$

$$2I_2 + 4Na_2S_2O_3 \rightarrow 2Na_2S_4O_6 + 4NaI$$

1 ml of 0.1 N $Na_2S_2O_3$ = 0.00355 g available chlorine

$$\% \text{ available chlorine} = \text{B.R.} \times \text{Normality of } Na_2S_2O_3 \times \frac{\text{Eq. wt. of } Cl_2}{1000} \times \frac{500}{50} \times \frac{100}{\text{wt. of sample (W)}}$$

$$= \text{B.R.} \times \frac{3.55}{W}.$$

16.9.2 Analysis of sodium hypochlorite

The estimation by above method expresses chlorates as well as hypochlorites as available chlorine. The errors due to chlorates can be avoided by titration with an N/10 solution of sodium arsenite (Na_2HAsO_3)

1 ml of 0.1N Na_2HAsO_3 = 0.003546 g chlorine.

16.9.3 Analysis of sodium chlorite

2 g sample is made up to 500 ml in a volumetric flask. 25 ml of solution is pipetted out and then 25 ml of 10% KI solution and of 10% H_2SO_4 are added. The content is titrated against 0.1N $Na_2S_2O_3$ solution using starch as an indicator till blue colour disappears completely.

$2NaClO_2 + 8KI + H_2SO_4 \rightarrow 2NaCl + K_2SO_4 + 8I + H_2O$

1 ml of 0.1N $Na_2S_2O_3$ = 0.00226 g $NaClO_2$

$$\% \ NaClO_2 = B.R. \times \text{normality of } Na_2S_2O_3 \times \frac{\text{Eq. wt. of } NaClO_2}{1000} \times \frac{500}{25} \times \frac{100}{W}$$

$$= B.R. \times \frac{4.52}{W}.$$

16.9.4 Analysis of hydrogen peroxide

10 ml of sample solution is diluted to 1000 ml with distilled water. 10 ml of this solution is pipetted out into a conical flask and 10 ml of 10% H_2SO_4 is added to it. This solution is then titrated against 0.1 N $KMnO_4$ till pink colour of permanganate solution persist.

$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

1 ml of 0.1N $KMnO_4$ = 0.0017 g H_2O_2

$$\% \ H_2O_2 = B.R. \times \text{Normality of } KMnO_4 \times \frac{\text{Eq. wt. of } H_2O_2}{1000} \times \frac{1000}{10} \times \frac{100}{10}$$

$$= B.R. \times 1.7$$

Generally, H_2O_2 concentration is expressed in volume. 10 volume H_2O_2 = 10 times its volume of O_2 which corresponds to 3% solution by weight of H_2O_2. To convert % H_2O_2 into volume of H_2O_2 following calculations can be used :

$$\text{Volume of } H_2O_2 = \% \text{ of } H_2O_2 \times \frac{112}{34}.$$

16.9.5 Analysis of stabilisers for peroxide bleach

The efficiency of a stabiliser for peroxide bleach is tested by titrimetric determination of the speed of decomposition of H_2O_2, in the presence and absence of stabiliser, during the bleaching of cotton. Bleaching baths containing 10 ml/l H_2O_2, 5 ml/l NaOH (67°Tw) and 0, 0.25, 0.5 and 1 g/l stabilisers are prepared by adding stabiliser, caustic soda and H_2O_2, in that order, to water. Cotton cloth pieces (5g) are bleached in this solutions at 90°C for 90 min, material to liquor ratio being 1:50. After replenishing water lost due to evaporation, about 25 ml samples are withdrawn after 0, 30, 60 and 90 min, cooled in ice water and a 5 ml aliquot is pipetted from these for analysis. It is diluted with 50 ml of distilled water, acidified with 10 ml of 2N H_2SO_4 and titrated with 0.1 N potassium permanganate to a permanent pink colour.

In the case of stabilisers which consume permanganate under these conditions, the determination is done iodometrically by adding 1g KI to the acidified solution and titrated the iodine liberated, after keeping in dark for 10 min, with 0.1N sodium thiosulphate using starch as an indicator.

1 ml 0.1 N $KMnO_4$ = 0.0017 g H_2O_2

1 ml 0.1 N $Na_2S_2O_3$ = 0.0017 g H_2O_2

16.9.6 Analysis of sodium hydrosulphite

2 g sample is dissolved in a mixture of 10 ml HCHO and 25 ml water in a 250 ml volumetric flask. The stoppered flask is allowed to stand for 5 min and the volume is made up to the mark. 25 ml of this solution is pipetted out and titrated against 0.1N I_2 solution using starch solution as an indicator till blue colour persists.

1 ml of 0.1 N I_2 = 0.00435 g $Na_2S_2O_4$

$$\% \, Na_2S_2O_4 = \text{B.R.} \times \frac{4.35}{W}.$$

16.9.7 Analysis of sodium bisulphite

10 g sample is accurately weighed and dissolved in 1 litre distilled water. To 10 ml of this solution 5 ml acetic acid is added and then titrated against 0.1 N I_2 solution using starch solution as an indicator. End point is judged when the colourless solution turns blue.

$NaHSO_3 + I_2 + H_2O \rightarrow NaHSO_4 + 2HI$

1 ml of 0.1 N I_2 = 0.0052 g $NaHSO_3$

% $NaHSO_3$ = B. R. × 52.

16.9.8 Estimation of sodium silicate

In a commercial sample of silicate, Na_2O (total alkali) and SiO_2 (silica) are determined. 5 g of sodium silicate is dissolved in 100 ml water. 10 ml of this solution is titrated against 0.5 N H_2SO_4 using Methyle Orange as an indicator.

1 ml 1N H_2SO_4 = 0.031 g Na_2O

For determination of silica, 20 ml of silicate solution is kept in an evaporating dish and then 20 ml of N HCl is added to it. The content is evaporated to dryness with constant stirring. After cooling 10 ml of N HCl is added and again evaporated to dryness. The content is baked (over a sand bath) at about 130°C to convert the silicic acid into silica. After cooling water is added to dissolve the soluble matter and then filtered through a weighed-ash filter paper, washed free from chloride (test the filtrate with dilute $AgNO_3$ solution). The content is incinerated and weighed as silica.

16.10 Assessment of Damage of Cellulose During Pre-treatment Processes

The damages that occur during various pre-treatment processes of cellulosic fibres can be detected by various chemical tests like fluidity, copper number, Methylene Blue absorption and silver nitrate staining etc.

16.10.1 Determination of fluidity of cellulose

The extent of chemical damage to cellulosic fibres is usually expressed from fluidity measurements, although with oxidative damage some problems arise. Fluidity is the inverse of viscosity of cellulose solution and is measured as rhes. Oxycellulose or hydrocellulose has equal effect upon viscosity and give overall degradation of cellulose. Degradation is always accompanied by a decrease in DP, therefore higher the viscosity the less is the damage which has been inflicted upon the fibre. Viscosity changes do not give a straight line plot in relation to loss of tensile strength. When fluidities are used, however, the curve is near enough to a straight line for all practical purposes.

Among the various solvents suggested for dissolution of cellulose, cuprammonium solution is recommended as a general solvent having 15 ± 0.1 g/l Cu, 200 ± 5g/l NH_3 and less than 0.5 g/l nitrous oxide. The fluidity in this solvent of the solution of cotton is given by

$$F = \frac{c}{t}$$

where, c is the viscometer constant. If it is necessary to apply kinetic energy correction, k,

$$F = \frac{c}{t - \frac{k}{t}}$$

The kinetic energy correction is unnecessary for times of flow greater than 200 sec. In actual practice 0.5 g of finely cut dry cotton sample is dissolved in 100 ml of standardised cuprammonium hydroxide solution. The viscometer (Fig. 16-2) is

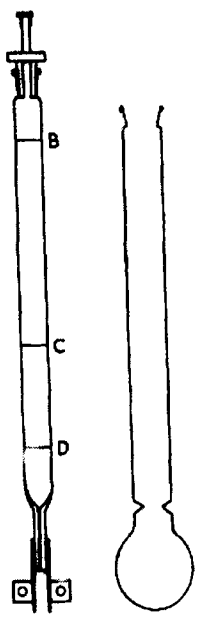


Figure 16-2. Shirley X-type viscometer and jacket.

used for dissolving as well as flow time of cellulose solution. The viscometer tube is calibrated. The three marks on the tube are timing marks. The ratio of the time of flow from BC to CD should be near unity. The viscometer is then wrapped with black cloth and wound on a cycle wheel which rotates at 4 r.p.m. overnight. Steel cylinder or Hg placed inside the cylinder falls from one end to the other during rotation. The established procedure [11,12] involves long agitation of cellulose with the solvent. A modified method is also described which gives only slightly less accurate results in a much shorter time [13].

Chemically undamaged cotton has a fluidity of 3 to 5. A value of 10 or more can be taken as an indication of excessive degradation during chemical pre-treatment processes. It is usual to work with 2% solution in the case of regenerated cellulose. Unprocessed viscose has a fluidity of 10 to 12. The fluidity values can be expressed in terms of DP of cellulose by the following equation [14]:

$$DP = 2160\ [(\log\eta_r + 1) - 0.267]$$

where η_r is the relative viscosity of 0.5% solution of cellulose in Cuoxam compared to the viscosity of the solvent. When the fluidity measurements in different solvents are compared, it is observed that the apparent DP of the degraded (oxidative) cotton is dependent on the alkalinity of the solvent [15] :

$$DP_{EWNN} < DP_{CUEN} < DP_{CUOXAM} < DP_{NO_3Al}$$

Fluidity results determined in Cuxam and Cuen for chemically damaged cotton are correlated with viscosity values obtained in Cadoxen and FeTNa solvents [16]. The comparison and conversion of the viscosity values to apparent cuprammonium fluidity is a quick method of determining degradation of cotton occured in pre-treatment processes [16].

16.10.2 Determination of copper number

Copper number is an expression of the reducing power of degraded celluloses. Oxidation of cellulose can produce ring fission of the glucose residues, resulting in the formation of aldehyde groups at carbon atoms 2 and 3. The aldehyde groups can reduce Fehling's solution to cuprous oxide. The latter may be determined quantitatively by allowing the oxide to reduce ferric alum to the ferrous state and determining the latter by titration with ammonium cerric sulphate. The copper number is thus the weight of copper from Cu^{2+} to Cu^{+} state by 100 g dry cellulose and is a measure of its inter and intra chain break down. Pure cellulose has a copper number of 0.2 - 0.3 and when fully degraded may be as high as 14. The importance of copper number has suffered a decline because it has been demonstrated that there is a poor correlation between increase in copper number and decrease in tensile strength.

Four solutions are prepared as follows :

Solution A : 100 g pure $CuSO_4$ dissolved in 1 litre H_2O.

Solution B : 50 g $NaHCO_3$ and 350 g Na_2CO_3 dissolved in 1 litre H_2O.

Solution C : 100 g ferric alum and 140 ml pure concentrated H_2SO_4 dissolved in 1 litre H_2O.

Solution D : N/100 cerric sulphate.

Solution A and B are mixed in proportion 5 to 95 and the mixture is boiled. 0.125 g finely cut dried sample is kept in a pyrex test tube and 100 ml of the mixture (A and B) is added to it. The test tube is immersed in a constant level water bath which is kept boiling. The test tube is covered with loose glass bulb during boiling. After 3 h test tubes are taken out, cooled and transferred onto Gooch crucible and filtered with suction. The sample is washed, first with dilute sodium carbonate solution (5 g/l) and subsequently with hot water . The residue is then washed with solution C twice with about 5 ml each time. The residue is then finally washed with about 10 ml of 2N H_2SO_4. Distilled water is added. The filtrate and washings are collected and then titrated with N/100 cerric sulphate solution using ferroin (2-3 drops) as indicator until the colour changes from red to pale blue.

1000 ml of N/100 cerric sulphate = 0.000635 g Cu (reduced)

$$\text{Copper Number} = \text{B.R.} \times 0.000635 \times \frac{100}{0.125}$$

$$= \text{B.R.} \times 0.508$$

The cuprous oxide reduces ferric alum as follows :

$$Cu^{+} + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$$

and final titration with cerric sulphate involves the oxidation $Fe^{2+} \rightarrow Fe^{3+}$ [18].

16.10.3 Methylene Blue absorption test

Methylene Blue test can also be used to differentiate between oxycellulose and hydrocellulose. Methylene Blue is a cationic dye. Standard cellulose generally has no affinity for Methylene Blue, but oxycellulose with the formation of carboxyl groups confer an affinity and can be sorbed onto cotton. For this purpose, Methylene Blue absorption tests are carried out both at pH of 7.0 and at a pH of 2.7 (acidic). Two pieces of fabrics to be tested are taken and treated one with Methylene Blue at a pH of 2.7 and the other at pH 7.0. If oxycellulose is present, the material will absorb less dye in the acid than in the neutral solution, whilst reverse is the case if hydrocellulose is present. The degree of staining will indicate the extent of degradation.

In another method, 1g cation free sample is treated with 100 ml of Methylene Blue solution (10 m. moles/l) buffered in presence of potassium dihydrogen phosphate (0.625 m. moles/l) and NaOH (0.4 m. moles/l). The contents of the flask are agitated for about 18 h at room temperature. The solution is poured off from the

cellulosic sample and preferably centrifuged. The supernatent solution is suitably diluted to determine the absorbance at 620 nm. The loss in concentration of the dye in the treating solution is found out by referring to the calibration graph and the carboxyl content of the cellulose sample is calculated and expressed as m.eq/100g dry cellulose.

If a dyed material is under test, the stripping of dye will be necessary before the test can be carried out. Alternatively, degradation can be determined by titration using an anionic dye which precipitates Methylene Blue from solution.

Scoured and bleached American cotton have carboxyl contents of 0.8-0.9; Egyptian cotton 1.16-1.74. Unbuffered Methylene Blue solutions give lower values viz., 0.45 and 0.65 respectively. Methylene Blue absorption of cotton depends on the ash alkalinity of the cotton and the value decreases as the ash alkalinity decreases.

16.10.4 Silver nitrate test

This qualitative test is also referred to as Harrison's test since he was the first to describe it in 1912. The test specimen is either boiled or padded with a reagent containing a mixture of silver nitrate (1%), sodium thiosulphate (4%) and sodium hydroxide (4%) and then steamed. Those parts where degradation takes place due to oxycellulose or hydrocellulose in a fabric will be stained black or dark grey due to the formation of silver by reduction.

16.10.5 Determination of acidic groups by iodometric method

1 g of bone dry cation freed sample is treated with 50 ml solution [NaCl (A.R.) 50 g, KI (CP) 83 g, KIO_3 (CP) 21.4 g, sodium thiosulphate crystals 4.96 g dissolved in 2 litres of water] in a stoppered flask. To this 25 ml of CO_2-free distilled water is added. A current of CO_2-free air is also bubbled through the solution and water washing the bubbling glass tube with 25 ml CO_2-free distilled water, the flask is stoppered and kept for 24 h. The contents in the flask are titrated with 0.02 N iodine solution using starch indicator. The end point is indicated by the appearance of a faint blue colour.

$$\text{Carboxyl content (m. eq. COOH/100g)} = \frac{1 \times (a - b) \times N \times 100 \times 1000}{1000 \times W}$$

where, a and b are the titration readings for blank and sample,
N = normality of iodine solution,
and W = bone dry weight of the sample.

16.11 Assessment of Damage of Wool

Wool fibre during its various pre-treatment stages also undergoes some kind of damage, the extent of which may be assessed by both physical and chemical methods. The very multiplicity of tests available is in itself evidence of the lack of a universal method for assessment of damage [19].

16.11.1 Microscopic test

Modification of the external scale structure of wool by chemical treatment can be examined visually with the aid of microscope.

Wool is immersed in a dilute solution of Methylene Blue (0.4 g/l) for 1 min and washed in water for 5 min and finally dried. The stained fibres are then cut into short lengths of about 1 mm and then mounted in a liquid paraffin and examined under microscope of about × 200. The degree of damage is then expressed in comparative numerical terms depending on the extent of staining.

Alternatively, damage to the outer layers (epicuticle) may be revealed by means Allwörden reaction [20]. When wool fibres are immersed in chlorine or bromine water, bubbles or blisters known as Allwörden sacs are formed on the surface. Damage to the fibre surface may show up by lessening the size of or eliminating altogether, the blisters. This test is particularly useful when damage caused by alkali treatment is severe.

16.11.2 Swelling test [21]

Wool fibre is immersed in a solution of sodium monohydrogen and dihydrogen phosphate at a pH of 5.95 for 1 h at 20°C. The samples are then centrifuged to remove the entrained liquor and then weighed wet and afterwards dried thoroughly and reweighed. The ratio of the weight of absorbed water to that of dry fibre i.e. retention of water will give the degree of swelling. The alkali solution will rupture the disulphide bonds in the polypeptide chains and thus the extent of swelling will give some idea of damage in wool.

16.11.3 Solubility test

In this method the amount of wool capable of being dissolved with a solution, which rupture the disulphide cross-links, is determined. Essentially it is a test which detects main chain breakage caused, most often, by action of acids on wool [21,22].

1 g wool (oven dry) is treated with 100 ml of 0.1 N solution NaOH at 65°C for 1 h. The sample is then rinsed with 2 litres of distilled water and dried to constant

weight at 105°C. The alkali solubility is then determined as the loss in weight of the test specimen expressed as percentage. Normal wool is expected to have about 12-13% solubility and values greater than 18% may be taken as suggesting that the sample has been damaged.

In the Krais-Viertel reagent test the wool is immersed in a solution of ammonia in caustic soda [23]. The test entails timing of the appearance of the characteristic swellings in this reagent. When the fibre has been damaged with acid, the time for appearance is decreased.

In the urea-bisulphite solubility test [24], wool is treated with a solution of urea (50%) and sodium bisulphite (3%) (pH adjusted to 7) at 60°C for 1h and then the residue is washed and dried till constant weight is obtained. Urea breaks the hydrogen bonds and bisulphite attacks the disulphide bonds in wool. Solubility in this method depends on the wool which had been treated in acidic or alkaline pH.

16.11.4 Spectrophotometric test [25, 26]

1g sample is extracted with 10 ml solution comprising isopropanol : pyridine : water 5:5:90. 2 ml of the wool extract solution is then reacted with 2 ml of ninhydrin solution (21.02 g NaOH, 62.4 ml propionic acid and 30 ml distilled water. After cooling 125 ml of methyl cellosolve and 18.75 ninhydrin is added and dissolved and the solution is made up to 250 ml) in capped test tube at 100°C for about 8 min. After reaction the solution is made up to 50 ml and the absorbance is measured in spectrophotometer at 570 nm against blank ninhydrin solution that contain no wool extract solution. The absorbance reading for the extract from the original clean wool is zero. The absorbance reading for the ninhydrin/wool extract reaction is directly related to the damage caused by sulphuric acid. The results correlate well with both alkali solubility and tensile strength test methods.

16.12 Determination of Degree of Mercerization

The effect of mercerization depends on the conditions of mercerization. A quantitative assessment of the degree of mercerization is carried out mainly in three different ways i.e. variation in the mercerized product, external appearance (lustre) and internal appearance (x-ray diagram) etc [26].

16.12.1 Determination of deconvolution count [27]

In this method cotton hairs are cut in large number of hair fragments 0.2 mm long. They are then mounted in liquid paraffin on a microscopic slide, and then

counted the proportion of fragments free from twist on convolution during mercerization. The result is expressed as percentage and is called "Deconvolution Count". If the figure is above 20, the fabric is mercerized. The ratio of the two sets of data may be used to estimate the degree of mercerization. The disadvantage of this method is that the extent of deconvolution is influenced by the maturity of cotton and by the structure of material that is twist of the yarn or weave of cloth.

16.12.2 Determination of swelling index [28]

Untwisting number of single yarn can give reliable means for estimating degree of swelling of cellulose in non-polar liquids such as carbon tetrachloride and benzene. Strong alkali solution and cadoxen (cadmium ethylene diamine complex of 3.6%) also causes large amount of untwisting. In this method, the yarn together with the weight (0.8 g) is hanged into the measuring cylinder containing sufficient amount of solvent as to dip the upper end of the yarn. The yarn is then allowed to untwist and the number of revolutions made by weight are measured for 3 min.

$$\text{Swelling index} = \frac{\text{Untwisting number in solvent}}{\text{Untwisting number in water}}$$

Swelling index increases with degree of mercerization. In this method there is no necessity of untreated sample.

16.12.3 Benzopurpurine test

In this method mercerized and unmercerized cotton samples are treated in a 0.5% solution of Benzopurpurine for 30 min at boiling temperature. The treated samples are then washed, dried and compared visually or spectrophotometrically. The mercerized sample is always more deeply dyed than the unmercerized. However, it is recommended that a standard swatch be calibrated so that the actual degree of mercerization can be assured.

16.12.4 Sodium hydroxide spotting test

In this method the undyed fabric is spotted with 30% solution of caustic soda and then both mercerized and undyed spotted fabric samples are dyed by using Benzopurpurine. If the fabric is fully mercerized, the spots will not be evident after dyeing. On the other hand, if the fabric is not mercerized or semi-mercerized, dark spots will be evident and the degree of mercerization can be evaluated on comparing the spots.

16.12.5 Goldthwait Red-Green test [29]

In this test a mixture of red and green direct dyes is used to compare the maturity of cotton fibre samples. Immature fibres dye red, and mature fibres green. Mercerization increases the fibre's affinity for green compound and ''causticization number'' can be assessed related to the strength of the green hue. Fabric treated with liquid ammonia ''under industrial mill condition'' dyes red.

16.12.6 Staining test

The fibre is immersed in iodine solution (20 g iodine in 100 ml of standard KI solution) for 3 min and rinsed thoroughly. Mercerized cotton is stained bluish black and unmercerized cotton remains white. Cotton fibres in the yarn bundle can be counted using a microscope and the ratio of dyed to undyed fibres can be used to determine the degree of mercerization. The iodine sorption value shows the largest increase for those samples treated in liquid ammonia with NH_3 removal by evaporation, followed by caustic mercerized samples, and last by those samples NH_3 treated and water quenched. Generally only minor differences in iodine sorption value are found between samples mercerized slack or under tension.

In another method [30] fabrics treated with several concentrations of NaOH are immersed in a mixture of 1.3 g/l Telon Fast Red AF-3G 150% (BAY), a low molecular weight acid dye, C.I Acid Red 151 and 1.4 g/l Benzo New Blue GS 140% (BAY), a large molecular weight direct dye, C.I. Direct Blue 10, liquor ratio 70:1 at pH 2 using H_2SO_4 for 10 min cold followed by washing off. Untreated cotton is stained red and becomes progressively bluer with increase in NaOH concentration.

16.12.7 Barium activity number [31-33]

Mercerized sample absorbs barium hydroxide (alkali) to a greater degree than sodium hydroxide and from practical point of view, barium hydroxide is more easy to estimate. The ratio of uptake for this reagent has been referred to barium activity number.

2 g mercerized and unmercerized samples are placed separately in two conical flask containing 30 ml of N/4 barium hydroxide and left for 2 h or preferably overnight. 10 ml of clear solution is withdrawn and titrated against N/10 HCl using phenolphthalein as indicator. A blank titration is also carried out on the measured barium hydroxide solution using Methyl Red as indicator.

$$\text{Barium activity number} = \frac{b - s}{b - u} \times 100$$

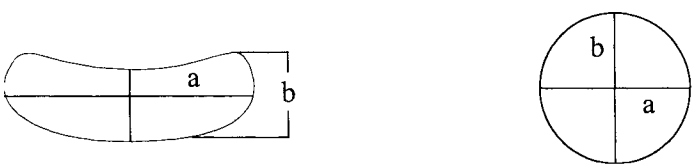
where, b = ml required for blank test,
s = ml required for mercerized cotton,
u = ml required for unmercerized cotton.

For exact estimation, correction should be made for the moisture regain of the sample. Barium activity number of unmercerized cotton is considered as 100 and semi-mercerized cotton ranges between 115 to 130 and that for completely mercerized cotton is about 155.

16.12.8 Determination of lustre [34, 35]

Pulfrich photometer, the Gorez Glarimeter comparative glass method and microscopic examination of cross-section of fibre are the qualitative methods for the assessment of degree of mercerization.

Mercerization increase the lustre and reduces the axial ratio (Fig. 16-3). Micro-



Before mercerization After mercerization

Figure 16-3. Cross-section of cotton fibre before and after mercerization.

scopic examination shows that the corss-section of the cotton fibre changes from eliptical to circular form due to mercerization. This can be measured as a ratio of two axes 'a' and 'b'. The axial ratio (a/b) of unmercerized cotton is about 2.2 to 2.6, whereas that of mercerized cotton is about 1.5 to 1.6. Caustic mercerized samples appear to give superior lustre than ammonia treated fibre.

The measurement of specular reflectance is considered as an accurate evaluation of lustre. Lustre can be determined from reflectance measurements with incident light inclined at 45°, the reflected light is measured either perpendicularly to the surface of the material (diffuse reflectance) or viewed at 45° symetrically to the incident light (specular reflectance). Lustre is therefore defined by the contrast ratio of the specular to diffuse reflectance [36, 37].

16.12.9 X-ray analysis

X-ray photograph of native cellulose (unmercerized) reveals the presence of two arcs close together and inside the prominent 002 arc. These reflections are

from $10\bar{1}$ plane and 101 plane, the latter being nearer the centre of the photograph. They are not as intense as 002 arcs. In case of completely mercerized or regenerated cellulose, X-ray photograph shows a change in position of two shorter arcs. The $10\bar{1}$ arc is much nearer to 002 arc and 101 arc is nearer the centre of the photograph. On the basis of this estimations it is estimated that mercerizing efficiency seldom exceeds 60-70% for yarn and 35-40% for cloth.

16.12.10 Infra-red analysis

Determination of infra-red crystallinity index at different wavelengths (1429 cm^{-1}/893 cm^{-1}) by the usual base line technique can be used [38]. When cellulose-II samples are considered, the 1372 cm^{-1}/2900 cm^{-1} ratio is more reliable index [39, 40]. A rapid method for estimation of the degree of mercerization has been developed using a near IR diffuse reflection technique [41].

16.13 Evaluation of Whitening Efficiency of Optical Brighteners

The estimation of optical whiteners in substrate is really a difficult problem, but the qualitative and quantitative estimation of fluorescent brightener in solution by examination of absorption and/or emission spectra have been detailed [42-46]. Since the brightener will differ in substantivity for a particular substrate with differences in their chemical structure, cost comparisons of performance can only be based upon evaluation of the treated substrates. Various techniques for such evaluation have been described [46-51].

16.13.1 Visual assessment

Visual assessment of a white object is based on a comparison of the test sample with a standard sample. A viewing angle of 45° is generally recommended and the position of the samples are changed several times during the test. Out of many white scales, Ciba-Geigy's ''Cotton white scale'' occupies a prominent position [52].

16.13.2 Extraction method

Generally optical brighteners on cotton are extracted from the fabric by suitable solvent like pyridine. The absorbance of the extracted solution of optical brighteners of unknown concentration is determined by using a uv-spectrophotometer, and by referring the calibration graph, the unknown concentration is determined. Optical brighteners can also be determined by extraction with alkaline cadoxen solution within narrow limits [53] and with relatively large errors (> 20%) in the uv range

[54]. This must place some doubt on results of fluorescent brightening agent concentrations determined in this way. A similar technique is also used to determine fluorescent brightening agents on nylon and acetate fibres [55]. A m-cresol-methanol mixture is used as solvent for nylon fibres and DMF for the acetate fibres. Extraction with a DMF-water mixture is recommended for cellulosic fibres.

16.13.3 Instrumental assessment

Thin-layer chromatography, tristumulus filter photometer and spectrophotometer are the most popular techniques for seperation, identification and quantitative analysis of fluorescent brightening agents, although some other instrumental techniques have been developed [56]. Spectrophotometers simply measure spectral reflectance, from which tristumulus values are calculated on the basis of spectral energy distribution of the light source and the C.I.E. spectral tristumulus values function . The L*, a*, b* values for the standard reference substrate and the sample are determined. The former values are substracted from the latter to get ΔL^*, Δa^* and Δb^* values. This determines the whiteness and tonal differences. The results obtained by this method are not always with full agreement with the results of subjective evaluation, and therefore it is used as an auxiliary method, especially in the determination of the concentration of the brightening agent on fibres.

16.14 Determination of the Degree of Heat-setting

16.14.1 Shrinkage test

Normally a square area is drawn on the heat-set material and measured. The marked cloth is boiled in soft water in the washing wheel for 30 min, centrifuged and air dried. The dimensions of the square are measured without ironing the dried fabric and the shrinkage is determined. A well set fabric should not show more than 1% residual shrinkage.

16.14.2 Crease-recovery angle

The determination of crease recovery angle before and after heat-setting of the fabric is done. The extent of crease-recovery of heat-set fabric before and after setting at and above 170-175°C will give idea of the degree of heat-setting.

16.14.3 Assessment of handle

Assessment of handle before and after setting gives an idea of the degree of heat-setting. In general, fabric becomes stiff after heat-setting. Stiffness is measured by bending length and compared with that of the unset fabric. The narrower

the difference of bending length between the set and unset fabrics, the better the setting.

16.14.4 Iodine absorption method

The degree of heat-setting of polyester fabrics can be correlated with their iodine absorption value. Heat-setting under industrial conditions in a taut form reduces the amorphous content of synthetic fibres. So, there will be a decrease in iodine sorption and increase in critical dissolution value [57].

16.15 Determination of Biodegradability of Surfactants [58]

The efficiency of a sewage treatment is often expressed as the percentage removal of the BOD, less often in terms of COD removal. Dividing the percent removal of the surfactant by the percent removal of the BOD or COD gives the biodegradability index of the surfactant.

The procedure for alkylbenzenesulphonates (ABS) and linear alkylbenzenesulphonates given by the soap and detergent association involves both a presumptive and a confirmatory test.

In the presumptive test, a nutrient medium, to which 30 mg/l test surfactant has been added, is inoculated with micro-organisms in a culture flask and aerated by a reciprocating shaker at 128 two-four inch strokes / min at 25 ± 3°C. After two 72 h adaptive transfers, in which 1 ml of the 72 h culture is transferred to 100 ml of a fresh nutrient medium plus surfactant, samples are taken at zero time, i.e. immediately after inoculation and mixing and on 7th and 8th days. A blank under the same conditions but without the surfactant is carried out side by side. The samples are then tested for the active content by the Methylene Blue method. If analysis is not done immediately, 1 ml formaldehyde per 100 ml should be added as preservative. If the percent degradation is less than 80, the sample is non-biodegradable. If above 90, the sample is biodegradable and in this case no further test is necessary. A value of 80-90% indicates the necessity of carrying out a confirmatory test. Although presumptive test is simple and inexpensive it suffers from the disadvantage in that it takes 14 days in all and that it does not measure rate per day or per hour, but only total degradation in one week.

In the confirmatory test, activated sludge from a domestic sewage treatment plant, test surfactant (20 mg/l) and synthetic sewage of composition

Glucose	13.0 g
Neutrient	13.0 g
Beef extract	13.0 g
K_3HPO_4	13.0 g
$(NH_4)_2SO_4$	2.5 g
Tap water	1 litre

are mixed in a specially designed vessel, brought to a steady state and aerated for 23 h. After 1 h settling, supernatant liquid is withdrawn and the same amount is replenished with synthetic sewage containing 20 mg / l surfactant. This is repeated for a minimum of 15 days after which the active content is determined by Methylene Blue method. The confirmatory method suffers from the disadvantage that the testing time exceeds the normal retention time in an activated sludge system in sewage plants.

16.15.1 Methylene Blue method

A 10 ml aliquot of a solution containing 0.625 g of 100% active content in 500 ml is pipetted in a 100 ml graduated glass stoppered cylinder and 25 ml of aqueous methylene blue indicator (The indicator is prepared by pipetting 10 ml of 0.3% solution of methylene blue hydrochloride into 500 ml water, adding 12 g concentrated H_2SO_4 and 50 g Na_2SO_4 and then diluting to 1 litre) and 15 ml of chloroform added. The solution is then titrated with 0.004 M cetyl pyridinium bromide, shaking mixture vigorously for 3 min after each addition. As the titration continues there is a slow transfer of blue colour from chloroform to aqueous layer. When the colour of the two layers has equalised the end point is reached.

$$\text{Active ingredient, \%} = \frac{a \times b \times m \times 5}{w}$$

where, a = ml of titrant consumed,
b = molarity of above solution,
m = molecular weight of active ingredient, and
w = weight of sample in g.

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