Investigation of Fibre Protection and Water Saving in the Wet Processing of Textiles

A thesis submitted to the University of Manchester for the degree of

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Abstract

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The aim of this research was to minimize the damage of textile fibres (wool and cotton), in the wet processing, such as bleaching and dyeing, and also seek to reduce fresh water usage during these processes.

Typically bleaching of textiles involves the application of oxidative and reductive whitening agents. However a detrimental side-effect is a reduction in their strength. Therefore the approach to developing robust processes is to optimize the chemical treatments and incorporate protective agents in to the treatment baths. This study has demonstrated the application of fibre protective agents were successful in maintaining fabric strength, as defined by flat abrasion, without affecting the improvement in fabric whiteness for both wool and cotton. While the protective mechanism for wool is probably based on restricting damage to the cell membrane proteins and minimizing internal lipid loss, the protective effect on cotton is less certain.

Colouration of wool requires elevated temperatures through boiling of aqueous treatment baths or steaming after printing. In this study the effect of blank dyeing of wool fabrics was examined and the extent of hydrothermal damage and yellowing established. In addition the potential effect of fibre protective agents, such as protein hydrolysates and formaldehyde-based agents, were assessed and their benefits in terms of fabric tensile strength, colour, mechanical properties related to fabric handle, and abrasion resistance determined. It was demonstrated that both protective agents offer fibre protection as individual additives and co-applicants.

Fresh water is a vital component in the processing of textiles. However water is a scarce commodity and the need for efficient use of it is important. Therefore in this study the use of simulated seawater as an alternative processing medium for bleaching and colouration was evaluated. It was found alkaline hydrogen peroxide bleaching of wool and cotton could be performed successfully in the seawater and benefits in terms of good whiteness and improved abrasion resistance achieved. Building on the previous fibre protection study the incorporation of Byco C into the salt water bleach bath was evaluated and flat abrasion strength benefits again demonstrated.

In this research a modified paper-based filter was be used as the "clean" industrial textile water effluent. Initially the filter paper based on poultry feathers was evaluated. The keratinous byproduct/waste material offers a cheap potential source of fibre and was successfully converted into paper. The strength and dye adsorption properties of the papers filters were assessed and it was observed that the important wet strength was considerably improved by the application of a cationic reactive polymer. Novel C_{30}-modified PVP based nanofibres were force spun and as evaluated as a dye absorbent for Direct and Disperse dyes. The nanofibre web offered significant potential for absorbing the comparable non-polar disperse dyes.

Declaration

No portion of this work has been submitted in support of any application for another degree or qualification of this or any other University or other institution of learning.

Bo Ning

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Chapter 1

Introduction

This chapter will introduce the textiles, chemicals and other materials employed in this research, as well as the related theories and background, and also the aims and objectives of this thesis.

1.1 Wool and cotton

1.1.1 Wool

Wool is the hair acquired from the skin of a sheep, and it is the most important animal fibre in the textile industry by far. Global wool production is approximately 1.3 million tonnes per year, which accounted for about 2.3% of total world fibre supply in 2003 [1].

1.1.1.1 Wool production and classification [2-4]

The quality of wool is determined by fibre diameter, crimp, yield, colour, and staple strength. Fibre diameter is the most important feature that determines the quality and price. The fineness of wool is classified as in Table 1.1:

Table 1.1 Wool classified by fibre diameter [5]

Classes	Fibre diameter Microns (1 microns=1/1000 mm)
Fine merino wools	17-20
merino wools	20-24
fine crossbred	24-28
medium crossbred	28-37
coarse crossbred	Over 37

The most important breed of sheep producing premium wools today is the Merino, originally from Spain, for the merino wool is the finest and softest wool available. Australia is the world's largest producer of wool, accounting for 27% of the world's greasy wool in 2003/2004. China, United States, New Zealand, Argentina, Turkey, Iran, United Kingdom, India are also important wool producing countries [1].

1.1.1.2 Fibre morphology of wool [2, 3, 6]

Fine wool fibres consists two kinds of cells, cuticle cells and cortical cells. Cuticle cells form the outer layer of the wool fibre and protect the wool fibre from external influences. Cortical cells account for approximate 90% of the weight of the whole fibre and there are mainly two types, the orthocortex and paracortex. The cuticular and cortical cells are separated by the cell membrane complex (CMC) which is composed of lipids and proteins. The cortical cells themselves contain smaller structural units called macrofibrils, which in turn are composed of microfibrils [2]. In coarse wool there is a third type of cells, the medulla, usually in the centre of the fibres, which is a cause of weakness in the fibre. It disappears as the quality of wool is improved [6]. The complex morphological structure of the wool fibre is shown in Figure 1.1.

1.1.1.2.1 The cuticle

The main feature of the cuticle is that the cuticle cells are overlapping in one direction, pointing from root to top [7]. Each cuticle cell is a nearly rectangular sheet, slightly bent, with a width of about $20\,\mu m$, a length of $30\,\mu m$, and a thickness of $0.5–0.8\,\mu m$ (at the scale edge). From cross-sections of about 50 fibres, it was determined that the weight fraction of the cuticle with respect to the whole fibre is between 6 and 16% [2]. The cuticle cell consists at least of four layers, the epicuticle, the A-layer and the B-layer of the exocuticle, and the endocuticle. The epicuticle is the outermost layer of the cuticle cell. It is a very thin membrane (3-6nm), which accounts only about 0.1%

for the weight of the wool fibre. It contains 78% protein, 5% lipids, 4% ash and a negligible amount of carbohydrate [8]. The next layer, the exocuticle, which represents about two-thirds of the cuticle consists of cystine-rich, highly crosslinked protein, and the A-layer is correspondingly more crosslinked than the B-layer. The endocuticle has the lowest cystine content and contains the non-keratinous protein, so it is more permeable to water and other reagents [2].
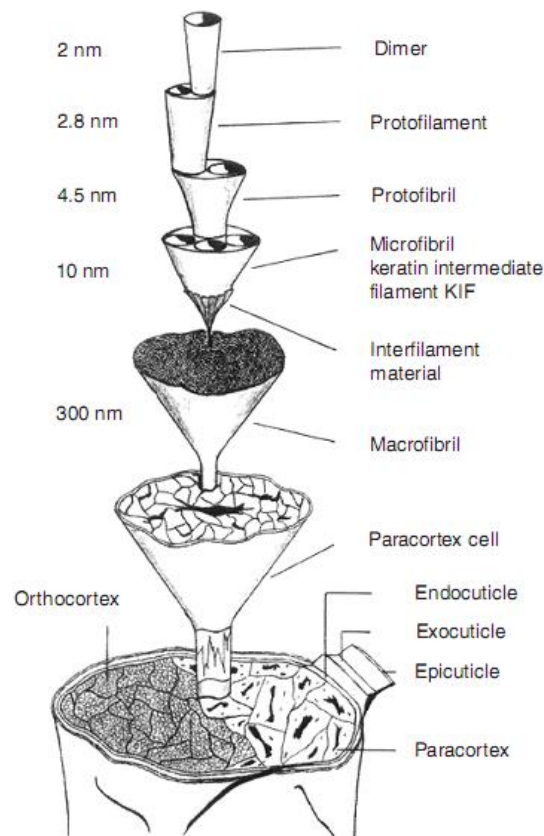
Figure 1.1 Morphological structure of the wool fibre [3]

1.1.1.2.2 The cell membrane complex [9, 10]

The function of the cell membrane complex (CMC) is to "hold" the cuticle and cortical cells together. It is about 25nm thick, and composed of lipids and proteins. The cell membrane complex is mechanically weak and can be easily modified by

chemical or mechanical action. It also provides a channel for aqueous chemicals to more easily penetrate the fibre and bypass the hard, cross-linked impermeable cuticle. The fibre may be disintegrated into individual cell by attacking the cell membrane complex with enzymes or formic acid.

1.1.1.2.3 The cortex

The cortex is the principal fibre component, which consists over 90% of the whole fibre. In many types of wool the cortex shows a bilateral structure, approximately half of the cross-section is formed of ortho-cells, whilst the remainder consists para-cells. The bilateral structure increases the differential dye-affinity and differential swelling of the wool fibre [7]. The para-cells contain a larger amount of sulphur than the ortho-cells and hence being tougher and more highly cross-linked, as clearly seen upon staining with silver nitrate and transmission electron microscopical inspection. The paracortex is always located on the inside and the orthocortex on the outside of the crimp wave. The cortex is composed of spindle-shaped cells with a length of 45–95 μm and a width of 2–6 μm, which give the wool its strength [11, 12].

1.1.1.2.4 The macrofibrils [13]

Each cortical cell is composed of 5–20 macrofibrils at the widest point, which are about 100–300nm wide. Macrofibrils are the main morphological component of the cortex cell, which account for about 85% of the mass.

1.1.1.2.5 The microfibrils [14]

The macrofibrils are composed of bundles of 500–800 highly organized, rod-like microfibrils (7-8nm in diameter), packed in an amorphous matrix, and are also called intermediate filaments (IFs).

1.1.1.3 Chemistry of wool

Wool is an animal fibre that is primarily composed of a group of proteins known as keratins, which consist of carbon, hydrogen, oxygen, nitrogen and sulphur. The concentration of sulphur is at least 2% in the keratins. When the wool is unwashed or greasy it also contains wool fat and suint or yolk. However on scouring/cleaning the wool still is not pure protein but rather typically is formed of 97% wool proteins, 2% structural lipids and 1% inorganic compounds, nucleic acids, and carbohydrates [6].
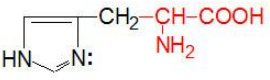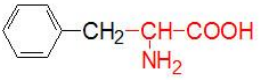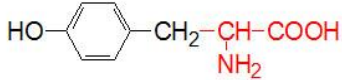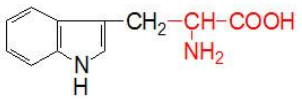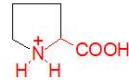
1.1.1.3.1 Amino acids of wool

There are many types of proteins present in the wool. The basic structural units of proteins are α-amino acids, which have the general formula in Figure 1.2 [3]. The proteins may be separated by chemical fraction into multi-membered protein classes, which can be distinguished by their characteristic amino acid composition. More than 20 amino acid residues are found in wool, which are characterized by their side chain groups (R). The side chain groups indicate influence the character of the amino acid, for example whether it is hydrophilic or hydrophobic, or acidic or basic [14].
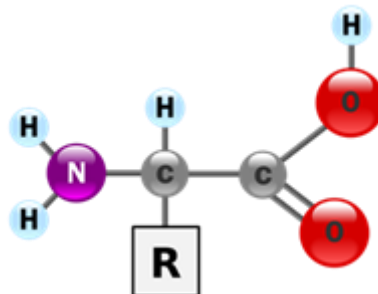
Figure 1.2 The general structure of an α-amino acid [3]

Table 1.2 Amino acids in wool [14]

Amino Acid	Structure	Amino Acid	Structure
Glycine	H–CH–COOH NH$_2$	Glutamic Acid	HOOC–CH$_2$–CH$_2$–CH–COOH NH$_2$
Alanine	CH$_3$–CH–COOH NH$_2$	Glutamine	H$_2$N–C–CH$_2$–CH$_2$–CH–COOH O NH$_2$
Valine	H$_3$C CH–CH–COOH H$_3$C NH$_2$	Arginine	HN–CH$_2$–CH$_2$–CH$_2$–CH–COOH C=NH NH$_2$ NH$_2$
Leucine	H$_3$C CH–CH$_2$–CH–COOH H$_3$C NH$_2$	Lysine	H$_2$N–(CH$_2$)$_4$–CH–COOH NH$_2$
Isoleucine	H$_3$C–H$_2$C CH–CH–COOH H$_3$C NH$_2$	Histidine	CH$_2$–CH–COOH NH$_2$
Serine	HO–CH$_2$–CH–COOH NH$_2$	Phenylalanine	CH$_2$–CH–COOH NH$_2$
Threonine	H$_3$C CH–CH–COOH HO NH$_2$	Tyrosine	HO–⬡–CH$_2$–CH–COOH NH$_2$
Cysteine	HS–CH$_2$–CH–COOH NH$_2$	Tryptophan	CH$_2$–CH–COOH NH$_2$
Methionine	H$_3$C–S–(CH$_2$)$_2$–CH–COOH NH$_2$	Proline	COOH
Aspartic Acid	HOOC–CH$_2$–CH–COOH NH$_2$	Cystine	2 x Cysteine
Asparagine	H$_2$N–C–CH$_2$–CH–COOH O NH$_2$		

The amino acids in wool can be broadly classified, Table 1.2, as non-polar with hydrocarbon side chains, including alanine, phenylalanine, glycine, valine, leucine and isoleucine. This imparts to wool hydrophobic character and generally has low chemical reactivity. In addition there are amino acids containing polar hydroxyl groups in their side chains, such as serine, tyrosine and threonine, and are chemically more reactive and hydrophilic. There are also acidic amino acids such as glutamic acid and aspartic acid, and basic amino acids such as lysine and araginine.

The proportions of acidic and basic groups as the side chain in the amino acid residues are approximately the same (800-850μmol/g) in wool [2], which is important for the fibre strength and cohesion. The aspartic and glutamic acids contain acidic carboxyl groups, while histidine, arginine and lysine contain imidazole, guanidino and amino functional groups. These side chains provide the most important effect on the reactivity of wool, especially in the dyeing properties.

Wool has a high content of sulphur, which is mainly derived from the amino acid cystine. The amino acid cystine has two sulphur atoms forming a disulphide bond [-S-S-], mainly between different protein chains or occasionally between different parts of the same protein chain, Figure 1.3. This is the most important crosslinking element of wool. In their ionised state, a deprotonated carboxylic acid group may be regarded as basic, and a protonated amino group as acidic.

1.1.1.3.2 The polymer system of wool

Proteins are formed by the condensation of *L*-α-amino acids via their carboxyl and amino groups so that amino acids are linked to form polymer chains by amide, or peptide – CO-NH- bonds. The various types of crosslinks and bonds, by which the individual peptide chains are held together, are shown in Figure 1.3 [3]. Hydrogen bonds, ionic bonds (or "salt linkages") and hydrophobic bonds are non-covalent, secondary (additional) bonds, which can occur within a single protein chain or between different chains. These bonds act like cross-links and make an important

contribution to fibre properties: ionic "salt links" exert maximum influence in the iso-ionic region; hydrophobic interactions and hydrogen bonding are strongest at low temperatures [3, 15]. However, maximum stability of the protein composite is imparted by covalent cross-links and these bonds are only cleaved under relatively severe conditions [15, 16]. The most thoroughly characterised cross-links in wool are the disulphide bonds, which stem from the incorporation of cystine residues (two cysteine linked via the thiol functionalities. The cystine inter-chain cross-links are responsible for the greater stability and lower solubility of keratin in water and other polar solvents, compared with most proteins. The second type of covalent cross-link in wool is the isopeptide bond, which may occur between the α-amino groups of lysine and the β- or γ- carboxyl groups of either aspartic or glutamic acid.

The ordered α-keratin and β-keratin structures are found regularly packed in the crystalline regions, which make up 30-40% of the fibre. These crystalline regions are embedded in an amorphous matrix (60-70% of fibre), which is highly cross-linked. Three distinct fractions of keratinous proteins have been identified in wool. The distribution of these proteins varies between the morphological components causing regions of the fibre to differ in their physical and chemical properties.

Low sulphur proteins make up 58% of the fibre and have an average sulphur content of 1.5%. They are mainly found in the crystalline regions since they are the only family of proteins with α-helical character.

High sulphur proteins make up 18% of the fibre and have a sulphur content of 5%. 8% of the fibre protein is composed of ultrahigh sulphur protein with a sulphur content of 8%. The high sulphur proteins are located in the amorphous regions of the fibre.

A third fraction contains high glycine-tyrosine proteins, which make up 6% of the fibre and their sulphur content is about 0.5-2%. Non-keratinous proteins, which make

up 17% of fibre mass are low in cystine and are easily degraded since they are only slightly cross-linked. In wool they are found as a network structure embedded in the keratinous proteins and are the chemical and physical weak regions of the fibre.
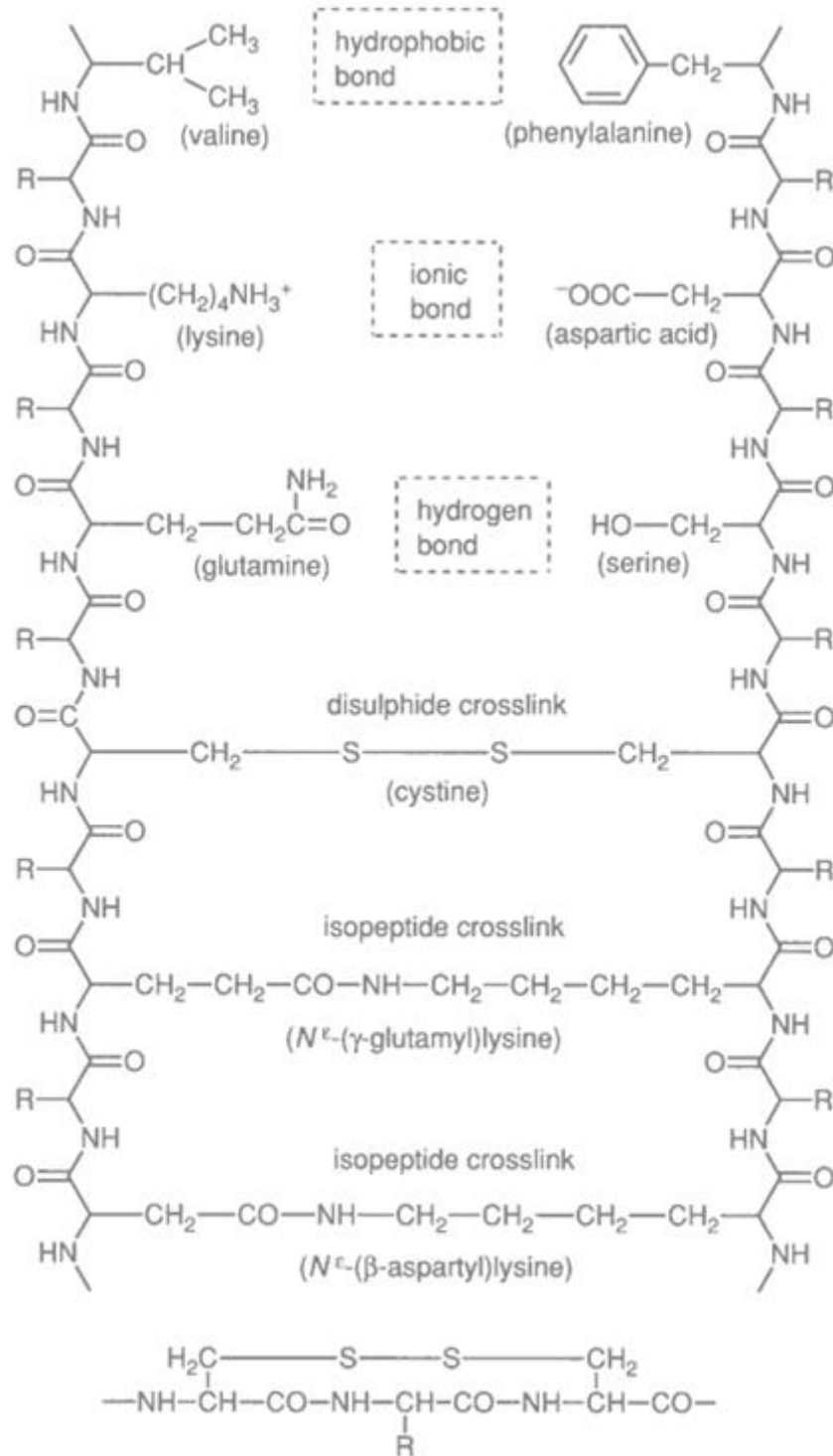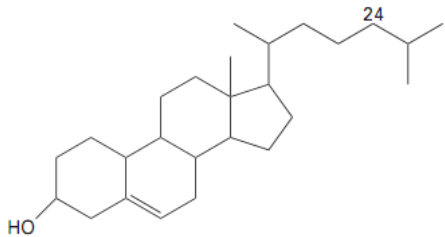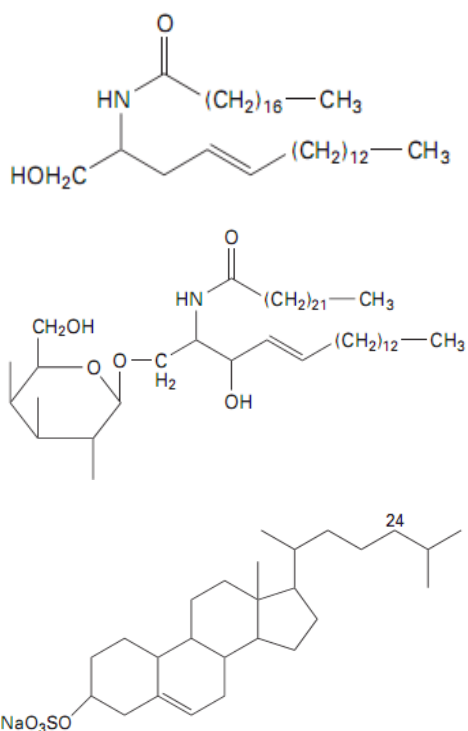
Figure 1.3 The main interchenic and intrachenic types of bonds in wool [3]

1.1.1.3.3 Wool lipids [17, 18]

Wool lipids include external and internal lipids. The external lipids are non-polar and almost all removed by scouring. Internal lipids consist of three major lipid classes: sterols (about 40%), polar lipids (about 30%) and fatty acid (about 25%) [14].

Table 1.3 Wool lipids [14]

Class/Name	Formula
Fatty acids	
Palmitic acid	$CH_3—(CH_2)_{14}—COOH$
Stearic acid	$CH_3—(CH_2)_{16}—COOH$
Oleic acid	$CH_3—(CH_2)_7—CH=CH—(CH_2)_7—COOH$
Protein bound fatty acid 18-Methyleicosanoic acid	$CH_3—CH_2—CH(CH_3)—(CH_2)_{16}—COOH$
Sterols Cholesterol Desmosterol (= 24-Dehydrocholesterol)	
Polar lipids Ceramide	
Cerebroside (Sphingolipid)	
Cholesterol sulphate	

The wool lipids have a great influence on the fibre properties although only present in small proportions. In particular, one fatty acid, 18-methyl eicosanoic acid (18-MEA), appears to be located as a surface layer and cannot be removed by exhaustive extraction with chloroform/methanol mixtures. It is likely to be attached to the cell surface proteins through ester or thioester linkages. It is considered a "Structural lipids of the wool fibre" [17, 18].

1.1.1.4 Structure and composition of the wool fibre surface and associated physicochemical properties

Historically, the epicuticle has been regarded as a unique component of the wool fibre but now it is known to be part of the resistant membrane system that surrounds all cuticle and cortical cells. The epicuticle of natural keratin fibres has an exterior lipid layer called the F-layer, which is regarded as an integral part of the proteinaceous epicuticle. The F-layer consists of palmitic (C16), stearic (C18), oleic (C18:1), eicosanoic (C20:1) and 18-methyleicosanoic acid (18-MEA), the latter being the main component of this fraction, 18-MEA represents approximately 70% of this layer by weight.

Epicuticle protein and lipid matrix
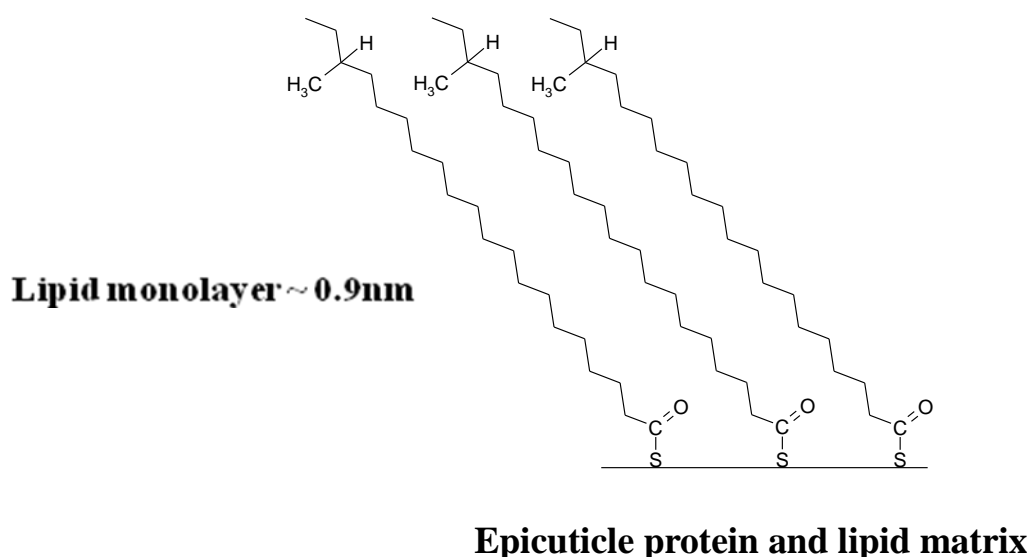
Figure 1.4 Model showing the arrangement of the protein and lipid components comprising the fibre cuticle surface membrane [19]

The fatty acids are linked through a thioester bond to cysteine residues or less commonly through an oxygen ester bond to serine or threonine residues. Some authors used the term fibre cuticle surface membrane (FCUSM) to describe the outermost surface layer of the mammalian fibres [19-21]. The diagram presented in Fig 1.4 shows this model, which consists of a monolayer of fatty acids linked to an underlying layer of highly cross-linked protein [19]. This model assumes a thickness of the surface layer (FCUSM) of approximately 6nm. Despite the wide range of estimates, it is generally agreed that the thickness of this surface layer is between 2 and 7nm. An interesting observation was that with fine fibres, more MEA is covalently bound than that theoretically required to form a monolayer on the surface [22]. In fine (16μm) Australian Merino wool fibres, the relative proportion of MEA is approximately 70% by weight of the bound fatty acids. It was also reported that as the fibre diameter increases (for a single-cuticle fibre) the amount of bound MEA as a proportion of total bound fatty acids decreases, approximately in a linear relationship, to 55% by weight for a 35μm fibre [22].

The importance of this lipid layer, particularly 18-MEA, has been extensively reviewed in terms of the hydrophobic character of the epicuticle [18, 23]. It functions as a highly resistant, hydrophobic, surface-protective barrier to water, and to attack from other chemical and biological agents. It has been also suggested that the bound lipids control not only the flexibility of the cuticle cells in itself but also the permeability of water into the cortex, and consequently play an important role in the hygroscopic control of the bulk fibre [18]. It must be emphasized that in spite of the FCUSM being a relatively minor component of mammalian fibres, its function in protection, wettability, friction and surface tension are crucial to the successful performance of fibres in the natural environment. Furthermore, this membrane is of increasing importance in industrial aspects of wool processing and fibre-damage considerations of human hair in the cosmetic industry. In the cosmetic industry, fibre damage in human hair is often associated with this membrane [18]. The function of

the MEA is still not fully understood, but considering its unusual occurrence together with the additional energy required by the cell to produce such a unique branched-chain rather than an abundant straight-chain fatty acid (e.g. palmitic acid), specific roles for this fatty acid are expected. It has been suggested that the methyl branch near the terminal (i.e. at the hydrophobic end) of the fatty acid could aid in improving the hydrophobic "umbrella" at the surface, especially given that a limited number of cysteine residues are available for covalent bond (thioester) formation in the underlying protein layer [20]. Also the existence of the branch may render the hydrophobic layer more resistant to biological degradation. 18-MEA is found to be sensitive to a number of surface oxidation processes, namely photo-oxidation [24], UV-irradiation and corona treatment [25], chlorination and plasma treatment [22, 26, 27], fluorination, UV/ozone treatment [26], bleaching [28, 29] and scouring and dyeing [22]. In all cases a decrease in 18-MEA was observed together with an associated increase in the wettability, indicating an increase of the hydrophilicity of the fibre. In addition the handle of the wool became harsher with these oxidative treatments.

1.1.2 Cotton

Cotton is the most important natural textile fibre in the world and accounts for about 40 % of the world total consumption of all textile fibres [30]. It is a seed hair of the plant called genus Gossypium, the purest form of cellulose exists in nature, which is a member of the natural order of Malvaceae [31].

1.1.2.1 The morphology of cotton [32, 33]

Cotton is a unique textile fibre due to its multilayer structure. The morphology of cotton is shown in Figure 1.5.
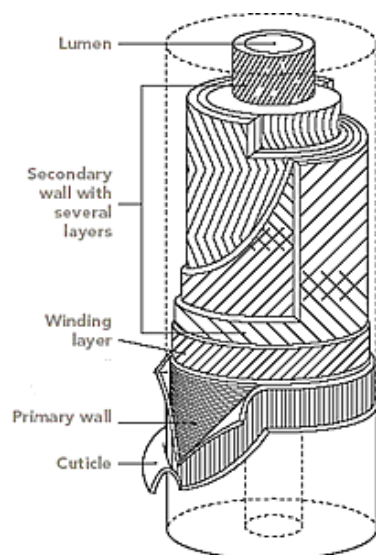
Figure 1.5 Morphology of the cotton [32]

The outer skin of cotton fibre is the cuticle. It is composed of fats, waxes and pectin, protecting the rest of the cotton fibre, and more or less removed during the scouring and bleaching processes. The primary wall contains the most of the non-cellulosic constituents of the fibre and an inner network of microfibrils. The winding layer, consists of helical microfibrils, is the thin layer inside the primary wall and associated with the secondary wall. Most of the weight of the fibre (about 95%) is formed by the secondary wall, which is composed of many layers of fibrils. The lumen is the hollow canal in the central part of the fibre, which is used to deposit the cell sap. When the sap is evaporated, the lumen collapses inward and imparts the twisted-ribbon longitudinal form and the kidney bean shape to the cotton fibre.

1.1.2.2 The chemical constitution of cotton

Cotton is composed of a linear polymer, which is typically 65-70% crystalline and 35-30% amorphous. Cotton cellulose polymer has a repeating unit called cellobiose, composed of two glucose unit. The degree of polymerization of cotton cellulose ranges from 6,000 to 10,000 [34].
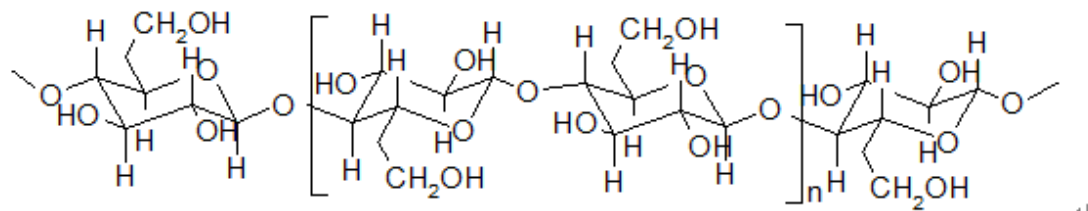
Figure 1.6 Repeating nature of cellulose polymer [34]
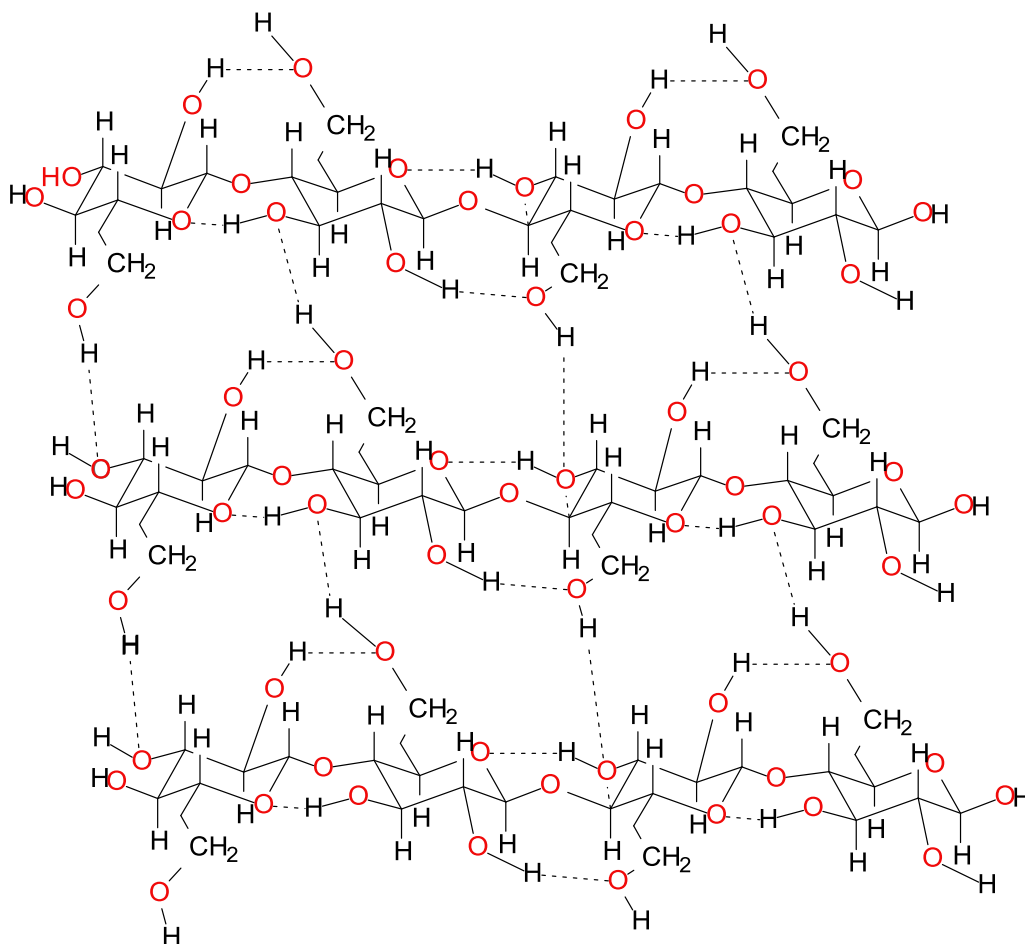
Figure 1.7 The intra and intermolecular hydrogen bonds within cellulose structure [32]

The cellulose structure of cotton contains both the intra- and intermolecular hydrogen bonds. Hydrogen bonding is relatively strong in the ordered crystalline region where chains are quite close together. In the amorphous regions, hydrogen bonding is relatively weak. Chemical cross-linkers can only penetrate the amorphous regions or the surface of crystalline regions, so the chemical modification and cross-linking can only occur in these regions [32].

1.2 Fibre damage during wet processing of wool and cotton

Wet processing improves the appearance, durability, and serviceability of fibres and fabrics by converting undyed and unfinished materials into finished consumer goods. Bleaching and dyeing are the most commonly used wet processing among the applications for wool and cotton fibres. However natural protein and cellulose fibres are harmed during the bleaching and dyeing procedures, therefore "optimised" treatments or additive chemicals are applied to these premium fibres to minimise the negative effect of aqueous processing on quality. The nature of the fibre damage that can occur during the bleaching and dyeing of wool and cotton and the relative methods that are utilised to minimise harmful effects are described in this section.

1.2.1 Fibre damage during bleaching

The natural colour of wool and cotton is not perfectly white, and with some wool fibres the most common shade may even close to the brownish black due to the presence of melanin pigments [5]. Bleaching processes are applied to these undesirable coloured fibres, either to meet a specific colour requirement or to increase the value of the fibre. Selection of the most suitable bleaching process depends on the factors such as the initial substrate colour, final colour required, machinery available, other pre- or post- processes or chemical treatments employed, and acceptable level of fibre damage. The limiting factors are predominantly the initial fabric colour and fibre damage.

1.2.1.1 Basics of bleaching [35]

The bleaching of wool can be achieved by either oxidation or reduction processes. Both may lead to damage arising from chemical reaction between the bleaching agents and the amino acids of wool fibre. Cotton can be bleached with hypochlorite, peroxide, and/or sodium chlorite. However, hydrogen peroxide is the most widely used oxidative bleaching agent for textile due to the environmental impact of the chlorine-based oxidative systems, in particular the formation of adsorbable organohalogens (AOX) [35]. Hydrogen peroxide is present in aqueous solution in a dissociative equilibrium with the perhydroxyl anion (HO_2^-, I) and the peroxodianion (O_2^-, II).

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad \text{(I)}$$
$$HO_2^- \leftrightarrow O_2^- + H^+ \quad \text{(II)}$$
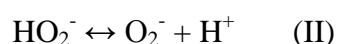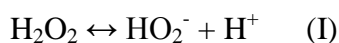
The addition of alkali, the most common activator, to an aqueous solution of hydrogen peroxide displaces the equilibrium of reaction (I) towards the right, favouring the formation of the perhydroxyl species; this then reacts further with hydrogen peroxide to give the superoxide ion, which has been suggested as an active agent responsible for bleaching effect [35].

Stabilisers are necessary to enhance the stability of both hydrogen peroxide and the active bleaching species in the bleach bath. Most common stabilisers used in wool bleaching are alkaline phosphates or organic derivatives. The rate of hydrogen peroxide decomposition can be accelerated by activators or retarded by stabilizers. Activators can be sodium hydroxide, sodium carbonate or ammonia, which can increase the pH value of the bleach bath. Stabilizers are the most common auxiliary present in protein and cellulosic fibre bleaching. They can maintain the internal pH value of fibre regardless of the pH value of the liquor and control the "useful"

breakdown of the peroxide. Sodium silicate, sodium pyrophosphate and tetrasodium pyrophosphate are effective commercial stabilizers.

1.2.1.2 Nature of fibre damage during bleaching

The aim of bleaching is to eliminate the natural colouration and yellowness of the fibre with consumers often requiring the 'maximum' whiteness possible. Natural colouration of fibres is often due to the inclusion of various pigments within the fibre. The majority of pigments, which are not removable by the scouring procedure and require bleaching [36, 37] are the protein-derived melanins. Melanins are highly cross-linked natural polymers of high molecular weight that are very stable to chemical attack. Moreover, the melanin pigments are usually present in the bulk of the fibre, the cortex, and not at the accessible surface. During the bleaching procedure, under conditions, which allow sufficient bleaching (destruction) of the pigment chromophore, oxidation of the keratin matrix also occurs and the more chemically sensitive keratin undergoes substantial damage. This is often referred as 'oxidative' or 'bleaching' damage [38, 39]. During the bleaching process with the most common bleaching agent – hydrogen peroxide, chemical and mechanical modifications occur resulting in an attack on the disulphide bond (III); a decrease in the sulphur content, a decrease in cross-linking, variation in the acid /base properties, shortening of the polypeptide chains, an increase in the protein solubility in alkali and urea-bisulphite, a decrease in the mechanical performance/durability of the fibre, and a decrease in weight.

$$W - CH_2 - S - S - CH_2 - W \quad \xrightarrow{\quad H_2O_2 \quad} \quad W - CH_2 - SO_3H + H_3O - S - CH_2 - W \quad (III)$$

Therefore the most distinct effects of bleaching are the increase in whiteness and associated damage. Bleaching methods are normally optimised to give the lowest level of fibre damage for any given degree of whiteness. Optimal processing conditions can be defined as impairing neither the molecular weight of the main chain molecules nor modifying or cleaving the disulphide cross-links.

Cystine oxidation of wool

There are a number of sites in the keratin fibre, which can be easily attacked by oxidising agents [40]. Disulphide bonds of cystine are one of the most susceptible oxidation sites in wool [41]. In bleaching processes, where hydrogen peroxide acts as the primary oxidising agent, of all the amino acids present in keratin, cystine undergoes relatively large scale modification [38] with oxidation of cystine to cysteic acid occurring. According to amino-acid analysis, extensive bleaching can reduce the content of half-cystine residues from 13.9% to 5%, which corresponds to approximately a 64 % reduction in the disulphide bond linkages [42, 43]. Two types of mechanisms for the oxidative degradation of disulphides exist, one involving -S-S- fission and the other -C-S- fission [44, 45]. The reaction may proceed with the disulphide crosslink remaining intact in the first two oxidation steps; this pathway can only be expected during oxidation under non-hydrolytical conditions. Secondly, under hydrolytical conditions cleavage of the disulphide crosslink occurs in the first oxidation step. The intermediate oxidation products cystine monoxide, cystine dioxide, cysteine sulphinic acid and cysteine-S-sulphonic acid have also been detected in various quantities in oxidised wool depending on the treatment conditions. Oxidation intermediates have been successfully detected by infrared spectroscopy, with absorptions at 1070cm^{-1} and 1120 cm^{-1} being assigned to –SO–S– and –SO_2 –S–, respectively [46, 47]. These absorptions are diagnostic for oxidation damage.

Cystine possesses characteristic reactivity up to the point that a significant part of wool's chemistry is identified specifically with that of the disulphide bond. Any change in cystine therefore affects the chemical properties and the quality of the fibre [41, 48]. The main source of permanent damage resides in the destruction of disulphide bonds, which not only opens the structure of fibre but also provides additional hydrophilic centres (anionic sites) in the form of cysteic acid residues, thus giving favourable conditions for destructive solubilisation [38, 49]. In addition, the new intermediate oxidation products of cystine behave as new reactive centres in wool [50].

1.2.2 Fibre damage during dyeing

1.2.2.1 Basics of wool dyeing [3]

The dyeing process depends on a number of important factors such as the character of the material to be dyed, solvent, properties of the dye and its concentrations, temperature, pressure, auxiliary products etc. The study of dyeing theories therefore cuts across a number of disciplines including surface and colloid chemistry, physical and polymer chemistry and extends into biological studies. Therefore it is not surprising that no unified theory of dyeing has been developed to account for all observed phenomena [51].

The presence of acidic and basic functional groups in the side chains of the proteins is the major influence in the dyeing of wool. The amino acids with basic functional groups are lysine, arginine, histidine and the N-terminal amino groups of the individual protein chains. The amino acids with an acidic functional group in the side chains are aspartic acid, glutamic acid and the C-terminus of the protein chains [52].

1.2.2.2 Nature of fibre damage during dyeing

Wool dyeing can be regarded as causing fibre degradation and is a reflection of the process usually being performed in water at the boil for periods of 1-8 hours within the pH range of 2-7. Wool dyeing is normally carried out at the boil to achieve uniform levelness, good penetration of the fibrous mass and individual fibres, optimum fastness properties, and excellent dyebath exhaustion.

Peptides, being natural polyamides formed from different amino acids, are subject to hydrolysis at the amide linkage [15], therefore damage to wool in hot, aqueous, acidic dye liquors occurs mainly by hydrolysis of peptide bonds, particularly at aspartic acid

( ) residues [15, 53]. Tryptophan ( ) peptide bonds
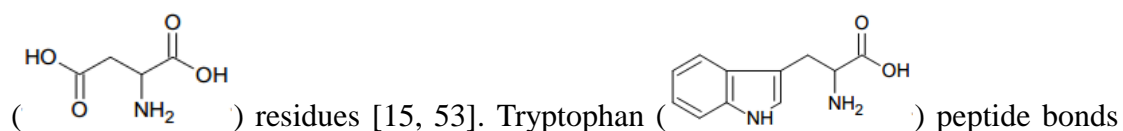
are also susceptible to acid hydrolysis [50]. There is strong evidence that the non-keratinous proteins in the wool fibre play an important role in determining the overall mechanical properties of the fibre. These non-keratinous proteins make up about 15% of the fibre mass. It is believed that preferential attack on these readily swollen region is a major factor in the impaired physical performance of wool often found after dyeing [53]. When wool is dyed at the boil soluble proteins, termed "wool gelatins" are extracted from the fibre. The wool gelatins have low cystine content, and are therefore believed to originate from the cell membrane complex and other non-keratinous regions. The yield of wool gelatins is regarded as a measure of the extent of wool damage. At a given liquor pH, the mass of non-keratinous material extracted from wool is proportional to treatment time, which is a clear indication of the damage when lengthy dyeing cycles are employed. Extraction of 2% o.w.f (on weight of fibre) of wool gelatins resulted in a decrease in a wet tensile strength of 25% [54], and it shows that although the amount of soluble protein extracted from wool dyeing is relatively small, the effect on physical properties can be large.

Compared to water-soluble proteins, the keratins show extraordinary resistance to hydrolytic degradation, attributable to the complex histological structure of the fibres, the nature of the proteins and especially the three dimensional network structures produced by disulphide cross-links. Amide bonds can be readily hydrolysed under acidic or alkaline conditions, whereas the cystine disulphide crosslink is increasingly cleaved by hydrolysis reactions at pH values greater than 3.

Thus in colouring wool the damaging effect of dyeing at pH 1.8-3 is mainly due to amide bond splitting, whereas above pH 3, the damage is increasingly associated with disulphide bond hydrolysis. When dyeing is performed on the alkaline side the associated degradation involves both disulphide and amide bond cleavage, Figure 1.8. The alkaline hydrolysis reaction shown in this figure is simplified, other reactions such as β-elimination to form dehydroalanine, which reacts further with cysteine to produce lanthionine, are also important [55].

41
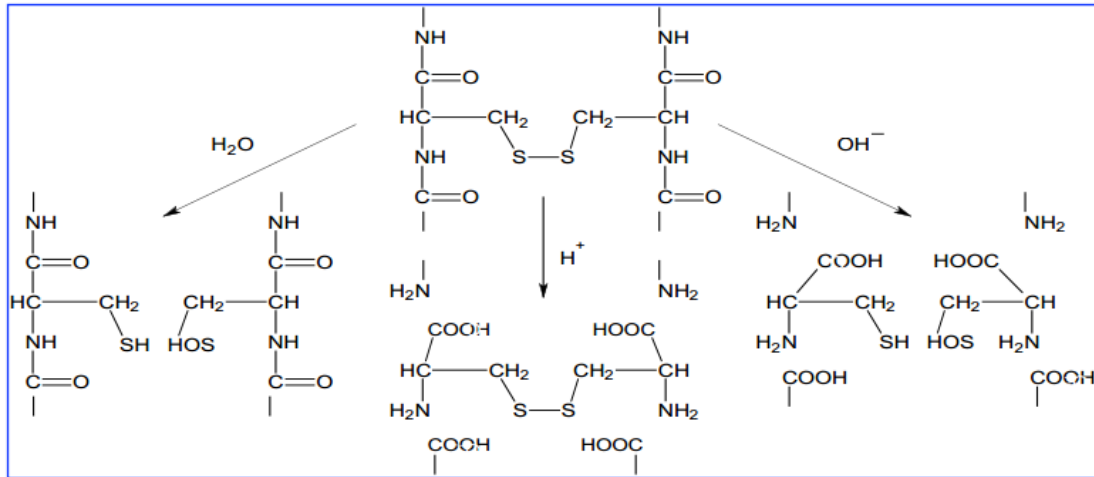
Figure 1.8 Keratin hydrolysis [55]

Disulphide bond hydrolysis is associated with the technically important wool setting reaction [53, 56]. The tendency for wool to acquire a permanent set in boiling water is well documented, but when this set is acquired during the dyeing process then the effect can either enhance the quality of the goods or detract from it. Examples of deleterious setting effects in dyeing include [53, 56]:

• Irreversible loss of bulk in package dyeing leading to yarn 'leanness';

• Improved yarn set and maintenance of bulk in hank dyeing;

• Formation of running marks and 'crows' feet' during winch dyeing of wool pieces;

• Flat setting of wool pieces during beam dyeing or in pad batch dyeing;

• Increased hygral expansion of piece dyed wool fabrics.

Effect of dyebath pH on wool damage

The wool fibre is amphoteric in character due to the approximately equal numbers of basic amino and acidic carboxyl groups in its side chains. At neutrality both types of group are fully ionised and the overall electrical charge carried by the fibre is zero.

$$H_3N^+ - wool - COOH \xrightleftharpoons{H^+} H_3N^+ - wool - COO^- \xrightleftharpoons{OH^-} H_2N - wool - COO^- \qquad \text{(IV)}$$

$$\textit{acidic} \qquad\qquad\qquad \textit{isoelectric} \qquad\qquad\qquad \textit{basic}$$
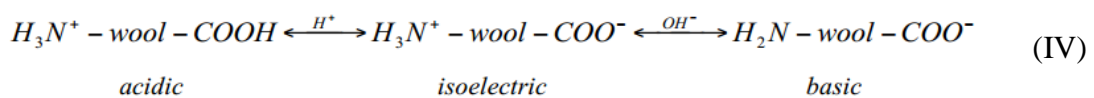
This condition is known as the isoelectric state. The importance of pH on damage during dyeing has been recognised for many years and it has been demonstrated that the level of damage is kept to a minimum when wool is dyed at a pH value within the isoelectric region of the fibre [46]. At this pH the wool fibre structure is maximally reinforced by salt linkages between protonated amino groups and carboxylate anions; additionally amide and disulphide bond hydrolysis is minimised.

From an extensive range of studies [52, 53], it was concluded that the optimum pH for wool dyeing is in the range pH 4-5 (i.e. the iso-ionic region). Although the effect of dyebath pH on fibre damage has been known for a considerable time, only recently dyes with specific application performance at or around the isoelectric region of wool have been marketed [55].

Effect of other factors in dyebath on wool damage

The dyeing time should be always kept to a minimum because the chemical damage is progressive [53, 56]. Similarly, high temperatures accelerate chemical degradation and so the temperature should be kept as low as practicable [53, 56]. It has been shown that in addition to being damaged chemically, wool fibres may be damaged physically as a result of severe bending prior to and during stock dyeing. Thus the influences of packing density and liquor circulation pressure have been investigated [53, 56] and it was found that these factors also important in dyeing. During dyeing bent wool fibres are boiled while compressed and this results in damage by two possible mechanisms:

1. As the bent fibres are boiled and then cooled, sharp bends in the fibres become set. This results in a concentration of stress at the inside of the bend curvature and when the fibres are subsequently extended, it effectively weakens the fibre;

2. A second mechanism involves fibre failure in bending. Fibres that are bent while dry and then immersed in hot water show signs of failure damage.

The severity of bending is determined by the extent to which the fibres are

compressed before and during dyeing, i.e. the packing density. This in turn is determined by the quantity of wool loaded into a given space and by the pressure exerted on the fibres by the circulating dye liquor. Therefore the liquor circulation pressure should be no higher than is necessary.

1.2.3 Fibre protection

There have been various techniques in reducing the negative effect of wet processing of wool and cotton. The method used in this research is the application of fibre protective agents [3].

1.2.3.1 Application of protein hydrolysates /derivatives as protective agents

An earlier observation of dyers that wool is less damaged after dyeing in previously used liquors compared to wool dyed in fresh liquors led to the development of fibre protective agents on basis of protein hydrolysates [3]. Proteins, protein hydrolysates and modified proteins can also be applied during textile finishing but surprisingly these derivatives are still little used in the industry. The protein material can be simply an amino acid; in most cases, however, oligopeptides or proteins of low-molecular weight obtained by acid or enzymatic hydrolysis from protein-containing materials, such as soya, waste leather, wool etc. Proteins and protein derivatives can be used as clearing agents, as fibre protective agents, protective colloids, surfactants and as dispersing agents [3]. From an environmental viewpoint, textile-finishing agents from renewable raw materials are gaining greater importance [3, 55]. Chemically protein-based surfactants are protein hydrolysates and protein derivatives such as protein fatty acid condensates, protein fatty amine condensates and quaternized protein derivatives. The acyl component of protein fatty acid condensates in most cases is a C12-acyl residue. These surfactants are used in wool processing as scouring, wetting, levelling and fibre protective agents. The opinion about the efficacy of protein based fibre protective agents is often controversial. Indeed with some protein

hydrolysates no elimination of the tensile strength loss occurred and only a small improvement was observed [57].

1.2.3.2 Application of formaldehyde based products

Cross-linking agents on the basis of formaldehyde and formaldehyde - releasing products has proved to be successful as fibre protective agents during acidic or HT - dyeing and during oxidative bleaching [53]. However increasingly the use of formaldehyde as a cross-linking agent has been questioned [53]. The use of formaldehyde as a fibre protective agent suffers from a number of disadvantages, the most significant are a harsh handle may be produced, reduction of some dyes, environmental limitations, unpleasant smell, the irritation of the mucous membranes of eyes, nose and mouth and it is probably carcinogenic [53].

1.3 Water saving in the textile industry

1.3.1 Water consumption in the textile industry

Water is a scarce natural resource [58]. Less than 0.5% of all the water on earth is available as fresh water and fresh water is only renewable by rainfall. Global consumption of water is rising rapidly due to the growing population, economic development and growing standards of living. Meanwhile, industrialization and urbanization have resulted in rapid deterioration of water quality. Lots of fresh water resources, such as rivers and lakes, are polluted due to the unregulated effluent disposal. As a result, the cost of water and effluent disposal has increased considerably over the last few decades. Also governmental policies and regulations regarding the quality of discharged wastewater are being better monitored and legislation tightened. So water saving and wastewater minimization are of great importance [58].

The textile industry involves the manufacture of fabrics from wool, cotton, and synthetic fibres. The main processes of the woollen textile industry are scouring,

dyeing, fulling, carbonizing, bleaching, and weaving, and that of cotton and synthetic textile industry are sizing, weaving, desizing, scouring, dyeing, and finishing [59]. It is obvious that a large amount of water is required in the textile industry to achieve the desirable properties for fabrics like colour, antistatic properties and ease of soil removal, and a large amount of wastewater is unavoidably produced [60].

There are some practices in the textile industry that can have a great effect on the characteristics of the wastewater, such as the segregation of waste streams, alkaline wool scouring, chemical sizing and colouration [59]. Accordingly the textile companies have already put a lot of emphasis on reconsidering their technological routines to control water consumption and treat their waste effluent to an increasingly high standard, because of the cost and stricter legislative requirements [60].

1.3.2 Textile effluent characteristics [59, 61, 62]

Water usage in the textile industry is mainly in scouring, dyeing, bleaching and finishing. Coupled to the aqueous demands there are chemical auxiliary reagents used which are diverse in chemical composition, ranging from inorganic compounds to polymers and organic products. Important pollutants in textile effluent are mainly colour, recalcitrant organics, toxicants and inhibitory compounds, surfactants, chlorinated compounds (AOX), pH, salts and in some cases heavy metals. Therefore ideally if water usage could be better regulated then the re-use of the chemical auxiliaries in exhausted baths would be beneficial as well.

The wastewaters generated in the textile industry, including wool, cotton and synthetics, are high in Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), and colour. There is a main difference between wool process wastewaters and those from the rest of the industry, is the release of wastewaters with high concentrations of suspended solids and grease from the wool-scouring operation. The characteristics of the process wastewaters from each pre-treatment sub-group are shown in Table 1.4.

Table 1.4 Wastewater characteristics of the textile industry [59]

Characteristics	Wool	Cotton and Synthetics
Industrial Operation	Year-round (batch)	Year-round (batch)
Flow	Intermittent [1]-Continuous	Intermittent [1]-Continuous
BOD	High	Average-High
TSS	High	Low-Average
TDS	High	High
COD	High	Average-High
Grit	Present	Absent
Cyanide	Absent	Absent
Chlorine Demand	High	High
pH	Basic	Basic
Colour	High	High
Turbidity	High	High
Explosives	Absent	Absent
Dissolved Gases	Absent	Absent
Detergents	Present	Present
Foaming	Present	Present
Heavy Metals	Present	Present
Colloidal Solids	Present	Present
Volatile Organics	Absent	Absent
Pesticides	Absent	Absent
Phosphorus	Present	Present
Nitrogen	Deficient	Deficient
Temperature	Normal-High [2]	Normal-High [2]
Phenol	Absent [3]	Absent [3]
Sulphides	Absent	Absent
Oil & Grease	High [5]	Absent-Present [4]
Coliform (Fecal)	Present	Absent

[1] Wastewater flow characterized by an intermittent flow over the day.

[2] Temperature equal to or higher than domestic wastewater. May affect design but not harmful to joint treatment processes.

[3] Phenol may be present in dye carriers.

[4] Oil present in wastewaters from synthetic textiles only.

[5] Wool processing wastewaters contain high concentration of animal grease.

1.3.3 Application of filtration in effluent treatment

Filtration is a very widely used process, where filtration is defined as 'a mechanism or device for separating one substance from another [63, 64]. Filtration may be used to separate contaminants from a fluid or separate value-added material, such as minerals, chemicals, or foodstuffs in a process operation [64]. In this research, the main application area is liquid filtration, which is designed to 'separate suspended particles from a fluid media by passing the solution through a porous membrane or medium' [59]. In addition in developing an active filter media dyestuffs and mineral ions may also be selectively removed.

1.3.3.1 Purposes of filtration [65]

There are two main purposes in filtration:

- To remove impurities from a fluid, and;
- To recover valuable materials from suspension in a fluid (usually a liquid).

The first 'clarification' normally uses finely porous filter media to remove as much of the impurity as possible. The second 'harvesting' usually employs coarser media because it is less concerned with the clarity of the filtrate but tries to recover the wanted materials as completely as possible.

1.3.3.2 Filtration Mechanism [64, 65]

There are four fundamental filtration mechanisms that can be distinguished and the following is a brief description of each.

1.3.3.2.1 Surface straining

The particles which are smaller than the pore diameters pass through the medium. Particles that are larger than the pores deposit on the surface of the filter, and remain

until mechanical removal. This type of separation is generally related to the media with uniform pore openings, but not associated with nonwoven filter media [64, 65].

Figure 1.9 Filtration by surface straining [65]

1.3.3.2.2 Depth Straining

This mechanism is for media that are relatively thick compared to their pore diameters and where the pore diameters vary significantly in their length. The particles will travel along the pores until they reach a necking point where the pore becomes too small for the particles to go any further. This mechanism can apply to felts and other nonwoven materials [64, 65].
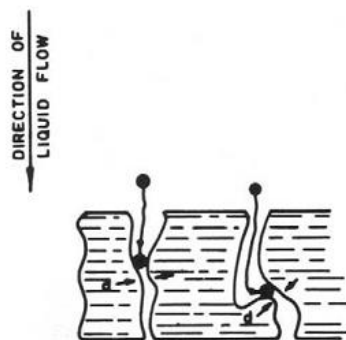
Figure 1.10 Filtration by depth straining [65]

1.3.3.2.3 Depth filtration

A particle can be removed from a fluid even though it may be smaller than the diameter at any point in the pore structure. It involves a complex mixture of physical mechanisms. Through inertial or hydraulic forces, or by Brownian (molecular) motion, the particles will be brought near to the pore wall and contact with it. Then they become attached to the pore wall, or to other particles already held to the pore wall by means of van der Waals and other surface forces. This mechanism is important for most media, especially high-efficiency air filters and deep bed (sand) filters [64, 65].
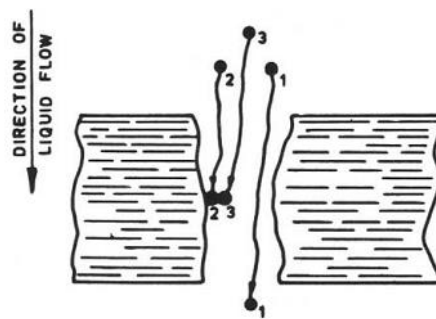
Figure 1.11 Depth filtration mechanism [65]

1.3.3.2.4 Cake Filtration

Cake or surface filtration involves the capture of particles on the surface of the medium [65]. It will build up as a thick layer of filter cake, which then acts as the filter medium for subsequent filtration. If some of the particles are larger than the pores, cake filtration may follow a period of surface straining. If the particles are all smaller than the pores, cake filtration can also occur due to the bridging of the particles, especially when the solid concentration is relatively high, above 2% by weight in a liquid [64, 65].
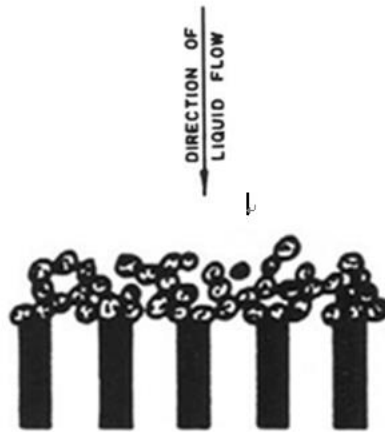
Figure 1.12 Cake filtration mechanism [65]

1.3.3.3 Filter Modification [59, 63]

A range of processes are available to engineer improved performance and achieve optimal filterability:

1.3.3.3.1 Use of Pre-coat and Filter Aids [63]

A pre-coat and or filter aids are often used to prevent deposited particles from being carried by flow impact into the pores of the filter media (or filter cake after formation) when there are colloidal particles in liquor clarification, thus reducing capacity. The pre-coat is used as a protective covering over the filter media to provide mechanical stability and still allow the particles to reach the pores, while the filter aid assists in particle separation and cake formation. Sometimes the pre-coat process is used to modify the use of a coarser filter media.

1.3.3.3.2 Coagulation

This is another approach to process colloidal or semi-colloidal particles. In the process of coagulation, the use of chemical additives results in alteration of the

physical structure of the suspended solids to the extent of losing their colloidal nature, agglomerating and the particles becoming larger and more filterable [59].

1.3.3.3.3 Temperature Control

Temperature has a direct impact on viscosity, which in turn affects the flow rate. Lower viscosity leads to liquor penetration into smaller voids and in shorter times. Temperature sometimes also plays a role in altering the particle form or composition, which in turn affects the clarification rate.

1.3.3.3.4 Control of pH

Proper pH control can result in clarification that might otherwise not be feasible, as it may affect alkalinity or acidity of the fluid, or some properties of the solids.

1.3.3.4 Filter media [65-67]

"A filter medium is any material that, under the operating conditions of the filter, is permeable to one or more components of a mixture, solution or suspension, and is impermeable to the remaining components" [65].

Any material that can be rendered permeable or made into a permeable form may be made into filter media, including:

- inorganic minerals;
- carbon and charcoal;
- glass;
- metals;
- metal oxides and other fired ceramic materials;
- natural organic fibres;
- synthetic organic fibres;

- synthetic sheet material [67].

The materials can be constructed into different structural forms as filter media: rod or bar, sheet, loosely packed or bonded fibres or granules, wire or monofilament, and so on. It is not necessary that a particular form of a material can be used as a filter medium in its original shape or format. However, not all permeable materials can be used as filter media, but inherent properties potentially enable them to be applied in this way, provided that the compatible filter is operating in an appropriate environment [65, 66].

Filter paper [63, 68]

The high porosity of paper enables its application as filter media. Paper can be used for the filtration of oils, aqueous fluids and gases. When untreated paper gets wet, there are two notable consequences. The fibres in the paper swell, then the spaces between them reduce and then the efficiency of filtration improves. Another consequence is the sharp drop in the mechanical strength, which is undesirable as a filter medium.

The main drawbacks of paper media are their high specific resistance and their limited mechanical strength. Filter papers are usually used in pleated form to offset the high specific resistance. Pleating reduces the flow velocity and hence the effective or overall resistance to flow. It also improves the rigidity of the element. The low mechanical strength of paper commonly limits the working pressure of filtration. This can be improved by rigid reinforcement, such as a wire mesh backing.

The filter papers used in industry are intended for general liquid filter application. They are often in filter press. Filter papers are used in the production of beverages, pharmaceuticals, light oils, syrups and other polishing process. Some of the filter papers are given added wet strength by the application of bonding agent, such as melamine formaldehyde or polyamide epichlorohydrin [63, 68]. The papers are

sometimes creped to increase the surface area for filtration. In addition, creping imparts more stretch and flexibility for the papers. Most industrial filter papers are made from wood pulp fibres with an average pore diameter between 5μm and 20μm [69]. Finer industrial filter papers are made with glass microfibres. Such papers require strengthening by binders such as latex, acrylic polymers or polyvinyl alcohol. The average pore diameter range from 3μm to 30μm [69]. Industrial filter papers can be impregnated with adsorbent or absorbent powders such as activated carbon, diatomaceous earth or perlite clay [63].

1.3.3.5 Application of filtration to wastewater treatment

Textile wastewaters are usually treated chemically and physically, and most commonly, in an activated sludge biochemical plant, but in order to have water that can be recycled in production cycles, especially dyeing processes, water needs further treatment. A filtration process can achieve this and it has been one of the popular treatments used in textile industry [70].

Despite the high cost of filtration techniques, it may be outweighed by the significant costs savings achieved through the reuse of permeate, salts and sizes. Costs can also be reduced by the use of pre-filters, regular cleaning to eliminate membrane fouling problems, and by choosing the most appropriate membrane system [71].

There are four main membrane systems used in textile industry: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). They are classified by their pore size, as in Table 1.13 [72]. These systems may be operated individually or in combination in order to increase the efficiency of separation and recycling. UF systems have been used for the recovery of polyvinyl alcohol (PVA) (sizing agent), indigo dyes and the purification of dilute caustic soda prior to evaporation, while NF systems have recently been applied in the removal of numerous pollutants, such as COD, colour and non-biodegradable contaminants. The permeate stream is recycled in order to use in the appropriate point. The concentrate would be treated by a

convenient method, such as wet air oxidation. RO systems are used in the recovery of both dyes and hot water in continuous dyeing. They are also applied as "polishing" step for UF/NF permeate [73].

	Cut-offs of different liquid filtration techniques							
Micrometer logarithmic scaled	0,001	0,01	0,1	1	10	100	1000	
Angstroms logarithmic scaled	1	10	100	1000	10^4	10^5	10^6	10^7
Molecular weight (Dextran in kD)	0,5	50	7.000					
Size ratio of substances to be separated	Atomic radius / Solved salts / Sugar / Pyrogens / Albumin (66 kD) / Viruses / Bacteria / Red blood cells / Yeast / Pollen / Human hair / Sand							
Separating process	Reverse osmosis / Nano filtration / Ultra filtration / Micro filtration / Particle filtration							

Figure 1.13 Cut-offs of different liquid filtration techniques [72]

1.3.4 Potential of sea water used in the wet processing of textile

Seawater is one of the most abundant substances present, which accounts for 97% of water on earth, and constantly circulates in the hydrological cycle [74].

1.3.4.1 The composition of seawater [75-77]

Seawater contains salts, dissolved gases, organic substance and undissolved suspended particles besides pure water. The presence of salts and other components

greatly affects the characteristics of seawater. Seawater is substantially different from freshwater by the amount of dissolved salts. The classification of natural waters based on the saline contents is shown in Table 1.5.

Table 1.5 Water classification based on salinity content [78]

Type	Total dissolved solids ppm	Note
Freshwater	<1500	Variable chemical composition
Brackish water	1500-10000	Variable chemical composition
Salt water	>10000	Variable chemical composition
Seawater	10000-45000	Fixed chemical composition
Standard seawater	35000	Fixed chemical composition

Table 1.6 Standard seawater composition [78]

Chemical ion	Concentration, ppm	% of total salt content
Chloride Cl^-	19345	55.0
Sodium Na^+	10752	30.6
Sulphate SO_4^{2-}	2701	7.6
Magnesium Mg^{2+}	1295	3.7
Calcium Ca^{2+}	416	1.2
Potassium K^+	390	1.1
Bicarbonate HCO_3^-	145	0.4
Bromide Br^-	66	0.2
Borate BO_3^{3-}	27	0.08
Strontium Sr^{2+}	13	0.04
Fluoride F^-	1	0.003

Some properties of the seawater is influenced by the addition of dissolved salts, such as the increase of the density, the decrease of the temperature of maximum density, and the reduction of the freezing point [76, 78].

The composition of seawater is variable with most known elements present in seawater. However the most common seawater composition contains eleven ions dissolved salts in seawater and contributes 99.9% of the total, Table 1.6.

1.3.4.2 The industrial use of seawater

Seawater, a widely available and inexpensive resource compared to freshwater, can be a promising alternative for several possible applications in industry, with the potential to improve the overall economics of the process [79].

There have already been some processes based on seawater used in the industry developed in the past few decades [79, 80]. The possible application of seawater directly in industry includes in cooling systems, air pollution control, and so on. It is obvious that the seawater used in the cooling system can save a large quantity of fresh water, but consideration should be taken due to the biological organisms such as bacteria and algae in the seawater may block pipes and expensive equipment [81]. Seawater has some advantages for the air pollution control as well. Seawater contains an excess of calcium and sodium carbonates in solution and is naturally alkaline, therefore it can be utilized for the removal of harmful ingredients in the waste gases such as sulphur dioxide [82, 83]. Seawater can also be used as a natural mineral source, for seawater contains a range of minerals that may supply the essential commercial nutrients and minerals required in some industrial processes. There are some recent reports about seawater applied in the pharmaceutical industry, in the production of thermostable alkaline proteases, and the fermentative production of biofuels, biochemicals and biopolymers [79, 84, 85]. Moreover, seawater desalination is considered a resource of potable water in the future. There has been some widely

applied and commercially proven desalination technologies, such as thermal (evaporative) and membrane based methods. Although the desalination of seawater is technologically well developed, the high economic costs due to the large amounts of energy required to remove salt ions from water and the high cost of transferring water long distance still remain a problem to the application of seawater desalination [80, 86, 87].

1.4 Feather- A potential fibrous resource

Feathers, which account for 5%-7% of the body weight of chickens, are an important by-product in poultry industry [88]. Previously feathers were commonly regarded as a waste material but progressively due to environmental pressure they are gradually being perceived as a potential source of valuable fibres. The question is how to use them effectively and identify the commercially viable end-uses.

1.4.1 Structure

There are several types of feathers [88]. The most common is the contour feather (Figure 1.14). The stiff, cylindrical, sharp-pointed 'midrib' is the shaft, or rachis and the branches arising from two sides of the shaft are the barbs. The individual barbs are slender and parallel and as a whole are considered as the feather vane. Individual barbs also have branching structure, Figure 1.15, and it is these smaller constituent fibre components that are commercially useful as fibres [88].

Figure 1.14 Contour feather [88]
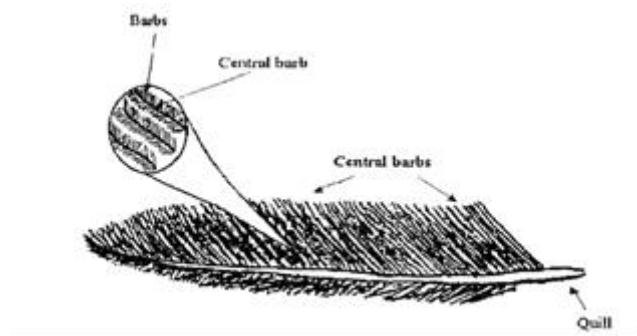
Figure 1.15 The hierarchical branching structure of feather [88]

1.4.2 Chemical composition

Feather contains about 91% protein (keratin), 1% lipids and 8% water [89]. The keratin in feather is β-keratin, very different from the α-keratins in hair, skin, hooves and nails. Hair α-keratin can be stretched to twice its length while feather keratin can only be stretched to approximately 6% before breaking. The β-keratin protein gradually twists, Figure 1.16.
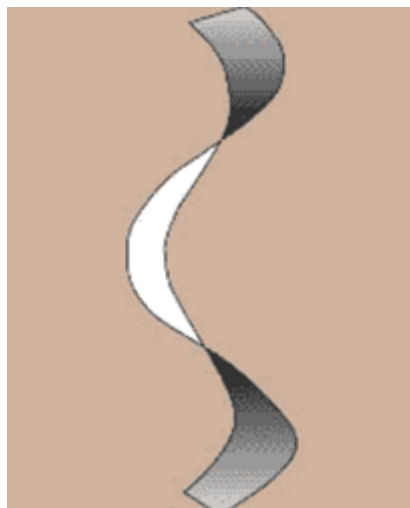
Figure 1.16 β-keratin twist [88]

β-keratin contains ordered α-helix and β-sheet structures and some disordered structures. The barbs have slightly more α-helix than β-sheet structure, while the β-sheet content is greater than in quill [88]. Feather keratins, like wool, are typically composed of 20 proteins varying in their relative amino acid content. The amino acid sequence is largely composed of cystine, glycine, proline, serine, and traces of histidine, lysine, and methionine [89]. The high content of cysteine (7%) makes the keratin stable by forming network structure through joining adjacent polypeptides by disulphide cross-links [88].

1.4.3 Physical properties of feather fibre [88]

The fibre diameter of feather is about 5-50 μm, with a fibre length between 3-13 mm and a fibre aspect ratio (length/diameter) in the range of 400-2600. The density of chicken feather fibres is always expressed as apparent density, as the feather fibre contains some air. The density of chicken fibre is reported as 0.89 g/cm^3 [88]. The chemical durability of feather is primarily determined by the keratin. Keratin has extensive cross-linking and strong covalent bonding within its structure, so the feather fibre shows good durability and resistance to degradation. The functions of feathers are closely related to their mechanical properties. It is reported that elasticity moduli of feather keratin ranges from 0.045 GPa to 10 GPa. The Young's modulus of chicken feather fibres was found to be in the range of 3 - 50 GPa and the tensile strength of oven-dried chicken feather fibres in the range of 41-130 MPa [88].

1.4.4 Feathers as potential filter media

There have already been a few reports about useful products manufactured from feathers, including diapers, filters, insulation, upholstery padding, paper, clothing and feather meal for animals [90].

It is reported that feather fibres can replace of some of the wood pulp to make paper products such as air filters and decorative paper and the feather fibres are even finer

than wood pulp. The thickness of feather fibres is only 5μm, while wood pulp fibres have a width of 10-20μm, then filters produced from feather fibre will have lower porosity and interstial spaces, creating greater numbers of pore. Therefore, filtration may be the first commercial value added product area for processed feathers. In particular it is possible that feather fibres can be used in both air and water filters. Moreover, with poultry feather fibre having good adsorbency properties, it has been demonstrated that heavy metals can be selectively removed from water [88]. In this study the removal of dyes has been examined.

1.5 Aims and objectives of the thesis

1.5.1 Minimize the damage of fibres in the wet processing of textiles

The wet processing of textile, such as bleaching and dyeing, would cause damage of textile fibres for various reasons. In this research, wool and cotton were evaluated in the process of bleaching or dyeing, the methods used to minimize the damage of textile fibres were:

• Optimize the chemical treatments

• Incorporate fibre protective agents

Hydrogen peroxide is the most widely used oxidative bleaching agent for textiles [35]. How the wool and cotton fibres affected by the hydrogen peroxide bleaching under various bleaching conditions was demonstrated in Chapter 4.

Protein hydrolysates/ derivatives, such as Byco C and Kerivas, were applied in the bleach bath as fibre protective agent to maintain the fabric strength. The results are shown in Chapter 5.Tensile strength, Martindale abrasion resistance, and Kawabata handle tests were used to check the mechanical properties of the wool and cotton fabrics, while the fabric whiteness was also examined for the whitening effect.

The effect of blank dyeing of wool fabrics was examined in Chapter 6. The extent of hydrothermal damage and yellowing established. Fibre protective agents, protein hydrolysates and formaldehyde-based agents, were applied in the dyebath, as individual additives or co-applicants. The fabric tensile strength, colour, handle, and abrasion resistance were assessed.

1.5.2 Reduce fresh water usage during the wet processing of textile

Fresh water is a scarce resource and the development of water saving treatments for textiles is important. Therefore two ways of saving water in the textile industry were demonstrated in this research.

The use of simulated seawater as an alternative processing medium for bleaching and colouration was evaluated in Chapter 7. The properties of the fabrics processed with simulated seawater, such as colour, tensile strength, abrasion resistance and handle were compared with those of the fabrics processed with distilled water.

Another way to save water in this research was the use of novel adsorbents in the removal of dye from effluent. The novel adsorbents evaluated were:

- modified paper-based filter
- Novel C30-modified PVP based nanofibres

The ability of dye adsorption for direct and disperse dyes was examined in Chapter 8.

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Chapter 2

Introduction to analytical techniques

2.1 Colour measurement

2.1.1 Colour Strength [1]

The colour strength for a given wavelength (λ) is:

$$K/S_\lambda = (1 - R_i)^2/2R_i \qquad \textbf{Equation 2-1}$$

R is the reflectance value (%) measured at the given wavelength.

The colour strength K/S can be calculated by measuring R with a spectrophotometer. Colour measurements usually measure the K/S values for a sample at 20nm increments from 400nm to 700nm. The K/S value is commonly defined by the most intense absorption wavelength.

2.1.2 CIE *L*a*b** [2, 3]

CIE is short for the Commission Internationale d'Eclairage (International Commission on Illumination), an international organisation concerned with lighting and colour. The CIE $L^*a^*b^*$ colour system is calculated on the principles of opponent pair theory. All colours can be described in terms of the unique colours, red, yellow, green and blue, the unique colours cannot be described with a combination of other colours. Then add black and white to the unique colours, three pairs of opponent colour are established, white/black, red/green, blue/yellow. L^* in the CIE $L^*a^*b^*$ colour system correlates with perceived lightness in the CIELAB colour space. A perfect white would have an L^* of 100, and a perfect black would have an L^* of 0. a^* correlates with red (+a^*) and green (-a^*), and b^* correlates with yellow (+b^*) and blue (-b^*).
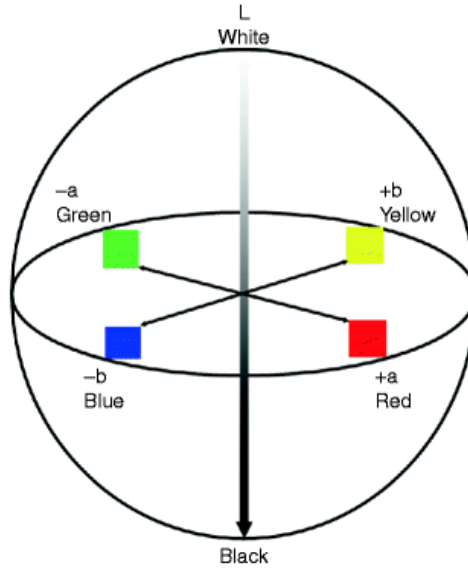
Figure 2.1 Representation of CIE $L^*a^*b^*$ colour space [2]

Colour differences can be calculated by subtracting the L^*, a^* and b^* values of the trial or batch from the standard:

$$\Delta L^* = \Delta L^*_{\text{trial}} - \Delta L^*_{\text{standard}}$$

$$\Delta a^* = \Delta a^*_{\text{trial}} - \Delta a^*_{\text{standard}}$$

$$\Delta b^* = \Delta b^*_{\text{trial}} - \Delta b^*_{\text{standard}}$$

The total CIE*LAB* colour difference, ΔE_{ab}, is given by

$$\Delta \mathbf{E}^*_{ab} = \sqrt{(\Delta \mathbf{L}^*)^2 + (\Delta \mathbf{a}^*)^2 + (\Delta \mathbf{b}^*)^2} \qquad \textbf{Equation 2-2}$$

2.1.3 CIE Whiteness Index and CIE Tint Index

The CIE Whiteness index is quite wide spread in the industry [4], while the CIE Tint Index is used to describe the particular shade of white [5].

It is strictly be used for D65 and illuminant C in combination with either $2°$ or $10°$ observer function [4].

The calculation is:

$$W_{CIE} = Y + 800(x_0 - x) + 1700(y_0 - y) \qquad \textbf{Equation 2-3}$$

$$T_{CIE} = 900(x_0 - x) - 650(y_0 - y)$$ **Equation 2-4**

Y: The tri-stimulus value for the sample

x and y: The colour chromaticity coordinates for the sample as this calculated using the illuminant/observer condition

x_0 and y_0: The colour coordinates of the achromatic point [5,6]

2.1.4 ASTM E313 Yellowness Index [2]

ASTM E313 has successfully been used for a variety of materials, including coatings, Plastics and Textiles.

The calculation is:

$$YI = 100(1 - 0.847\,Z/Y)$$ **Equation 2-5**

X, Y and Z are the tri-stimulus values for the calculated for illuminant C.

2.2 Absorption Spectrometry

Absorption spectrometry is based on the measurement of transmittance or absorbance of solutions contained in transparent cells having a certain path length. The concentration of an analyte is linearly related to absorbance by the equation below, also known as the Beer Lambert Law of light absorption [7]:

$$A = -\log T = \log(I_0/I) = klc$$ **Equation 2-6**

A –absorbance

T –transmittance

I –radiation intensity transmitted by solution

I_0 –radiation intensity transmitted by solvent

c –concentration in the solution of the absorbing substance (dye in solution)

l – path length (cell length)

k –absorption coefficient

In simple terms, the Beer-Lambert Law states that the amount of radiant energy absorbed is proportional to the concentration of the analyte. If the cell path length equals 1.0 cm, then the equation can be written as:

$$A = kc \qquad \textbf{Equation 2-7}$$

Therefore at a particular wavelength a graph of absorbance against concentration should be a straight line. The Beer-Lambert Law also applies to a medium containing more than one absorbing substance provided there is no interaction among the various species. The total absorbance for a multi-component system is given by the equation below. This feature can be used to measure the absorbance of bichromatic and trichromatic dye mixtures.

$$A_{Total} = A_1 + A_2 + \cdots + A_n = k_1 lc_1 + k_2 lc_2 + \cdots + k_n lc_n \qquad \textbf{Equation 2-8}$$

2.3 Scanning Electron Microscopy (SEM) [8]

SEM was used to characterise the surface topography of a wide variety of materials including wool fibres. The SEM technique enables high magnification, excellent depth of focus and relatively simple sample preparation [9]. Textile fibres are usually non-conductive, so they have to be coated with a thin conducting film to eliminate the possible 'charging'. The depth of coating should be monitored in order to ensure that surface details are not masked with an excessively thick coating.

2.3.1 SEM principle

Scanning Electron Microscopy is based on the interaction between a beam of electrons (accelerated to 1-50keV) and the solid surface onto which it impinges. When the incident electron beam arrives at the specimen surface it interacts with its component atoms and a number of different types of particles or radiation, according to the type of interaction occurring, are emitted, Figure 2.2. There are two main types of interaction that may occur:

1. The electron beam strikes the nucleus of the atoms of the specimen under investigation;
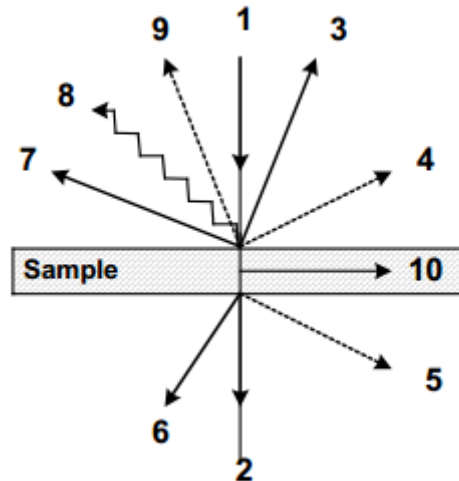
1. Incident electron beam

2. Unscattered electrons

3. Backscattered primary electrons

4. Secondary electrons

5. Inelastically scattered electrons

6. Elastically scattered electrons

7. Light

8. X-rays

9. Auger electrons

10. Absorbed electrons

Figure 2.2 Principal interactions occurring when electronds impinge of the sample substrate surface in the SEM [8]

2. The electron beam misses the nucleus and collides with their associated electrons. When an electron from the beam encounters a nucleus in the sample, the resultant Coulombic attraction results in the deflection of the electron's path, known as Rutherford elastic scattering. A few of these electrons will be completely

backscattered, re-emerging from the incident surface of the sample. Since the scattering angle is strongly dependent on the atomic number of the nucleus involved, the primary electrons arriving at a given detector position can be used to yield images containing both topological and compositional information. The high-energy incident electrons can also interact with the loosely bound conduction band electrons in the sample. The amount of energy given to these secondary electrons as a result of the interactions is small, and so they have a very limited range in the sample (a few nm). Because of this, only those secondary electrons that are produced within a very short distance of the surface are able to escape from the sample. This means that this detection mode provides high resolution topographical images, making this the most widely used of the SEM modes.

Another possible way in which a beam electron can interact with an atom is by the ionisation of an inner shell electron. The resultant vacancy is filled by an outer electron, which can release its energy either via an Auger electron or (more importantly here) by emitting an X-ray. This produces characteristic lines in the X-ray spectrum corresponding to the electronic transitions involved. Since these lines are specific to a given element, the composition of the material can be deduced. This can be used to both provide qualitative and quantitative information about the elements present at a given point on the sample, or alternatively it is possible to map the abundance of a particular element as a function of position.

2.3.2 SEM instrumentation

Figure 2.3 shows the schematic diagram of an SEM instrument, which is both a scanning electron microscope (uses electron detector unit) and a scanning electron microprobe (uses X-ray detector unit).
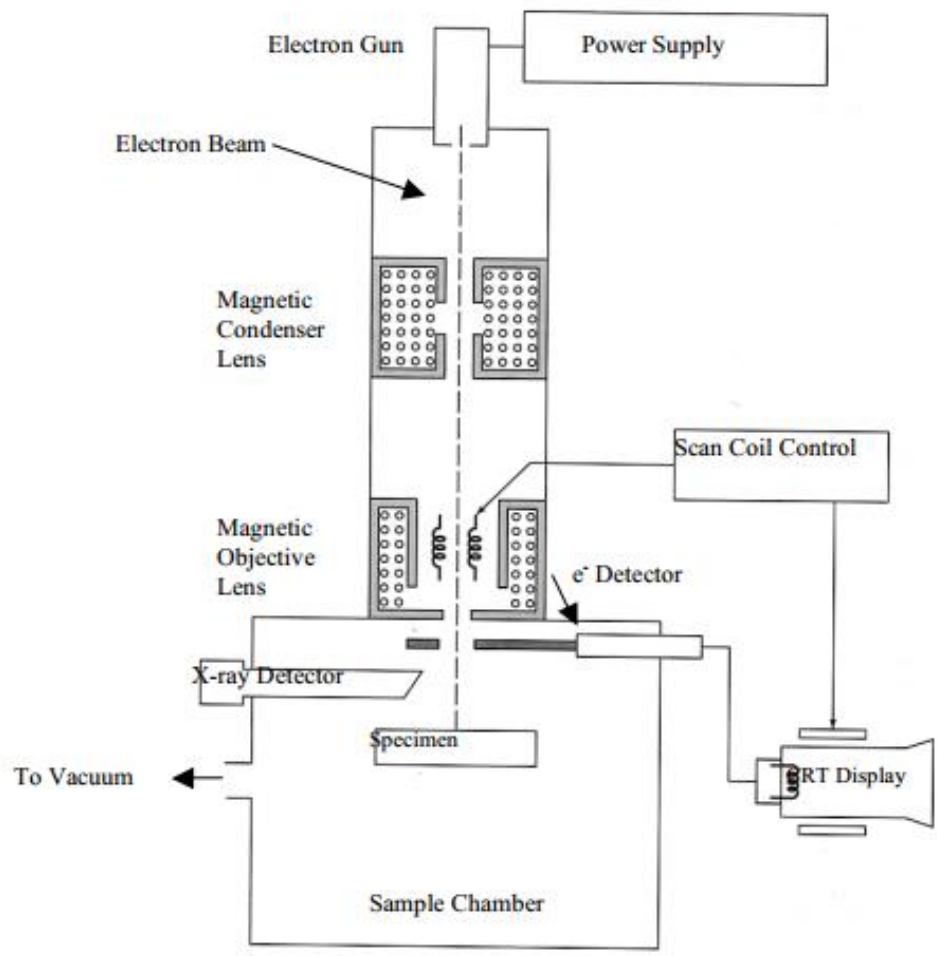
Figure 2.3 Typical schematic diagram of an SEM instrument [8]

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Chapter 3

Experimental

3.1 Bleaching of wool and cotton

All bleaching experiments were performed in sealed, stainless steel 500ml dye pots using a Mathis Labomat BFA laboratory dyeing machine.

3.1.1 Materials

3.1.1.1 Fabrics

100% wool botany serge fabric ($187g/m^2$) was supplied by Whaley's Ltd, Bradford.

100% scoured and bleached plain woven cotton fabric, $135g/m^2$, was supplied by Phoenix Calico Limited, UK.

100% scoured unbleached plain woven cotton fabric, $138g/m^2$, was supplied by Phoenix Calico Limited, UK.

3.1.1.2 Chemicals

Table 3.1 Chemicals used in hydrogen peroxide bleaching experiments

Chemical	Formula	Grade	Manufaturer
Hydrogen peroxide 50% (by wt)	H_2O_2	Laboratory reagent	Aldrich
Tetrasodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	Laboratory reagent	Aldrich
Eriopon R (non-ionic wetting agent)	Commercial Product	Commercial grade	Aldrich
Sodium carbonate	Na_2CO_3	Laboratory reagent	Aldrich
Citric acid	$C_6H_8O_7$	Laboratory reagent	Aldrich
Sodium silicate	Na_2SiO_3	Laboratory reagent	Aldrich
Caustic soda	$NaOH$	Laboratory reagent	Aldrich
Soda ash	Na_2CO_3	Laboratory reagent	Aldrich
Blankit IN	Commercial Product	Commercial grade	BASF

The chemicals used in hydrogen peroxide bleaching experiments are listed in Table 3.1.

3.1.2 Hydrogen peroxide bleaching procedures for wool and cotton

Method 1

Alkaline hydrogen peroxide bleaching: The wool and cotton fabrics were bleached at pH 9, 20-30g/L hydrogen peroxide, 4g/L tetrasodium pyrophosphate, 1g/L non-ionic wetting agent (Eriopon R), 60℃, 0.5-2 hours, and a fabric: liquor ratio of 1:20.

Acidic hydrogen peroxide bleaching: The wool fabrics were also bleached at pH 5 (adjust with sodium carbonate), 20-30g/L hydrogen peroxide, 2g/L citric acid, 80℃, 0.5-2 hours, and a fabric: liquor ratio of 1:20.

Method 2

Higher temperature bleaching: Another bleaching method for cotton fabrics was using 7g/L sodium silicate, 1.2mls/L caustic soda, 1.8g/L soda ash, 5g/L hydrogen peroxide, 85℃, 0.5-2 hour, and a fabric: liquor ratio of 1:15.

After bleaching, the fabrics were rinsed in distilled water and dried at atmospheric conditions (20-25 ℃).

3.1.3 Reductive bleaching procedures for wool

After the hydrogen peroxide bleaching, the wool fabrics were then bleached in 6g/L Blankit IN (reductive bleaching agent) for 1 hour at 60℃, and a wool: liquor ratio of 1:20. After bleaching, the fabrics were rinsed with warm water, cold water, 1 ml/L hydrogen peroxide for 10 minutes and cold water, then dried at atmospheric conditions (20-25 ℃).

3.1.4 Application of fibre protective agents

Protein hydrolysates and protein derivative products were applied as potential fibre protective agents in the bleach bath. The fibre protective agents used in this study are commercial products, supplied by Corda Chemicals, Table 3.2.

Table 3.2 Fibre protective agents used in hydrogen peroxide bleaching experiments

Commercial name	Chemical nature
Keravis^{TM}	Hydrolysed vegetable protein
Tannic acid	Tannin
Byco C	Hydrolysed wheat protein
Voluminis^{TM}	Hydrolyzed wheat protein

The amounts of protective agent that have been introduced to the bleach bath were as follows:

- Byco C: 1, 2, 3 and 5% o.w.f;
- Keravis^{TM}: 1, 2, 3 and 5% o.w.f;
- Tannic acid: 0.5, 1.0, 1.5 and 2% o.w.f.

Voluminis^{TM} was applied on some of the bleached wool fabrics for 10 minutes at room temperature and a wool: liquor ratio of 1:20. The amounts of Voluminis applied were 0.5, 1.0, and 2.0% o.w.f.

3.2 Blank dyeing of wool

All the blank dyeing experiments were performed in sealed, stainless steel 500ml dye pots using a Mathis Labomat BFA laboratory dyeing machine.

3.2.1 Materials

3.2.1.1 Fabrics

100% wool botany serge fabric ($187g/m^2$) was supplied by Whaley's Ltd, Bradford.

3.2.1.2 Chemicals

The chemicals used in blank dyeing experiments are listed in Table 3.3.

Table 3.3 Chemicals used in blank dyeing experiments

Chemical	Formula	Grade	Manufaturer
Acetic acid	CH_3COOH	Laboratory reagent	Aldrich
Sodium acetate	CH3COONa	Laboratory reagent	Aldrich

3.2.2 Dyeing procedures

The wool fabric was dyed at pH 4.5-5.0 (adjust with acetic acid), 1g/L sodium acetate at 100-130 ℃, for 30-60 minutes, and a wool: liquor ratio of 1:20. The wool fabric was also dyed at pH 6.0-7.0 (adjust with acetic acid), 1g/L sodium acetate at 100-130 ℃, for 30-60 minutes, and a wool: liquor ratio of 1:20. After dyeing, the fabrics were rinsed in distilled water and dried at atmospheric conditions (20-25 ℃).

3.2.3 Application of fibre protective agents

Byco C, and Irgasol HTW (DMEU) were applied as protective agent in the dye bath. Irgasol HTW is a formaldehyde-based commercial product, supplied by Ciba. The amounts of protective agent that have been introduced to the dye bath were as follows:

- Byco C: 1, 2,5 and 8% o.w.f;
- Irgasol HTW: 1, 3 and 5% o.w.f.

3.3 Wet processing of wool and cotton in simulated seawater

The simulated seawater was used in the wet processing of wool and cotton instead of distilled water in this study. The concentration of common salt, sodium chloride, in the simulated seawater is 23.96g/L, as the simulated seawater recipe in some papers [1, 2]. The common salt used in this research is laboratory reagent, supplied by Aldrich.

3.4 Dye removal from effluent

3.4.1 Dye adsorption of modified paper filters

3.4.1.1 Handsheet preparation of modified filter papers

The modified paper filters used in this experiment were handsheets made of wood pulp and processed clean chicken feathers.

The wood pulp used in the study consisted of 70% Hardwood fibre (Eno Birch) and 30% Softwood fibre (Lapponia Pine), soaked for 4 hours in 2000mLs water and dispersed in a British Standard Disintegrator for 50,000 revolutions as described in TAPPI T205. The pulp solution was then thickened to 10% consistency and beaten in a PFI mill for 3000 revolutions according to TAPPI T248. After diluting back to 1.3% and a further dispersion the stock was then ready for paper making [3].

Table 3.4 Processing conditions for feathers

Beater roll setting	Time mins	Amperes	Kw/h Reading
20 turns up*	10	13	8806.3
5 turns up	18	14.5	
1 turns up	7	18	
1 turns down	50	20	
20 turns up			8810.3

*20 turns up refers to 5mm above datum.

The chicken feathers were beaten in a Hollander Beater. The net weight of chicken feather processed was 7 kilograms. The details are shown in Table 3.4.

In assessing the dye adsorption by the modified filter paper a range of cellulose/additive compositions were manufactured. They were made in the sheet machine, Figure 3.1, according to TAPPI T205 sp-95 and were specified as 60 g/m^2 (oven dry weight) and 200 mm square in size [4].
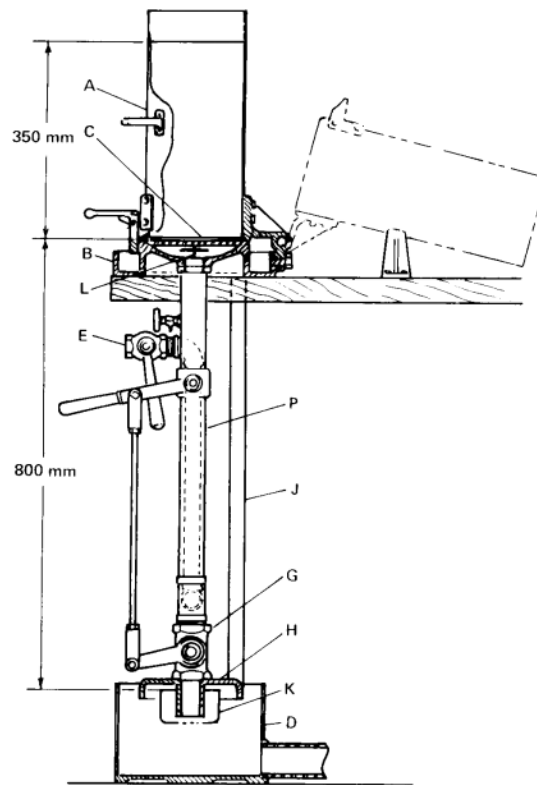
Figure 3.1 Sheet machine [4]

A—Cylindrical deckle
B—Base
C—Wire-covered grid plate
D—Cylinder
E—Water supply valve
G—Drainage valve
H—Crossbar
J—PVC drain pipe
K—Overflow vessel
L—Four-fin baffle
P—Drainage pipe

The compositions of the handsheets are listed in Table 3.5. Cellulous represents the wood pulp. EKA (Cationic Polyamide Epichlorohydrin) was applied as the wet strength additive in this study.

Table 3.5 Compositions of paper with additives in the percentage on the weight of paper.

Cellulose %	Eka %
100	0
99.8	0.2
99.6	0.4
99.4	0.6
99.2	0.8
99.0	1
98.5	1.5
98.0	2
97.5	2.5
97.0	3

Cellulose %	Feathers %	Eka %
90.0	10	0
89.8	10	0.2
89.6	10	0.4
89.4	10	0.6
89.2	10	0.8
89.0	10	1
88.5	10	1.5
88.0	10	2
87.5	10	2.5
87.0	10	3

3.4.1.2 Dye adsorption of modified paper filters

The adsorption characteristics of the paper was assessed using the polyazo C. I. Direct Red 80, Figure 3.2 and the stilbene-type dye C. I. Direct Orange 39, Figure 3.3. Both dyes are manufactured by Classic Dyestuffs Inc.
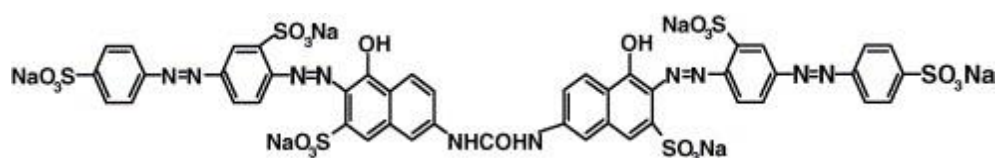
Figure 3.2 Structure of C. I. Direct Red 80 [5]
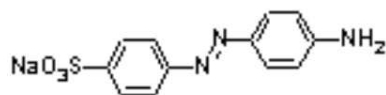
Figure 3.3 Structure of C. I. Direct Orange 39 [6]

Dye adsorption procedures

400mLs of the 0.1g/L dye solution was placed in a beaker (diameter large enough so that the paper can lie flat inside) and set to stir slowly with a magnetic stirrer. The pH of the solution was adjusted to pH 7 and pH 4, and the filter paper placed in the dye solution, and left in the stirring solution for 5 minutes. The paper was removed and left to dry at atmospheric conditions (20-25 °C). For each sample the transmittance of the dye solution was measured before and after exhaustion, then the UV-visible absorbance of the dye solution could be calculated. Each measurement was made in triplicate. Once the paper was dry the K/S value for the paper at λ_{max} was calculated from the measurement of the reflectance of the paper, again triplicate measurements were performed.

3.4.2 Dye adsorption of modified PVP nanofibres

In this study we used a solid hydrophobic PVP polymer, which was forcespun into solid nanofibres to make the novel C_{30}-modified PVP nanofibres. The dye adsorption of the nanofibres was assessed using the same two dyes with these used in the dye adsorption of modified paper filters (polyazo C. I. Direct Red 80, and the stilbene-type dye C. I. Direct Orange 39), and C. I. Disperse Red 60 in addition, Figure 3.4.
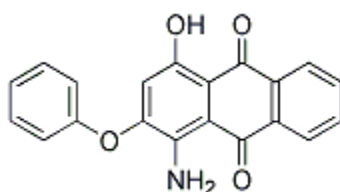
Figure 3.4 Structure of C. I. Disperse Red 60 [7]

Dye adsorption procedures

The dye adsorption experiments were carried out in sealed, stainless steel 50ml dye pots using a Mathis Labomat BFA laboratory dyeing machine. The modified PVP nanofibres were applied in 0.33g/L dye solution, 1g/L wetting agent (Tinovetin), set at 30°C and 40°C, for 30 minutes and a nanofibre: liquor ratio of 1:20. The nanofibres were filtered out with Buchner funnel and dried at atmospheric conditions (20-25 °C). The UV-visible absorbance of the dye solution was measured before and after exhaustion for each sample and the K/S value of the dry nanofibres at λ_{max} were measured.

3.5 Measurements of physical and mechanical properties

3.5.1 Whiteness and yellowness measurements

The CIE Whiteness Index and ASTM E 313 Yellowness Index were measured using a DataColor 600 Spectrophotometer. A dry fabric was measured in a four-folded state at 4 points, and twice on each side, obtaining an average value.

3.5.2 Colour strength

The colour strength, K/S, of the paper filters and PVP nanofibres was determined by measuring the fabric reflectance by DataColor 600 Spectrophotometer. A dry paper was measured at 4 points, twice on each side, obtaining an average value. Due to the form and fragility of the PVP nanofibres, the nanofibre webs were measured only once.

3.5.3 Absorbance measurements

The dye solution was measured by a Phillips PU8700 series UV/Vis Spectrophotometer. The light absorption spectrum of the dye solution before and after the adsorption by the paper filter and nanofibres was measured at the wavelength of

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maximum dye absorption, λ_{max}. The measuring parameters of the UV-Vis Spectrophotometer were set as: absorbance mode, start/stop: 200-750nm, bandwidth: 2.0nm/auto, scan speed: 2000nm/min.

3.5.4 Tensile strength measurements

A test specimen of specified dimensions was extended at a constant rate until rupture using an Instron tensile testing apparatus that measures the maximum force, the elongation at maximum force, the force at rupture and the elongation at rupture, then the tensile strength could be calculated.

3.5.4.1 Experimental details of fabric samples [8]

- The width of the test specimen was 50 mm (excluding any fringe) and the length of test specimen was long enough to allow a gauge length of 150 mm.
- All samples were conditioned at 65% relative humidity and 20 °C for at least 24 hours before testing.
- Gauge length - 150 mm.
- Rate of extension - 100mm/min.
- Number of test - 5 for each sample.

3.5.4.2 Experimental details of paper samples [9]

- Sampling

Width of the test piece - 15 mm

Length of the test piece - the test piece was clamped without handling the section of the test piece between the lines of clamping.

- All samples were conditioned at 50% relative humidity and 23 °C for at least 24 hours before testing.
- The test length (the distance between the clamping lines) - 180 mm

- Constant rate of elongation- 10 mm/minute

- Number of tests - 10 for each sample

Wet strength measurement of paper

Prior to testing the strips were soaked in water for 1 hour. All other details were the same as in the dry strength test of paper [10].

3.5.5 Martindale Abrasion Resistance

A circular fabric specimen, mounted in a specimen holder with foam backing and subjected to a defined load, was rubbed against an abrasive medium (standard fabric) in a translational movement tracing a Lissajous figure, the specimen holder being additionally freely rotatable around its own axis perpendicular to the plane of the specimen. The evaluation of the abrasion resistance of the textile fabric was determined at regular inspection intervals to two yarns broken.

Fabrics test conditions

The sample diameter of the test specimens was 38mm and the diameter of the abradant fabric was at least 140 mm. The diameter of the woven wool felt was 140mm and the diameter of the specimen holder foam backing was 38mm. The fabrics were conditioned to a relative humidity of 65% and temperature of 20 ℃. The breakdown point of the woven fabrics was when two separate threads were completely broken [11].

3.5.6 Kawabata Evaluation System (KES) [12]

How the fabric feels is described as its handle or 'fabric hand'. It is one of the most important factors in the evaluation of fabrics in the apparel market. The Kawabata Evaluation System (KES) was designed to provide an objective evaluation of the handle value of fabric. The system measures the low-stress mechanical and surface properties of fabrics with highly sensitive instruments, including fabric bending,

shearing, tensile, compressive stiffness, smoothness and frictional properties, and the results are expressed in 16 measured or calculated parameters. The Kawabata Evaluation System (KES) provides a unique capability to predict human response, as well as provides an understanding of how the fibre, yarn, fabric construction and finish affect the concept of comfort of the fabric.

Table 3.6 List of KES-F parameters [13]

Property block	Symbol	Description	Unit
Tensile	LT	Linearity of extension curve	-
	WT	Tensile energy	$g.cm/cm^2$
	RT	Tensile resilience	%
	EMT	Extension at 500g/cm load	%
Shear	G	Shear stiffness	g/cm.deg
	2HG	Shear hysteresis (0.5°)	g/cm
	2HG5	Shear hysteresis (5°)	g/cm
Bending	B	Bending stiffness	$g.cm^2/cm$
	2HB	Bending Hysteresis	g.cm/cm
Surface	MIU	Coefficient of friction	-
	MMD	Mean deviation of MIU	-
	SMD	Geometrical roughness	μm
Compression	LC	Linearity of compression curve	-
	WC	Compression energy	$g.cm/cm^2$
	RC	Compression resilience	%
	To	Thickness at $0.5g/cm^2$ pressure	mm
	Tm	Thickness at $50g/cm^2$ pressure	mm
Weight	W	Weight per unit area	mg/cm^2
Primary handle values (PHV)	KOSHI	Stiffness	-
	NUMERI	Smoothness	-
	FUKURAMI	Fullness	-
	T.H.V.	Total hand value	-

The standard sample size used for testing is 20cm x 20cm, although a sample size of 15cm x 15cm was analysed where specified due to material size constraints. The samples were conditioned to a relative humidity of 65% and temperature of 20°C for at least 24 hours before testing.

3.5.7 Scanning Electron Microscopy (SEM)

The fabric samples were attached to the SEM mounting stubs with copper adhesive tape to increase the conductivity of the sample. Then the samples were coated in the sputter coater with a gold cathode before they are transferred into the microscope. The surface of the sample was deposited about a 40 nm gold layer to prevent the accumulation of electric charge. The coating conditions were 2.4 kV, 18-20 mA, three minutes, 3-4 times. The main SEM parameters were: working voltage 5~8kV; auto. beam scale 1~10, working distance 8~10 mm; magnification 500~3000 times.

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Chapter 4

Effect of hydrogen peroxide bleaching on wool and cotton

4.1 Hydrogen peroxide bleaching of wool

100% wool botany serge fabrics were bleached with hydrogen peroxide under alkaline and acid conditions as described in Section 3.1.2 method 1. The CIE Whiteness, tensile strength and abrasion resistance were measured several times for each sample, as mentioned in Section 3.5. The values shown in the tables are mean values.

A lot of wool fabrics were used in this research, when one batch of wool fabrics was used up, another batch of wool fabrics would be used. Three batches of wool fabrics (named Wool 1, Wool 2 and wool 3) were used. These wool fabrics are technically the same, but have slight difference in whiteness tensile strength and abrasion resistance properties. All the wool fabrics mentioned in this chapter are Wool 1.

4.1.1 Alkaline hydrogen peroxide bleaching of wool

4.1.1.1 Effect of alkaline hydrogen peroxide bleaching on the wool whiteness

The original wool fabrics were not quite white. Then the wool fabrics bleached under alkaline conditions showed an obvious increase in CIE Whiteness, Table 4.1. This whitening effect increased with hydrogen peroxide concentration and bleaching time.

Table 4.1 Effect of alkaline hydrogen peroxide bleaching on the whiteness of wool fabric.

pH	Hydrogen peroxide	Temperature	Time	CIE Whiteness
	g/L	℃	hour	
Original Fabric				15.3
9	20	60	1	35.8
9	20	60	1.5	39.5
9	20	60	2	41.4
9	30	60	0.5	38.8
9	30	60	1	38.5
9	30	60	2	43.7

4.1.1.2 Effect of alkaline hydrogen peroxide bleaching on the wool tensile strength

Examination of the tensile data for bleached fabrics indicated that the effect of bleaching was to decrease the fabric tenacity [1], the tensile strength after the hydrogen peroxide bleaching, and the decrease increased with hydrogen peroxide concentration and bleaching time.

Table 4.2 Effect of alkaline hydrogen peroxide bleaching on the tensile strength of wool fabric

pH	Hydrogen peroxide	Temperature	Time	Tensile Strength
	g/L	℃	hour	kN/m
Original Fabric				7.1
9	20	60	1	7.1
9	20	60	2	6.9
9	30	60	1	6.7
9	30	60	2	6.6

4.1.1.3 Effect of alkaline hydrogen peroxide bleaching on the wool abrasion resistance

The effect of bleaching was to reduce the abrasion resistance of the wool fabric, Table 4.3. The detrimental effect increased with hydrogen peroxide concentration and bleaching time.

Table 4.3 Effect of alkaline hydrogen peroxide bleaching on the abrasion resistance of wool fabric

pH	Hydrogen peroxide	Temperature	Time	Number of rubs to end point*
	g/L	℃	hour	
Original Fabric				20000
9	20	60	1	15500
9	20	60	1.5	15000
9	20	60	2	12667
9	30	60	0.5	15250
9	30	60	1	13000
9	30	60	2	14667

*Test continued until two yarns broken.

4.1.2 Acid hydrogen peroxide bleaching of wool

4.1.2.1 Effect of acid hydrogen peroxide bleaching on the wool whiteness

The CIE Whiteness of the wool fabrics showed smaller increase after bleaching under acid hydrogen peroxide bleaching conditions, Table 4.4, compared to the alkaline bleaching. Although again the whitening effect increased with hydrogen peroxide concentration but surprisingly did not increase with bleaching time.

Table 4.4 Effect of acid hydrogen peroxide bleaching on the whiteness of wool fabric

pH	Hydrogen peroxide	Temperature	Time	CIE Whiteness
	g/L	℃	hour	
Original Fabric				15.3
5	20	80	0.5	29.2
5	20	80	1	28.9
5	20	80	1.5	23.9
5	30	80	0.5	29.6
5	30	80	1	20.0

4.1.2.2 Effect of acid hydrogen peroxide bleaching on the wool tensile strength

Examination of the tensile data for wool fabrics bleached at 80^0C did not show an obvious decrease in strength.

Table 4.5 Effect of acid hydrogen peroxide bleaching on the tensile strength of wool fabric.

pH	Hydrogen peroxide	Temperature	Time	Tensile Strength
	g/L	℃	hour	kN/m
Original Fabric				7.2
5	20	80	0.5	7.0
5	20	80	1	7.0
5	20	80	1.5	7.0
5	30	80	0.5	7.1
5	30	80	1	6.7

4.1.2.3 Effect of acid hydrogen peroxide bleaching on the wool abrasion resistance

The abrasion resistance data reduced considerably on the wool fabric bleached under acidic conditions, the number of rubs to end point dropped at least half of the number

of the original wool fabric, Table 4.6. The detrimental effect kept rising with hydrogen peroxide concentration and bleaching time. The Martindale flat abrasion test appears to be a more sensitive indicator of strength loss caused by oxidative bleaching.

Table 4.6 Effect of acid hydrogen peroxide bleaching on the abrasion resistance of wool fabric.

pH	Hydrogen peroxide	Temperature	Time	Number of rubs to end point*
	g/L	℃	hour	
Original Fabric				20000
5	20	80	0.5	10000
5	20	80	1	9750
5	20	80	1.5	8750
5	30	80	0.5	8500
5	30	80	1	8000

*Test continued until two yarns broken.

4.2 Hydrogen peroxide bleaching on cotton

100% scoured and bleached plain woven cotton fabrics were bleached with under alkaline conditions as described in Section 3.1.2 Method 1 for better whiteness. While 100% scoured unbleached plain woven cotton fabrics were bleached using Method 1 under alkaline conditions and Method 2 as well. The CIE Whiteness, tensile strength and abrasion resistance were measured as mentioned in Section 3.5. The values shown in the tables are mean values of several tests.

4.2.1 Hydrogen peroxide bleaching on scoured and bleached cotton

One batch of cotton fabrics were used up after the hydrogen peroxide bleaching, so another batch were used to be the control group. The two batches of fabrics are technically the same, but have slight difference in whiteness and tensile strength.

4.2.1.1 Effect of hydrogen peroxide bleaching on the cotton whiteness

The scoured and bleached cotton already had a high whiteness, but the whiteness was still increased a little after the hydrogen peroxide bleaching, Table 4.7.

Table 4.7 Effect of hydrogen peroxide bleaching on the whiteness of scoured and bleached cotton

pH	Temperature	Time	CIE Whiteness			
	℃	hour	20 g/L hydrogen peroxide		No hydrogen peroxide	
Original Fabric			71.3		83.7	
9	60	1	79.8	+11.9%	85.2	+1.8%
9	60	1.5	81.4	+14.1%	81.9	-2.2%
9	60	2	81.0	+13.6%	83.4	-0.4%

4.2.1.2 Effect of hydrogen peroxide bleaching on the cotton tensile strength

Table 4.8 Effect of hydrogen peroxide bleaching on the tensile strength of scoured and bleached cotton

pH	Temperature	Time	Tensile Strength			
			kN/m			
	℃	hour	20 g/l hydrogen peroxide		No hydrogen peroxide	
Original Fabric			8.7		12.1	
9	60	1	8.5	-3.1%	12.1	-0.1%
9	60	1.5	9.0	+3.5%	12.9	+7.1%
9	60	2	9.6	+9.9%	12.9	+7.0%

The tensile data of scoured and bleached cotton fabrics showed a small amount of initial decrease due to the oxidative damage [2], but with longer processing time the strength increased most likely due to fabric consolidation and shrinkage [3], Table 4.8.

The fabrics in the control group were processed at the same conditions with the hydrogen peroxide bleaching, except no hydrogen peroxide was applied, their tensile data indicated the similar tendency with the bleached fabrics, only 2.9-3.6% difference in terms of change rate. Therefore, the hydrogen peroxide had little effect on the tensile strength in this case.

4.2.1.3 Effect of hydrogen peroxide bleaching on the cotton abrasion resistance

The abrasion resistance of the cotton fabrics in the control group increased, probably due to fabric consolidation and shrinkage. However compared to the control group, the bleached fabrics increase to a lesser extent probably due to the hydrogen peroxide cause the strength loss of the bleached cotton fabrics [4, 5].

Table 4.9 Effect of hydrogen peroxide bleaching on the abrasion resistance of scoured and bleached cotton

pH	Temperature	Time	Number of rubs to end point			
	℃	hour	20 g/l hydrogen peroxide		No hydrogen peroxide	
Original Fabric			16750		16750	
9	60	1	17500	+4.5%	19000	+13.4%
9	60	1.5	17500	+4.5%	18500	+10.4%
9	60	2	17333	+3.5%	18750	+11.9%

4.2.2 Hydrogen peroxide bleaching on scoured unbleached cotton

4.2.2.1 Effect of hydrogen peroxide bleaching on the cotton whiteness

The whiteness of scoured unbleached cotton increased considerably after bleaching. The whitening effect increased with the bleaching time.

Table 4.10 Effect of hydrogen peroxide bleaching on the whiteness of scoured unbleached cotton

pH	Temperature	Time	CIE Whiteness	
	℃	hour	20 g/L hydrogen peroxide	No hydrogen peroxide
Original Fabric			4.0	
9	60	1	32.2	4.6
9	60	1.5	40.8	6.3
9	60	2	46.2	6.2

4.2.2.2 Effect of hydrogen peroxide bleaching on the cotton tensile strength

Examination of the tensile data for the scoured unbleached cotton fabrics showed only an increase in the strength of the control fabrics due to the probable effect of the fabric consolidation and shrinkage, Table 4.11. Meanwhile, the data of the bleached fabrics showed a relatively smaller increase due to the oxidative damage, caused by oxycellulose formation of cotton fibres [6], reducing the effect of the fabric consolidation and shrinkage on fabric strength.

Table 4.11 Effect of hydrogen peroxide bleaching on the tensile strength of scoured unbleached cotton

pH	Temperature	Time	Tensile Strength	
			kN/m	
	℃	hour	20 g/L hydrogen peroxide	No hydrogen peroxide
Original Fabric			12.2	12.2
9	60	1	13.4	14.3
9	60	1.5	14.0	14.3
9	60	2	14.5	14.4

4.2.2.3 Effect of hydrogen peroxide bleaching on the cotton abrasion resistance

The abrasion resistance of the cotton fabrics increased considerably after the

processing of the fabrics with and without hydrogen peroxide, in all probability due to fabric consolidation and shrinkage. The number of rubs at which the specimen breaks down varied to a small extent between the bleached fabrics and the fabrics in the control group. This suggested that the hydrogen peroxide appeared to have little influence on the abrasion resistance on this experimental fabric.

Table 4.12 Effect of hydrogen peroxide bleaching on the abrasion resistance of scoured unbleached cotton

pH	Temperature	Time	Number of rubs to end point	
	℃	hour	20 g/L hydrogen peroxide	No hydrogen peroxide
Original Fabric			13250	
9	60	1	22000	19250
9	60	1.5	21000	20000
9	60	2	21250	19750

4.2.3 Higher temperature bleaching on scoured unbleached cotton

4.2.3.1 Effect of higher temperature bleaching on the cotton whiteness

Table 4.13 Effect of higher temperature bleaching on the whiteness of scoured unbleached cotton

Temperature	Time	CIE Whiteness	
℃	minute	Bleached fabric	Control Group
Original		4.0	
85	30	48.1	4.4
	45	53.2	4.9
	60	55.6	4.1
	90	62.9	4.3

This higher temperature bleaching method clearly increased the whiteness of the scoured cotton, Table 4.13, to a much greater extent than the lower temperature bleaching system, Table 4.10. Further the whitening effect improved with the bleaching time for the higher temperature bleaching method.

4.2.3.2 Effect of higher temperature bleaching on the cotton tensile strength

The scoured cotton bleached with the higher temperature method showed a small increase in the tensile strength of the bleached fabrics and the control fabrics. The increased tensile strength was around 15% for the control group, which was most due to some fabric consolidation and shrinkage [7]. In contrast the bleached cotton had about a 10% increase of the tensile strength, a little lower than that of the control group, indicated that there was a little oxidative damage to the tensile strength of the bleached cotton fabrics [4].

Table 4.14 Effect of higher temperature bleaching on the tensile strength of scoured unbleached cotton

Temperature	Time	Increase percentage of tensile strength	
℃	minute	Bleached fabric	Control Group
85	30	6.5%	18.6%
	45	11.9%	12.9%
	60	11.0%	17.4%
	90	9.3%	17.7%

4.2.3.3 Effect of bleaching higher temperature bleaching on the cotton abrasion resistance

Examination of the abrasion resistance data for the scoured cotton fabrics showed a considerable increase in the processed fabrics for both the bleached and control fabrics, and the percentage increased with the processing time, most probably due to

the consolidation.

Table 4.15 Effect of higher temperature bleaching on the abrasion resistance of scoured unbleached cotton

Temperature	Time	Increase percentage of number of rubs to end point	
℃	minute	Bleached fabric	Control Group
85	30	49.1%	37.7%
	45	60.0%	54.0%
	60	53.5%	60.4%
	90	60.0%	66.0%

4.3 Conclusions

The alkaline hydrogen peroxide bleaching had a good whitening effect on the wool fabrics, and the whitening effect increased with hydrogen peroxide concentration and bleaching time. While the tensile strength and abrasion resistance decreased to some extent. The detrimental effect of the tensile strength and abrasion resistance also increased with hydrogen peroxide concentration and bleaching time.

The wool fabrics bleached under acidic conditions showed a smaller increase in CIE Whiteness compared to the alkaline bleaching. The whitening effect still increased with hydrogen peroxide concentration but did not increase with bleaching time. The tensile strength did not have an obvious decrease with hydrogen peroxide concentration or bleaching time and is perhaps why acid peroxide bleaching was developed to achieve a balance of whiteness and strength maintenance. The flat abrasion of the wool fabrics bleached under acid condition decreased much more than that of the fabrics bleached under alkaline condition, and the fabric strength also decreased with hydrogen peroxide concentration and bleaching time. The Martindale flat abrasion test appears to be a more sensitive indicator of strength loss caused by oxidative bleaching.

The effect on bleaching on the CIE Whiteness of the scoured and already bleached cotton fabrics was to maintain the whiteness of the pre-bleached fabrics but to clearly improve the whiteness of thescoured unbleached cotton. The bleaching at higher temperature imparted a better whiteness on the scoured unbleached fabrics, however the effect of bleaching on the strength of the fabrics was more complex due to the fabric consolidation and shrinkage occurring during the aqueous treatment. Nevertheless the oxidative peroxide bleaching still reduced the strength lower than that observed for the control fabrics.

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Chapter 5

Effect of fibre protective agents on wool and cotton bleaching

5.1 Effect of Keravis™ on bleaching of wool

5.1.1 Effect of Keravis™ on the whiteness of bleached wool fabric

Keravis™ is hydrolysed vegetable protein PG-Propyl Silanetriol which is designed to deliver optimal anti-breakage benefits [1, 2]. It is a multifaceted protein based complex which acts on all of the three fundamental parameters of hair strength: tensile properties, bending modulus and cuticle abrasion. The unique chemical composition of Keravis™ allows it to penetrate into the hair cortex, building strength from within, while providing film forming effects to reinforce, lubricate and protect the surface of the hair. These properties combine to strengthen the hair, thus, helping to reduce the degree of damage hair sustains from chemical treatments, environmental stresses or styling practices.

The incorporation of Keravis™ into the bleach formulation did not adversely affect whiteness, Table 5.1.

Table 5.1 Effect of Keravis™ on the whiteness of bleached wool fabric

pH	Hydrogen peroxide	Temperature	Time	CIE Whiteness			
	g/L	℃	hour	With no Keravis™	with 3% Keravis™	with 5% Keravis™	with 10% Keravis™
Original fabric				15.3			
9	20	60	1	32.8	34.2	35.1	34.6
			2	39.3	38.8	39.2	39.6
	30		1	38.2	37.3	37.8	37.2
			2	42.5	41.2	41.8	41.1

Wool 2 was used in this section.

5.1.2 Effect of Keravis™ on the abrasion resistance of bleached wool fabric

The application of Keravis™ in the bleach bath had a marginally beneficial effect in mainatining the wool fabric strength, Table 5.2, which can be seen from the increase in the number of rubs to end point of the bleached wool fabrics with 5% o.w.f. applied Keravis™, for both 1 hour and 2 hours of bleaching time.

Table 5.2 Effect of Keravis™ on the abrasion resistance of bleached wool fabric

pH	Hydrogen peroxide g/L	Temperature ℃	Time hour	Keravis™ %	Number of rubs to end point
Original fabric					20000
9	20	60	1	0	12000
				3	12667
				5	13000
			2	0	10500
				3	11500
				5	11750

5.2 Effect of tannic acid on bleaching of wool fabric

Tannic acid is a known antioxidant and it was anticipated it may have a beneficial effect on the properties of the bleached wool [3]. Previous studies indicate it can protect against hypochlorite and peroxide attack on wool and cotton. However it is apparent that increasing the tannic acid concentration in the alkaline bleach reduced the efficiency of the bleaching process, Table 5.3, suggesting the tannic acid reacts with the peroxide and interferes with the whitening process.

Table 5.3 Effect of tannic acid on the whiteness of wool fabric bleached under alkaline condition

pH	Hydrogen peroxide g/L	Temperature ℃	Time hour	CIE Whiteness		
				With no tannic acid	With 1% tannic acid	With 2% tannic acid
Original fabric				20.8		
9	20	60	1	37.2	27.6	21.1
			2	41.2	31.3	23.7
	30		1	41.1	30.9	26.1
			2	44.7	35.4	29.6

Wool 1 was used in this section.

While the tannic acid reduced the alkaline bleaching efficiency it is apparent that the acid peroxide performance was far more dramatically affected, Table 5.4. In fact the black colour of the tannic acid stained the wool resulting in a negative effect on fabric whiteness.

Table 5.4 Effect of tannic acid on the whiteness of wool fabric bleached under acid condition

pH	Hydrogen peroxide g/L	Temperature ℃	Time hour	CIE Whiteness		
				With no tannic acid	With 1% tannic acid	With 2% tannic acid
Original fabric				20.8		
5	20	80	1	23.6	15.0	7.1
			2	23.6	12.8	5.7
	30		1	29.7	18.3	9.2
			2	18.8	14.6	7.5

5.3 Effect of Byco C on bleaching of wool fabric

Byco C (Croda Gelatins, UK) is a type of hydrolysed protein made from gelatine by enzymic hydrolysis, and has various industrial uses such as growth media, nutrition, emulsions and so on [4]. Gelatine is a protein derived from the hydrolysis of collagen and its chemical structure is shown in Figure 5.1.
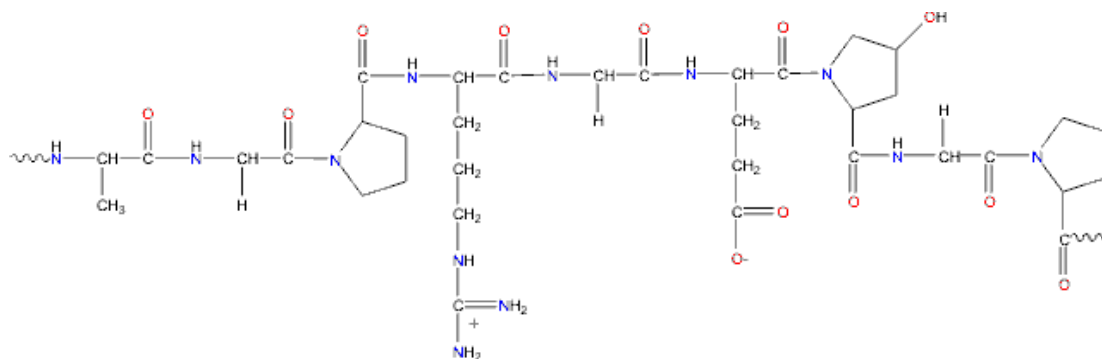
Figure 5.1 Chemical structure of gelatine [5]

5.3.1 Effect of Byco C on oxidative bleaching of wool fabric

5.3.1.1 Effect of Byco C on the whiteness of oxidative bleached wool fabric

Table 5.5 Effect of Byco C on the whiteness of wool fabric bleached under alkaline condition

pH	Hydrogen peroxide	Temperature	Time	CIE Whiteness		
	g/L	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
	Original			15.3		
9	20	60	1	35.8	35.7	34.5
			1.5	39.5	38.6	39.7
			2	41.4	41.7	40.6
	30		0.5	38.8	37.9	35.0
			1	38.5	39.7	39.8
			2	43.7	42.7	43.0

Wool 2 was used in this section.

Examination of the CIE whiteness values for the wool fabrics bleached under alkaline condition indicated that the incorporation of Byco C into the bleaching formulation had little effect on the overall improvement in fabric whiteness, Table 5.5.

The incorporation of Byco C into the bleaching bath again similarly had little effect on the overall improvement in fabric whiteness under acid conditions, Table 5.6.

Table 5.6 Effect of Byco C on the whiteness of wool fabric bleached under acid condition

pH	Hydrogen peroxide	Temperature	Time	CIE Whiteness		
	g/L	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
Original				15.3		
5	20	80	0.5	29.2	30.3	29.1
			1	28.9	29.8	28.2
			1.5	23.9	28.4	25.7
	30		0.5	29.6	30.6	31.1
			1	20.0	27.8	26.3

5.3.1.2 Effect of Byco C on the tensile strength of oxidative bleached wool fabric

Table 5.7 Effect of Byco C on the tensile strength of wool fabric bleached under alkaline conditions

pH	Hydrogen peroxide	Temperature	Time	Tensile Strength kN/m		
	g/l	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
Original				7.1		
9	20	60	1	6.9	6.9	6.6
			2	6.7	6.6	6.7
	30		1	6.6	6.5	6.6
			2	6.5	6.5	6.6

The tensile data for bleached fabrics showed that the effect of incorporating the Byco C into the 60℃ alkaline treatments was relatively small and offered no significant benefits or fibre protection, Table 5.7.

The effect of incorporating the Byco C into the 80℃ acid treatments was also small, Table 5.8, the tensile strength data of the wool fabrics bleached with 3% and 5% Byco C slightly increased , and did not greatly appear to maintain the wool's tensile strength.

Table 5.8 Effect of Byco C on the tensile strength of wool fabric bleached under acid conditions

pH	Hydrogen peroxide	Temperature	Time	Tensile Strength kN/m		
	g/l	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
Original fabric				7.6		
5	20	80	0.5	7.0	7.4	7.3
			1	7.0	7.0	7.0
			1.5	7.0	7.0	7.1
	30		0.5	7.1	7.3	7.1
			1	6.7	6.8	6.9

5.3.1.3 Effect of Byco C on the abrasion resistance of oxidative bleached wool fabric

The abrasion resistance data of the wool fabric bleached under alkaline condition showed that the addition of the Byco C to the bleach bath clearly reduced the strength loss or maintained the strength of the bleached wool fabric, in effect it functioned as a fibre protective agent.

Table 5.9 Effect of Byco C on the abrasion resistance of wool fabric bleached under alkaline condition

pH	Hydrogen peroxide	Temperature	Time	Number of Rubs to End Point		
	g/L	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
Original				20000		
9	20	60	1	15500	20500	20500
			1.5	15000	17333	18500
			2	12667	12500	15500
	30		0.5	15250	18000	19000
			1	13000	13000	17500
			2	14667	15000	17333

Table 5.10 Effect of Byco C on the abrasion resistance of wool fabric bleached under acid conditions

pH	Hydrogen peroxide	Temperature	Time	Number of Rubs to End Point		
	g/L	℃	hour	With no Byco C	With 3% Byco C	With 5% Byco C
Original				20000		
5	20	80	0.5	10000	10500	11500
			1	9750	10000	11000
			1.5	8750	10250	10750
	30		0.5	8500	9667	10500
			1	8000	10000	10250

The effect of incorporating the Byco C into the 80^0C acid bleaching treatments was also beneficial to maintaining the strength of the wool fabrics. The Byco C functioned as a fibre protective agent under this condition as well, Table 5.10.

5.3.2 Effect of Byco C on oxidative and reductive bleaching of wool fabric

The wool fabrics were first oxidatively bleached for 1 hour using Method 1 Alkaline

hydrogen peroxide bleaching in Section 3.1.2, then reductively bleached as described in Section 3.1.3.

5.3.2.1 Effect of Byco C on the whiteness of oxidative and reductive bleached wool fabric

The reductive bleaching process, after the oxidative bleaching, can further whiten wool fabrics [6], and this was apparent in the CIE whiteness data obtained in this study, Table 5.11. The incorporation of Byco C did not have a deleterious effect on the whitening in both bleaching steps.

Table 5.11 Effect of Byco C on the whiteness of oxidative and reductive bleached wool fabric

Hydrogen peroxide	Byco C in oxiditive bleaching	CIE Whiteness			
		No reductive bleaching	Reductive bleaching with no Byco C	Reductive bleaching with Byco C	
g/L	%	bleaching		3% Byco C	5% Byco C
Original		2.8			
20	0	26.5	42.7		
	3	26.3	44.0	42.6	
	5	26.9	44.8		43.8
30	0	27.5	49.5		
	3	29.3	49.2	47.2	
	5	28.8	48.5		49.1

Wool 3 was used in this section.

5.3.2.2 Effect of Byco C on the tensile strength of oxidative and reductive bleached wool fabric

The tensile strength values of the oxidative and reductive bleached wool fabrics did not have much difference with that of just oxidative bleached ones. While the tensile values of the fabrics bleached with Byco C were most slightly higher than that of the

fabrics bleached without Byco C, it appeared in oxidative bleaching as well as oxidative and reductive bleaching.

Table 5.12 Effect of Byco C on the tensile strength of oxidative and reductive bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Tensile Strength (kN/m)			
		No reductive bleaching	Reductive bleaching with no Byco C	Reductive bleaching with Byco C	
g/L	%			3% Byco C	5% Byco C
Original		6.9			
20	0	6.5	6.6		
	3	6.6	6.6	6.8	
	5	6.6	6.6		6.8
30	0	6.7	6.6		
	3	6.4	6.8	6.7	
	5	6.6	6.7		6.8

5.3.2.3 Effect of Byco C on the abrasion resistance of oxidative and reductive bleached wool fabric

Table 5.13 Effect of Byco C on the abrasion resistance of oxidative and reductive bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Number of rubs to end point			
		No reductive bleaching	Reductive bleaching with no Byco C	Reductive bleaching with Byco C	
g/L	%			3% Byco C	5% Byco C
Original		20000			
20	0	15500	12250		
	3	20500	13000	13500	
	5	20500	12500		14500
30	0	13000	11000		
	3	13000	12000	12250	
	5	17500	13000		12500

The reductive bleaching process clearly lowered the flat abrasion performance of the oxidatively bleached wool fabrics, which was evident by the reduction in the number of rubs to end point, Table 5.13. The application of Byco C in the bleach bath still can be regarded as the fibre protective agent for both of the bleaching process.

5.3.3 Effect of Voluminis^{TM} on bleached wool fabric

Voluminis™ is a novel and optimized copolymer of hydrolyzed wheat protein and a cationic monomer [7]. The parent hydrolyzed protein is functional in its own right providing substantivity and moisturization both on the surface but primarily inside the hair cortex. By combining the properties of the hydrolyzed protein with a cationic polymer through controlled copolymerization, it is claimed that the highly functional cationic derivative provides hair volumization from rinse-off systems through a combination of substantivity without build-up, film formation, controlled charge repulsion and reduction in fiber-fiber cohesion.

5.3.3.1 Effect of Voluminis^{TM} on oxidatively bleached wool fabric

The wool fabrics were first oxidatively bleached using Method 1 Alkaline hydrogen peroxide bleaching in Section 3.1.2, then processed with Voluminis^{TM} as described in Section 3.1.4.

Effect of Voluminis on the whiteness of oxidative bleached wool fabric
The application of Voluminis^{TM} on just oxidative bleached wool had only very small effect on the CIE whiteness data. Generally the 0.5% Voluminis^{TM} decreased the CIE whiteness value slightly, and then with the increase of the amount of Voluminis^{TM} to 2.0%, the CIE whiteness values showed a small increase.

Table 5.14 Effect of Voluminis on the whiteness of oxidative bleached wool fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	CIE Whiteness			
					Voluminis^{TM}			
	g/L	℃	hour	%	0%	0.5%	1.0%	2.0%
Original					2.8			
9	30	60	1	0	27.5	25.8	27.2	27.8
				3	29.3	27.8	28.0	29.8
				5	28.8	25.4	28.1	30.7
			2	0	33.7	31.3	32.6	35.2
				3	34.3	32.6	33.8	34.0
				5	33.6	32.1	32.5	35.7

Wool 3 was used in this section.

Effect of Voluminis^{TM} on the KES-F of oxidative bleached wool fabric

Surprisingly the effect of Voluminis^{TM} on the primary hand values in the KES-F was only marginal, Table 5.15. The reason for this behaviour is not certain at present.

Table 5.15 Effect of Voluminis^{TM} on the KES-F of oxidative bleached wool fabric

Time	Byco C	Voluminis^{TM}	KOSHI	NUMERI	FUKURAMI
hour	%	%			
Original			3.2	6.7	5.9
1	0	0.0	2.1	7.5	8.1
		2.0	2.3	6.8	7.7
	3	0.0	2.1	7.1	8.0
		2.0	2.0	7.1	8.0
	5	0.0	1.8	7.3	8.6
		2.0	2.3	6.5	7.6
2	0	0.0	2.1	7.5	8.1
		2.0	2.3	6.3	7.7
	3	0.0	2.4	7.3	8.0
		2.0	2.3	6.5	7.5
	5	0.0	2.2	7.1	7.9
		2.0	2.3	6.7	7.5

5.3.3.2 Effect of Voluminis[TM] on oxidatively and reductively bleached wool

The wool fabrics were oxidatively bleached for 1 hour using Method 1 Alkaline hydrogen peroxide bleaching in Section 3.1.2 at first, and reductively bleached as described in Section 3.1.3, then processed with Voluminis[TM] as described in Section 3.1.4.

Effect of Voluminis[TM] on the whiteness of oxidatively and reductively bleached wool fabric

The CIE whiteness values showed the added Voluminis[TM] increased the fabric whiteness on oxidative and reductive bleached wool and the CIE whiteness value increased with the amount of Voluminis[TM] applied, Table 5.16.

Table 5.16 Effect of Voluminis[TM] on the whiteness of oxidative and reductive bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	CIE Whiteness			
				Voluminis[TM] (%)			
g/L	%	g/L	%	0.0	0.5	1.0	2.0
Original				2.8			
20	0	6	0	42.7	46.8	46.9	47.2
	3		0	44.0	45.8	46.4	45.0
			3	42.6	45.1	45.8	44.9
	5		0	44.8	45.2	45.8	46.3
			5	43.8	44.3	44.8	44.9
30	0		0	49.5	50.1	48.5	49.8
	3		0	49.2	50.0	49.8	48.5
			3	47.2	48.6	48.4	49.2
	5		0	48.5	49.5	50.6	50.7
			5	49.1	49.3	49.7	48.8

Effect of Voluminis^{TM} on the tensile strength of oxidatively and reductively bleached wool fabric

Examination of the tensile data indicated that the application of Voluminis^{TM} on the oxidative and reductive bleached wool fabric had little effect on the fabric strength retention, while the Byco C did offer some fibre protection in the both oxidative and reductive bleaching, Table 5.17.

Table 5.17 Effect of Voluminis^{TM} on the tensile strength of oxidatively and reductively bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Tensile Strength	
				kN/m	
g/L	%	g/L	%	No Voluminis^{TM}	2% Voluminis^{TM}
Original				6.9	
20	0	6	0	6.6	7.1
	3		0	6.6	7.2
			3	6.8	7.0
	5		0	6.6	7.1
			5	6.8	7.1
30	0		0	6.6	7.2
	3		0	6.8	7.1
			3	6.7	6.9
	5		0	6.7	6.9
			5	6.8	7.1

Effect of Voluminis^{TM} on the abrasion resistance of oxidatively and reductively bleached wool fabric

The effect of Voluminis^{TM} on the abrasion resistance of the oxidatively and reductively bleached wool fabric was variable, with some sample yarn failure end points increasing while others decreased, Table 5.18. It was hoped the electrostatic repulsion would reduce fibre engagement but it was not evident from the single

additive treatment. In contrast the incorporation of Byco C clearly reduced the strength loss, and the effect increased with the amount of Byco C applied.

Table 5.18 Effect of Voluminis^{TM} on the abrasion resistance of oxidatively and reductively bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Number of rubs to end point	
g/L	%	g/L	%	No Voluminis^{TM}	2% Voluminis^{TM}
Original				20000	
20	0	6	0	12250	12000
	3		0	13000	12750
			3	13500	14500
	5		0	12500	13500
			5	14500	14500
30	0		0	11000	12000
	3		0	12000	12500
			3	12250	13500
	5		0	13000	12250
			5	12500	14250

Effect of Voluminis^{TM} on the KES-F of oxidative and reductive bleached wool fabric

Examination of the KES-F data of various processed wool fabrics showed 2% Voluminis increased the fabric stiffness, decreased the fabric smoothness and fullness, and accordingly, the total hand value was decreased. The application of Byco C did not have obvious effect on the handle of the wool fabrics, Table 5.19.

Table 5.19 Effect of Voluminis^TM on the KES-F of oxidative and reductive bleached wool fabric

KES-F Parameters		1	2	3	4	5	6	7
EMT	%	8.32	11.29	12.37	13.90	12.08	12.47	15.13
B	g.cm^2/cm	0.103	0.105	0.100	0.093	0.105	0.101	0.096
2HB	g.cm/cm	0.0378	0.0432	0.0441	0.0513	0.0537	0.0540	0.0575
G	g/cm.deg	0.35	0.30	0.30	0.38	0.30	0.29	0.35
2HG5	g/cm	0.62	0.36	0.56	0.95	0.44	0.57	0.83
MMD		0.0159	0.0194	0.0186	0.0223	0.0176	0.0182	0.0203
SMD	μm	3.16	4.60	4.99	5.16	4.24	5.05	5.39
RC	%	62.99	55.95	50.44	48.04	56.07	50.16	48.24
T	mm	0.716	0.585	1.127	1.300	0.544	1.133	1.313
W	mg/cm^2	20.1	19.7	21.7	20.6	19.6	21.7	21.3
KOSHI		3.20	2.37	1.79	1.84	2.68	1.72	1.87
NUMERI		6.74	7.65	7.62	6.11	7.93	7.69	6.42
FUKURAMI		5.87	7.26	8.55	8.15	7.45	8.69	8.43

[1] Original wool fabric

[2] Oxidative bleached wool fabric with no Byco C

[3] Oxidative and reductive bleached wool fabric with no Byco C

[4] Oxidative and reductive bleached wool fabric with no Byco C, then treated with 2% Voluminis

[5] Oxidative bleached wool fabric with 3% Byco C

[6] Oxidative (3% Byco C) and reductive bleached (no Byco C) wool fabric

[7] Oxidative (3% Byco C) and reductive bleached (no Byco C) wool fabric, then treated with 2% Voluminis

5.4 Effect of Byco C in the bleach bath on bleaching of cotton fabric

5.4.1 Effect of Byco C in the bleach bath on bleaching of scoured and bleached cotton fabric

5.4.1.1 Effect of Byco C in the bleach bath on the whiteness of scoured and bleached cotton fabric

The CIE whiteness data in Table 5.20 showed the application of Byco C, up to 5%, in the bleach bath did not adversely affect the fabric whiteness.

Table 5.20 Effect of Byco C on the whiteness of scoured and bleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C (%)		
	g/l	℃	hour	0	3	5
Original Fabric				71.3		
9	20	60	1	79.8	79.9	79.6
			1.5	81.4	79.6	80.9
			2	81.0	81.3	81.1

5.4.1.2 Effect of Byco C in the bleach bath on the tensile strength of scoured and bleached cotton fabric

Examination of the tensile data for the scoured and bleached cotton fabrics did not show an obvious effect of the Byco C on the fabric strength maintenance. It is apparent fabric shrinkage and consolidation was occurring, hence a fabric strength increase was observed.

Table 5.21 Effect of Byco C on the tensile strength of scoured and bleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	Breaking Load	Tensile Strength
	g/L	℃	hour	%	N	kN/m
Original Fabric					436.8	8.7
9	20	60	1	0	423.4	8.5
				3	465.2	9.3
				5	463.4	9.3
			1.5	0	451.9	9.0
				3	449.4	9.0
				5	465.8	9.3
			2	0	480.2	9.6
				3	432.9	8.7
				5	461.3	9.2

5.4.1.3 Effect of Byco C in the bleach bath on the abrasion resistance of scoured and bleached cotton fabric

The incorporation of Byco C in the bleach bath clearly reduced the strength loss of the bleached fabrics, and the number of rubs to end point increased with the amount of Byco C applied, Table 5.22.

Table 5.22 Effect of Byco C on the abrasion resistance of scoured and bleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	Number of rubs to end point
	g/L	℃	hour	%	
Original Fabric					16750
9	20	60	1	0	17500
				3	18750
				5	20500
			1.5	0	17500
				3	18750
				5	20000
			2	0	17333
				3	19250
				5	19500

5.4.2 Effect of Byco C on bleaching of scoured unbleached cotton fabric

5.4.2.1 Effect of Byco C in the bleach bath on the whiteness of scoured unbleached cotton fabric

The incorporation of Byco C into the hydrogen peroxide bleaching bath at 60 ℃ for the scoured unbleached cotton did adversely affect the fabric whiteness according to the CIE whiteness data, Table 5.23. The Byco C appears to be reducing the efficiency of bleaching at this relatively low processing for cotton.

Table 5.23 Effect of Byco C on the whiteness of scoured unbleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	CIE Whiteness
	g/L	℃	hour	%	
Original fabric					6.0
9	20	60	1	0	32.2
				3	31.8
				5	30.0
			1.5	0	40.8
				3	38.6
				5	36.8
			2	0	46.2
				3	41.0
				5	38.3

5.4.2.2 Effect of Byco C in the bleach bath on the tensile strength of scoured unbleached cotton fabric

The tensile data of the bleached cotton fabrics indicated that the strength properties were protected by the application of Byco C, but the breaking load and tensile strength increase was relatively small.

Table 5.24 Effect of Byco C on the tensile strength of scoured unbleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	Breaking Load	Tensile Strength
	g/l	℃	hour	%	N	kN/m
Original fabric					609.4	12.2
9	20	60	1	0	667.9	13.4
				3	699.6	14.0
				5	685.7	13.7
			1.5	0	698.4	14.0
				3	723.4	14.9
				5	756.6	15.1
			2	0	726.6	14.5
				3	731.5	14.6
				5	723.0	14.5

5.4.2.3 Effect of Byco C in the bleach bath on the abrasion resistance of scoured unbleached cotton fabric

Examination of the abrasion resistance data of the bleached cotton fabrics showed that the addition of the Byco C to the bleach bath clearly reduced the strength loss or maintained the strength of the bleached fabrics. The number of rubs to end point increased with the amount of Byco C applied in the bleach bath.

Table 5.25 Effect of Byco C on the abrasion resistance of scoured unbleached cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	Number of rubs to end point
	g/L	℃	hour	%	
Original fabric					13250
9	20	60	1	0	22000
				3	23000
				5	23250
			1.5	0	21000
				3	23000
				5	23750
			2	0	21250
				3	22750
				5	23250

5.4.3 Effect of Byco C in the bleach bath on scoured unbleached cotton fabric bleached with higher temperature method

5.4.3.1 Effect of Byco C in the bleach bath on the whiteness of scoured unbleached cotton fabric

In general the CIE whiteness values of the cotton fabrics were not influenced by the addition of Byco C in the bleach bath treatment at 85℃,Table5.26.

Table 5.26 Effect of Byco C in the bleach bath on the whiteness of scoured unbleached cotton fabric

Temperature	Time	Byco C	CIE Whiteness
℃	minute	%	
Original fabric			1.5
85	30	0	48.1
		3	42.7
		5	51.5
	45	0	53.2
		3	55.7
		5	52.4
	60	0	55.6
		3	59.4
		5	55.5
	90	0	62.9
		3	61.0
		5	57.7

5.4.3.2 Effect of Byco C in the bleach bath on the tensile strength of scoured unbleached cotton fabric

Examination of the tensile data for cotton fabrics bleached at 85℃ showed an increase in strength with the incorporation of Byco C into the treatment bath, Table 5.27. The breaking load and tensile strength reached the peak with the 3% Byco C addition in the 30 minutes bleaching process, while the breaking load and tensile strength of the cotton fabrics bleached for 60 minutes increased up to the application of 5% Byco C.

Table 5.27 Effect of Byco C in the bleach bath on the tensile strength of scoured unbleached cotton fabric

Temperature	Time	Byco C	Breaking Load	Tensile Strength
℃	minute	%	N	kN/m
Original			609.4	12.2
85	30	0	649.3	13.0
		1	664.0	12.3
		2	656.0	13.1
		3	680.0	13.6
		5	655.5	13.1
	60	0	676.2	13.5
		1	693.4	13.9
		2	692.1	13.8
		3	705.8	14.1
		5	731.7	14.6

5.4.3.3 Effect of Byco C in the bleach bath on the abrasion resistance of scoured unbleached cotton fabric

Table 5.28 Effect of Byco C in the bleach bath on the abrasion resistance of scoured unbleached cotton fabric

Temperature	Time	Byco C	Number of rubs to end point
℃	minute	%	
Original fabric			13250
85	30	0	19750
		3	20500
		5	20750
	45	0	20000
		3	20750
		5	21500
	60	0	20333
		3	20250
		5	21500
	90	0	20000
		3	22500
		5	23500

The flat abrasion data of the scoured unbleached cotton fabrics bleached at 85℃ indicated that the fabric strength was marginally increased with the incorporation of Byco C in the bleach bath, with the fabric strength increasing with the amount of Byco C added, Table 5.28.

5.5 Conclusions

The incorporation of Byco C and Keravis into the bleach formulation did not adversely affect the whiteness but did have a beneficial effect in protecting the wool fabric during bleaching of wool and cotton. In contrast the application of tannic acid did reduce the whitening effect of the hydrogen peroxide bleaching. The effect of incorporating the protein hydrolysate on the bleached fabric's tensile strength was minimal and reflects the different fibre failure mechanisms for flat abrasion and tensile breaking.

The application of Voluminis on just oxidative bleached wool did not have much effect on the fabric whiteness and handle. While the Voluminis increased the fabric whiteness on oxidative and reductive bleached wool and the effect on fabric handle was unclear.

The application of Byco C did not obviously affect the fabric whiteness and tensile strength for the scoured and bleached cotton, while it had a beneficial effect on the flat abrasion of cotton fabrics.

The incorporation of Byco C in both bleaching methods for the scoured unbleached cotton did not affect the final fabric whiteness and maintained the flat abrasion performance. The tensile strength was not influenced much by Byco C in the 60℃ bleaching method, but showed an increase tendency with the rising amount of Byco C in the 85℃ bleaching method.

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Chapter 6

Effect of fibre protective agents on wool during dyeing

6.1 Effect of blank dyeing on wool fabric

The blank dyeing of wool fabrics were processed as described in Section 3.2.

The dyeing of wool fabrics is normally carried out at the boil, however the blend fabrics containing wool and other material could be subjected to higher temperature, for example, polyester [1]. So the temperature of dyeing in this study was up to 130℃.

6.1.1 Effect of blank dyeing on the yellowness of wool fabric

Colouration of wool requires elevated temperatures which would cause hydrothermal damage and yellowing. The ASTM E313 Yellowness Index of the wool fabric was examined to evaluate the extent of the fabric damage.

Table 6.1 Effect of blank dyeing at pH 4.5-5.0 on the yellowness of wool fabric

pH	Temperature	Time	Yellowness Index
	℃	Minutes	
Original fabric			23.7
4.5 - 5.0	100	30	25.0
		60	26.4
	110	30	32.9
		60	35.0
	120	30	35.8
		60	42.2
	130	30	43.9

Wool 3 was used in this section.

The Yellowness Index of the wool fabric dyed at pH 4.5-5.0, 100℃ increased with

the increase of temperature, particularly at above 100℃ and with extended immersion times, Table 6.1. The increase in yellowness was due the degradation of the tyrosine, tryptophan, histidine and cysteine [2, 3].

The yellowing behaviour of the wool fabrics dyed at pH 6.0-7.0 was similar to that of the wool fabrics dyed at pH 4.5-5.0. However the yellowness index of the wool fabric dyed at pH 6.0-7.0 was relatively higher due to the higher hydroxyl concentration and greater hydrothermal damage. Similarly the yellowness indices difference between the wool fabrics dyed at the two pH ranges increased with the temperature, Table 6.2.

Table 6.2 Effect of blank dyeing at pH 6.0-7.0 on the yellowness of wool fabric

pH	Temperature	Time	Yellowness Index
	℃	Minutes	
Original fabric			23.7
6.0 - 7.0	100	30	26.7
		60	28.7
	110	30	27.9
		60	37.7
	120	30	38.1
		60	45.9
	130	30	48.6

6.1.2 KES-F analysis of the effect of blank dyeing on the handle of wool fabric

Examination of the KES-F data showed the effect of aqueous treatment was to increase the fabric's extensibility, thickness and weight and decrease the bending rigidity, Table 6.3, due to wet relaxation of the fabric. With extended dyeing at elevated temperature the fabric bending and shear increased and the shear hysteresis at 5° also showed a big increase due to hydrothermal damage causing fabric handle deterioration. The 2HG5 values have been closely identified with subjective perception of fabric softness and are related to yarn deformation and recovery [4, 5].

Table 6.3 KES-F analysis of the effect of blank dyeing at pH 4.5-5.0 on the mechanical properties of wool fabric

KES-F Parameters		Original	1	2	3
EMT	%	6.80	14.20	13.10	17.73
RT	%	63.77	54.39	59.45	48.59
B	$g.cm^2/cm$	0.159	0.147	0.144	0.185
2HB	g.cm/cm	0.0671	0.0791	0.0688	0.1156
G	g/cm.deg	0.46	0.46	0.45	0.72
2HG5	g/cm	0.85	0.81	0.84	1.63
WC	$g.cm/cm^2$	0.446	0.748	0.763	0.644
RC	%	54.12	47.22	47.09	48.37
T	mm	1.18	1.74	1.72	1.69
W	mg/cm^2	23.96	28.00	28.80	33.33

[1] Wool fabric dyed at 110℃ for 30 minutes
[2] Wool fabric dyed at 110℃ for 60 minutes
[3] Wool fabric dyed at 120℃ for 30 minutes

Examination of the KES-F data showed the handle the wool fabrics dyed at pH 6.0-7.0 were worse than those dyed at pH4.5-5.0, especially for the dyeing temperature of 120℃, Table 6.4. The increased damage to the wool at the higher pH was due to increased amide hydrolysis and degradation to the cysteine residues resulting in embrittlement and stiffening of the fabric.

Table 6.4 KES-F analysis of the effect of blank dyeing at pH 6.0-7.0 on the mechanical properties of wool fabric

KES-F Parameters		Original	4	5
EMT	%	6.80	14.43	24.27
RT	%	63.77	53.39	65.13
B	$g.cm^2/cm$	0.159	0.146	0.224
2HB	g.cm/cm	0.0671	0.0643	0.1501
G	g/cm.deg	0.46	0.48	0.92
2HG5	g/cm	0.85	0.82	2.22
RC	%	54.12	47.39	45.92
T	mm	1.18	1.66	1.77
W	mg/cm^2	23.96	29.24	36.18

[4] Wool fabric dyed at 110℃ for 60 minutes
[5] Wool fabric dyed at 120℃ for 30 minutes

6.1.3 Effect of blank dyeing on the abrasion resistance of wool fabric

Examination of the abrasion resistance data showed the fabric strength dropped considerably when the wool fabrics dyed at pH 4.5-5.0, Table 6.5. The fabrics became very weak after dyeing at 120℃ and 130℃, and the number of rubs to end point decreased significantly with the dyeing time at higher temperature. The degradation was related to peptide bond hydrolysis and hydrothermal damage to the cysteine linkage reducing fabric strength.

Table 6.5 Effect of blank dyeing at pH 4.5-5.0 on the abrasion resistance of wool fabric

pH	Temperature ℃	Time Minutes	Number of rubs to end point
Original			19250
4.5 - 5.0	100	30	13000
		60	14250
	110	30	15250
		60	15750
	120	30	7000
		60	3750
	130	30	<1000

The numbers of rubs to end point of the wool fabrics dyed at pH 6.0-7.0 were similarly decreased when the dyeing temperature was 100℃ or 110℃, Table 6.6. The yarn breakage also dropped sharply when the dyeing temperature increased to 120℃ or 130℃. It is clear that the dyeing time had a significant effect on the abrasion resistance of the wool fabrics dyed at 110℃, 120℃ and 130℃ and that the Martindale flat abrasion test was particularly sensitive to hydrothermal damage. This is perhaps a reflection of the sensitivity of the low-sulphur proteins and lipid loss in the CMC causing fracture between the cortical cells.

Table 6.6 Effect of blank dyeing at pH 6.0-7.0 on the abrasion resistance of wool fabric

pH	Temperature	Time	Number of rubs
	℃	Minutes	to end point
Original			19250
6.0 - 7.0	100	30	15500
		60	16250
	110	30	16000
		60	9250
	120	30	6500
		60	3000
	130	30	<1000

6.2 Effect of Byco C on wool fabric during blank dyeing

6.2.1 Effect of Byco C on the yellowness of dyed wool fabric

The effect of the incorporating Byco C in the dye bath at pH 4.5-5.0 was not obvious in terms of adversely affecting the yellowness index under various dyeing conditions, Table 6.7.

Table 6.7 Effect of Byco C on the yellowness of dyed wool fabric at pH 4.5-5.0

pH	Temperature	Time	Yellowness Index				
			Byco C (%)				
	℃	Minutes	0	1	2	5	8
Original fabric			23.7				
4.5 - 5.0	100	30	25.0	25.3	26.0	25.6	
		60	26.4	27.6	27.1	27.5	
	110	30	35.0	33.0	33.2	29.2	
		60	32.9	32.0	31.6	30.1	
	120	30	35.8		30.6	34.5	33.6
		60	42.2		39.9	38.1	37.4
	130	30	43.9		46.9	33.7	42.8

Wool 3 was used in this section.

Similarly the yellowness data of the wool fabrics dyed at pH 6.0-7.0 was unaffected by the application of the Byco C in the dye bath, Table 6.8.

Table 6.8 Effect of Byco C on the yellowness of dyed wool fabric at pH 6.0-7.0

pH	Temperature	Time	Yellowness Index				
			Byco C (%)				
	℃	Minutes	0	1	2	5	8
Original fabric			23.7				
6.0 - 7.0	100	30	26.7	27.8	26.8	27.2	
		60	28.7	29.0	27.6	29.0	
	110	30	27.9	31.1	29.8	30.2	
		60	37.7	38.6	38.6	34.0	
	120	30	38.1		35.4	33.3	31.2
		60	45.9		46.0	37.6	47.1
	130	30	48.6		48.8	47.3	46.2

6.2.2 KES-F Analysis of the effect of Byco C on the mechanical properties of dyed wool fabric

Table 6.9 Effect of Byco C on the KES-F properties of wool fabric dyed at pH 4.5-5.0, 110℃

KES-F Parameters		Original	1	2	3	4
EMT	%	6.8	14.2	13.0	13.1	12.6
RT	%	63.8	54.44	57.4	59.5	57.6
B	g.cm^2/cm	0.159	0.147	0.142	0.144	0.162
2HB	g.cm/cm	0.0671	0.0791	0.0672	0.0688	0.0767
G	g/cm.deg	0.46	0.46	0.50	0.45	0.43
2HG5	g/cm	0.85	0.81	0.83	0.84	0.75
RC	%	54.1	47.2	47.0	47.1	48.0
T	mm	1.18	1.74	1.73	1.72	1.70
W	mg/cm^2	23.96	28.00	28.31	28.80	**28.04**

[1] Wool fabric dyed for 30 minutes without Byco C
[2] Wool fabric dyed for 30 minutes with 5% Byco C
[3] Wool fabric dyed for 60 minutes without Byco C
[4] Wool fabric dyed for 60 minutes with 5% Byco C

Examination of the KES-F data of the wool fabrics dyed at pH 4.5-5.0, 110℃ showed 5% of Byco C applied in the dye bath had little effect on the handle properties, Table 6.9. The aqueous treatment increased extensibility, fabric thickness and weight and decreased bending rigidity.

The handle of the wool fabrics dyed at pH 4.5-5.0, 120℃ were improved by the application of Byco C in the tensile, bending, shear and compression properties, Table 6.10, with the improvement increased with the amount of Byco C applied in the dye bath.

Table 6.10 Effect of Byco C on the KES-F of dyed wool fabric at pH 4.5-5.0, 120℃

KES-F Parameters		Original	5	6	7
EMT	%	6.80	17.73	15.28	13.82
RT	%	63.77	48.59	53.52	54.90
B	g.cm^2/cm	0.159	0.185	0.140	0.140
2HB	g.cm/cm	0.0671	0.1156	0.0658	0.0672
G	g/cm.deg	0.46	0.72	0.52	0.47
2HG5	g/cm	0.85	1.63	0.99	0.91
RC	%	54.1	48.4	48.9	48.5
T	mm	1.18	1.69	1.71	1.67
W	mg/cm^2	23.96	33.33	29.33	**29.64**

[5]Wool fabric dyed for 30 minutes without Byco C
[6] Wool fabric dyed for 30 minutes with 5% Byco C
[7] Wool fabric dyed for 30 minutes with 8% Byco C

The application of Byco C in the dye bath showed little effect on the fabric handle properties of the wool fabrics dyed at pH 6.0-7.0, 110℃, Table 6.11. The beneficial effect, in terms of B, G and 2HG5, of Byco C increased considerably when the dyeing temperature was raised to 120℃, but the KES-F data indicated that increasing the

amount of Byco C did not have great effect on the fabric handle properties of the wool fabrics dyed at 120℃.

Table 6.11 Effect of Byco C on the KES-F of dyed wool fabric at pH 6.0-7.0

KES-F Parameters		Original	8	9	10	11	12
EM	%	6.80	14.43	13.50	24.27	14.55	14.85
RT	%	63.77	53.39	56.05	65.13	54.23	56.29
B	g.cm^2/cm	0.159	0.146	0.136	0.224	0.145	0.145
2HB	g.cm/cm	0.0671	0.0643	0.0623	0.1501	0.0648	0.0646
G	g/cm.deg	0.46	0.48	0.44	0.92	0.47	0.44
2HG5	g/cm	0.85	0.82	0.69	2.22	0.85	0.77
RC	%	54.1	47.4	48.3	45.9	46.6	48.2
T	mm	1.18	1.66	1.68	1.77	1.65	1.64
W	mg/cm^2	23.96	29.24	28.49	36.18	29.16	28.80

[8] Wool fabric dyed at 110℃ for 60 minutes without Byco C
[9] Wool fabric dyed at 110℃ for 60 minutes with 5% Byco C
[10] Wool fabric dyed at 120℃ for 30 minutes without Byco C
[11] Wool fabric dyed at 120℃ for 30 minutes with 5% Byco C
[12] Wool fabric dyed at 120℃ for 30 minutes with 8% Byco C

6.2.3 Effect of Byco C on the abrasion resistance of dyed wool fabric

Examination of the abrasion resistance data indicated that the application of Byco C in the dye bath had improved the fabric strength of the wool fabric dyed at pH 4.5-5.0, Table 6.12. The number of rubs to end point generally increased with the amount of Byco C applied at 100-120℃. The effect of Byco C increased with dyeing time of the wool fabrics dyed at 100℃ and 110℃. The wool fabrics dyed at 130℃ were too weak to show any potential beneficial effect of the Byco C.

Table 6.12 Effect of Byco C on the abrasion resistance of wool fabric dyed at pH 4.5-5.0

pH	Temperature	Time	Number of rubs to end point				
			Byco C (%)				
	℃	Minutes	0	1	2	5	8
Original			19250				
4.5 - 5.0	100	30	13000	14250	13333	14500	
		60	14250	14000	15250	17000	
	110	30	15250	16000	15500	17750	
		60	15750	16500	17250	18250	
	120	30	7000			10000	10000
		60	3750		6250	7000	7000
	130	30	<1000	<1000	<1000	<1000	

The flat abrasion of wool fabrics dyed under the higher pH 6.0-7.0, 100-120℃ was obviously enhanced by the application of Byco C, Table 6.13. The increasing amount of Byco C applied in the dye bath up to 8% had a beneficial effect on the abrasion resistance, especially for the wool fabrics dyed at 120℃. The dyeing time did not have an obvious influence on the effect of Byco C. The effect of Byco C at 130℃ on the fabric strength was not able to be established due to the wool fabric being too weak.

Table 6.13 Effect of Byco C on the abrasion resistance of wool fabric dyed at pH 6.0-7.0

pH	Temperature	Time	Number of rubs to end point				
			Byco C (%)				
	℃	Minutes	0	1	2	5	8
Original			19250				
6.0 - 7.0	100	30	15500	16000	17250	18250	
		60	16250	16500	16750	17750	
	110	30	16000	16000	17000	18000	
		60	9250	10750	10250	12250	
	120	30	6500		10500	13250	14000
		60	3000		3000	8500	
	130	30	<1000		<1000	<1000	<1000

6.2.4 Effect of Byco C on the SEM analysis of dyed wool fabrics after Martindale abrasion testing

The SEM micrographs, Figures 6.1(a-l) showed the fibrillation of the wool fibres dyed without or with 5% Byco C after Martindale abrasion testing. The fatigue failure occurred mostly along the intercellular boundaries suggesting the cell boundaries still constitute were the preferred fission planes. However it is apparent that the abrasion resistance of wool fabrics dyed with 5% Byco C was much higher than that of wool fabrics dyed with no Byco C.
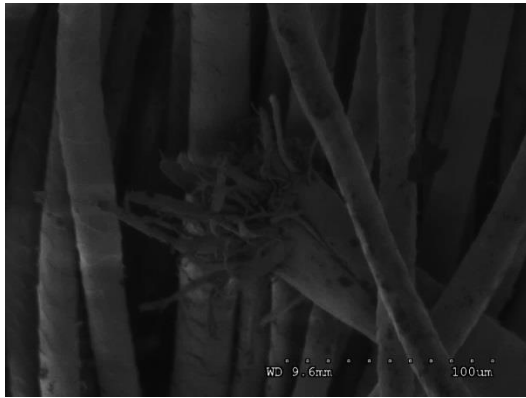
Figure 6.1(a) Wool dyed at pH4.5-5.0, 30 minutes, 100℃, no Byco C

Figure 6.1(b) Wool dyed at pH4.5-5.0, 30minutes, 100℃, 5% Byco C

Figure 6.1(c) Wool dyed at pH4.5-5.0, 60 minutes, 100℃, no Byco C

Figure 6.1(d) Wool dyed at pH4.5-5.0, 60 minutes, 100℃, 5% Byco C
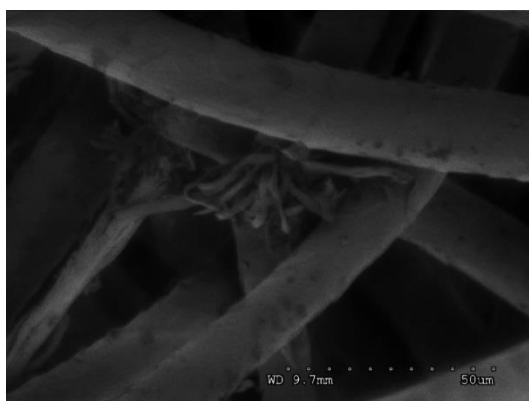
Figure 6.1(e) Wool dyed at pH6.0-7.0, 30 minutes, 100℃, no Byco C
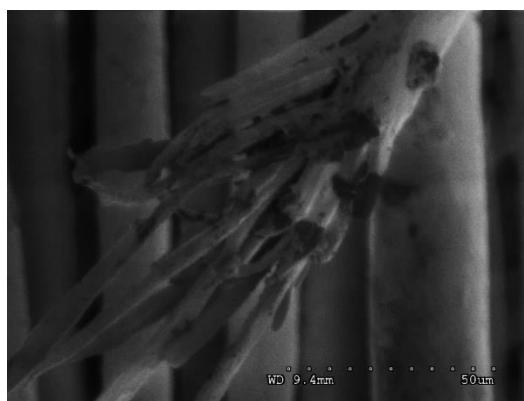
Figure 6.1(f) Wool dyed at pH6.0-7.0, 30 minutes, 100℃, 5% Byco C
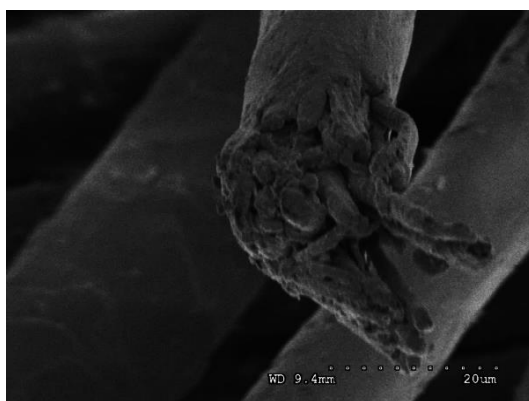
Figure 6.1(g) Wool dyed at pH6.0-7.0, 60 minutes, 100℃, no Byco C
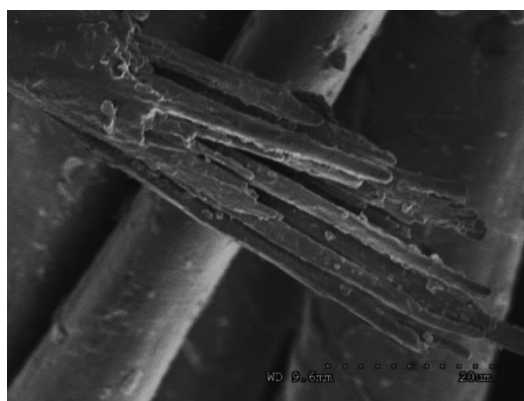
Figure 6.1(h) Wool dyed at pH6.0-7.0, 60 minutes, 100℃, 5% Byco C

Figure 6.1(i) Wool dyed at pH6.0-7.0, 30 minutes, 110℃, no Byco C
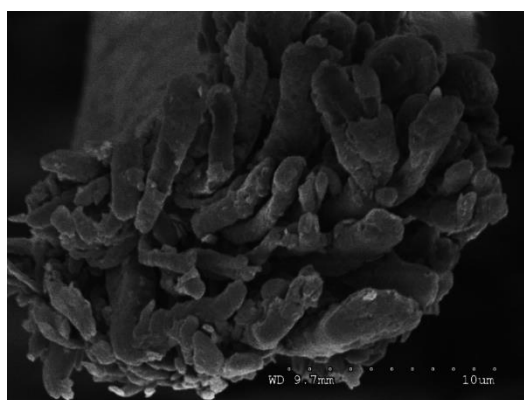
Figure 6.1(j) Wool dyed at pH6.0-7.0, 30 minutes, 110℃, 5% Byco C
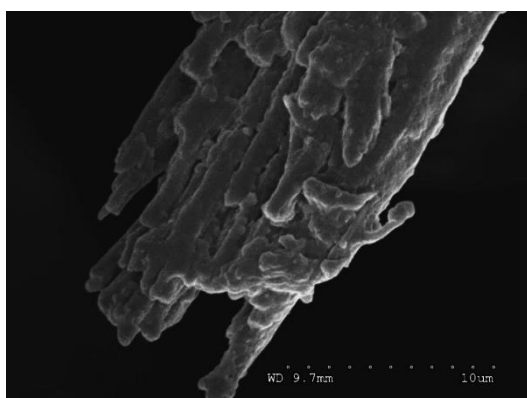
Figure 6.1(k) Wool dyed at pH6.0-7.0, 60 minutes, 110℃, no Byco C

Figure 6.1(l) Wool dyed at pH6.0-7.0, 60 minutes, 110℃, 5% Byco C

Figure 6.1 SEM micrographs of dyed wool fabrics after Martindale abrasion testing.

6.2.5 Effect of Byco C on the shrinkage of dyed wool fabric

The shrinkage (%S) of dyed wool fabric was calculated using the following equation:

$$\%S = (A_0 - A_1)/A_0 \times 100 \qquad \textbf{Equation 6-1}$$

Where A_0 and A_1 are the length of the wool fabric in weft direction before and after the blank dyeing, respectively.

The wool fabrics treated at elevated aqueous temperatures had obviously shrunk when they were dyed at high temperature, above 120℃, Table 6.14. The shrinkage of the fabric was more obvious with increased dyeing temperature and time and the wool fabrics dyed at pH 4.5-5.0 shrunk less than those dyed pH 6.0-7.0. This latter effect was due to less damage and greater fibre cohesion in the isoelectric region. The shrinkage data in Table 6.14 showed the incorporation of Byco C into the dyebath decreased the shrinkage of the dyed wool fabric at pH 4.5-5.0, 120℃, although in general the effect appeared to be independent of Byco C concentration. The application of Byco C in the dye bath at 130℃ had only a marginal effect on the

fabric shrinkage.

Table 6.14 Effect of Byco C on the shrinkage of dyed wool fabric at pH 4.5-5.0

pH	Temperature	Time	Byco C	Shrinkage
	℃	Minutes	%	%
4.5 - 5.0	120	30	0	14.6
			2	10.9
			5	11.8
			8	11.4
		60	0	23.3
			2	16.3
			5	13.0
			8	11.8
	130	30	0	32.7
			2	35.9
			8	35.5

Table 6.15 Effect of Byco C on the shrinkage of wool fabric dyed at pH 6.0-7.0

pH	Temperature	Time	Byco C	Shrinkage
	℃	Minutes	%	%
6.0-7.0	120	30	0	21.4
			2	13.6
			5	11.8
			8	11.8
		60	0	22.8
			2	23.8
			5	8.8
	130	30	0	36.8
			2	37.2
			5	36.8
			8	36.4

The shrinkage of wool fabrics dyed at pH 6.0-7.0, 120℃ was greatly decreased by the incorporation of Byco C into the dyebath with the shrinkage generally reduced with the increased with the amount of Byco C applied. The shrinkage of the wool fabric dyed at pH 6.0-7.0, 130℃ was not greatly affected by the Byco C used in the dye bath since the degradation of the sacrificial gelatin was probably too rapid to benefit the fibre. The shrinkage data is shown in Table 6.15.

6.3 Effect of Irgasol HTW on wool fabric during blank dyeing

Irgasol HTW is a formaldehyde-based reagent that is used as fibre protective agent in wool dyeing. Its protective effect is based on the formation of methylene bridge crosslinking reactions between adjacent thiol groups (both free and produced during hydrolysis) or amino groups on wool polypeptide chains [6]. The active constituent of HTW is dimethylolethylene urea (DMEU), which reacts with wool to produce stable -S-CH_2-S- and -NH-CH_2-NH- bonds that replace the disulphide crosslinks and polypeptide bonds broken by hydrolysis [7].

6.3.1 Effect of Irgasol HTW on the yellowness of dyed wool fabric

The incorporation of Irgasol HTW into the dyebath had little effect on the yellowness index of wool fabrics dyed at pH 4, Table 6.16.

Table 6.16 Effect of Irgasol HTW on the yellowness of wool fabric dyed at pH 4

pH	Temperature	Time	HTW	Yellowness Index
	℃	Minutes	%	
Original				23.7
4	120	30	0	35.8
			1	36.2
			3	31.8
			5	36.2
		60	0	44.9
			1	42.8
			3	42.4
			5	41.0

Wool 3 was used in this section.

The yellowness index data of the wool fabrics dyed at pH 7, Table 6.17, showed the application of Irgasol HTW did not have obvious effect on the wool colour. Similarly the dyeing time had little influence on the effect of HTW in terms of yellowness.

Table 6.17 Effect of Irgasol HTW on the yellowness of wool fabric dyed at pH 7

pH	Temperature	Time	HTW	Yellowness Index
	℃	Minutes	%	
Original				23.7
7	120	30	0	38.1
			1	35.9
			3	34.2
			5	37.3
		60	0	45.9
			1	45.8
			3	39.2
			5	40.2

6.3.2 Effect of Irgasol HTW on the abrasion resistance of dyed wool fabric

Table 6.18 Effect of Irgasol HTW on the abrasion resistance of wool dyed at pH 4

pH	Temperature	Time	HTW	Number of rubs to end point
	℃	Minutes	%	
Original				19250
4	120	30	0	7000
			1	16750
			3	19250
			5	22500
		60	0	3000
			1	2000
			3	12250
			5	16667

The effect of Irgasol HTW on the flat abrasion was to clearly reduce the strength loss, Table 6.18. The number of rubs to end point increased with increasing Irgasol HTW

application levels in the dye bath at pH 4. The wool fabric dyed at 120℃ for 30 minutes with 5% Irgasol HTW had even better abrasion resistance than the original wool fabric.

The abrasion resistance of the wool fabrics dyed at pH 7 also improved considerably with the application of Irgasol HTW, but was significantly less effective than the wool fabrics dyed at pH 4, Table 6.19. This is a reflection of the increased hydrothermal damage to the wool at pH 7 and the cross-linker having less effect.

Table 6.19 Effect of Irgasol HTW on the abrasion resistance of wool fabric dyed at pH 7

pH	Temperature ℃	Time Minutes	HTW %	Number of rubs to end point
Original				19250
7	120	30	0	6500
			1	9250
			3	14750
			5	13750
		60	0	3000
			1	1750
			3	11750
			5	11250

6.4 Effect of Irgasol HTW and Byco C on wool fabric during blank dyeing

6.4.1 Effect of Irgasol HTW and Byco C on the yellowness of dyed wool fabric

The co-application of Irgasol HTW and Byco C had a variable effect on the yellowness index of the wool fabrics dyed at pH 4, and the dyeing time had little

influence on the effect of Irgasol HTW and Byco C co-applied in the dye bath.

Table 6.20 Effect of Irgasol HTW and Byco C on the yellowness of wool fabric dyed at pH 4

pH	Temperature	Time	HTW	Yellowness Index	
	℃	Minutes	%	Without Byco C	With 5% Byco C
Original				23.7	
4	120	30	0	35.8	34.5
			1	36.2	39.0
			3	31.8	40.1
			5	36.2	37.6
		60	0	44.9	38.1
			1	42.8	38.9
			3	42.4	47.1
			5	41.0	44.2

Wool 3 was used in this section.

Similarly the yellowness data in Table 6.21 showed the co-application of Irgasol HTW and Byco C had little beneficial effect on the yellowness of the wool fabrics dyed at pH 7.

Table 6.21 Effect of HTW and Byco C on the yellowness of wool fabric dyed at pH 7

pH	Temperature	Time	HTW	Yellowness Index	
	℃	Minutes	%	Without Byco C	With 5% Byco C
Original				23.7	
7	120	30	0	38.1	36.6
			1	35.9	34.2
			3	34.2	32.8
			5	37.3	35.5
		60	0	45.9	39.0
			1	45.8	35.3
			3	39.2	40.9
			5	40.2	41.0

6.4.2 Effect of Irgasol HTW and Byco C on the abrasion resistance of dyed wool fabric

Examination of the abrasion resistance data indicated that the co-application of Irgasol HTW and Byco C had better protective effect than the application of Byco C alone, but worse than the application of only Irgasol HTW in the dye bath for the wool fabrics dyed at pH 4, Table 6.22.

Table 6.22 Effect of Irgasol HTW and Byco C on the abrasion resistance of wool fabric dyed at pH 4

pH	Temperature ℃	Time Minutes	HTW %	Number of rubs to end point	
				Without Byco C	With 5% Byco C
Original				19250	
4	120	30	0	7000	10000
			1	16750	12250
			3	19250	16750
			5	22500	20500
		60	0	3000	7000
			1	2000	11500
			3	12250	10750
			5	16667	10000

Similarly the abrasion resistance of the wool fabrics dyed at pH 7 was clearly improved by the application of Irgasol HTW and Byco C together in the dye bath, compared with the Irgasol HTW and Byco C applied individually. The number of rubs to end point increased to a large extent with the amount of Irgasol HTW in the application of Irgasol HTW and Byco C together. The effect of HTW and Byco C of the flat abrasion was decreased considerably over longer dyeing time, Table 6.23.

Table 6.23 Effect of Irgasol HTW and Byco C on the abrasion resistance of wool fabric dyed at pH 7

pH	Temperature	Time	HTW	Number of rubs to end point	
	℃	Minutes	%	Without Byco C	With 5% Byco C
Original				19250	
7	120	30	0	6500	7500
			1	9250	12000
			3	14750	21333
			5	13750	22750
		60	0	3000	8000
			1	1750	12500
			3	11750	9250
			5	11250	13250

6.5 Conclusions

The effect of dyeing of wool fabrics at elevated temperature was increase the yellowness, harshen the handle and decrease the flat abrasion performance of the wool fabric. The wool fabrics dyed at pH 6.0-7.0 showed poorer handle, yellowness and abrasion properties than those dyed at pH 4.5-5.0, due to increased hydrothermal damage.

The incorporation of Byco C had little effect on the yellowness of the dyed wool fabrics, but did improve the handle and flat abrasion properties inder various dyeing conditions, including pH value 4.5-5.0 and 6.0-7.0, 100-120℃, 30 and 60 minutes. The flat abrasion generally improved with the amount of Byco C applied in the dye bath. The wool fabrics clearly shrunk at 120℃ and 130℃ but this shrinkage of the dyed wool fabrics was decreased by the co-application of Byco C. The effect of Byco C was better at pH 6.0-7.0 than at pH 4.5-5.0 when the wool fabrics were dyed at 120℃. The abrasion resistance and the shrinkage tests showed the wool fabrics dyed at 130℃ were not influenced by the application of Byco C.

When Irgasol HTW was applied in the dye bath for the wool fabrics dyeing at pH 4 and 7, 120℃ for 30 and 60 minutes the yellowness was not obviously affected by the application of HTW, while the abrasion resistance did improve significantly. The effect of Irgasol HTW in abrasion resistance was significantly better at pH 4, and the increase was better as the amount of HTW increased.

The co-application of Irgasol HTW and Byco C together in the dye bath had little influence on the yellowness of the wool fabrics dyed at pH 4 and 7, 120℃ for 30 and 60 minutes. The flat abrasion of the wool fabrics dyed at pH 4 showed the joint effect of Irgasol HTW and Byco was better than the single effect of Byco C, but worse than that of Irgasol HTW applied individually. The difference between the single use of Irgasol HTW and the use of Irgasol HTW and Byco C together was enlarged by the dyeing time. The effect of Irgasol HTW and Byco C together was better than the individual use of Irgasol HTW or Byco C at pH 7 in terms of flat abrasion. The dyeing time enhanced the effect of HTW and Byco C together, and the effect also improved with the amount of HTW in the joint application of HTW and Byco C.

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Chapter 7

Effect of wet processing of wool and cotton in simulated seawater

7.1 Effect of wool bleaching in simulated seawater

7.1.1 Effect of hydrogen peroxide bleaching of wool in simulated seawater

The whiteness data in Table 7.1 showed the wool fabrics bleached under alkaline condition in simulated seawater had little difference to those bleached in distilled water. The simulated seawater did not affect the hydrogen peroxide bleaching effect or the effect of Byco C on fabric whiteness.

Table 7.1 Comparison of effect of distilled water and salt water on the whiteness of wool fabric bleached under alkaline condition

pH	Hydrogen peroxide	Temperature	Time	Byco C	CIE Whiteness	
	g/L	℃	hour	%	Distilled water	Salt water
Original fabric					2.8	
9	20	60	1	0	25.4	26.5
				3	27.8	26.3
				5	26.9	26.9
			2	0	30.3	29.5
				3	31.0	31.3
				5	30.0	31.3
	30		1	0	28.2	28.1
				3	30.3	30.6
				5	29.6	29.0
			2	0	33.6	34.3
				3	32.1	34.3
				5	32.8	34.5

Wool 3 was used in the experiments for this table.

The whitening effect of the wool fabrics bleached under acid condition was generally increased in the simulated seawater medium, instead distilled water, Table 7.2. The co-application of Byco C did not diminish the bleaching action in most cases in simulated seawater or distilled water.

Table 7.2 Comparison of effect of distilled water and salt water on the whiteness of wool fabric bleached under acidic conditions

pH	Hydrogen peroxide	Temperature	Time	Byco C	CIE Whiteness			
	g/l	℃	hour	%	Distilled water		Salt water	
Original fabric					15.3		2.8	
5	20	80	0.5	0	29.2	+13.9	22.3	+19.5
				3	30.3	+15.0	22.5	+19.7
				5	29.1	+13.8	22.2	+19.4
			1	0	28.9	+13.6	20.1	+17.3
				3	29.8	+14.5	17.0	+14.2
				5	28.2	+12.9	21.7	+18.9
			1.5	0	23.9	+8.6	11.2	+8.4
				3	28.4	+13.1	15.2	+12.4
				5	25.7	+10.4	8.1	+5.3
	30		0.5	0	29.6	+14.3	26.4	+23.6
				3	30.6	+15.3	20.7	+17.9
				5	31.1	+15.8	19.7	+16.9
			1	0	20.0	+4.7	18.0	+15.2
				3	27.8	+12.5	17.1	+14.3
				5	26.3	+11.0	8.8	+6.0

Wool 1 was used in the experiments with distilled water while Wool 3 was used in the experiments with salt water for this table. "+" means the CIE Whiteness value of the fabrics increased after bleaching.

The application of Keravis[TM] in the simulated seawater hydrogen peroxide bleach bath under alkaline conditions did not affect the whiteness of the wool, Table 7.3.

Table 7.3 Comparison of the effect of bleaching wool under alkaline conditions in distilled water and salt water on the whiteness of wool fabric

pH	Hydrogen peroxide g/L	Temperature ℃	Time hour	Keravis™ %	CIE Whiteness Distilled Water	CIE Whiteness Salt Water
		Original fabric			8.8	
9	20	60	1	0	32.8	35.0
				5	35.1	35.0
				10	34.6	35.6
			2	0	39.3	38.2
				5	39.2	36.6
				10	39.6	39.9
	30		1	0	38.2	38.1
				5	37.8	37.8
				10	37.2	37.5
			2	0	42.5	41.5
				5	41.8	41.6
				10	41.1	41.7

Wool 2 was used in the experiments for this table.

Table 7.4 Comparison of effect of bleaching wool in distilled water and salt water on the tensile strength of the wool fabric

pH	Hydrogen peroxide g/L	Temperature ℃	Time hour	Byco C %	Tensile Strength (kN/m) Distilled water	Tensile Strength (kN/m) Salt water
		Original fabric			7.1	
9	20	60	1	0	6.9	7.0
				3	6.9	6.9
				5	6.6	6.7
			2	0	6.7	7.0
				3	6.6	7.2
				5	6.7	7.2
	30		1	0	6.6	7.0
				3	6.5	6.9
				5	6.6	7.1
			2	0	6.5	7.0
				3	6.5	7.0
				5	6.6	7.0

Wool 3 was used in the experiments for this table.

Examination of the tensile data of the bleached wool fabrics, Table 7.4, showed little difference between the wool fabrics bleached in simulated seawater and those bleached in distilled water, with or without the incorporation of Byco C.

The abrasion resistance performance of the wool fabrics bleached in simulated seawater was better than that observed for the wool fabrics bleached in distilled water, Table 7.5. Further the co-application of Byco C still had beneficial effect on the flat abrasion of the bleached wool fabrics, and the effect increased with the amount of Byco C.

Table 7.5 Comparison of the effect of bleaching wool fabric in distilled water and simulated salt water on the abrasion resistance of bleached wool fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	Number of rubs to end point	
	g/L	℃	hour	%	Distilled water	Salt water
Original fabric					20000	19000
9	20	60	1	0	15500	18000
				3	20500	18500
				5	20500	20000
			1.5	0	15000	17250
				3	17333	18250
				5	18500	19000
			2	0	12667	16500
				3	12500	16667
				5	15500	19000
	30		0.5	0	15250	17750
				3	18000	18333
				5	19000	20500
			1	0	13000	17500
				3	13000	19750
				5	17500	19333
			2	0	14667	15500
				3	15000	17500
				5	17333	16250

Wool 3 was used in the experiments for this table.

7.1.2 Effect of oxidative and reductive bleaching of wool in simulated seawater

The whiteness of the oxidatively and reductively bleached wool fabrics was not influenced by the use of simulated seawater, Table 7.6. The Byco C applied in the oxidative bleaching and reductive bleaching stages using simulated seawater did not affect the whitening effect.

Table 7.6 Comparison of effect of distilled water and salt water on the whiteness of oxidatively and reductively bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	CIE Whitness	
g/L	%	g/L	%	Distilled water	Salt water
Original				2.8	
20	0	6	0	42.7	44.2
	3		0	44.0	43.7
			3	42.6	46.1
	5		0	44.8	45.9
			5	43.8	44.7
30	0		0	49.5	50.4
	3		0	49.2	49.9
			3	47.2	48.3
	5		0	48.5	48.2
			5	49.1	47.9

Wool 3 was used in this section.

The difference in the tensile strength between the wool fabrics bleached in simulated seawater and those bleached in distilled water was relatively small, Table 7.7. The application of Byco C in both bleaching steps was not affected by the simulated seawater.

Table 7.7 Comparison of the effect of oxidatively and reductively bleaching wool fabric in distilled water and salt water on the fabric tensile strength

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Tensile Strength	
g/L	%	g/L	%	Distilled water	Salt water
Original				6.9	
20	0	6	0	6.6	7.0
	3		0	6.6	7.0
			3	6.8	6.6
	5		0	6.6	6.7
			5	6.8	6.9
30	0		0	6.6	6.8
	3		0	6.8	6.8
			3	6.7	6.6
	5		0	6.7	6.8
			5	6.8	6.9

Table 7.8 Comparison of effect of distilled water and salt water on the abrasion resistance of oxidative and reductive bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Number of rubs to end point	
g/L	%	g/L	%	Distilled water	Salt water
Original				20000	
20	0	6	0	12250	11250
	3		0	13000	12500
			3	13500	12250
	5		0	12500	13250
			5	14500	13250
30	0		0	11000	10750
	3		0	12000	11250
			3	12250	12500
	5		0	13000	12000
			5	12500	13250

Examination of the abrasion resistance of the oxidatively and reductively bleached wool fabrics showed the simulated seawater had little effect on the fabric strength. The application of Byco C in the bleach bath still increased the flat abrasion of the bleached wool fabrics, and the increasing amount of Byco C had positive effect on the flat abrasion as well in both distilled water and simulated seawater.

7.1.3 Effect of Voluminis[TM] on bleaching wool in simulated seawater

7.1.3.1 Effect of Voluminis[TM] on oxidatively bleached wool in simulated seawater

The CIE whiteness value of the oxidatively bleached wool processed with Voluminis[TM] showed little difference using simulated seawater and distilled water. The application of Voluminis[TM] and Byco C were both not affected by the simulated seawater.

Table 7.9 Comparison of the effect of distilled water and salt water on the whiteness of oxidative bleached wool fabric processed with Voluminis[TM]

pH	Hydrogen peroxide	Temperature	Time	Byco C	Voluminis[TM]	CIE Whiteness	
	g/L	℃	hour	%	%	Distilled water	Salt water
Original						2.8	
9	30	60	1	0	0.0	27.5	30.6
					2.0	27.8	27.2
				3	0.0	29.3	30.9
					2.0	29.8	29.4
				5	0.0	28.8	31.9
					2.0	30.7	30.5
			2	0	0.0	33.7	32.9
					2.0	35.2	32.5
				3	0.0	34.3	34.3
					2.0	34.0	33.9
				5	0.0	33.6	34.9
					2.0	35.7	34.5

Wool 3 was used in this section.

Table 7.10 Effect of oxidatively bleaching wool fabric in distilled water with Voluminis[TM] on the KES-F measured properties

Time hour	Byco C %	Voluminis[TM] %	KOSHI	NUMERI	FUKURAMI
Original			3.2	6.7	5.9
1	0	0.0	2.1	7.5	8.1
		2.0	2.3	6.8	7.7
	3	0.0	2.1	7.1	8.0
		2.0	2.0	7.1	8.0
	5	0.0	1.8	7.3	8.6
		2.0	2.3	6.5	7.6
2	0	0.0	2.1	7.5	8.1
		2.0	2.3	6.3	7.7
	3	0.0	2.4	7.3	8.0
		2.0	2.3	6.5	7.5
	5	0.0	2.2	7.1	7.9
		2.0	2.3	6.7	7.5

Table 7.11 Effect of oxidatively bleaching wool fabric in salt water with Voluminis[TM] on the KES-F properties

Time hour	Byco C %	Voluminis[TM] %	KOSHI	NUMERI	FUKURAMI
Original			3.2	6.7	5.9
1	0	0.0	2.6	7.0	7.6
		2.0	2.2	6.5	7.4
	3	0.0	2.3	6.2	7.1
		2.0	2.1	7.2	7.9
	5	0.0	2.5	6.3	7.3
		2.0	1.6	6.9	7.9
2	0	0.0	2.4	6.5	7.4
		2.0	2.3	6.2	7.1
	3	0.0	2.5	6.9	7.6
		2.0	2.9	4.8	6.5
	5	0.0	2.0	7.2	7.9
		2.0	2.5	6.4	7.6

The KES-F data of the oxidative bleached wool fabric processed with Voluminis[TM] indicated that the wool fabrics were only slightly affected by treatment in the simulated seawater. In general the mechanical properties varied unpredictably but all the differences were at relatively small in size, Table 7.10 and Table 7.11.

7.1.3.2 Effect of Voluminis[TM] and Byco C on the oxidative and reductive bleaching of wool in simulated seawater

The oxidative and reductive bleaching of wool in the presence of Voluminis[TM] in simulated sea water in comparison to bleaching in distilled did not affect the overall whiteness of the wool fabrics, Table 7.12. The application of Byco C in both bleach baths showed the whiteness was not affected by the simulated seawater medium.

Table 7.12 Comparison of the effect of oxidative and reductive bleaching of wool fabric, in the presence/absence of Voluminis[TM] and Byco C, in distilled water and salt water on the fabric whiteness

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Voluminis[TM]	CIE Whiteness	
g/L	%	g/L	%	%	Distilled water	Salt water
20	0	6	0	2.0	47.2	47.7
	3		0		45.0	48.1
			3		44.9	48.0
	5		0		46.3	47.6
			5		44.9	47.3
30	0		0		49.8	49.7
	3		0		48.5	47.9
			3		49.2	50.2
	5		0		50.7	49.3
			5		48.8	48.0

Wool 3 was used in this section.

The tensile strength of the oxidatively and reductively bleached wool fabric processed with Voluminis^{TM} in simulated sea water and all processed in distilled water showed little difference between the wool fabrics, Table 7.13. The effect of Byco C on the fabric whiteness was also not affected by bleaching in simulated seawater.

Table 7.13 Comparison of the effect of oxidative and reductive bleaching of wool fabric, in the presence/absence of Voluminis^{TM} and Byco C, in distilled water and salt water on the fabric tensile strength

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Voluminis^{TM}	Tensile Strength (kN/m)	
g/L	%	g/L	%	%	Distilled water	Salt water
20	0	6	0	2.0	7.1	7.3
	3		0		7.2	7.1
			3		7.0	7.1
	5		0		7.1	7.0
			5		7.1	7.1
30	0		0		7.2	7.0
	3		0		7.1	7.1
			3		6.9	7.3
	5		0		6.9	7.0
			5		7.1	7.0

Examination of the flat abrasion of the oxidatively and reductively bleached wool fabric processed with Voluminis^{TM} showed a slight decrease for the wool fabrics processed in the simulated sea water. The largest decrease amount was only 1000 rubs, about 5% of the original total rubs. The number of rubs to end point still generally increased with the amount of Byco C applied in the bleach bath, both oxidative and reductive, for the wool fabrics processed in simulated sea water.

Table 7.14 Comparison of the oxidative and reductive bleaching of wool fabric, in the presence/absence of Voluminis^{TM} and Byco C, in distilled water and salt water on the abrasion resistance of oxidative and reductively bleached wool fabric

Hydrogen peroxide	Byco C in oxidative bleaching	Blankit IN	Byco C in reductive bleaching	Voluminis^{TM}	Number of rubs to end point	
g/L	%	g/L	%	%	Distilled water	Salt water
20	0	6	0	2.0	12000	11750
	3		0		12750	11750
			3		14500	13500
	5		0		13500	12500
			5		14500	14000
30	0		0		12000	11000
	3		0		12500	12750
			3		13500	13250
	5		0		12250	13500
			5		14250	13000

Examination of the flat abrasion of the oxidatively and reductively bleached wool fabric processed with Voluminis^{TM} showed a slight decrease for the wool fabrics processed in the simulated sea water. The largest decrease amount was only 1000 rubs, about 5% of the original total rubs. The number of rubs to end point still generally increased with the amount of Byco C applied in the bleach bath, both oxidative and reductive, for the wool fabrics processed in simulated sea water.

7.2 Effect of wool dyeing in simulated seawater

Wool fabrics dyed at pH4.5-5.0 in simulated sea water were not influenced by the salty medium in terms of fabric whiteness. The flat abrasion was affected slightly, with some abrasion end point levels of the dyed wool fabrics higher in simulated seawater than those dyed in distilled water. The abrasion resistance still improved with the amount of Byco C.

Table 7.15 Comparison of effect of dyeing distilled water and salt water on the yellowness and abrasion resistance of wool fabric dyed at pH 4.5-5.0

pH	Temp.	Time	Byco C	Yellowness Index		Number of rubs to end point	
	℃	Minutes	%	Distilled water	Salt water	Distilled water	Salt water
Original				23.7		19250	
4.5 -5.0	100	30	0	25.0	24.7	13000	14333
			1	25.3	25.2	14250	14750
			2	26.0	25.6	13333	15000
			5	25.6	26.4	14500	15000
		60	0	26.4	26.7	14250	14750
			1	27.6	28.4	14000	15000
			2	27.1	26.7	15250	15250
			5	27.5	26.7	17000	15500
	110	30	0	35.0	29.8	15250	15000
			1	33.0	30.5	16000	15667
			2	33.2	30.7	15500	17000
			5	29.2	29.3	17750	17250
		60	0	32.9	29.7	15750	15000
			1	32.0	28.6	16500	16250
			2	31.6	30.9	17250	16500
			5	30.1	29.4	18250	16750

Wool 3 was used in this section.

Examination of the yellowness of the wool fabrics dyed at pH 6.0-7.0 showed the simulated seawater did not influence the base level yellowness values, with or without Byco C in the dye bath. The abrasion resistance was not affected as well. The number of rubs to end point still increased with the amount of Byco C.

Table 7.16 Comparison of effect of distilled water and salt water on the yellowness and abrasion resistance of wool fabric dyed at pH 6.0-7.0

| pH | Temp. | Time | Byco C | Yellowness Index | | Number of rubs to end point | |
	℃	Minutes	%	Distilled water	Salt water	Distilled water	Salt water
6.0 -7.0	Original			23.7		19250	
	100	30	0	26.7	25.4	15500	15500
			1	27.8	26.0	16000	16333
			2	26.8	25.6	17250	17000
			5	27.2	25.9	18250	18250
		60	0	28.7	28.1	16250	15750
			1	29.0	28.0	16500	16750
			2	27.6	26.9	16750	17000
			5	29.0	28.1	17750	18750
	110	30	0	27.9	28.8	16000	13250
			1	31.1	28.8	16000	13500
			2	29.8	29.7	17000	14250
			5	30.2	29.4	18000	15250
		60	0	37.7	35.3	9250	9750
			1	38.6	35.0	10750	11500
			2	38.6	36.0	10250	10750
			5	34.0	31.5	12250	11750

7.3 Effect of cotton bleaching in simulated seawater

7.3.1 Effect of hydrogen peroxide bleaching in simulated seawater on scoured unbleached cotton fabric

100% scoured unbleached plain woven cotton fabrics were bleached using Method 1 under alkaline conditions as described in Section 3.1.2.

Examination of the fabric whiteness values showed the bleaching effect of the 60℃ bleaching method was not affected by the simulated seawater, Table 7.17, in fact there is some evidence for an improvement in whiteness. The effect of Byco C was similarly not affected in terms of whiteness.

Table 7.17 Comparison of the effect of hydrogen peroxide bleaching cotton fabric in distilled water and salt water at 60℃ on the whiteness of cotton fabric

pH	Hydrogen peroxide	Temperature	Time	Byco C	CIE Whiteness	
	g/L	℃	hour	%	Distilled water	Salt water
Original fabric					6.00	
9	20	60	1	0	32.2	36.6
				3	31.8	32.1
				5	30.0	33.8
			1.5	0	40.8	42.9
				3	38.6	38.0
				5	36.8	36.8
			2	0	46.2	41.6
				3	41.0	40.6
				5	38.3	38.2

7.3.2 Effect of bleaching scoured unbleached cotton bleached at 85℃ in simulated seawater

100% scoured unbleached plain woven cotton fabrics were bleached using Method 2 as described in Section 3.1.2.

According to the data in Table 7.18, the effect of bleaching at 85℃ in simulated seawater had a small effect on the whiteness, flat abrasion and tensile properties of the scoured cotton fabrics. The application of Byco C still had beneficial effect On the flat abrasion, and the number of rubs to end point increased with the amount of Byco C applied in the bleach bath.

Table 7.18 Comparison of the effect of bleaching cotton fabric at 85 ℃ in distilled water and salt water on the whiteness, tensile strength and abrasion resistance of cotton fabric

Temperature	Time	Byco C	CIE Whiteness		Number of rubs to end point		Tensile Strength	
℃	minute	%	Distilled water	Salt water	Distilled water	Salt water	Distilled water	Salt water
Original fabric			1.50		12500		11.2	
85	30	0	48.1	46.9	19750	18667		
		3	42.7	43.0	20500	20750		
		5	51.5	45.5	20750	21250		
	45	0	53.2	52.8	20000	20000	12.5	12.0
		3	55.7	51.1	20750	22333	12.3	12.6
		5	52.4	53.3	21500	23000	12.6	12.3
	60	0	55.6	62.0	20333	19500		
		3	56.9	55.6	20250	20750		
		5	55.5	55.8	21500	21500		
	90	0	62.9	63.2	20000	20750	12.2	12.3
		3	61.0	62.4	22500	22500	12.9	12.5
		5	57.7	64.6	23500	22500	12.8	12.3

7.4 Conclusions

Bleaching wool in simulated seawater instead of distilled water under alkaline conditions resulted in the whiteness of the wool fabric being improved. In contrast bleaching under acidic conditions it was found the whiteness of the wool deteriorated. The wool fabrics bleached in salt water showed similar tensile strength to comparable fabrics bleached in distilled water. However the application of Byco C during the bleaching process had a beneficial effect on the flat abrasion performance of wool fabrics. The effect of bleaching on the handle of wool fabrics was not obviously influenced by salt water.

The beneficial effect of Byco C was also observed with an oxidative/reductive bleaching process for wool although the improvement was not as great as observed with peroxide bleaching alone.

The effect of novel protein-based reagents such as Voluminis or Keravis on the properties of bleached wool fabric whether by application in simulated sea water or distilled water was minimal.

The wool fabrics dyed at pH 4.5-5.0 and pH 6.0-7.0, 100 and 110℃ were not affected by using simulated seawater instead of distilled water in terms of yellowness and abrasion resistance. The co-application of Byco C still had a positive effect on the abrasion resistance, which also improved with increasing the application levels of the Byco C.

The whiteness and abrasion resistance of scoured cotton was not affected when the salt water was used instead of distilled water in both bleaching methods. The application of Byco C still had beneficial effect in the flat abrasion, and the abrasion resistance improved with the amount of Byco C applied in the bleach bath.

Chapter 8

Effect of novel adsorbents in the removal of dye from effluent

8.1 Dye adsorption of modified paper

The development of improved textile processing involves examining the entire application and how it can be better engineered. That improved processing can be based on the use/reuse of water, incorporating fibre protective agents into treatment baths or using waste extracted from the textile material during processing. In this study as part of the water reuse strategy waste protein material, i.e. feathers have been used as the base material for a filter media in order to remove unexhausted dye and allow the reuse of the aqueous treatment bath. In the development of the paper substrate the wet strength and dye receptivity have investigated in order to produce a more effective filter media.

8.1.1 The effect of EKA on modified paper

Papers are often used in liquid filtration in industry [1]. However the mechanical strength of the untreated paper decreases rapidly when the paper gets wet, which is clearly undesirable in liquid filtration [1]. Therefore it is necessary to impart to industrial filter papers added wet strength by incorporating a bonding agent, such as melamine formaldehyde or polyamide epichlorohydrin, into the wet formation process of papers [2, 3]. Accordingly EKA (Cationic Polyamide Epichlorohydrin) was applied as the wet strength additive in this study.

The effect of incorporating the wet strength additive EKA into the paper was unsurprisingly to increase the wet strength, Table 8.1, with an optimal level of approximately 2% of the reactive cationic polyamide epichlorohydrin in the paper being identified.

Table 8.1 Mechanical properties of paper produced from cellulose and EKA

Ratio Cellulose:EKA	Grammage (g/m^2)	Thickness (μm)	Tensile strength (kN/m)	Zero span index (Nm/g)	Wet tensile strength (kN/m)
100:0	66.6	90	4.8	191.6	0.06
99.8:0.2	59.7	88	4.5	193.5	0.38
99.6:0.4	61.7	90	4.9	198.5	0.40
99.4:0.6	50.7	75	4.0	205.9	0.34
99.2:0.8	59.3	85	4.9	205.8	0.47
99.0:1.0	58.0	84	4.7	200.9	0.44
98.5:1.5	57.6	82	4.4	200.2	0.61
98.0:2.0	60.3	84	4.7	200.8	0.64
97.5:2.5	60.1	85	4.8	202.5	0.64
97.0:3.0	58.9	83	4.5	198.9	0.65

Coupled to the wet strength benefits it was apparent that the tensile strength and the zero span strength were not affected indicating that the strength of the individual cellulosic fibres was not reduced or the interfibre cohesion reduced with the addition of EKA.

The next phase in the filter media development involved was the evaluation of a mixed cellulose, feather and EKA paper which could offer better wet strength but also better dye adsorption. The results indicates the presence of feather material reduces the tensile strength and zero span strength but that the EKA effectively introduced good wet strength back into the paper, Table 8.2. It is evident from the data that while the grammage values were comparable to the cellulose/EKA paper the presence of the feathers significantly increased the paper thickness creating a bulkier substrate. In addition the tensile strength and zero span strengths were reduced due to the lower interfibre bonding between the feather and cellulosic fibres. However once again the EKA additive increased the wet strength to an acceptable level.

Table 8.2 Mechanical properties of paper produced from a mixture of cellulose, feathers and EKA

Ratio Cellulose:Feather:EKA	Grammage (g/m^2)	Thickness (μm)	Tensile strength (kN/m)	Zero span index (Nm/g)	Wet tensile strength (kN/m)
90.0:10.0:0	58.2	143	3.1	169.1	0.06
89.8:10.0:0.2	59.1	135	3.0	166.7	0.18
89.6:10.0:0.4	58.0	136	3.1	159.1	0.25
89.4:10.0:0.6	58.9	146	3.1	166.9	0.27
89.2:10.0:0.8	59.4	137	3.0	157.3	0.44
89.0:10.0:1.0	64.2	145	3.2	162.5	0.49
88.5:10.0:1.5	60.5	156	3.1	171.0	0.38
88.0:10.0:2.0	60.3	132	3.1	158.7	0.41
87.5:10.0:2.5	61.8	137	3.0	158.0	0.38
87.0:10.0:3.0	56.2	133	2.7	158.3	0.38

8.1.2 The adsorption of direct dyes at pH7

8.1.2.1 UV-Visible Analysis of Exhausted Dye Solution

It was apparent from the dyebath absorption values that relatively little dye is being absorbed but that this is a reflection of the amount of absorbent present, Table 8.3. Similarly for the Direct Red 80 dye, relatively little dye absorption was apparent due to the excess of dye relative to the absorbent, Table 8.4. Nevertheless it is apparent that the presence of the cationic EKA and feathers does increase the capacity for the dye to be transferred from solution onto the filter paper.

Table 8.3 UV-Visible analysis of C. I. Direct Orange 39 exhausted dyebath

Ratio of Paper Components		Absorbance at λ_{max}, (420nm)
Original Dyebath		2.7
Cellulose & EKA	100:0	2.7
	99.8:0.2	2.6
	99.6:0.4	2.6
	99.2:0.8	2.6
	98.5:1.5	2.5
	97.0:3.0	2.5
Cellulose, Feathers & EKA	90.0:10.0:0	2.6
	89.8:10.0:0.2	2.6
	89.6:10.0:0.4	2.4
	89.2:10.0:0.8	2.3
	88.5:10.0:1.5	2.3
	87.0:10.0:3.0	2.3

Table 8.4 UV-Visible analysis of C. I. Direct Red 80 exhausted dyebath

Ratio of Paper Components		Absorbance at λ_{max}, (540nm)
Original Dyebath		2.1
Cellulose & EKA	100:0	2.1
	99.8:0.2	2.1
	99.6:0.4	2.0
	99.2:0.8	2.0
	98.5:1.5	2.0
	97.0:3.0	2.0
Cellulose, Feathers & EKA	90.0:10.0:0	2.0
	89.8:10.0:0.2	2.0
	89.6:10.0:0.4	2.0
	89.2:10.0:0.8	2.0
	88.5:10.0:1.5	2.0
	87.0:10.0:3.0	1.9

8.1.2.2 K/S Values of Paper with Absorbed Direct Dye

The effect of incorporating the positively charged EKA into the cellulose-based paper was to increase the C. I. Direct Orange 39 dye binding due to the electrostatic attraction of the negatively charged dye to the cationic polymer [4], Table 8.5 and Figure 8.1. Similarly the C. I. Direct Red 80 dye has increased affinity for the modified paper, Table 8.6 and Figure 8.2. The effect of incorporating the feathers into the paper was to increase dye adsorption but the effect needs to be fully evaluated using a range of pH conditions, particularly at pH4-5 where the protein will be fully cationised and have maximum potential for dye adsorption.

Table 8.5 K/S values of paper with absorbed C. I. Direct Orange 39

Ratio of Paper Components		K/S value at λ_{max}, (440nm)
Cellulose & EKA	100:0	1.25
	99.8:0.2	1.29
	99.6:0.4	1.45
	99.2:0.8	1.60
	98.5:1.5	1.84
	97.0:3.0	2.09
Cellulose, Feathers & EKA	90.0:10.0:0	1.27
	89.8:10.0:0.2	1.40
	89.6:10.0:0.4	1.59
	89.2:10.0:0.8	1.87
	88.5:10.0:1.5	1.74
	87.0:10.0:3.0	2.22

Figure 8.1 Paper absorbed C. I. Direct Orange 39

The left one contains 0.2% Eka; the right one contains 3.0% Eka.

Table 8.6 K/S values of paper with absorbed C. I. Direct Red 80

Ratio of Paper Components		K/S value at λ_{max}, (540nm)
Cellulose & EKA	100:00:00	0.63
	99.8:0.2	0.80
	99.6:0.4	0.95
	99.2:0.8	1.25
	98.5:1.5	1.46
	97.0:3.0	1.48
Cellulose, Feathers & EKA	90.0:10.0:0	0.70
	89.8:10.0:0.2	0.84
	89.6:10.0:0.4	0.87
	89.2:10.0:0.8	1.38
	88.5:10.0:1.5	1.35
	87.0:10.0:3.0	1.69

Figure 8.2 Paper absorbed C. I. Direct Red 80

The left one contains 0.2% Eka; the right one contains 3.0% Eka.

8.1.3 The adsorption of direct dyes at pH4

8.1.3.1 UV-Visible Analysis of Exhausted Dye Solution

Table 8.7 UV-Visible analysis of C. I. Direct Orange 39 exhausted dyebath

Ratio of Paper Components		Absorbance at λ_{max},(420nm)
Original Dyebath		3.03
Cellulose & EKA	100:0	2.89
	99.8:0.2	2.85
	99.6:0.4	2.85
	99.2:0.8	2.78
	98.5:1.5	2.74
	97.0:3.0	2.76
Cellulose, Feathers & EKA	90.0:10.0:0	2.80
	89.8:10.0:0.2	2.82
	89.6:10.0:0.4	2.81
	89.2:10.0:0.8	2.75
	88.5:10.0:1.5	2.77
	87.0:10.0:3.0	2.74

Table 8.8 UV-Visible analysis of C. I. Direct Red 80 exhausted dyebath

Ratio of Paper Components		Absorbance at λ_{max},(540nm)
Original Dyebath		2.30
Cellulose & EKA	100:0	2.21
	99.8:0.2	2.20
	99.6:0.4	2.18
	99.2:0.8	2.15
	98.5:1.5	2.12
	97.0:3.0	2.15
Cellulose, Feathers & EKA	90.0:10.0:0	2.15
	89.8:10.0:0.2	2.14
	89.6:10.0:0.4	2.14
	89.2:10.0:0.8	2.10
	88.5:10.0:1.5	2.11
	87.0:10.0:3.0	2.06

The values of the dyebath adsorption showed a small amount of dye was absorbed in the modified papers for C. I. Direct Orange 39 dye, and the papers made from cellulose and EKA absorbed about the same amount of dyes with the papers made from Cellulose, Feathers and EKA, Table 8.7. Similarly for the C. I. Direct Red 80 dye, not much dye adsorption occurred but was a reflection of the excess of dye relative to the absorbent, Table 8.8.

8.1.3.2 K/S Values of Paper with Absorbed Direct Dye

The K/S values of paper with absorbed C. I. Direct Orange 39 dye increased with the amount of positively charged EKA, Table 8.9. Similarly the C. I. Direct Red 80 dye also had increased affinity for the modified paper, Table 8.10. The K/S values also increased with the feather/cellulosic/EKA material for both direct dyes, which showed the effect of incorporating the feathers into the paper under acid condition, where the protein was cationised and "available" for dye adsorption. However no increased adsorption benefit was seen above that of the EKA addition and the feather addition just provided alternative cheap fibrous filler within the typical cellulosic filter media.

Table 8.9 K/S values of paper with absorbed C. I. Direct Orange 39

Ratio of Paper Components		K/S value at λ_{max}, (440nm)
Cellulose & EKA	100:0	1.24
	99.8:0.2	1.53
	99.6:0.4	1.53
	99.2:0.8	1.69
	98.5:1.5	2.04
	97.0:3.0	2.05
Cellulose, Feathers & EKA	90.0:10.0:0	1.28
	89.8:10.0:0.2	1.27
	89.6:10.0:0.4	1.43
	89.2:10.0:0.8	1.84
	88.5:10.0:1.5	1.93
	87.0:10.0:3.0	2.26

Table 8.10 K/S values of paper with absorbed C. I. Direct Red 80

Ratio of Paper Components		K/S value at λ_{max}, (540nm)
Cellulose & EKA	100:0	0.77
	99.8:0.2	0.79
	99.6:0.4	1.02
	99.2:0.8	1.30
	98.5:1.5	1.36
	97.0:3.0	1.39
Cellulose, Feathers & EKA	90.0:10.0:0	0.75
	89.8:10.0:0.2	0.88
	89.6:10.0:0.4	0.94
	89.2:10.0:0.8	1.52
	88.5:10.0:1.5	1.57
	87.0:10.0:3.0	1.61

8.2 Dye adsorption of PVP nanofibres

Polyvinylpyrrolidone (PVP) is commonly used in laundry formulations as a dye scavenging agent to prevent cross-staining of whites with fugitive dye from coloured garments during the aqueous laundering process [5]. However PVP is water soluble and cannot be used as a solid filter media in removing dye from exhausted dyebaths. Therefore in this study we used a solid hydrophobic PVP polymer, which was forcespun into solid nanofibres, and investigated their potential as dye adsorbents. The melting point of the nanofibres was approximately 50℃ and so the upper temperature threshold for filtration was limited.

8.2.1 The adsorption of direct dyes

Examination of the dyebath absorption values indicated a small amount of dye was exhausted onto the nanofibre web, and that the PVP nanofibres absorbed more dye when the temperature increased from 30℃ to 40℃, Table 8.11.The K/S values of the

nanofibres used for dye adsorption of C. I. Direct Orange 39 dye were relatively small, while that of C. I. Direct Red 80 dye were a little higher, and showed a K/S increase with the temperature, Table 8.12. It is apparent that the nature of the dye will influence the dye exhaustion onto the nanofibre, especially as this fibre is based on a hydrophobic PVP derivative.

Table 8.11 UV-Visible analysis of exhausted dyebath and K/S values of nanofibres used for dye adsorption of C. I. Direct Orange 39

Temperature ℃	Absorbance at λ_{max},(540nm)	K/S value at λ_{max}, (520nm)
Original Dyebath	2.84	
30	2.78	0.10
40	2.67	0.12

Table 8.12 UV-Visible analysis of exhausted dyebath and K/S values of nanofibres used for dye adsorption of C. I. Direct Red 80

Temperature ℃	Absorbance at λ_{max},(420nm)	K/S value at λ_{max}, (420nm)
Original Dyebath	2.58	
30	2.53	0.16
40	2.47	0.31

8.2.2 The adsorption of disperse dyes

Disperse dyes are widely used in the colouration of polyester and cellulose acetate fibres [6, 7]. However the research literature for removal of disperse dyes from exhausted is very limited [6, 7]. The dye absorption values for the C. I. Disperse Red 60 decreased significantly after the immersion of the PVP nanofibres in the dyebath and the effect of raising the bath temperature was greater transfer of the disperse dye onto the fibres. Associated with increased dye removal from solution was the increase in the colour strength, K/S, values of the nanofibres. The high surface area and low

glass transition of the PVP fibres suggests that these fibres have significant potential for absorbing hydrophobic materials from dye effluent baths.

Table 8.13 UV-Visible analysis of exhausted dyebath and K/S values of nanofibres used for dye adsorption of C. I. Disperse Red 60

Temperature ℃	Absorbance at λ_{max},(590nm)	K/S value at λ_{max}, (520nm)
Original Dyebath	1.63	
30	1.58	1.14
40	0.91	1.76

8.3 Conclusions

The wet strength of paper filter media was increased by the incorporating the wet strength additive EKA (cationic polyamide epichlorohydrin) into the paper substrate, without reduce the strength of the individual cellulosic fibres and the interfibre cohesion. Incorporating 2% of EKA into the cellulosic pulp provided the optimum level of wet strength. The addition feather pulp unfortunately decreased the paper strength but the presence of the EKA in the mixed paper material still had a significant beneficial effect on the resultant paper's wet strength.

The effect of the EKA and feather addition into the paper filter media was apparent from the UV-Visible analysis of exhausted dyebath and K/S values of the papers, where the Direct anionic dye was transferred from solution onto the cationic paper and demonstrated the potential for cleaning dye effluent. The effect of acid pH on the feather was minimal and so increased dye exhaustion was observed for both direct dyes.

The potential use of the PVP nanofibres as a possible filter media for the adsorption for direct dyes and disperse dyes was clear. However due to the hydrophobic nature of

the fibres it was apparent that the adsorption of non-polar disperse dyes was preferred. This colourant adsorption was greater at higher temperature, 40 ℃, due better transfer from the dyebath solution onto the high surface area fibres.

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Chapter 9

Conclusions and further research

9.1 Conclusions

The overall aims of the project were to develop wet processing technology that addressed the need for better water usage, lowered damage to wool and cotton during bleaching and dyeing and identified novel filtration materials that could potentially improve the recycling of aqueous treatment baths. Therefore the project has been successful in regard to those broad objectives and this section will outline the overall conclusions.

The effect of bleaching was to increase fabric whiteness but reduce the wool fabric's flat abrasion performance due to degradation of the wool protein and probable loss of internal lipids. The incorporation of protein derivative Byco C into the bleach formulation, both for oxidative and oxidative/reductive bleaching, did not adversely affect whiteness and did have a beneficial effect in protecting the wool fabric from bleach danmage. The effect of incorporating the protein hydrolysate on the bleached fabric's tensile strength was surprisingly minimal and reflects the different fibre failure mechanisms for flat abrasion and tensile breaking. The bleaching effect for wool was better under alkaline condition than under acidic conditions and was due to the increased dissociation of hydrogen peroxide under alkaline conditions giving rise to more reactive oxidative bleaching agents. The incorporation of another cross-linking protein derivative, Keravis^{TM}, imparted only a marginal improvement on the bleached fabric properties.

The incorporation of Voluminis^{TM}, a "bulking" protein, into the oxidative bleaching system for wool did not have much effect on the fabric whiteness and handle. Similarly the known anti-oxidant tannic acid had no beneficial effect on the bleaching of wool and actually decomposed the hydrogen peroxide resulting a poorer whitening effect.

The blank dyeing of wool fabrics at elevated temperature caused yellowing of the wool fabric, damaged the handle and lowered the flat abrasion properties. This effect was most obvious with increasing temperature and under neutral pH dyeing conditions. The incorporation of Byco C and Irgasol HTW into the dyebath had little effect on the yellowness of the dyed wool fabrics, and improved the handle and flat abrasion properties of the treated fabrics. The associated shrinkage of the wool fabrics during high temperature aqueous conditions was effectively controlled by the co-application of Byco C into the dyebath. The Byco C probably functions as a sacrificial protein and maintains the protein balance between solution and fibre. The application of the cross-linking Irgasol HTW and Byco C together in the dyebath also had beneficial effect on the flat abrasion of dyed wool fabrics. The combined effect was enhanced at pH 7, while at pH 4, the joint effect of Irgasol HTW and Byco was better than the individual effect of Byco C, but worse than that of Irgasol HTW alone. In providing a commercial option based on effectiveness and avoiding the use of formaldehyde the application of Byco C was best.

Fresh water is a scarce resource and the development of water less or water-free treatments for textiles are an urgent technology goal. However the use of more abundant saltwater (simulated seawater) as an alternative aqueous medium, instead of fresh water, for bleach processing has not been examined previously. In addition the combination of fibre protection in seawater media has also not been examined for wool and cotton previously. Therefore this study has identified a potentially useful approach to tackling a global challenge.

The relative whiteness of the resultant wool fabrics after bleaching in simulated seawater was not adversely affected. Indeed the wool fabrics bleached in salt water were overall whiter than those bleached in distilled water and with comparable tensile strength but better abrasion resistance. The nature of this improvement is currently uncertain but is most likely related to lipid retention and less damage to the cell membrane complex proteins. Further improvements in the flat abrasion performance could still be achieved by incorporating Byco C into the simulated seawater treatment

bath. The effect of bleaching on the handle of wool fabrics was not obviously influenced by salt water.

Dyeing of wool fabrics in simulated seawater was investigated and the potential benefits in terms of whiteness and abrasion resistance examined. It was clear that the wool fabrics were not obviously affected in terms of yellowness and abrasion resistance. However the addition of Byco C into the dyebath still had a positive effect on the flat abrasion of wool fabrics.

The whiteness of scoured cotton was increased considerably after bleaching with the higher temperature bleaching method having a better whitening effect. The incorporation of Byco C into bleaching baths did not adversely affect the fabric whiteness but did have a beneficial effect in increasing the flat abrasion performance. Similar to wool processing the tensile strength was not influenced greatly by Byco C in the 60℃ bleaching method, but showed increase protection with the increasing amounts of Byco C in the 85℃ bleaching treatment.

The scoured and bleached cotton already had a high whiteness, but the fabric whiteness still increased marginally after the second bleaching. The application of Byco C did not obviously affect the fabric whiteness and tensile strength, while it again had a beneficial effect on the flat abrasion of cotton fabrics.

The whiteness of cotton was not affected when the simulated sea water was used instead of distilled water in both bleaching methods. The abrasion resistance of the cotton fabrics bleached with 85℃ method was not affected. The incorporation of Byco C into the bleaching treatment baths still had a beneficial effect on the flat abrasion of the scoured cotton fabrics. Again the nature of this protective effect is uncertain at this stage.

The second theme of the thesis was to evaluate novel filter media which could improve the recycling of dyebath and bleach bath effluent. A series of papers with different cellulose/feather/wet strength additive compositions were made in this study and the dry strength of each paper was examined. It was found that the addition of

feather material had a detrimental effect on the paper strength (tensile and zero span), and in particular wet strength. However papers containing a cationic reactive polymer, EKA, which has the potential for cellulosic crosslinking, had a beneficial effect and increased wet strength. The combination of feather and EKA together with the cellulose pulp had reasonable strength under dry and wet conditions and maybe a viable option for further use as a dye adsorption filter medium.

Examination of the dye adsorption characteristics of the EKA treated pure cellulose and cellulose/feather combination under neutral and acidic conditions showed that increasing the cationicity of the paper increased dye adsorption for the EKA papers. The dye adsorption improved slightly under acidic conditions.

Hydrophobic PVP/1-triacontene nanofibres were manufactured through force spinning and evaluated for their effectiveness in adsorbing Direct dyes and Disperse dyes. Examination of the dye adsorption characteristics of the nanofibres indicated that the disperse dye was absorbed to a much higher extent.

9.2 Future work

Further work can be done in establishing the strength improvements of the wool and cotton fabrics through the use of fibre protective agents during the wet processing and the potential use of seawater as a the wet processing medium for textiles. In particular bleaching, dye bath recycling and wider wet processing in seawater needs further study. In addition the observed improvements in the flat abrasion of the wool and cotton fabric can be further investigated in particular:

- Develop an understanding of the action of proteins in protecting wool and cotton fabric during bleaching and dyeing and their impact on the fibre mechanical strength;

- Evaluate the effect of any potential cellulosic sacrificial agents (e.g. carboxymethylcellulose, alginates etc) on the bleaching of cotton and whether

any benefits are similarly evident in terms of whiteness and flat abrasion performance;

- The dyeing of cotton and wool in seawater needs to be investigated further, particularly in the presence of Byco C. Clearly any effect on colour needs to be established;

- During bleaching and dyeing of wool protein is lost into solution and if the bath is recycled the dissolved protein can give protection during wet processing. The effect of recycling and adding Byco C should be explored further;

- The bleaching of cotton and wool in seawater should be investigated with a view to recycling and replenishing the hydrogen peroxide concentration and minimising seawater usage;

- In understanding the protective action of the proteins and cellulosic materials the bulk and surface chemistry can be explored by X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR) Spectroscopy in order to relate fabric handle to surface and bulk properties;

- Similarly in developing an understanding of the potential for saltwater for textile processing the effect of laundering in saltwater can also be evaluated and the benefits of reducing dye loss, in particular from Direct dyed cotton;

- As part of the domestic laundering the effect of recycling with a combined chemically selective and mechanical filter will be assessed.

The utilisation of modified paper filters manufactured from waste poultry feathers, wood pulp, and EKA will can be evaluated as a dye adsorption medium under a range of acidic conditions ~ pH 3.0-6.0 in order to explore the potential of the feather material as a dye adsorbent. In addition its use as a combination filter media with the microfiltration media should also be explored with a view water effluent clean-up and preliminary filtration of actual seawater.

The potential for nanofibres as effective dye adsorption media can be further evaluated further and the role of polymer composition and immersion conditions on dye exhaustion established.