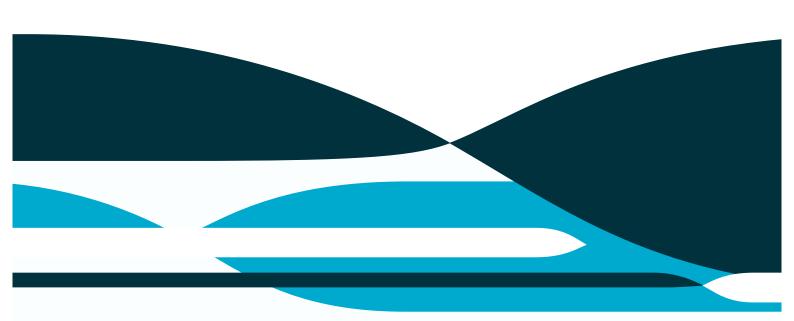# Review of the Dyeing Ability in Australian Cotton

Final Report – CMSE1214

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Copyright and disclaimer

Important disclaimer

Contents

Acknowledgments

1 Executive summary

The dyeing of cotton is influenced by chemical and physical interactions between dye molecules and the substrate, many of which are not well understood. This project reviews current knowledge of the relationships between the fibre properties of cotton, including surface and structural properties, and dye uptake by cotton fibres. Where available, research specifically pertaining to the dyeing ability of Australian cotton is reviewed.

The aim of this review is to guide the CRDC and researchers in understanding the issues associated with cotton dyeing and the current gaps in knowledge. Understanding and resolving these issues provides better quality, both in terms of breeding fibre with improved dyeing ability and improving dyed quality in mills. Increasing understanding around cotton's dyeing ability also improves prospects for better water and energy efficiencies associated with dyeing cotton, and thereby the 'social' license to use cotton as a textile.

The review has been conducted in response to anecdotal information gathered over time from mills reporting colour appearance and dye uptake differences using Australian cotton (Gordon et al, 2002, Gordon et al, 2004 and Yang and Gordon, 2010).

While a large amount of research has been conducted in this area, there remain questions about the effect of the structural properties of cotton cellulose on dye uptake kinetics and substantivity, i.e. the adherence of the dye molecule to the substrate being dyed. The structural properties in question include the species of wax and associated chromophores on the outer surface of the fibre, the non-cellulosic fractions, e.g. pectins, within the fibre structure and the fine structure of cotton cellulose itself. The review concludes that there remains a gap in understanding how these surface and structural attributes affect dye uptake and dyed appearance in cotton.

Focus is given to research that describes cotton's structural morphology, its cellulose structure and surface chemistry properties and the physical properties currently used to assess the dyeing ability of cotton. An overview of the dyeing of cotton including the dyestuffs used and procedures for preparing and dyeing cotton is given. This is followed by a review of research on the central issues that affect cotton dyeing. The central issues, as identified, are control of shade variation and water and energy consumption by the dyeing process.

Recommendations for further research work and its relevance to the Australian cotton industry conclude the review.

2 Introduction

Cotton is the most widely used natural fibre in the textile industry. However, over the last decades there has been a steady decline in the percentage of textiles derived from cotton with a corresponding rise in synthetic material. Figure 2-1 shows the proportion of fibre types produced for the world market. In 2013 cotton accounted for just less than 31% of the world fibre production (FAO-ICAC, 2013).

Use of synthetic fibres over natural fibres is advantageous to textile manufacturers as there is no reliance on crops, they are often cheaper and chemical alteration of fibre properties is often easier. From a consumer point of view, synthetic fibres are appealing again for their cheaper price, and also for fabric properties such as wrinkle resistance, moisture wicking and softness. It is vital to the cotton industry that fibre properties influencing textile processing be optimized in order for cotton to remain competitive with synthetic fibres.
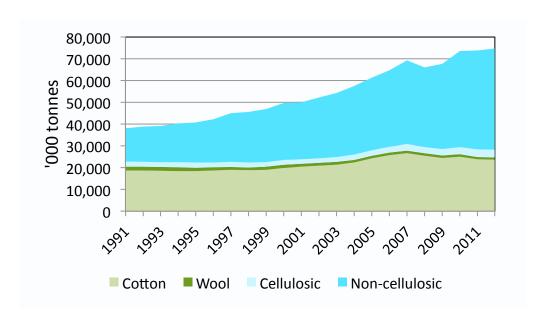
Figure 2-1: World fibre production (FAO-ICAC, 2013)

Dyeing is an important step in textile processing, imparting colour to the product. Dyeing is influenced by complex chemical and physical interactions between the dyestuff and the substrate. These are the origin of sources of shade variation and they must be carefully regulated to ensure the repeatability of colour shades between batches. Off-shade dyeing can lead to issues in later processing such as barré in fabrics. In some cases shade variation can be fixed with further over-dyeing but significant variation occasionally results in whole batch losses, both situations being costly for dye-houses.

Despite the level of care applied in dyeing there are still instances of cotton dyeing off shade for no clear reason. In their survey of international mills using Australian cotton, Gordon et al., (2004) found that any mills reported episodes where cotton with seemingly identical properties exhibited different dyeing behaviour. Reports of shade variation between processing lots of cotton continue to arise.

3 The Cotton Fibre

3.1 Cotton fibre development

Each cotton fibre is a single seed hair, harvested from domesticated species of plant in the genus *Gossypium*. The plants from one species, *Gossypium hirsutum*, are the source of over 90% of cotton produced globally. Another species, *Gossypium barbadense*, makes up another 8% of cotton fibre and is known for producing long, fine fibres. The other two domesticated species, *Gossypium aboreum* and *Gossypium herbaceum*, are of little commercial importance internationally.

Cotton is an annual summer crop, preferentially growing in hot climates with low humidity. Cotton is grown in approximately 75 countries worldwide. The three largest producers are China, India and the United States. The three largest exporters of cotton are currently the United States, India and Uzbekistan (Cotton Australia, 2013b).

The majority of cotton consumption is by developing countries such as China and India, accounting for over half of all cotton consumption globally (Cotton Australia, 2013b).

Cotton fibres are harvested from a seed pod or cotton fruit known as a boll. It takes 4-5 months for the cotton plant to grow from seed to boll opening. Cotton flower buds develop a few weeks after plants grow, with flowers opening a few weeks after that. The day of flowering is known as anthesis, with fibre development often described in days post-anthesis (dpa). Cotton fibre development occurs in four overlapping stages; initiation, elongation, secondary wall deposition, and maturation (see Figure 3.1, (Lee et al., 2007)).

The initiation stage of development starts when the flowers open, marking the start of fibre growth. The fibres extend longitudinally during the elongation stage, with final fibre length reached at 21-35 dpa. It is also during this stage that the outer layers of the fibre develop, establishing fibre diameter. Secondary wall deposition commences at around 21 dpa, continuing for 3-6 weeks. At maturity the bolls open, exposing the cotton fibres to the elements and drying them out.

At maturity the bolls are harvested. Nowadays this is mostly done mechanically but harvesting is still done by hand in some parts of the world. The bolls are then ginned to separate the fibre from the seed, and the fibres packed into bales for transport to mills or export.
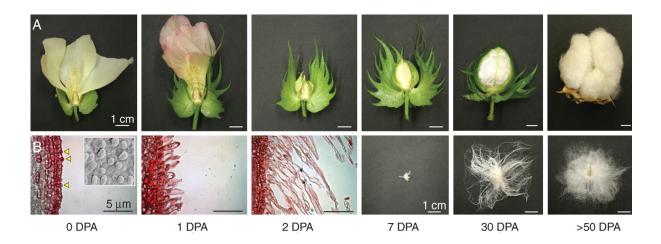
Figure 3-1: Cotton fibre development from initiation (0 dpa) to maturation (50+ dpa) (adapted from Lee, Woodward and Chen 2007).

3.2 Morphology of cotton structure

Chemical analyses of samples of mature cotton fibre are shown in Table 3-1 (McCall and Jurgens (1951)). These show the major constituent of cotton fibre is cellulose, with the thick and dominant secondary wall (in mature fibres) being nearly pure cellulose. The other substances are thought to be almost entirely confined to the primary wall and residual protoplasm in the lumen. The primary wall also contains much cellulose. Waxes, pectins, ash including metal ions and nitrogenous substances are also contained in this thin primary wall.

Table 3-1: Analysis of Cottons; Dry Basis (McCall and Jurgens, 1951)

Constituent	Empire	Wilds	Stoneville 2B	Unknown mature	Unknown Immature	Unknown (Mebane)
Cellulose (%)	95.30	93.42	95.58	96.41	92.44	94.93
Total sugars (%)	0.07	0.25	0.18	0.17	0.13	0.11
Reducing sugars (%)	0.01	0.17	0.04	0.02	0.03	0.02
Total N (%)	0.17	0.26	0.18	0.16	0.32	0.19
Wax (%)	0.73	1.07	0.69	0.45	1.14	0.57
Ash (%)	0.86	1.32	1.00	0.79	1.32	1.16

The cotton fibre structure has a layered structure. Figure 3-2 shows a drawing of the widely accepted structure of the cellulose layers in a cotton fibre (United States Department of Agriculture, 2012). The drawing is a representation based on photographic evidence by light and electron microscopy and evidence of the fibril angle by x-ray diffraction.
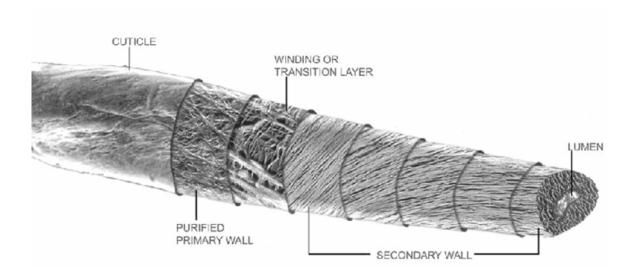
Figure 3-2: The layered structure of the cotton fibre (United States Department of Agriculture, 2012)

The outermost layer of the cotton fibre is the cuticle, a waxy layer coating the fibre. As well as wax, other surface chemical components present in this layer include sugars, salts, pectins, and metal ions (Wakelyn et al., 2007). The cuticle protects the fibre, acting as a waterproof coating. Intermingled with the cuticle is the primary cell wall; it is not uncommon for these two layers to be regarded as one (Etters, 1999, Maxwell et al., 2003). This layer consists mostly of cellulose, and non cellulosic materials including pectins, waxes and proteins (Maxwell et al., 2003). The cellulose is arranged in fine strands forming a network of capillaries. The combined cuticle and primary wall contribute only around 1% of the total fibre thickness (Etters, 1999)

A lacy network of cellulose micro-fibrils called the winding layer separates the primary and secondary cell walls. Although regarded as the first layer of the secondary wall, or the S1 layer, it differs in structure from both the primary wall and the remaining secondary wall layers with the cellulose strands aligned at a different angle. The secondary cell wall is composed almost entirely of cellulose, and makes up 90% of the total fibre weight (Heine and Hocker, 1995). The bulk of the cotton fibre is found in the second or S2 layer of the secondary cell wall. After the fibre diameter is established during elongation the secondary wall cellulose is deposited in layers of tightly packed cellulose strands.

The final or S3 layer of the secondary wall separates the S2 layer from the hollow lumen in the centre of the fibre, and is accordingly referred to as the lumen wall. During growth the lumen is filled with protoplast which dries up on boll opening, leaving a hollow bean-shaped cavity.

However, the layered model of the cotton fibre's cellulose structure offers little insight or connection to the fibre's chemical and physical properties. Unlike the growth rings in trees, the extent of each layer and its properties is difficult to measure in cotton and as such the 'layered' model has not been used to describe tensile, dye uptake or chemical reactivity properties in cotton fibre. Nor has the organisation or fine structure of the cellulose, i.e. the specific geometry, organisation and contribution of the cellulose units (fibrils and micro-fibrils) within each layer and along the fibre length. The way these organisational structures might change under genetic or environmental influence also remains a question. Here unto is the largely unmeasured connection between the structural properties of cotton cellulose and the dynamic uptake of dye-stuffs and the substantivity of dyes in the cotton fibre structure.

3.3 Cotton cellulose

As per Table 3-1, mature the cotton fibre is estimated to be composed almost 95% of pure cellulose. Cellulose is a polymer of D-gluco-pyranose units, an isomer of glucose, joined together in unbranched chains by β (1→4)-glycosidic bonds (Figure 3-3). The repeated unit of the chain is cellobiose, formed from two glucose molecules. The number of glucose units linked together to form the cellulose chain is described as the degree of polymerization. In cotton fibre the degree of polymerization ranges on average from 10,000-15,000 glucose units. Each chain has a reducing end with a free hemi-acetal group and a non-reducing end with an alcohol group.

Figure 3-3: The structure of cellulose chain.

The chains of cellulose are held together by hydrogen bonds between the hydrogen atoms of hydroxyl groups on adjacent chains (Figure 3-4, (Zhou and Wu, 2012)). The cellulose chains are arranged into crystalline strands known as micro-fibrils or crystallites, which are further arranged into the said cellulosic layers of the cotton fibre. Chapter 6 in the book 'Fibre Structure' entitled 'The Development of Ideas of Fine Structure' gives a still relevant overview of the theories proposed for the fine structure of crystalline fibres (Hearle, 1963). A still pertinent observation by Hearle in that chapter is that theories of fine structure are imprecise and often imperfectly visualised.

The imprecise knowledge around fibre structure is promulgated by the view that cotton fibres are said to contain two types of cellulose; crystalline and amorphous, in various ratios depending on genotype and maturity or degree of cell wall thickening (Figure 3-4, (Zhou and Wu, 2012)). While this view is not incorrect it does not promote questions about how this structure is ordered, or how it affects other properties of the fibre. Crystallinity is measured indirectly as an index. A high number means that the cellulose is crystalline and that it has a highly ordered, tightly packed structure. It is then said that hydrogen bonds holding the chains (fibrils) together are most extensive in these regions. A 'proof' of this is that many reagents, including water and consequently dye solutions, cannot penetrate the intra-crystalline regions of cellulose, with only the surface of crystalline regions being accessible (Ciolacu et al., 2011).

On the other hand, amorphous cellulose is said to have no definite crystalline form. Regions containing amorphous cellulose are more accessible to water and other substances, with many reagents only able to penetrate amorphous regions. Accordingly, amorphous cellulose is sometimes referred to as accessible cellulose.

The primary cell wall has a higher proportion of amorphous cellulose than the secondary cell wall. Hence, immature fibres are more 'accessible' than mature fibres due to having a greater ratio of amorphous cellulose. However, immature fibres also have a smaller total cellulose content due to less

developed secondary cell walls, so there is a smaller available surface area for dyes to bind to and as such they don't hold colour as well (Smith, 1991).

Four parameters of cotton cellulose's crystalline structure are usually measured to describe its nature. These are (a) crystallite orientation, (b) crystallite size (dimensions), (c) crystal lattice type and (d) the degree of crystallinity or order.

Crystallite orientation, or the mean alignment of the molecular chains in the crystalline regions with respect to the fibre axis, is measured by x-ray diffraction (XRD) (see Figure 3-5); the angular width of azimuthal curves at either the half-maximum angle or the 40% angle. Crystallite size is determined using the radial width of the arcs in the x-ray pattern (as in Figure 3-5), or by the levelling off degree of polymerisation after acid –hydrolysis.

Crystal lattice type is determined by the x-ray pattern itself against patterns for native cellulose (cellulose I), cellulose II (mercerised cotton) and celluloses III and IV. The shift in lattice configuration from I to IV is associated with a decrease in crystallinity. Descriptions of these configurations can be found in the comprehensive review of cellulose structure by Krassig (1985).

Crystallinity is measured using either acid-hydrolysis or dissolution technique from which the percentage of un-hydrolysed cellulose residue is plotted against the period of hydrolysis or using a viscometry measurement applied to the solution, or by using XRD or infrared (IR) spectroscopy. Various aspects of these measurements are used to determine the degree of crystallinity, e.g. intensities of interferences (for XRD) or the ratio of absorption at various wavelengths (for IR spectroscopy). Raman spectroscopy has been used to measure polymorphism, e.g. where the crystalline structure has more than one form. The application of differential scanning calorimetry (DSC) on cellulose is difficult because of the cellulose's complexity and highly crystalline structure. Table 3-2 lists aspects of crystalline structure measured by a range of instrumental and analysis methods.

Table 3-2: Common techniques employed for the characterisation of cellulose

Technique	Information
XRD	Crystallite size; crystallinity index
Raman spectroscopy	Crystallinity - polymorphs
Synchrotron XRD	Crystal structure, fibril angle
FTIR & FT-Raman	Chemical composition
DSC	Thermal degradation
Theoretical modelling	Conformation; dynamics
Electron microscopy	Crystallite size (surface)

While it is intuitive to propose that crystallinity and cotton's fine structure is important to the dyeing ability of cotton there is little research linking cotton's structure, crystallinity or otherwise, to dye uptake. There is a presumption that is not substantiated that only the amorphous regions of cellulose take up water and reagents (dyes).

Examples of research linking dye uptake and cellulose crystal structure include: Nelson and Mares (1965) who collected developing cotton fibres (20 to 50 dpa) and used the Goldthwaite test (see Section 4.2), chemical adsorption techniques and XRD to measure the changes in development of the fibre. The data were interpreted as indicating the high crystallinity of mature cotton fibre does not suddenly appear when the fibre first dries as the boll opens, but begins to develop concurrently with the deposition of cellulose during the period of wall thickening, and reaches the final high value by crystallization of an additional small fraction of cellulose upon initial drying. The dyeing tests were used to indicate changes in fibre development rather than a measure of dyeing and crystallinity interactions.

Datar et al (1973) found 'structure of *herbaceum* cotton was different to *hirsutum* cotton of similar maturity. Structure was defined in terms of micropore (void) size, convolution angle, birefringency and tensile properties – uptake of a large molecule dye was used to measure void size.

Wall (1988) used near infrared reflectance (NIR) spectroscopy in her PhD to analyse differences in cellulose for cotton samples with different dye take-ups. Wall found the reflectance spectra at wavelengths associated with the -OH and C=OjC-H combination bands in cellulose had the best regressions with dye uptake but that (i) only 60% of the variation in dye uptake could be measured by NIR spectra, and (ii) the best relationships between NIR spectra and fibre properties were with maturity and fineness (micronaire) – see also Section 3.5. The conclusion from this work was that further research was needed to identify the remaining 40% of the variation influencing the dye uptake of cotton.

In all these efforts only integrated, average values are used to link 'crystallinity' to dye uptake. No consideration is taken of the fine detail, e.g. fibril size, fibrillar angle, or to the variation in fine structure (the polymorphism) within and between fibres, largely because of the research effort required to measure these details.
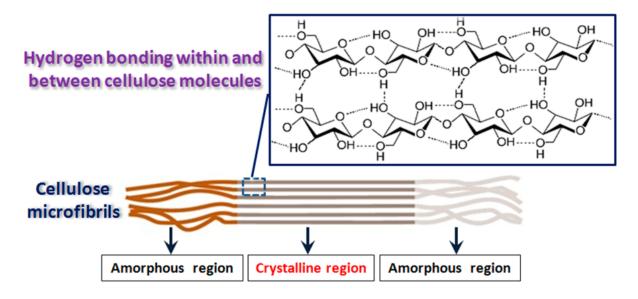

Figure 3-4: Hydrogen bonding between cellulose chains and the differential arrangement of cellulose microfibrils in amorphous and crystalline regions (Zhou and Wu, 2012).
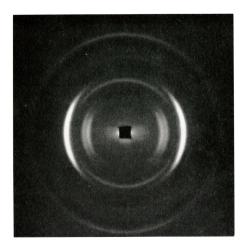
Figure 3-5: X-ray pattern diffraction – native cotton cellulose (Segal, 1971)

3.4 Cotton surface chemistry

The outer layers of the cotton fibre, the cuticle and the primary cell wall, contain various non-cellulosic compounds, making up nearly 4% of the cotton surface (Buchert et al., 2001). Most apparent of these are waxes, but there are also pectins, xyloglucans and other sugars, and various amino acids, proteins, organic acids, and inorganic salts.

Cotton wax consists of a mixture of high molecular weight long-chain saturated fatty acids and alcohols, resins, hydrocarbons (both saturated and unsaturated), sterols, and sterol glucosides (Wakelyn et al., 2007). Wax has the greatest effect on dyeing ability as it acts as an impermeable barrier, preventing water and dye molecules from penetrating the fibre. Cotton is scoured before dyeing to remove wax and other non-cellulosic impurities, but sometimes despite this process a residual waxy layer sometimes remains (Mitchell et al., 2005).
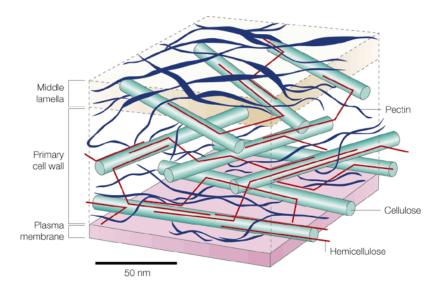
Levels of cotton wax appear to be influenced by both genetic and environmental factors. A 2002 study by Gordon et al., (2002) found statistically significant variation in cotton wax content between fibres of the same variety grown in different regions, highlighting environmental effects on cotton development. Some cottons in this study that suffered heat or water stress during growth were found to have lower micronaire values. Additionally, the composition of cotton wax was not uniform, with some of the stressed cottons having high concentrations of a wax containing high levels of hydrocarbon which could not be removed easily by conventional scouring methods.

The presence of wax is thought to be beneficial in the mechanical processing of cotton such as spinning, acting as a natural lubricant and reducing fibre breakage during cleaning and drafting. However, work by Cui et al. (2002) found no significant correlation between wax content and fibre breakage. This work found wax to be significantly correlated with micronaire but no other fibre property (Cui et al., 2002). This was backed up the following year in work by Gamble (2003). Gamble's work also found an inverse relationship between micronaire and pectin content, and linear relationships between micronaire and salt and sugar contents (Gamble, 2003).

3.4.1 NON-CELLULOSICS

Hemicelluloses are estimated to make up approximately 1.4% of the cotton surface (Buchert et al., 2001). Hemicelluloses are polysaccharides with a backbone structurally similar to that of cellulose, but unlike cellulose may contain residues other than glucose. Additionally, the chain lengths of hemicelluloses are shorter and may be branched. Hemicelluloses also have a more amorphous structure, making them more reactive to reagents. Types of hemicelluloses found in cotton include pectin and xyloglucan.

Pectin is a generic term used to describe a family of polysaccharides containing 1,4-α-D-galacturonic acid, including homogalacturonans, rhamnogalacturonans, and substituted galacturonans. Pectin acts as a cement, binding the non-cellulosic surface components of cotton within the cellulosic matrix of the primary cell wall (Figure 3-6, (Smith, 2001)), as well as partially contributing to the hydrophobic character of the cuticle and primary wall (Etters, 1999).

Nature Reviews | Molecular Cell Biology

Figure 3-6: Generic structure of a plant primary cell wall (Smith, 2001).

Xyloglucans are found in the primary cell wall of all higher plants. Xyloglucans are suggested to play an important role in cell enlargement, decreasing in concentration during plant growth. It is for this reason that xyloglucans are regarded as a key component of the primary cell wall.
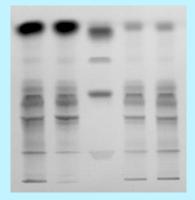
Australian research on cotton wax – 1992-2002

Between 1992 and 1994 the CRDC commissioned fibre-to-fabric trials to examine the effect of variety and environment upon spinning ability, yarn properties and dye uptake (Steadman, 1994 and 1995). While the trials found variation in dye uptake was due predominantly to a combination of fibre maturity and fineness (linear density) the trials also showed the strong effect of pre-bleaching on dye uptake. Fabrics that were dyed without bleaching took up much less dye than fabrics that had been bleached, and fabrics that had been bleached took up less dye than fabrics that had been scoured and then bleached. However, variation in dye uptake results, measured as percent reflectance, suggested that other factors besides maturity and fineness had an effect on dye uptake. Spinners and dyers associated with the project suggested that the variation was due to differences in cotton wax, which on some samples was more difficult to remove than on others (Jones, 1996, Dawson, 1996).

Preliminary work on a more formal survey began in late 2000 in response to continued concerns from industry, which were re-stated at the Fibre-to-Fabric Meetings held in that year (Galmes, 2000). A preliminary survey of a small number of cotton varieties from Australian Cotton Research Institute (ACRI) trial plots at Emerald, Breeza and Narrabri was undertaken. Fibre samples were subject to an abbreviated solvent extraction procedure using 95% ethanol solution. Extracts, which contained polar and non-polar constituents, were then expressed as a percentage of the fibre weight. While the results of this survey confirmed the strong relationship between the percent extractable matter and specific surface area (micronaire) that has previously been found, the results also showed that there was a fair degree of spread from this relationship. The degree of spread prompted questions about other factors that govern the amount (and type) of wax found on cotton.

In a more formal study initiated in 2001 the wax from a wide range of Australian cotton varieties grown across different regions was extracted using the method by Conrad (1944) in order to measure the amount of wax and determine whether there were chemical differences in the wax extracts. The wide range of cotton varieties and regions examined meant that the dependency of wax content on varietal (genetic) and regional (environmental) factors could be investigated.

The results showed that while both variety and region contribute to the amount of wax found on the fibre, the chemical composition of the wax extracts was very similar across all samples tested. The exception to this was an extract from a low micronaire cotton (3.8) sample that had much higher concentrations of hydrocarbon wax. It was noted this did not occur for all low micronaire (values ≤ 3.8) cottons and that the only apparent difference between the low micronaire samples was that the sample with the high concentrations of hydrocarbon wax was subject to heat and water stress at some point during fibre growth.

High Performance Thin Layer Chromotography of cotton wax extracted from Sicala 40 cotton. Lanes 1 & 2 (Brookstead) show high concentrations of long chain hydrocarbon waxes in the low micronaire cotton, 4 & 5 (Walgett), 3: Standard lipid mixture.

3.5 Properties used to predict dyeing ability

While the surface and structural properties of cotton fibre might be important to how a fibre will dye these properties are not easily measured. As such, the fibre properties used to class and market cotton are used. Today cotton is most commonly graded using an automated high volume instrument (HVI) line, the instruments of which measure fibre bundle length, strength, uniformity, micronaire, colour and trash content. As HVI lines have become the standard classification system for cotton, the test parameters are also used by mills in the selection of cotton to purchase from growers.

Fibre properties are determined by the cotton genotype, growth environment and interactions between them, as well as the metabolic rate of the plant during development (Bradow and Davidonis, 2000). Properties such as length, strength and fineness are for the most part determined by genetics but environmental factors can influence overall fibre quality (Bradow and Davidonis, 2000). The most important fibre properties in relation to dyeing ability are colour and micronaire. Discolouration of cotton can arise from numerous causes potentially indicating fibre quality issues, which may affect dyeing ability. Micronaire is closely related to maturity. These two factors are considered the major parameters effecting shade and are used to predict dyeing ability of cotton accordingly.

3.5.1 COLOUR

Naturally white cotton may become discoloured during growth due to factors such as weather conditions, microbial or insect damage, and disease. Additionally, fibre discolouration can arise from poor moisture and temperature conditions during storage. Colour variation in cotton fibre may suggest variation in other physical properties that may have an effect on processing and quality of the end product and result in a lower market value (Cui et al., 2014, Matusiak and Walawska, 2010). Discolouration due to fibre deterioration can affect the ability of cotton to take up dyes and other treatments (Matusiak and Walawska, 2010). Discolouration can sometimes be reduced or eliminated by bleaching, minimizing its impact on dyeing ability. Work by Bradow and Bauer in 1998 found growth environment to be the main influence on colour of both raw and dyed cotton fibres. Temperature was a big influence with higher temperatures correlating with increased whiteness and decreased yellowness in raw fibre (Bradow and Bauer, 1998). The same paper found that although genotype did not have a significant influence on the colour of raw fibre, it did effect the colour of dyed fabrics (Bradow and Bauer, 1998).

Raw fibre colour is measured instrumentally in terms of yellowness (+b) and reflectance (Rd). Yellowness gives a measure of the level of pigmentation of the cotton based on the yellow/blue (+b/-b) axis in the CIE LAB colour space. Reflectance is a measure of brightness and is important to the overall appearance of cotton in terms of lustre. Immature fibres appear duller than mature fibres as their shape does not reflect light as efficiently (Gordon et al., 2004). Australian cottons have been reported to be less lustrous than some African cottons and therefore appear duller (Gordon et al., 2004).

A 2010 study by Matusiak and Walawska found agreement between classer and HVI grading of cotton grown outside the USA (central Asia) to be insufficient. They suggest that HVI may not be the best measure for this property and an alternative method is needed (Matusiak and Walawska, 2010). Ultimately the colour of fibres, yarns, and fabrics will be visually scrutinized, hence instrumental methods of determining fibre colour should be correlated with the human eye (Bradow and Davidonis, 2000).

3.5.2 MICRONAIRE

Micronaire is a measure of the specific surface area of a fibre determined by measuring the air permeability of a constant mass of cotton fibres that is compressed to a fixed volume (Cotton Incorporated, 2014). Micronaire is a function of maturity and fineness, with maturity referring to the degree of cell wall thickening and fineness referring to linear density of the fibre. The ideal range of micronaire values for upland type cotton is between 3.8-4.2 units. Higher micronaire fibres tend to be coarse, and accordingly result in coarser yarns. Low micronaire cotton fibres are more prone to breaking and tangling. The latter is particularly problematic as it can lead to the formation of neps; tangled clumps of fibres which may also contain foreign matter such as trash or seed coat fragments. Neps are problematic as they lead to imperfections and irregularities in yarns and fabrics. Neps are often resistant to dyeing and may appear in fabrics as pale or white specks. A low micronaire value may result from immaturity or genetic fineness, whereas high micronaire can result from coarseness or thicker, more developed secondary cell walls; hence relying on micronaire alone is an insufficient method of quantifying maturity (Paudel et al., 2013).

Micronaire is one of the two factors most heavily influencing dyeing ability of cotton, with studies conducted at the International Centre for Textile Research recommending cotton fibre to be used in fabrics from multiple sources varying by no more than 0.2 micronaire units to avoid dyeing ability issues such as streaking (Chellamani et al., 2001).

3.5.3 MATURITY

Maturity has a greater influence on fabric appearance and defects than any other fibre property. Maturity is not a chronological term but rather an expression of cell wall thickness. Fibre maturity can be described as the thickness of the secondary cell wall in relation to the fibre diameter. Maturity is expressed as a maturity ratio, with a value of 0.85-0.95 being considered as mature. Immature fibres behave differently to mature fibres which consequently causes differences in dyed appearance (Figure 3-7, from Bange et al., 2009). In immature fibres the secondary cell wall cellulose, which is the part of the cotton fibre that primarily takes up dye, is under developed causing the fibres to accept dye differently (Smith, 1991).

Shade variation is also influenced by chemical differences in immature fibres effecting affinity for the dye stuffs, and optical effects due to different reflectance properties. Several types of defects in dyed fabrics result from immature fibres including poor shade repeatability, piece-to-piece shading, filling bands, warp streaks, and barre (Smith, 1991). These problems can generally be controlled by measures such as fibre blending, separation of fibres from different sources, or adjusting dyeing recipes to compensate for the immature fibre (Smith, 1991).

Within a fabric, dyed appearance is dependent not only on the average maturity of the fibres, but also the distribution of immature fibres, with localized areas with immature fibres appearing as white specks which may not be correctable (Smith, 1991). Both bulk and localized defects in dyed fabrics can be very costly to manufacturers.

Figure 3-7: Shade variation between cottons of different maturities dyed with the same colour (from Bange et al., 2009).

Maturity has been well studied, as may be expected by the dramatic impacts on quality of the end product caused by this property. The paper by Smith (1991) acknowledged that although maturity is related to fibre properties influencing dye uptake, such as secondary wall thickness and fineness, it does not give a direct indication of dyeing ability, with the exception of dyeing defects directly related to immature fibres such as barré and white specks. This paper states that other properties, such as order, crystallinity and morphology, may be equally important if not more so than maturity in regards to dyeing ability (although these were not measured) (Smith, 1991).

Bradow et al. undertook a series of studies in the late 90's – early 00's on environmental effects on cotton development. Maturity was found to be quite sensitive to growth environment, particularly temperature, regardless of whether genotype was taken into consideration (Bradow et al., 1996b). Further work from this group found relationships between maturity and both yarn elongation percentage and dye uptake (Bradow and Bauer, 1998). They emphasise the need for reliable maturity testing for prediction of dye defects related to individual immature fibres, and not bulk fibre properties, suggesting that further modeling of effects of growth environment on maturity is required (Bradow et al., 1996a).

The need to review maturity testing procedures in terms of dyeing ability is also demonstrated in work by Pellow et al. (1996) which showed fine fibres that would be rejected by mills on the basis of high micronaire to uptake dye more successfully than lower micronaire fibres. In this case the high micronaire of the fibres was related to high maturity and not coarseness (Pellow et al., 1996).

In the late 2000's CSIRO developed the SiroMat instrument, which uses polarized light microscopy to directly measure maturity. This instrument was found to give strong predictions of dye shade variation, even between fibres with high maturity ratios (within the range of 0.90-0.98) (Gordon et al., 2008). This work found there to be shade variation between dyed fibres with as little as 0.05 units maturity difference.

The SiroMat instrument was replaced in 2010 with the Cottonscope instrument which also combined the CSIRO Cottonscan technology (Naylor et al., 2011). The Cottonscope measures average maturity, linear density, micronaire and ribbon width and also reports the distribution of fibre maturity and ribbon width within a specimen.

Rebenfeld and Wu (1961) used ratios of green and red direct dye extracts (the Goldthwaite differential dye test – see section 4.2) to indicate structural properties of cotton but described as differences in

fibre maturity. The method of extracting the dyestuffs from the fibre and measurement of the extract were proposed as providing more objective and therefore more accurate assessment of fibre maturity by the Goldthwaite dye test.

Thompson and Hsieh (1998) investigated the 'maturity' of fibre via the Goldthewaite test on seed cotton – fibres were separated and segregated on basis off their position on fibre. The chalazal end of the fibre was least mature and fibres with high seed fibre weights were most mature.

3.5.4 FINENESS

The term fineness can refer to a number of different aspects of the cotton fibre. Biologically speaking, fineness refers to the perimeter of the cotton fibre. More commonly however, fineness refers to the linear density, or mass per unit length of a cotton fibre. This property is expressed in millitex, or micrograms per metre. Finer fibres can improve performance properties of yarns and fabrics due to having a greater number of fibres within the yarn cross-section but may be more susceptible to breakage and tangling. In addition, fabrics and yarns made from finer fibres have enhanced lustre as they have more reflective surfaces per unit area (Bradow and Davidonis, 2000). Typically, finer fibres have lower micronaire values but this is not necessarily always true, with some fine fibres having higher micronaire values due to higher maturity (Pellow et al., 1996).

4 The Dyeing of Cotton

Cotton has been used in textiles as early as 3000 BC and dyed for just as long. Historically natural dyes were used such as plant and animal extracts, and mineral pigments. The first synthetic dyes were developed in 1856 by Sir William Henry Perkin, triggering a boom in dye manufacture (Aspland, 1992a). Nowadays there are many types of dyes available for use on cotton textiles including direct, vat, sulfur, azoic and reactive dyes.

4.1 The dyeing process

The absorption of dyes by cotton during the dyeing process can be described as a chemical equilibrium as in equation 1 below (King, 2006).

$$D_{bath} \rightleftharpoons D_{fibre} \qquad [1]$$

In this simplified model, dyes are generally described as substantive if at the end of the dyeing process D_{fibre} (the amount of dye on the fibre) is much larger than D_{bath} (the amount of dye in the dye bath).

Substantivity is favoured by the formation of multiple dye-fibre bonds. This bonding in the case of cotton dyes is hydrogen bonding between suitable hydrogen donor groups on the dyes and lone pairs on the oxygen atom of the cellulosic hydroxyl group. The necessity for the formation of a number of these bonds combined with the highly crystalline structure of cotton, places very specific requirements on the structure of cotton dyes, in particular on the higher molecular weight direct and reactive dyes. In general the most useful dyes are found to be those which can adopt an elongated and coplanar configuration in which the number of hydrogen bonds is maximised and the cellulose crystal structure is not disrupted.

The alternative approaches to attaining acceptable fastness are the formation of an insoluble coloured complex (azoic, sulphur and vat dyes) or the formation of dye-fibre covalent bonds (reactive dyes). These dyes will be discussed later in the chapter; however the same principles apply to the dye absorption process regardless of subsequent chemical reactions.

The dyeing process occurs by various methods depending on the type of dye. For reactive dyes the process occurs in three steps: exhaustion, fixation and washing off. During exhaustion the dye is taken up by the substrate to its maximum capacity or equilibrium.

Salt is added to help exhaust the bath by pushing the dye into the substrate. The lower the affinity for the dye the more salt is required.

Typically, the dye is added at room temperature and the dye-bath gradually heated to set dyeing and fixation temperature. In the fixation stage the covalent bonds between the dye and the fibre form. An alkali, such as sodium hydroxide or soda ash, is added to the dye-bath, which converts the hydroxyl groups on the cotton cellulose to the reactive anionic form. The addition of the alkali triggers a shift in equilibrium between the dye in the substrate and in the bath. Equilibrium is reached when all free dye molecules have been bound to the substrate or have hydrolyzed in the bath, and no further increase in colour depth occurs. The final step of the process, washing off, requires all unfixed, hydrolyzed dye to

be removed from the substrate. This can be a lengthy process, depending on the substantivity of the dye, requiring washes at various temperatures and in some cases even further scouring.

4.1.1 ELECTROSTATIC EFFECTS AND THE USE OF SALT

When textile fibres are immersed in an aqueous dye-bath there is a rearrangement of charge groups at the interface between the fibre and the aqueous environment. This invariably leads to the fibre surface acquiring an initial negative charge, the so-called zeta potential (Ribitsch, 1998). Since most textile dyes are sulfonated to provide aqueous solubility they also have a negative charge in solution and there is an electrostatic barrier to overcome in order for the dyes to diffuse through the fibre-water interface.

In cotton dyeing, the only widely used method of overcoming this electrostatic barrier is the addition to the dye-bath of large quantities of salt, generally sodium chloride or sodium sulphate. The presence of electrolyte is well known to reduce the extent of the electrostatic field around a charged surface (Hunter, 1981). The mechanism of the salt effect is the dynamic adsorption of counter-ions (i.e. sodium), which leads to a reduction in the effective surface charge of the fibre. Figure 4-1 illustrates the effect of salt on dye uptake.
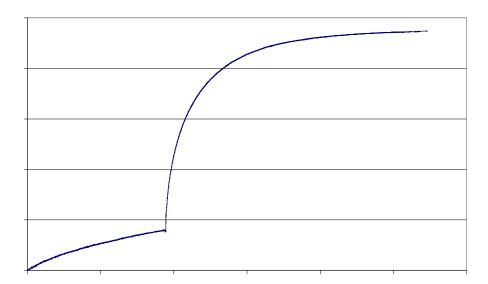

Figure 4-1: Exhaustion of direct cotton dye- effect of salt addition (uptake of 1% CI Direct Blue 71 with 8 g/L sodium chloride added at 80°C for 60 minutes) (King, 2006)

It can be seen that there is an initial adsorption of dye, but dye uptake approaches approximately 20% asymptotically. The addition of salt results in rapid exhaustion of dye to yield a much higher and commercially practical uptake. The addition of salt as well as affecting the rate of dyeing by reducing the electrostatic repulsion increases the overall uptake of dye by reducing its solubility in the dye-bath.

4.1.2 EQUILIBRIUM AND LIQUOR RATIO

As previously referred to, the cotton dyeing process is an approach to equilibrium, and at the completion of the process there is a distribution of dye between the fibre and the dye bath. The

equilibrium concentration of dye in each of the two phases is governed by various physical effects such as the amount of electrolyte in the dye-bath and the substantivity of the particular dye structure. One practical consequence of the equilibrium between dye-bath and fibre is the effect of the relative amounts of the two phases, the so-called liquor to goods ratio or liquor ratio. Higher liquor ratios allow more dye to remain in the dye-bath at the completion of the dyeing process; the implication of this is a lesser depth of shade and more dye in the effluent from the dye-house. Figure 4-2 shows the effect of liquor ratio on the uptake of a typical direct dye.
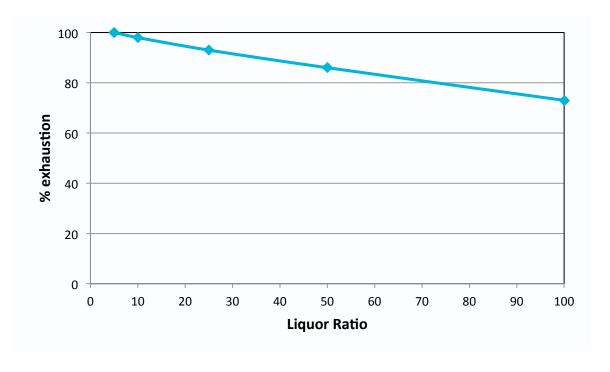

Figure 4-2: Effect of liquor ratio on dye uptake (uptake of 1% CI Direct Blue 71 with 8 g/L sodium chloride at 80oC for 60 minutes) (King, 2006)

It can be seen that there are high levels of dye uptake only at quite low liquor ratios and that the exhaustion of the dye varies significantly with small changes in liquor ratio. In order to get reproducible shades in cotton dyeing, liquor ratio is one of the many aspects that have to be consistent from laboratory to bulk and from one dyeing to the next. The lowest liquor ratios are those obtained in modern jet dyeing equipment and these are claimed to be as low as 2:1. Typical package dyeing liquor ratios are between 10 and 20 to 1. In continuous and semi-continuous dyeing methods the liquor ratios are typically less than one and thus even higher fixation levels are obtained.

4.1.3   EFFECT OF TEMPERATURE ON DYEING

Studies of dyeing have shown that the absorption of dyes by cotton is an exothermic process. The implication of this fact is that if dyeing is carried out to equilibrium, then lower temperatures favour higher exhaustion of dyes. One might conclude from this that dyeing should be carried out at room temperature, however the other effect of dyeing temperature is on the rate of dye uptake; this kinetic effect has more practical significance, although the thermodynamic effect should not be neglected. The rate of dye uptake increases appreciably with temperature and approximately doubles for every ten degree temperature rise. The dyeing temperature must be high enough for equilibrium and fixation to occur in a short enough time for practical operation of the dye house. An additional constraint is that if the rate of dyeing is too rapid severe unlevel dyeing can occur. This is due to the fact that timescale of dyeing will be similar to the time in which dye liquor circulates in the dyeing machine. Thus the choice of dyeing temperature is a compromise (Perkins, 1996); all dye manufacturers provide recommended

dyeing temperature profiles for particular dyes based on studies in their research laboratories and practical experience.

4.2 Types of dyes

This section introduces the main types of dyes used in the dyeing of cotton textiles.

4.2.1 DIRECT DYES

Direct dyes have previously been quite popular due to their ease of application and full range of available shades but recent years have seen a shift towards other dye classes, particularly reactive dyes. Direct dyes are water soluble anionic dyes that are drawn in to the substrate on addition of electrolyte to the dye-bath (Aspland, 1991). Once the dye molecules have entered the fibres they are held in by intermolecular forces including Van der Waals interactions and hydrogen bonds. The dye molecules are relatively large with a long and flat shape, allowing them to lie parallel to the cellulose chains. The large size of the molecules also increases the substantivity between the dye and the fibre by increasing the number of intermolecular bonds that can form.

Direct dyes can have good light fastness but may not produce the most vibrant results and have average wash fastness (Aspland, 1991).

A laboratory dye procedure can be used to test differences in the maturity of cotton fibres (Goldthwaite, 1947). The test involves dyeing a loose bundle of fibres with two direct dyes in completion. The dyes recommended for the test were diphenyl fast red and chloratine fast green. The effects of the test are dependent upon competition between the two dyes for absorption sites in cotton cellulose, upon the relative rates of stripping (desorption) and different optical effects arising from the variation in wall thickness. Mature fibres are coloured red and immature fibres appear from a greyish to distinct green. The procedure was developed by Goldthwaite et al., (1947).

Rebenfeld and Wu (1961) devised a chemical method for extracting the Goldthwaite dyes and determining their concentration via a standard curve. This method was said to be more objective and sensitive to the relative amounts of dyes taken up.

4.2.2 VAT DYES

Vat dyes are the oldest type of dyes in existence. The most common vat dye is the indigo used to colour denim, however nowadays synthetic indigo is used over natural indigo (Aspland, 1992c).

Vat dyes work via a reduction-oxidation reaction. The dye is sold as a water insoluble pigment which is solubilized on addition of a reducing agent. The fabric is added to the dye-bath and on exposure to air or an oxidizing agent the dye reverts to the water-insoluble form. Vat dyes typically have a high wash fastness but low abrasion resistance which can be improved with treatment of the fabric (Aspland, 1992c). A notable exception to this is indigo, which is known for poor wash and fastness properties. This is due to different application methods to other vat dyes and consumer demand for denim fabrics with a worn appearance (Aspland, 1992c). Some vat dyes react with light causing accelerated fibre degradation, known as photochemical tendering. One theory explaining this degradation suggests the light converts the dye into an excited state allowing it to continually withdraw electrons from the fibre while remaining in its oxidized form due to oxygen exposure from the air (Baumgarte, 1974). Another

Certain azoic dyes can break down under reductive conditions to release a group of defined aromatic amines, which are carcinogenic. Consumer goods which contain listed aromatic amines originating from azoic dyes were prohibited from manufacture and sale in the European Union (EU) countries in September 2003.

theory proposes the formation of a highly active singlet oxygen species is responsible for the tendering

Only very few azoic dyes are affected in this way, with it been estimated that less than 4% of known azoic dye structures would release the corresponding amines (Chakraborty, 2010). Additionally over the last few years all reputable dye manufacturers have stopped manufacturing these dyes and test institutes report the vast majority of samples tested today comply with the EU Directive. Those consumer goods containing azoic dyes that, by reductive cleavage of one or more azoic groups, may release one or more of the listed aromatic amines are forbidden. Detectable concentrations of any amine should not exceed 30 ppm in the finished article or the dyed part thereof.

(Baumgarte, 1974). Particular dyes known for this degradation are some yellow, orange and brown shades, and certain dye combinations (Chakraborty, 2010).

4.2.3 SULFUR DYES

Sulfur dyes are another popular type of dye due to their low price and good wash fastness. Sulfur black is a particularly common dye due to its cost and depth of colour (Aspland, 1992b). Application of sulfur dyes is similar to that of vat dyes, with coloration occurring by a reduction then oxidation reaction however oxidating agents may be required to return the dye to an insoluble form. Some colours are not available as sulfur dyes and as sulfur dyes can be of a reductive nature and are also reductive dyes they are subject to the same photochemical tendering (Shenai and Rao, 1973).

(Puentener and Page, 2004)

As of June 2014 there was no Australian legislation banning sale of goods containing these dyes

4.2.4 AZOIC DYES

Azoic dyes are a class of dyes containing an insoluble azo group (R-N=N-R'), which acts as the chromophore. The dyes are produced by reaction of a napthol compound and a diazo-compound. Azoic dyes may be applied as direct, vat or reactive dyes. Azoic dyes are known for their particularly bright colours and high wash fastness but can have poor abrasion resistance. They are used in wide range of textile applications and (even) as food colourings.

4.2.5 REACTIVE DYES

Reactive dyes first appeared on the market in 1956 and have since become increasingly popular in the textile industry, particularly in the dyeing of cellulosic fibres for which they are now the most commonly used dye type. Reactive dyes are a class of dye that form covalent bonds with the substrate, chemically binding them to it. Covalent bonds are much stronger than the intermolecular forces that hold other dyes.

The two major reactive groups in commercial reactive dyes are the chloro-triazine and vinyl sulfone groups (Figures 4-1 and 4-2) (Buschle-Diller and Traore, 1998). Dyes may be mono-functional or multi-functional, with the latter containing two or more reactive groups that may be the same or different.

Figure 4-3: The structure of a dichlorotriazine group

Figure 4-4: The structure of a vinyl sulfone group

The reaction between the dyestuff and the cotton fibre proceeds via a different mechanism for each reactive group. For the chlorotriazine group, the reaction occurs by nucleophilic substitution, forming an ether bond (Figures 4-3). For the vinyl sulfone group, the reaction proceeds by nucleophilic addition, creating an ester (Figure 4-4). The dye initially has a sulfatoethylsulphone group, becoming the vinyl sulfone form on elimination of a bisulphate anion.

Figure 4-5: The nucleophilic substitution mechanism of chlorotriazine dyes

Reactive dyestuffs and lyocell

Lyocell is a 'new-generation' regenerated cellulose fibre developed in the 1980s by Courtaulds (now Acordis-Lenzing).

A key discovery made early in the development of lyocell was that multi-functional reactive dyes could cross-link the fibre and thereby prevent or inhibit the fibrillation of the fibre. Since manipulation of this fibrillation is critical in the development of lyocell fabric aesthetics understanding how to control this cross-linking by the dyestuffs was important.

Figure 4-6: The nucleophilic addition mechanism of vinyl sulfone dyes

Chromophoric groups used in reactive dyes include anthraquinone, phthalocyanine, formazin, oxazine and azo groups, with the latter estimated to make up around 66% of reactive dyes (Bhatti et al., 2012). Typically, reactive dye molecules are smaller in size than other dye types (such as direct dyes) and can have a low affinity for the cotton fibre, causing low levels of dye-bath exhaustion.

Large amounts of salt are required to drive the dye into the fibre (whether it be cotton or a regenerated cellulose fibre like lyocell), which together with poor exhaustion rates raises environmental concerns about dye-bath effluent. However, some low salt reactive dyes have a larger molecular size and therefore enhanced substantivity by inter-molecular attraction.

Reactive dyes typically have good wash fastness and light fastness, and a full range of shades is available (Aspland, 1992a). Compared to other dye classes reactive dyes can have longer processing times and be more costly, however prices have fallen with their increasing popularity. As they are important in dyeing of cotton reactive dyes will be the main focus for this review.

4.3 Pre and post dyeing procedures

Cotton may be dyed in fibre, yarn or fabric forms. There are then processes applied pre and post dyeing to affect dye uptake, fabric handle and appearance, and the functionality of these forms.

4.3.1 PRETREATMENTS

Pre-treatment can involve multiple processing steps including singeing, desizing, scouring, bleaching and mercerization. Singeing is performed on yarns and fabrics to burn off stray fibres not tightly bound in the yarn or fabric. It is commonly applied to yarns for weaving or woven fabrics, which are expected to have low hairiness and a smooth, clean fabric hand.

Desizing is done to remove starches and other sizes that may have been applied to the yarn or fabric in previous processing steps, commonly prior to weaving to stiffen and strengthen the warp yarns, and involves treatment with amylase enzymes, oxidizing agents, or acids.

Scouring, which is very common, is performed to remove cotton wax and other impurities that may inhibit dye uptake. Traditionally scouring is done under alkaline conditions, using strong sodium hydroxide solutions or alkaline detergents at high temperatures. The scouring solution may also contain other reagents such as wetting agents, dispersing agents and chelating agents. Many rinses are often required to thoroughly remove the scouring solution, with acetic acid often added to neutralize the alkali. The relatively harsh conditions can cause damage to the cotton fibres if not properly controlled. Scouring consumes a lot of water and energy, and is a main contributor of organic pollutants in textile effluent (Etters, 1999). Hence, there is a growing research trend towards bio-scouring with enzymes including cellulases and pectinases.

Bleaching further removes impurities from cotton, particularly those that may have caused discolouration or yellowness. Discolouration prior to dyeing can cause differential results in the end product. Bleaching provides a uniform white base and helps ensure dyeing is even. Bleaching is especially important in dyeing of pale shades.

Bleaching of cotton is typically done using hydrogen peroxide at high temperatures. Like scouring, the harsh nature of conventional bleaching is of environmental concern and research is being done into finding alternative methodologies such as enzyme treatments (Eren et al., 2009).

4.3.2   ENZYME TREATMENTS

Enzyme treatments are designed to be a gentler method of scouring cotton with a lesser environmental impact due to lower water use and fewer chemicals required. Enzymes have been used for various applications in the textile industry since the early 1900s. The first enzyme treatments utilised amylase enzymes as a method of desizing fabrics. Starch removal remained the only application of enzymes in textile processing until the 1980s when cellulase enzymes started being used to de-fuzz the surface of cellulosic fabrics and to create aesthetic effects such as stonewash-look denim. From the 1990s catalase enzymes have been used to neutralize hydrogen peroxide after bleaching.

Since the 1980s scouring of cotton has been tested with a variety of different enzyme types, targeting different components in the cotton fibre, both as individual enzymes and in various combinations. Additionally, studies have found use of surfactants, particularly nonionic ones, to enhance the enzymatic reaction process (Ooshima et al., 1986, Sawada et al., 1998). Some of the enzyme types that have been used include cellulases, pectinases, proteases, lipases, cutinases and xylanases.

Cellulases catalyse the hydrolysis of cellulose into smaller sugars, eventually breaking it down to glucose. Treatment of cotton with cellulases is designed to degrade the outer layers of cellulose, loosening the cuticle and primary wall, where much of the noncellulosic material in cotton is located. Cellulases are commonly produced by fungi and bacteria found in soil such as *Trichoderma*, *Penicillium*, and *Fusarium* (Araujo et al., 2008).

There are different types of cellulases that have different mechanisms of action which are generally used in combination to degrade cellulose. Types of cellulases include exoglucanases which cleave cellulose from the crystalline ends of chains, and exoglucanases which randomly cleave cellulose from within chains in the amorphous regions. Cellulases may be classed as acidic, neutral, or alkaline depending on the pH at which they have optimum activity. On the basis of weight loss Rössner (cited in

Hartzell & Hsieh, 1998) deemed cellulases to be the most effective enzyme for the removal of impurities from cotton fibre. However, a significant decrease in strength was observed (Hartzell and Hsieh, 1998). A multi-enzyme study by Hartzell & Hsieh (1998) found cellulases to be the only enzyme to produce noticeable improvements in wettability and water retention properties when applied alone on raw cotton.

Pectinases, which break down pectin, are regarded by many being the most effective singular enzyme for bio-scouring applications, producing promising results without the weight and strength losses caused by cellulases (Sawada et al., 1998, Wang et al., 2007). Pectin has a structural role in the primary wall of cotton fibre, cementing non-cellulosic components within the cellulose of the primary cell wall. Degradation of pectin facilitates removal of the cuticle and the non-cellulosic material in the underlying primary wall. Pectinases are mostly produced by saprophytes (organisms that obtain nutrients from dead organic matter) and fungi and bacteria pathogenic to plants. There are three types of pectinases; pectin esterases which catalyze pectin ester hydrolysis to produce pectic acid, polygalacturonases that hydrolyze α-1,4-glycosidic bonds and polygalaturonate lyases, which cleave pectin chains. Pectinases are classed as either alkaline or acidic according to the pH at which they have optimum activity. It has been shown that alkaline pectinases are more effective than acidic pectinases in the scouring of cotton (Tzanov et al., 2001). Pectinase scouring of cotton has been found to be most effective and efficient when combined with an initial treatment to disrupt and remove the surface wax layer, such as *n*-hexane extraction (Agrawal et al., 2007).

The potential use in cotton scouring of proteases, lipases, cutinases and xylanases has also been investigated, but not to the same extent as that of cellulases and pectinases. Protease treatment is designed to break down the proteins found in the cuticle of cotton fibre, loosening it. Lipases and cutinases break down the fats and fatty acids respectively found in cotton wax. Xylanases break down hemicellulosic materials.

Enzyme treatments have been demonstrated to be just as effective as conventional alkaline scouring for many textile applications. However, they have still not been widely introduced in industry despite researchers predicting this as early as 15 years ago (Etters, 1999, Kim et al., 2006, Kalantzi et al., 2009). Kalantzi et al. (2009) put this down to unresolved issues including higher costs, longer treatment times, and incomplete removal of waxes. Some issues relating to dyeing ability have been reported when enzymatic treatments have been compared to conventional scouring including shade difference in light shades on unbleached fabric (Losonczi et al., 2004) and slight unevenness in dyed fabric appearance (Wang et al., 2007). For medium to dark shades little difference in shade is observable and can be reduced in light shades by bleaching (Losonczi et al., 2004). Additionally there is no significant difference in fastness properties (Wang et al., 2007).

4.3.3 MERCERIZING

Mercerization is a chemical process designed to swell cellulosic fibres, improving dye affinity, lustre and strength in cotton. The original patent granted to John Mercer in 1851 describes a method of changing the properties of cotton fabric, yarn or fibres by treatment with concentrated (25% w/w) caustic soda (sodium hydroxide). Following removal of the alkali by neutralisation with acid and rinsing with water, the effects of the treatment on the properties of cotton were found to be permanent to subsequent wet finishing or washing processes. The contorted and flattened tape-like cross-sections of raw cotton were converted into smoother, less convoluted fibre shapes having more elliptical cross-sections. There was also an increase in strength and a large increase in the affinity for dyestuffs. The effect was good dye coverage of immature fibres. The latter was regarded by Mercer as the major benefit of his invention. The disadvantage of the treatment was a contraction in fibre length of up to 18%, which was accompanied by an increase in fibre diameter. With an already short fibre, the decrease in fibre length

limited the commercial success of Mercer's process, which is now more commonly called slack mercerisation.

In 1889, Lowe discovered that preventing fibre shrinkage during the caustic soda treatment produced fibres with a substantially rounder cross-section. There was also an increase in the affinity for dyes and an increase in fibre strength. Unlike Mercer's method, however, preventing shrinkage during the treatment produced a high degree of fibre lustre. Lowe's discovery improved the usefulness of Mercer's process and turned it into the true mercerisation process, carried out under tension, we know today. Mercerization is not a routine step in cotton pre-treatment and is most commonly used for embroidery and crochet yarns, with some use in clothing.

The requirement to maintain tension throughout the treatment and rinsing steps has restricted the application of mercerisation under tension to yarns and fabrics. It has been recognised for many years, however, that the mercerisation of cotton yarn or fabric may produce an uneven treatment (Kim et al., 1984). One problem is due to incomplete penetration of concentrated solutions of sodium hydroxide into tightly woven fabrics and into the centre of high twist yarns. It is related both to the high viscosity of the sodium hydroxide solution and also to the very high level of swelling of cotton in the alkali, which by causing the yarn and fabric structure to close up impedes efficient penetration of the reagent.

The above factors contribute to exposed surface fibres, especially free fibre ends, often being better treated than fibres buried inside yarns. Another factor is related to yarn geometry (Kim et al., 1984). Individual fibres within a yarn do not occupy a constant radial position, but are distributed from the outside to the core, with some protruding from the yarn surface. The effect of this is that, when stretched, all the fibres do not extend to the same extent, with those towards the surface undergoing less extension than those nearer the core. Uneven treatment can lead to an uneven uptake of dyes, with a subsequent effect on fabric appearance.

4.3.4 FINISHING

Finishing involves chemical or mechanical treatments of the dyed substrate (usually the cotton fabric) to improve appearance, handle, texture or performance (Shamey and Hussein, 2005). Chemical treatments may be used to impart properties such as resistance to wrinkles, water absorbency, water repellency, absorption of odours and fire retardency, as well as enzyme treatments to de-fuzz a fabric or yield special visual effects such as stonewash look denim. Examples of mechanical finishing of cotton include the pre-shrinking of fabrics and shearing to remove hair and loose threads.

Mercerised cotton sliver – CSIRO 2003/04

A new process developed (and patented) by CSIRO enabled cotton sliver to be mercerised in a continuous operation, without fibre shrinkage (Arnold and Rippon, 2004). In this system (see Figure 4-5 below) cotton sliver is held between two continuous belts as it is transported by means of a series of small diameter rollers through the treatment and rinsing baths. The belts, which are made of a material that is resistant to the action of concentrated aqueous sodium hydroxide, are slightly elastic and follow a circuitous path around the rollers. The belts have an open construction, which enables the sodium hydroxide solution to penetrate into the sliver and also allows the alkali to be rinsed from the fibres with water and then neutralised with dilute acid.

The belts are pulled through the system by a pair of driven rollers at the output end (C). This produces tension in the belts back to the input rollers at A. The tension in the belts, together with their alternating left and right curvatures around the rollers, produces a compressive force on the sliver. The resulting friction between the fibres and the two belts prevents fibre shrinkage in the mercerising liquor. The nip rollers at B squeeze much of the mercerising liquor from the sliver, returning it to the treatment bath prior to the rinsing stage. In order to avoid shrinkage during rinsing, compression of the fibres must also be maintained while the sliver is transported through the rinsing water.

In order to maximise the efficiency of alkali removal, a counter-current flow of fresh water is maintained from the exit end of the rinsing tank. The rinsing stage reduces the concentration of sodium hydroxide below the level at which fibre shrinkage occurs. It is not necessary, therefore, to maintain tension on the sliver after the exit rollers at C. Although not shown in Figure 4-5, residual alkali is neutralised by passing the sliver through a bath of dilute acetic acid maintained at pH 5. The treated cotton is then given a final aqueous rinse before it is dried.
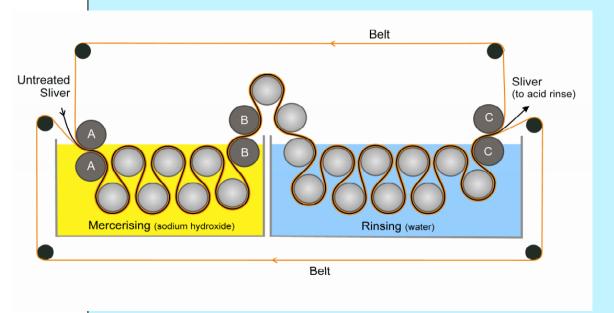

Figure 4-7: Schematic diagram of CSIRO continuous cotton sliver mercerising system

5 Dyeing issues

Although dyeing has been done throughout history there is still much scope for process improvement. Many issues in dyeing ability relate to concern for the environment and repeatability of results.

5.1 Environmental issues

Environmental issues in dyeing revolve around water and energy consumption, and the pollution of waterways with dye effluent. Dyeing can be a very inefficient process with several wet processing steps required from initial pre-treatment to washing off, all of which use water and energy. Research is being done to increase productivity of dyeing, reducing the amount of water and energy required, by looking toward process alterations such as one-bath multi-step processes and lower water dyeing utilizing other solvents such as supercritical fluids (Eren et al., 2009, Presa and Tavcer, 2009, Ozcan et al., 2008).

Many chemicals are involved in the dyeing process including harsh alkaline pre-treatments, bleach, dyes and salts. A lot of research has been carried out regarding the plausibility of replacing chemical scouring and bleaching with enzyme-based bio-scouring treatments using enzymes such as cellulases and pectinases. Although many studies have shown the potential of bio-scouring on a laboratory scale (Li and Hardin, 1997, Kim et al., 2006, Kalantzi et al., 2009), these treatments have not been widely implemented in industry. Kalantzi et al. (2009) put this down to higher cost, longer treatment times, incomplete removal of waxes, and some limitations in dyeing of darker shades. Polluted wastewaters from dye-houses can be of serious environmental concern, particularly in developing countries. Residual dye in waters poses a hazard to both humans and animals (particularly fish), as well as effecting aquatic plant growth due to colour in the water reducing light transmittance (Akbari et al., 2002).

As well as dye, these waters also contain other potentially harmful chemicals including detergents, surfactants and other additives. Work has been done to remediate dye effluent removing some of the chemicals and allowing it to be recycled utilizing methods such as coagulation/flocculation, nano-filtration and bioremediation by bacterial consortiums (Akbari et al., 2002, Avlonitis et al., 2008, Phugare et al., 2011, Khouni et al., 2011). Also of environmental concern are the large amounts of salt often required to drive the dye-stuff into the cotton fibre, which can increase salinity in waterways, harming aquatic organisms. Methods are being developed for low or salt-free dyeing including the synthesis of novel dyes and chemical modification of the cotton fibres (Zheng et al., 2012, Dehabadi et al., 2013).

5.2 Shade variation

Shade variation is a major problem faced by all dye-houses. Although care is taken to replicate dyeing procedure, repeatability and precision of the procedure is not the only source of variation. Shade differences are also an expensive problem, costing both time and money to fix, and potentially causing whole batch losses (Smith, 1991).

A 1992 report by Cooper and Taylor found variation in dyeing ability to be greatest in raw cotton fibre, decreasing with each stage of processing, and recommended that different colour standards be used at each stage accordingly. However, quantification of fibre dyeing ability variation is not straight forward,

with the same paper noting that some dye-stuffs appear more sensitive to fibre variability than others (Cooper and Taylor, 1992).

There are many fibre related sources of shade variation which have been discussed in sections 3.3 – 3.5. There are currently no standard testing methods designed to rapidly assess the dyeing ability of raw cotton samples (Estur and Knappe, Gordon et al., 2004).

5.2.1 BARRÉ

One of the most common and perplexing quality control problems is barré the name given to faults in fabric, often knit fabric, defined by repetitive yarn direction streaks. The factors that cause or contribute to barré are varied and diverse. Barré can be caused by physical, optical or dye differences in the yarns, geometric differences in the fabric structure or by any combination of these differences. All barré is the consequence of largely only subtle differences in yarn reflectance between individual yarns in the knit structure. According to surveys by Uster Technologies (2013) barré defects are caused by fibre property variations (70%), yarn count variation (10%), yarn twist variation (10%) and yarn hairiness variation (10%).

Prevention of barré
As outlined, barré is caused by inconsistencies in materials, equipment or processing. To prevent barré occurring, consistency must be maintained through all phases of textile production. Stock yarns should be properly and carefully labelled to avoid mix ups. Inventories should be controlled on a first in/first out basis. All equipment should be properly maintained and periodically checked. Before beginning full scale production, sample dyeings ought to be done.

6 Conclusion

The literature reviewed shows a large amount of research has been conducted in the area of dye uptake/dyed yarn/fabric appearance and the relationship between these attributes and basic fibre properties. It is understood that fibre fineness and maturity can contribute to more than 60% of the variation in shade seen in yarn and fabric. However, it is also understood there are gaps in knowledge linking the effect of fibre properties including other aspects of maturity and fineness, e.g. distribution of maturity within a specimen, surface colour (Rd, +b and UV), waxes, pectins and cellulose structure, on dye uptake by fibres.

By far and away the largest gaps in knowledge relate to details about cotton's fine structure and how this affects dye uptake and substantivity. At the moment four parameters of cotton cellulose's crystalline structure are typically measured to determine its nature. These are (a) crystallite orientation, (b) crystallite size (dimensions), (c) crystal lattice type and (d) the degree of crystallinity or order. While these attributes represent a level of detail about a fibre's cellulose structure, they are either, ill-defined and inconsistent between different methods of measurement, or do not relate enough of the structure to be of value, e.g. the scale of the distances between cellulose 'sheets' and/or 'layers' between which dye molecules could diffuse; the structure and organisation of cellulose fibrils within the sheets or 'layers'; the effect of non-cellulosic fractions on dye uptake; where non-cellulosic fractions are found in the fibre; the variation in cellulose structure along the length of a fibre?

In light of recent Australian industry focus on high quality 'premium' fibre for fine count yarns and reports from partner mills about off-shade dyeing, attention needs to be applied to understanding the above questions and relationships. Improving information and understanding would allow the cotton industry as a whole to more readily tackle the issues of dyeing cotton consistently, and furthermore improve cotton's environmental footprint in terms of water, salt and energy use.

A focus on dyeing can also help reveal the structural properties of cotton and support new research directions into affecting new structural and surface properties of cotton fibre cellulose.

On an industrial level, information about dyeing and fibre properties allows the development of predictive tests and models to help manage dyeing in order to preserve/enhance fibre quality, and hence yarn and fabric quality.

It is recommended that the industry via CRDC and other agencies continue to focus on quantifying the dyeing properties of (Australian) cotton, with particular focus on understanding cotton's cellulose substrate and surface properties and their interaction with dyeing kinetics and dye substantivity.

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