The Influence of Woven Fabric Structures on the Continuous Dyeing of Lyocell Fabrics with Reactive Dyes

A thesis submitted by

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In accordance with the requirements for the degree of

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To my Parents and Grandparents

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Abstract

Tencel, a regenerated cellulosic fibre is synthesised by an environmental friendly process. It can be dyed by the same dye types as recommended for other cellulosic fibres. The behaviour of reactive dyes on Tencel woven fabric varies with the type and the density of woven fabric. The highly crystalline Tencel fibre is less easy to dye uniformly by the continuous dyeing methods because of the short time of contact between the dye and fibre.

The purpose of this work is to investigate the influences of weave structure on dyeing of standard Tencel fabric using reactive dyes applied by continuous dyeing methods. Programmes are developed using Matlab software to measure the fabric porosity and uniformity of fibre coloration (UFC) in the yarns of the woven fabric. UFC is also measured subjectively. Firstly, fabrics of four different weave structures (plain, 2/1, 3/1, 5/1 twill fabric) are studied. The visual depth and UFC standard deviation values is highest for the 2/1 twill fabric, gradually reducing towards the 5/1 twill fabric. Secondly, nine plain weave fabrics of different fabric densities are dyed using different padding procedures - a liquor temperature of 40°C with a 1 min dwell time and with a 5 min dwell time, and liquor at room temperature without any dwell time. The padded fabrics are then fixed by pad-steam, pad-dry-steam, pad-batch and pad-dry-thermosol continuous dyeing processes. To improve colour depth the plain weave fabrics are given a caustic pre-treatment and their dyeing characteristics are compared with untreated fabrics. The causticised fabrics are dyed using the same padding procedures, for comparison.

The optimum dyeing procedure is found to be padding with a dwell time of 1 min in liquor at 40°C after caustic pre-treatment to achieve the highest visual depth, dye uptake, and uniformity of fibre coloration. The fibrillation tendency of the Tencel plain weave fabrics is also reduced using this procedure. Numerical relationships are established to enable the prediction of dyeing properties such as colour strength, UFC for fabrics of different weave structures, applied by the various continuous dyeing processes.

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CHAPTER 1: INTRODUCTION

1 Introduction

1.1 Background

Most abundant fibres used in the world are the cellulose fibres. Cellulose fibres offer comfort, excellent water absorbency, wide application, and are completely biodegradable [1]. There are two sources of cellulosic fibres, one which is obtained directly from the natural resources such as cotton; and others which are regenerated from the wood of trees (natural resources) such as viscose, modal, cupramonium, and lyocell (Tencel) fibres. Wood pulp is a renewable resource and is not suitable for food production [1]. However, there are some other new fibres also in use, such as bamboo (regenerated cellulose) and banana (bast fibre), etc.

For wet processing (dyeing and finishing) of conventional fibres, large amounts of energy, water and chemicals are consumed. Additionally the transportation requires more fuels [2]. The introduction of lyocell and other new fibres (bamboo and banana, etc) help to sustain the clean environment and minimize energy usage.

Bamboo fibre is biodegradable, hygroscopic, cool and soft, gas permeable, ultraviolet resistant and has unique and natural antibiotic and antibacterial finishes. It is manufactured using wood with sodium hydroxide and sodium sulfite. The recycling of the chemical wastes is required at extra cost and time [3]. The properties of bamboo fibres are similar to viscose fibres.

Banana fibre is extracted from the bark of banana tree, has high strength, less elongation, good lustre, light weight and is biodegradable. However, it is used mainly for making ropes, mats and other composite materials [4].

Lyocell fibres are manufactured using wood pulp and an amine oxide solvent. The 99.5% recovery of the amine oxide makes the lyocell fibres very valuable. The lyocell fibres or filaments are renewable, sustainable, biodegradable, biopolymer, antibacterial, and have excellent moisture management, and dry and wet tenacity [5]. The lyocell fibre has a high rate of water absorption because of the small and quite uniform voids in the nanometer range [6]. Lyocell fibres were introduced in 1994 as sustainable and biodegradable regenerated cellulosic fibres produced by an environmentally friendly process and were commercialized under the trade name Tencel [7, 8]. The properties of Tencel fibre are almost similar to the cotton fibre. On the contrary, this fibre has many advantages over cotton fibre [9]. The replacement of cotton fibre by Tencel fibre can improve the environmental friendliness [5]. Tencel fibre minimizes water consumption 20 times and has high production compared to conventional cotton fibre. The cultivation of cotton fibre has toxic impacts on fresh water and the soil; use of Tencel fibre helps to decrease impact on the soil and water.

Tencel garments are very regular and have less impurities, because of the regular fibre linear density and staple length [9]. Lenzing is the main manufacturer of Tencel fibres, and it is going to expand production of Tencel fibres in 2010, at Heiligenkreuz (Austria) by 10,000 tons to 60,000 tons per year, and the pulp production to a capacity of 260,000 tons [10].

Tencel regenerated cellulosic fibres can be dyed by the same dye types as for other cellulosic fibres, such as cotton and viscose. Extensive work has been carried out on its dyeing behaviour [11-14]. Much work has been done using mono, bi and multi-functional reactive dyes applied by exhaust method [12, 15]. Exhaust dyeing requires high temperature, more time and has low production as compared to the continuous dyeing methods. Functional reactive dyes have advantage of minimizing the fibrillation tendency. The wet abrasion causes the Tencel fibres to fibrillate because of its highly oriented crystalline regions and weak lateral link between the crystallites [16, 17].

Continuous dyeing is a fast method of dyeing and is useful for dyeing bulk quantities of fabric. In this method fabric is passed in between nip rollers, and then dye is fixed in the fabric by steaming, batching, curing in some cases, along with intermediate drying. Cotton fabrics, using reactive dyes are most commonly dyed by the pad-steam and pad-batch methods. It has been found [11] Tencel fabrics gave good results when dyed by pad-batch method. The pad-dry-thermosol process is most commonly used for dyeing the cellulosic and man-made blend fabric. The selection of the continuous dyeing method depends on the application and types of dye.

Moreover, it has been reported that fabric construction changes the dyeing behaviour [18] but not much work has been reported on the behaviour of reactive dyes on Tencel fabrics of different fabric constructions and structure. The fabric parameters such as fabric porosity, cover factor and density, can impart positive and negative effects on dyeing, such as non-uniformity of dye penetration or dye diffusion in the fabric. Very loosely woven fabric and very tightly woven fabric can both give less dye uptake and non-uniform dye penetration depending on the dye chemistry.

On a world-wide scale, one third of the dyes used for cellulose fibres are reactive dyes [14]. Differences in weave structure (plain and twill) and density leads to differences in liquor flow through the fabrics, and when a dyer uses a recipe for a reference fabric construction to dye a fabric of different construction, the final colour depth obtained can be different [18].

The dyeing properties of cellulose fabrics are improved by pre-treatment process such as plasma treatment, acid donor, cationic fixing agent and caustic treatment. Caustic pre-treatment, at a particular percentage and temperature, is very effective for improving the dye penetration into the filaments of woven fabric. Caustic swells fibres and increases the accessible sites for reactive dyes [19-21]. However, in all pre-treatment processes, Tencel fabric was dyed by the exhaust method. The difference in dyeing methods (continuous and exhaust) is also an important factor effect on the dyeing of Tencel fabric.

The problem of dyeing the Tencel fabric can be greater in continuous dyeing, because dye liquor has a much shorter time available to penetrate all the fibres of the fabric completely. In exhaust dyeing, dye liquor is efficiently circulated through the fabric and at a higher temperature. There is a greater potential for unlevelness to occur, especially in tightly woven fabrics (low porosity) in continuous dyeing processes.

Therefore, the purpose of this work is to assess the extent at which fabric properties, in terms of weave structure and other parameters such as porosity and fabric density, influence the levelness and the depth of shade, when reactive dyes are applied by exhaust and continuous methods.

However, it was hard to measure the correct fabric properties such as % porosity (inter-yarn zone) using geometrical formulas which give only approximate values. Similarly, it was difficult to measure dye penetration visually using yarn cross-sectional images. In this research, work has been done to measure the uniformity of fibre coloration (UFC), in a systematic manner by subjective and objective methods. A numerical relationship between the fabric density and dyeing behaviour (visual depth and uniformity of fibre coloration) has been developed. This model helps to predict the dyeing behaviour of Tencel plain weave fabric composed of varying fabric densities dyed by continuous dyeing methods. The detailed aims of the research are discussed in next section.

1.2 Research Aims

The aim of this research was to investigate the behaviour of reactive dyes applied by continuous methods on Tencel fabrics of different woven structures. The objectives are summarized as follows:

- To dye Tencel woven fabric using selected reactive dyes by exhaust and continuous dyeing processes, such as pad-steam, pad-dry-steam, pad-dry-thermosol, and pad-batch.
- To develop a dyeing method in order to improve the dye uptake.
- To develop a numerical technique for analyzing the porosity of woven fabric.
- To develop a numerical technique for measuring the uniformity of dye penetration in the woven fabric.
- To develop an understanding of the relationship between visual depth of different weave structures and densities of woven fabric.
- To develop a numerical technique for predicting the dyeing behaviour such as colour depth and UFC of plain weave fabrics dyed by continuous dyeing methods.

In order to accomplish these tasks, a specific research plan was followed. First, four different types of Tencel woven fabric constructions (plain, twill 2/1, twill 3/1 and twill 5/1) were dyed using selected reactive dyes, by exhaust and continuous methods. Second, only one type of Tencel woven fabric structure, i.e. plain weave fabric, was studied, at nine different fabric densities. These fabrics were dyed with Levafix CA and Remazol (DyStar) dyes, by continuous dyeing methods. Third, the dyeing methods were then altered to establish the optimum for maximum visual depth and dye uniformity in continuous dyeing processes. Both absorbance and reflectance spectroscopic techniques were used to analyze the properties of the dye solutions and determine the amount of dye present and fixed on dyed fabrics. Optical microscopic studies were performed to analyze the uniformity of dye in the filaments of yarn of the woven fabric and then software was developed to calculate the uniformity of dye in different dyeing processes and woven fabrics. Scanning electron microscopy was used to examine the fibrillation on the fabrics after dyeing. Several other tests, including colour fastness to rubbing, and to washing, tensile strength, abrasion resistance and bending length tests were carried out with a view to characterize the influences of different dyeing methods and different fabric constructions of the fabrics. Equations were developed to predict the dyeing behaviour (colour depth and UFC) of Tencel plain weave fabrics dyed by continuous dyeing methods using selected reactive dyes.

1.3 Thesis Contribution

The contribution of the thesis can be summarized as follows.

Much work has been reported on the dyeing of Tencel woven and knitted fabrics. Most work has been done on the exhaust method of dyeing, but very little work on dyeing by continuous methods, especially in pale shades has been done. Aditionally, no work has been carried out to compare the dyeing behaviours of fabrics of different weave structures.

In this thesis initially the structural characteristics of woven fabrics were assessed by using established formulas and numerical method, discussed in Chapter 5. The fabric assessment, such as ends and picks per cm, fabric weight in gram per square meter, cover factor and porosity were measured in four different weave structures and nine different weave densities of plain Tencel woven fabric. These values were used to analyze the dyeing behaviour of different dyes on the woven fabric.

The cross-sectional views of yarn were analyzed using Olympus software and then by statistical method developed in this thesis. These analyses were used to assess the uniformity of fibre colouration.

The visual depth of reactive dyes applied by exhaust process was higher than the continuous processes but there was not as much difference in dye uptake in both dyeing methods. Moreover, visually at high thread density fabric had very high visual depth but under microscope it was found that the dye molecules were not penetrated properly to all fibres of the yarns of the woven fabric. For this reason a new method of continuous dyeing was designed to overcome the problems of depth and levelness.

1.4 Thesis Outline

This thesis is arranged in eight chapters. Chapter 1 is about the background, contribution, aims of research and publications. The literature about lyocell fibres is reviewed in chapter 2. It contains history of lyocell fibres, general description of the chemistry of cellulosic fibres, including lyocell, its method of manufacture, types, morphology, properties, application, advantages and fibrillation behaviour of lyocell fibres. Chapter 3 reports previous studies about pre-treatment processes, such as cationic fixing agent, plasma treatment, enzymatic treatment and alkali treatment. Additionally it reports the behaviour of different dyes on Tencel fabric, the chemistry of reactive dyes and dyeing methods and its assessment such as fastness, absorbance, Integ value and uniformity of fibre coloration. Chapter 4 gives a general review of woven fabrics such as plain, twill and their derivatives. Additionally fabric parameters, such as thread density, linear density and their influence on fabric weight, cover factor, porosity, abrasion resistance, fabric strength, fabric stiffness and on dyeing are explained. Chapter 5 introduces the experimental procedures, dyeing methods and assessment methods of this study. In the Chapter 6, the results of fabric assessments of different weave structure (Plain, Twill 2/1, Twill 3/1 and Twill 5/1) of Tencel fabric are examined and discussed. The visual depth of dyed fabric, exhaustion and fixation percentage in exhaust and continuous methods, uniformity of fibre coloration, microspectrophotometry and effect of weave on the dyeing are also discussed. In the Chapter 7, the results of dyeing Tencel plain weave fabrics of different weave densities are discussed. The results of continuous dyeing after caustic treatment and without caustic treatment and their assessment including visual depth, dye uptake, uniformity of fibre colouration, by both subjective and objective assessment, rubbing and washing fastness, tensile strength, fabric stiffness, abrasion resistance, fibrillation, effect of caustic treatment and the equations use to predict the dyeing behaviour versus fabric density are also discussed. Chapter 8 concludes the experimental results of the whole study, summaries the finding of the current research and gives suggestion of the future works.

1.5 Publication

- Wardman, R H, Syed, U and Taylor, J, The Influence of weave structure on the dyeing behaviour of reactive dye on Tencel fabrics, AUTEX 2009 World Textile Conference, Đzmir, Turkey, 28th May, 2009, p. 368 – 373.

- Syed, U, Wardman, RH, and Taylor, J, The Influence of NaOH and continuous dyeing behaviour on the reactive dyes on lyocell fabrics, AUTEX 2010 World Textile Conference, Vilnius, Lithuania, 21st - 23rd June, 2010.

CHAPTER 2: LYOCELL FIBRE

2 Lyocell Fibre

2.1 History of Lyocell Fibre

Lyo is a Greek word which means dissolve [22]. Lyocell fibre brand name, Tencel, is a natural man-made or regenerated cellulosic staple fibre or filament spun by a solvent spinning process [8, 22]. The solvent spinning technique is both simpler and more environmentally sound, since it uses a non-toxic solvent, an amine oxide that is recycled in the manufacturing process with the 99.5% recovery. Cellulose fibres made from such solutions have been given by BISFA (International Bureau for Standardization of Man-Made Fibres) [23] and the EU commission a generic name lyocell with short form CLY [22]. BISFA defines lyocell as a cellulose fibre obtained by a spinning process from an organic solvent, a mixture of an organic chemical and water [23].

The lyocell process was awarded the “Environmental Award 2000” in the category "Technology for sustainable developments" by the European Union. It has been recognized that the manufacturing of lyocell fibre has low environmental and ecological impact. Bleach is commonly required in fabric manufacturing, especially for cotton but the high quality lyocell products contain no free chlorine and are sold as so-called "TCF - products".

Lyocell is a biodegradable fibre and N-Methylmorpholine-N-oxide (NMMO) is the suitable solvent for lyocell fibre manufacturing. According to Meister et al [24] degradation of NMMO occurs in several steps. Initially NMMO is reduced to N-methyl-morpholine (NMM), which takes 28 days. Then, NMM is reduced to morpholine, which is further degraded. Knapp et al [25] reported that morpholine up to 8.7 g l^{-1} did not give toxic effect on bacteria while Calamari et al [26] showed morpholine has toxic effect on aquatic organisms, particularly on algae.

Although, the history of Tencel fibre is not as old as cotton, work on finding a suitable solvent for cellulose started in 1939, when Graenacher et al [27], reported that a tertiary amine oxide was capable of dissolving up to 10% cellulose. 30 years later, Johnson [28] patented cyclic amine oxides, particularly NMMO, as a solvents for cellulose. The ENKA group [22], and McCorsley and Varga [29, 30] revealed that NMMO has good solvent power for cellulose. They developed a method of producing highly concentrated (up to 23%) cellulose with NMMO and water solution. The water was later eliminated by vacuum [29].

Courtaulds started an investigation to develop new cellulosic fibres in the early 1980s [31]. It was first produced commercially in the United States in 1992 by Courtaulds, which then become Acordis fibres. The fibre was given a generic name lyocell in the United States in 1996. By this time, there was one other major lyocell producer in the world, Austrian company Lenzing AG [1, 8, 32].

Young Soo in 2002 [33] and 2003 [34] reported that regenerated cellulosic fibres could be manufactured by using ascidians tunics (97% α-cellulose, 918 DP) with NMMO/water and antioxidant (N-propyl gallate). Fibre had good tenacity both dry and wet, at particular concentration of cellulose (up to 3 - 6 % by weight) but then it decreased because of fibre defects during manufacturing. However it was not mentioned whether it is toxic or not, but during manufacturing process NaOCl was used which is non- environment friendly.

Lyocell fibres are marketed under different brand names depending on the manufacturing companies [22] such as:

Brand name	**Company**
Tencel	Lenzing, Austria.
Alceru	TITK, Germany.
Newcell	Akzo Nobel, Germany.
Orcel	Russian Res .Inst.

Today there is only one company, Lenzing, making fibres on a commercial scale. It is currently manufacturing the fibres in [8]: Heligenkreuz (Austria), Grimsby (U.K), Mobile (U.S.A).

2.2 Chemistry of Cellulose

Knowledge of the structural features of cellulose substrates is essential for analyzing the effects of physical and chemical properties. The property of cellulose fibres depends on the chemical nature of cellulose molecule, its structure and morphology in a solid state (fibrous form).

In textile fibres, cellulose may exist in different crystalline forms, known as cellulose-I, cellulose-II, cellulose-III and cellulose-IV. Lyocell is a regenerated cellulosic-II fibre [35, 36], however under certain condition cellulose-IV is observed [37].

The structural features of Tencel fibre can easily be defined by categories into three different structure levels as shown in Figure 2.1;

- The molecular level.
- The supermolecular level.
- The morphological level/ ultrastructure.

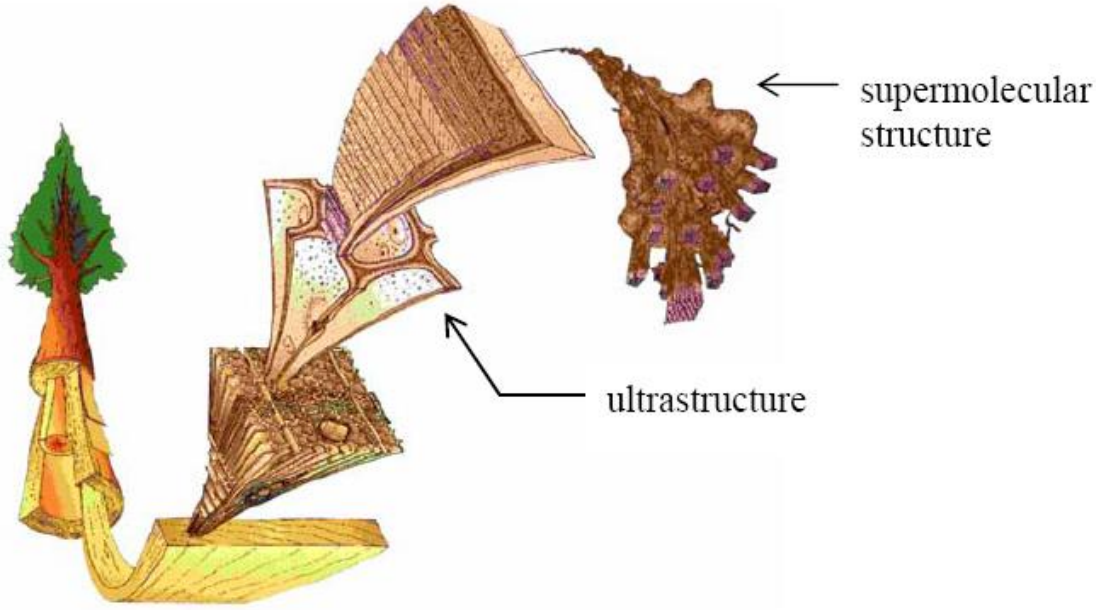


Figure 2.1 Structure level of cellulose fibre [38]

2.2.1 *Molecular Level*

Study of the chemical constitution, steric conformation, molecular weight, functional hydroxyl groups or functional sites, and their intra and intermolecular attractions all are under the heading of molecular level.

The cellulosic chain is composed of 1,4-ß-D polyanhydro glucopyranose as shown in Figure 2.2.

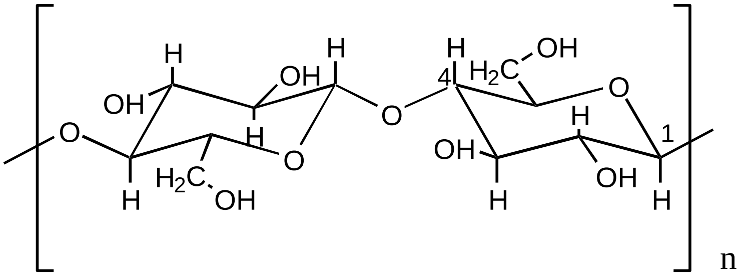


Figure 2.2 Cellulose chemical structure [39]

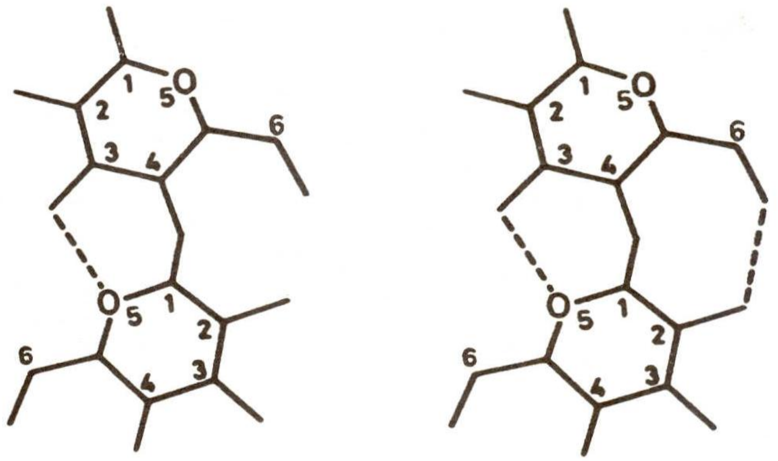
It has been confirmed [39] by x-ray crystallography studies and nuclear magnetic resonance studies that the ß-D glucose exists in the pyranose form and also in the $^4C_1$ chain formation containing lowest energy conformation for ß-D glucosepyranose. The repeating unit (n) of cellulose chain is cellobiose, which is composed of two glucose units. The number of glucose units in the chain is called the degree of polymerization (DP). The number of glucose units in cellulose is 1000 to 15000, depending on its source. However, DP reduces during extraction and purification processes.

Three reactive hydroxyl groups, one primary hydroxyl and two secondary hydroxyl groups are present in the cellulose chains in each repeating units. These hydroxyl groups undergo substitution reactions such as etherification and esterification. Intramolecular hydrogen bonding has an influence on the reactivity of hydroxyl groups. The hydroxyl group on the C(3) is less reactive in etherification because of the pyranose O(5) group than the hydroxyl group on C(2) atoms.

The cellulose microfibrils are formed due to the molecular attraction forces (van der Waal's forces) of the hydroxyl groups on C(3) and C(6) of neighbouring molecular chain.

The cellulose in different sources has the same basic composition and chemical constitution, but differs widely in chain length (DP). The molar mass of cellulose is always quoted as an average molar mass. The molar mass has an influence on viscosity or shear behaviour of solutions and also has an effect on the degradation kinetics and tenacity.

The cellulose structure may form intra and intermolecular bonds. Intramolecular bonds are formed in two different ways. One is in between the hydrogen bond of OH-group of C(3) and pyranose ring oxygen O(5) having a bond length 2.75 ^{0}A [40] as shown in Figure 2.3 (a) [39]. The second is in between the hydroxyl groups of the carbon atoms C(2) and C(6) having a bond length 2.87 ^{0}A [40] as shown in Figure 2.3 (b).



(a) (b)

Figure 2.3 Intra hydrogen bonding according to (a) Linang and Marchessault and (b) Blackwell et al [39]

The intramolecular bond has an influence on the chain stiffness and rigidity and on the chemical reactivity of hydroxyl groups. It helps to stabilize the “two-fold screw axis” or “two-fold helical” structure.

The inter-chain hydrogen bond links one chain of cellobiose to another [40, 41] . In the cellulose structure the O(6)-H and O(3) form an intermolecular hydrogen bond with a bond length of 2.79 ^{0}A. Hydrogen bonding occurs at 020 planes, no hydrogen bond is formed along the unit cell diagonals. Successive sheets of cellulose are staggered and making the same manner. The cellulose chain is directional, which allows for parallel and anti parallel packing [40].

Discuss later in Section 2.3, the Tencel fibre is composed of cellulose, made by extrusion from solution in NMMO and water [42]. Therefore, the intermolecular attraction of these molecules is higher than in the single molecule. It was observed that the increases of temperature decrease the interaction force (Brownian law). Cellulose molecules act as a modified solvent form in the NMMO-water system [42]. In solution initially hydrogen bonds between the cellulose chains are ruptured. Then, the interaction between the donator-acceptor of the N→O dipole and the hydroxyl groups of cellulose occurs.

Consequently, the type of pulp and its cellulose concentration leads to different interaction states in the solution. The aggregation of cellulose chains in the solution depends upon the DP and cellulose concentration. The increase of DP and cellulose concentration decreases the bonding with NMMO. On the average each glucose unit interacts with nine NMMO molecules [42].

Pulp of high molecular mass, even in small quantity, changes the rheological behaviour of cellulose-NMMO solution and has an influence on the solubility of the solution which decreases with increases in the molar mass.

2.2.2 Supermolecular Structure

The supermolecular level of cellulose means aggregation of chain molecules to elementary crystal and fibrils, degree of order inside and around these fibrils, perfection of their orientation with respect to the fibre axis, etc.

The basic element of supermolecular structure is the parallel arrangement of crystallites and crystallite strands. Crystallites and crystallite strand arrangements are formed due to the ability of the hydroxyl groups to form with one another secondary valence hydrogen bonds.

Swiss biologist Nägeli in 1856 initially proposed the structure of cellulose fibre as a “micelle structure”. Then according to Mark et al [40]; length of cellulose chain was determined by the length of micelle (elongated rod). The chain consists of 100 to 150 glucose units; 40-60 such chains bound by associated forces, formed one crystallite (micelle). The micelles are oriented along the fibre axis at an angle dependent upon the plant species. According to them chemical reactions were taking place on the surface of micelles and within the micelles. During reactions, the reagents act not only on the group lying on the surface of the micelles, but also penetrate inside the micelles. This was further confirmed by two different x-ray diagrams, one due to the surface reaction and the other due to the penetration of reagents. However, their theory failed to explain the swelling of cellulose i.e. nature of the intermicellar forces which hold the micelles together during penetration. Staudiner [39] in the early thirties described the cellulose as a “fringe micellar structure” as shown in Figure 2.4 .

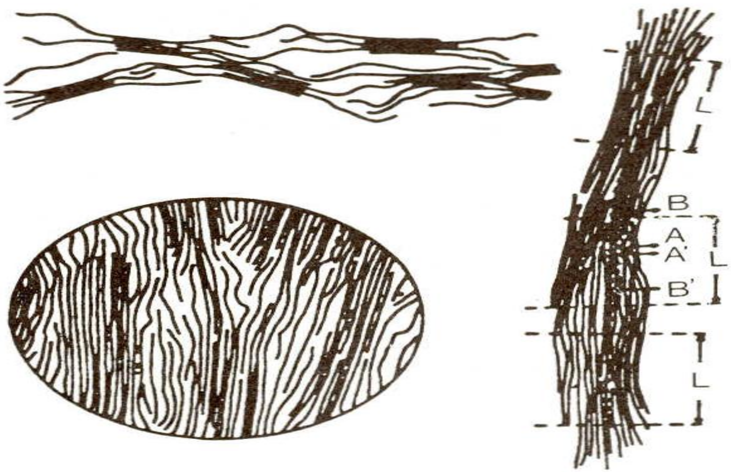


Figure 2.4 Fringe micellar [39]

His structural concept was of micelles forming crystalline domains in an amorphous matrix. It was supported by the x-ray diffraction of cellulose and was very valuable for understanding the solid state polymer. However, it did not consider the distinct fibrillar nature of fibrous substrates.

These fibrillar elements were discovered by light microscopy. It was found that fibrous substrates are composed of fibrillar elements. These fibrillar elements are called “macro-fibrils” and their dimensions vary from a few tenths of micron up to several microns in diameter. These macro fibrils are aggregates, much thinner and more basic fibrillar units, having 3 to 20 nm cross dimension as shown in Figure 2.5.

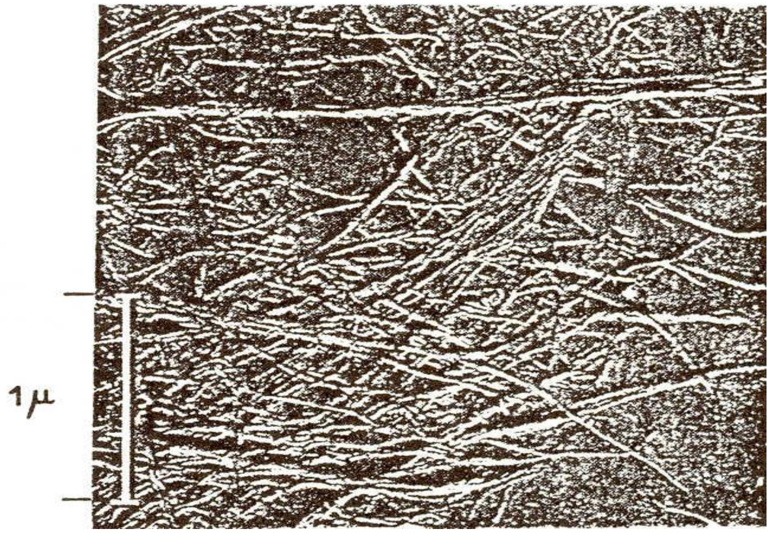


Figure 2.5 Electron micrograph of the fibrillar structure of cellulose fibres

Elementary fibrils that are present in all natural and synthetic fibres act as small building blocks to form “elementary crystalline units”. In case of regenerated cellulosic fibres they have a dimension of 15 to 20 nm. In 1950s Hess, Frey-Wyssling, Kartky and others, and finally Hearle [39] proposed the structural model called “fringe-fibrillar model” as shown in Figure 2.6. The network of elementary fibrils and their secondary are more or less random aggregations. The internal cohesion is established by the transition of the long cellulose molecules form crystallite (represented by the small rectangles) in the elementary fibrils.

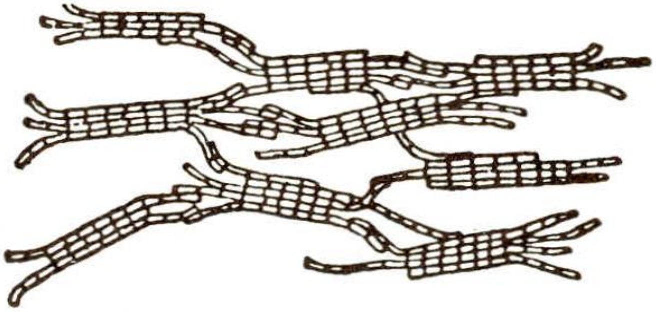
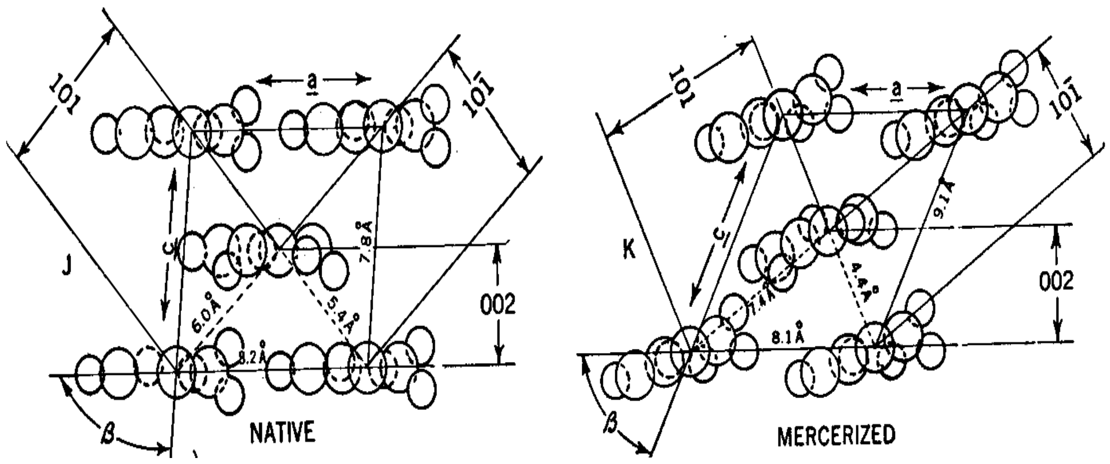


Figure 2.6 Fringe –fibrillar model of fibre structure [39]

2.2.2.1 Polymorphic Lattice Structure / Unit cell structure

The unit cell structure of native cellulose was first proposed by Meyar, Mark and Misch in 1926. According to their model each unit cell of cellulose molecule composed of cellobiose segments arranged in parallel chains [39] as shown in Figure 2.7 (a).



(a) (b)

Figure 2.7 Unit cell structure (a) cellulose - I and (b) cellulose - II

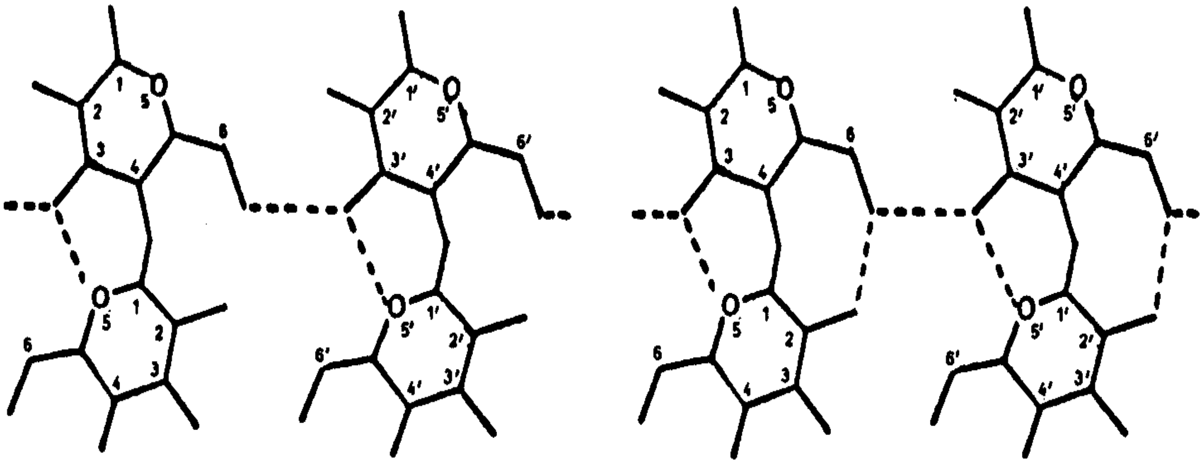
Andress first gave the concept of unit cell arrangement of mercerized cotton and regenerated cellulosic fibre. According to his concept mercerized cotton and regenerated cellulose fibre was composed of cellulose-II anti-parallel chain arrangement as compared to the parallel chain arrangement of cellulose-I as shown in Figure 2.7(b). Cellulose-I has the following parameters a = 8.35 ^{0}A, b = 10.3 ^{0}A and c = 7.9 ^{0}A, where b defines the length of cellobiose residues along the fibre axis [40]. Cellulose II [40] has the following parameters a = 8.14 ^{0}A, b = 10.3 ^{0}A, and c = 9.14 ^{0}A and ß = 62^{0}. Mercerization modifies spacing in the intermiceller structure of the native cellulose-I and changes it into cellulose-II structure. Cellulose-II is a very stable structure and when heated up to 260 ^{0}C.

2.2.2.1.1 Cellulose-I

Blackwell et al [39], described cellulose as a distinct sheet like structure with very dense hydrogen bond packing. They assumed that there are two hydrogen bridges as shown in Figure 2.8:

1. Between the hydroxyl group on the carbon atom C(3) and the ring oxygen atom O(5') of the neighbouring glucose unit.

2. Between the hydroxyl group on the carbon atom C(2) and the primary hydroxyl group on the carbon atom C(6') of the neighbouring base unit.



(a) (b)

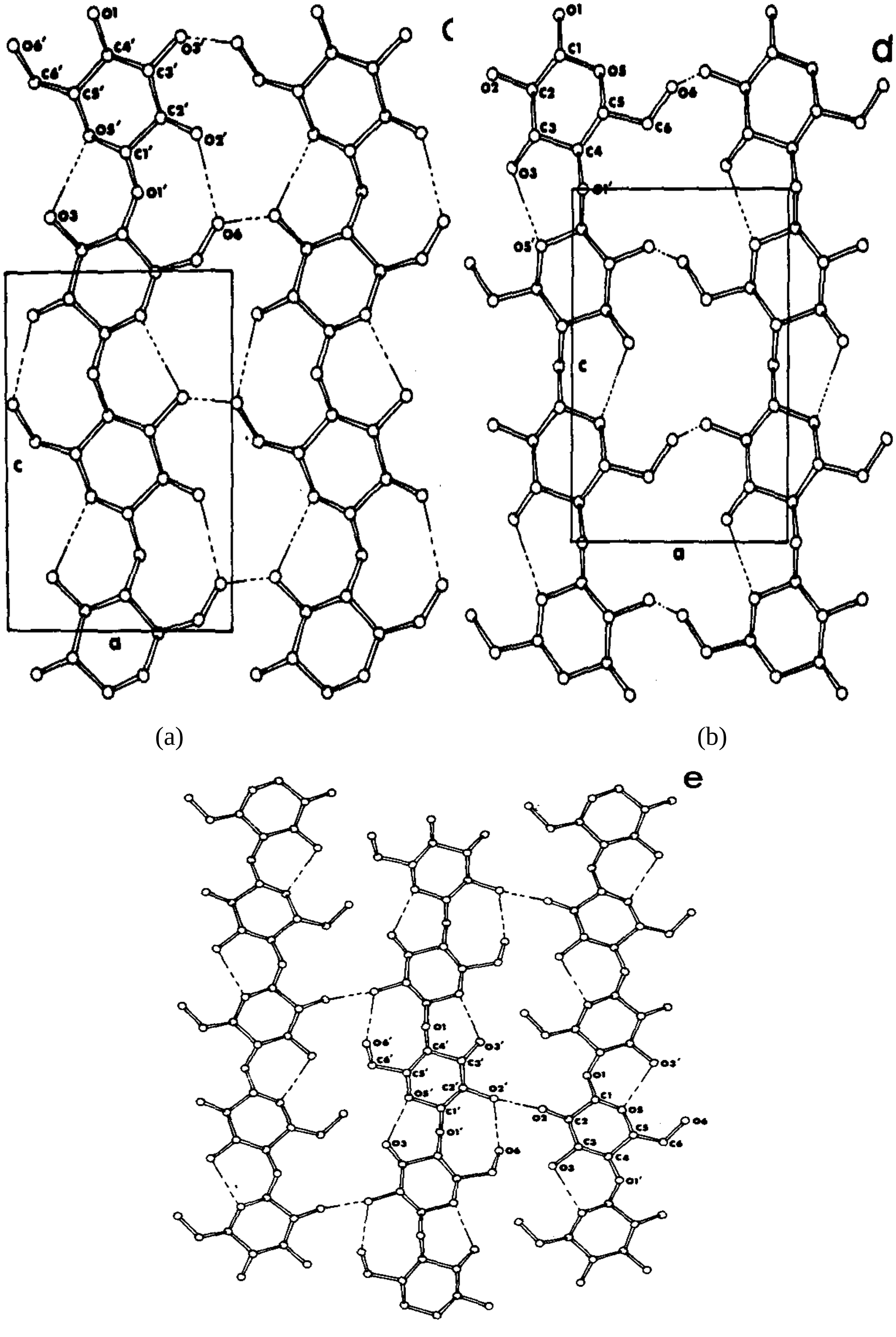
Figure 2.8 Intermolecular hydrogen bonds under the 002-lattice planes of cellulose-I (a) Liang and Marchessault (b) Blackwell et al

They also proposed the intraplaner hydrogen bonds between the hydroxyl group on C(6) and C(3’’). The OO2-planes are held together by van-der-Waal’s forces.

2.2.2.1.2 Cellulose –II

According to Blackwell et al [39] the intramolecular hydrogen bonds are formed in a similar way as in the cellulose-I structure. The interplanar bonding is assumed to be hydrogen bridges from hydroxyl groups C(6) to hydroxyl groups on C(3’’) alternating in direction for “down” chain neighbouring one another in the centre plane OO2-plane as shown in Figure 2.9 (a) and another hydrogen bonds from the hydroxyl groups on C(6) to hydroxyl groups on C(2’’) for “up” chains neighbouring one another in the corner OO2-planes as shown in Figure 2.9(b). They also assumed the 101-planes in which hydroxyl groups on the carbon atoms C(2) and C(2’’) from each second glucose unit of centre “down” and corner “up” chains thus hydrogen bonds are formed between the neighbouring anti parallel chains.

Cellulose-II lattices have strong interplanar bonding and an average bond length of the hydrogen bridges is 2.72 ^{0}A as compared to 2.80 ^{0}A [40] in cellulose-I. Cellulose–II is denser (the density of cellulose crystal is 1.58 gm cm^{-3} [32]) than the cellulose-I because of the greater involvement of hydrogen bonds.



(a)

(b)

(c)

Figure 2.9 Hydrogen bonding network: (a) in the 002-plane for centre "down" chains; (b) in the 002-plane for corner "up" chains; (c) between anti-parallel chains in the 101^{-}-plane

In addition, cellulose-II has higher hygroscopicity, and is more easily hydrolyzed by acids and ester.

2.2.2.1.3 Cellulose-III

When the reaction product of cellulose fibre with liquid ammonia is decomposed then the cellulose-III structure is formed. The cellulose-III lattice structure is closely related to cellulose-II structure.

2.2.2.1.4 Cellulose-IV

Cellulose-IV lattice is formed when regenerated cellulose fibre is treated with suitable liquid at high temperature under stretch or tension. The structure of cellulose-IV is closely related to cellulose-I.

The lattices differ from each other by internal secondary bonding, though little difference has been observed in the chemical and physical properties. The following Table 2.1 illustrates the dimension of unit cell of cellulose I to IV.

Table 2.1 The unit cell structure of polymorphic forms of cellulose [43]

Type of cellulose/axis	***a (°A)***	***b (°A)***	***c (°A)***	***ß***
Cellulose-I	8.35	10.35	7.5 A	84^0
Cellulose-II	8.1	10.3	9.1 A	$62^{\,0}$
Cellulose-III	7.74	10.3	9.9 A	$58^{\,0}$
Cellulose-IV	8.11	10.3	7.9 A	90^0

2.2.2.2 Orientation of Regenerated Cellulosic Fibre

The elementary crystallites or fibrils and accessible interlinking regions of fibre are responsible for the adsorption, exchange or substitution behaviour of fibre.

The elementary fibrils are a strand of elementary crystallites. They are surrounded by a layer of disordered or amorphous unit cells and also the molecules in the outer layer of the unit cells. Kratky [40] suggested the extremities of two chains (a, a') as shown in Figure 2.10; are held together by a strong bond in the crystalline region and act as a continuous chain. The breaking of fibre occurs due to the breaking of bond that joins the two chain extremities.

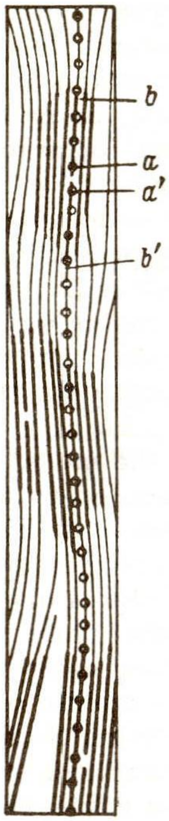


Figure 2.10 Micellar structure according to Kratky, a and a' chain ends; b and b' limits of the oriented segment

The degree of crystallinity depends on the origin and type of regenerated cellulosic fibre. If the cellulose is precipitated quickly from solution when it is extended into the spin bath liquor, it forms crystalline units separated by liquid filled amorphous regions [8, 36]. Lyocell fibre is characterized by high degree of cystallanity 80% [35] to 90% [44] and long and thin crystallites [8, 44]. It consists of well oriented amorphous region 20% [35] to 10% [44] resulting very high dry and wet tenacity [36]. The high modulus of lyocell fibres results in low shrinkage [8], while lyocell staple fibre has low modulus [34] means it can shrink to a greater extent than lyocell filament fibre. The effect of increase in crystallinity is shown in Table 2.2 and increase in fibre orientation (Table 2.3) on regenerated cellulosic fibres.

Table 2.2 Effect of increasing crystallinity on properties of cellulose fibres[43]

Increases	Decreases
Tensile strength	Elongation
Young’s modulus	Moisture sorption
Hardness	Swelling
Dimensional stability	Dye sorption
Density	Toughness
	Chemical reactivity
	Flexibility

Table 2.3 Effect of increasing orientation on fibre properties [43]

Increases	Decreases	Little or no effect
Tensile strength	Total elongation	Sorption of water
Transverse swelling	Reversible elongation	Elastic limit
Recovery after wet stretching	Longitudinal swelling	
Young’s modulus	Dyeing absorption	
Rigidity	Plasticity	
Refractive index	Crease resistance	
Gloss	Chemical reactivity	

2.3 Manufacturing Method of Lyocell Fibre

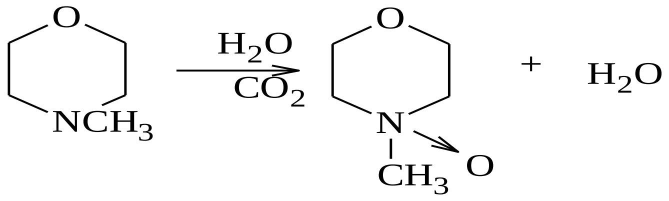
2.3.1 Raw Material

The main ingredient used for lyocell fibres manufacturing is cellulose, a natural polymer found in the cells of all plants. It forms basis for other plant derived fibres such as cotton, hemp and linen. The cellulose for lyocell manufacturing is derived from the pulp of hardwood trees [1], beech and eucalyptus being primarily used to produce Tencel fibre [45]. The trees grow to a height of up to 40 meters, planted in so-called “wood farms”. There is no artificial irrigation or gene manipulation and no pesticides are used [45].

The pulp is typically produced from a mix of trees, chosen for their low colour and amount of contaminants. Some other common tree species used for manufacturing the lyocell fibres are oak and birch. These trees are grown on managed tree farms, generally on land that is not suitable for other agricultural uses. The variation in wood pulp imparts a difference in the physical characteristics of lyocell fabrics and their intermediates. The higher the degree of polymerization of lyocell fibres lower will be fibrillation, higher the strength and the dimensional stability [46].

The solvent used in the manufacturing process is an amine oxide, N-methylmorpholine-N-oxide (NMMO) [47]. It belongs to the family of cyclic, aliphatic and tertiary amine oxides. As shown in the Scheme 2.1, the nitrogen carries the cyclic and aliphatic group and oxygen atom. The N-O bond has high energy (222 kJ mol^{-1}), polarity (responsible for high hydrophilicity) and has ability to form hydrogen bonds.

NMMO is an effective solvent for cellulose due to its high polarity and weak N-O bond. The maximum dissolution of cellulose with NMMO depends upon the degree of polymerization of cellulose. However, NMMO is able to form a slurry with cellulose and water when the cellulose contents lie in between 4 to 17 % by weight [47].



N-methylmorpholine N-methylmorpholine-N-oxide

Scheme 2.1 Structure of N-methylmorpholine-N-oxide

The cellulose-NMMO-water system exhibits viscoelastic properties, similar to molten polymers [42, 47]. NMMO is a strong oxidant, sensitive to heat and catalysts (catalyst break the N-O bond) [47].

The NMMO solvent can be decomposed during the reaction with cellulose and water, two forms of degraded NMMO are N-methylmorpholine (NMM,2) and morpholine (M,3) as shown in Scheme 2.2 [48]. However, the degradation of NMMO can be avoided using mechanical agitation (reduce and maintain an optimum temperature at which degradation does not happen) and using stabilizer additives such as gallic acid propylester (GPE) [42] and propylgallate (PG) [47] and organic or inorganic bases [49].

The melting point of pure NMMO is at 170ºC [42], and by differential scanning calorimetry it is at 184 ºC [47].

N-Methylmorpholine(NMM,2) Morpholine (M,3)

Scheme 2.2 Main degradation products of NMMO [48]

Water is another key ingredient in producing lyocell fibre. Dilute aqueous solution of the amine oxide with water is used to completely dissolve the pulp fibres and to coagulate the spin fibres. Water is also used for washing the spin filaments after coagulation. Different finishing agents, lubricant such as soap or silicone are generally used [32].

2.3.2 Manufacturing Process

The major steps for manufacturing the lyocell staple or filament fibres are shown in Figure 2.11.

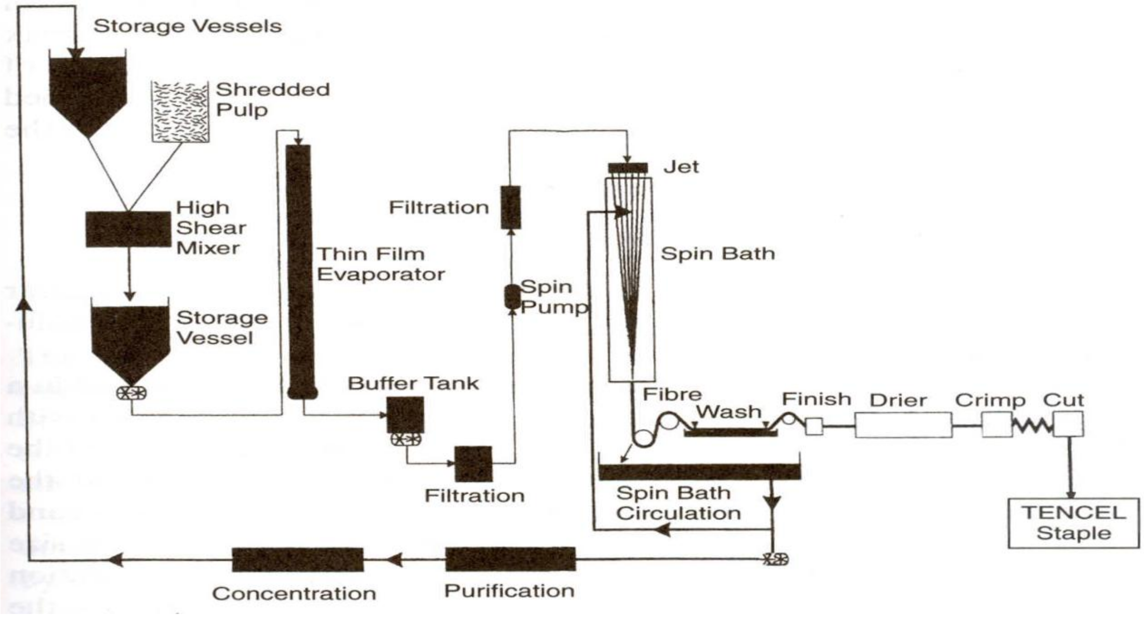


Figure 2.11 Manufacturing process of Tencel [32]

The various steps of the process are detailed below.

2.3.2.1 Preparation of Wood Pulp

- For manufacturing the high quality of lyocell fibres, pulp in the range 100 - 1000 units DP (degree of polymerization) are required. For Tencel pulp of 500 to 550 units DP is used.
- The trees are cut to 20 ft (6.1m) lengths and debarked by high-pressure jets of water.
- Next, the logs are fed into a chipper; a machine that chops them into squares little bigger than postage stamps.
- Then the chips are loaded into a vat of chemical digesters that soften them into a wet pulp.
- The wet pulp is washed with water, and may be bleached. Then, it is dried in huge sheets, and finally rolled onto spools; weighing some 500 lb (227 kg) and the sheets have a thickness of poster board paper.

2.3.2.2 Dissolving Cellulose

- After unrolling the spools of cellulose they are broken into one inch squares.
- These squares are loaded into a heated, pressurized vessel filled with the 76 - 78% N-methylmorpholine N-oxide solution with water, which is reclaimed and recycled in a "closed loop" spinning process conserving energy and water.
- Up to 99% of solvent is recovered and reused [28].

2.3.2.3 Filtering

- After a short time soaking in the solvent, cellulose dissolves into a clear solution.
- It is pumped out through a filter, to insure that all the impurities are removed.
- Impurities are materials such as pulp feedstock, undissolved pulp fibres or sand and ash (inorganic compound) [32].

- The solution is passed through two types of filters. One is a media candle filter element which consists of sets of sintered steels and other is candle filter elements associated with spinning machine [32].

2.3.2.4 Spinning

- The filter solution is pumped through spinnerets, pierced with small holes as shown in Figure 2.11.
- When the cellulose is forced through it, long strands of fibres come out.
- These fibres are then immersed in another solution or spin bath containing diluted amine oxide.
- The filaments are drawn from the air gap with a ratio between 4 and 20, in order to get consistent fibre properties. Below a draw ration of 4 the tenacity of lyocell fibre is low and above 20 spinning properties are decreased [42].

2.3.2.5 Washing

- The sets of fibre strands are washed with hot de-mineralized water in a series of washing baths. The level of washing liquor is maintained by counter current feeding as shown in Figure 2.12.
- After washing the filaments may be treated with bleaching agent, and finishing agent which may be soap or silicone. The filament could be treated with other chemicals to obtain the specific fibre properties.

2.3.2.6 Drying and Finishing

- The lyocell fibres next passes to drying perforated drums, where water is evaporated from the filaments.

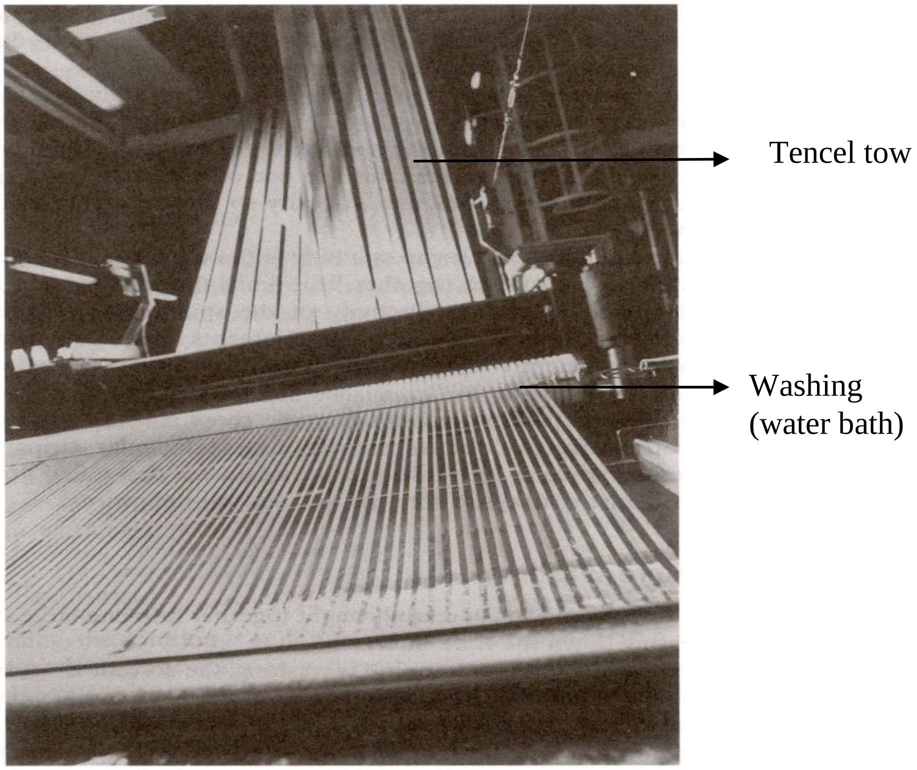


Figure 2.12 Tencel tow washing process [32]

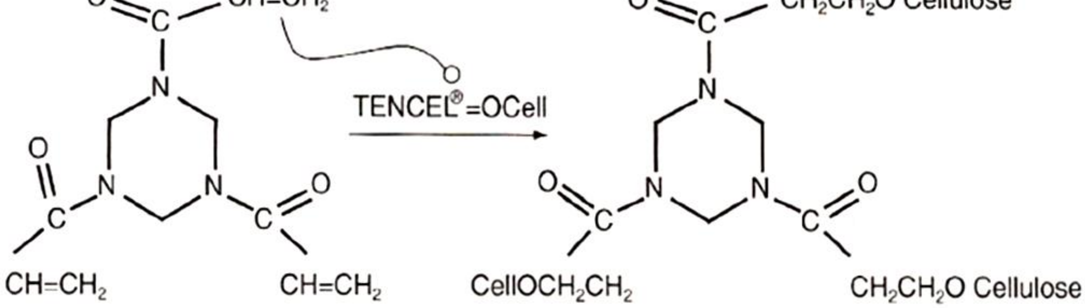
When comparing the properties of lyocell staple and filament fibres, the staple fibres has 50% less modulus of elasticity but there is not as much variation in tenacity and elongation at break. This is because of variation in molecular orientation and the difference between the direction of preferred orientation and the fibre axis. Moreover, staple fibre is permanently deformed during converting from filament to staple fibre [50]. The crimping particularly stuffer box causes structure damage (kink band) and decreases the strength and modulus of elasticity [51].

The entire manufacturing process, from unrolling the raw cellulose and to the baling of fibres, takes only about two hours. After this, lyocell fibres may be processed in a wide assortment of ways. It may be spun with other fibres, such as cotton or wool. The yarn can be woven or knit such as any other fabric, and given a variety of finishes, from soft and suede-like to silky [1, 32]. Additives such as surfactants change the fibre structure and properties.

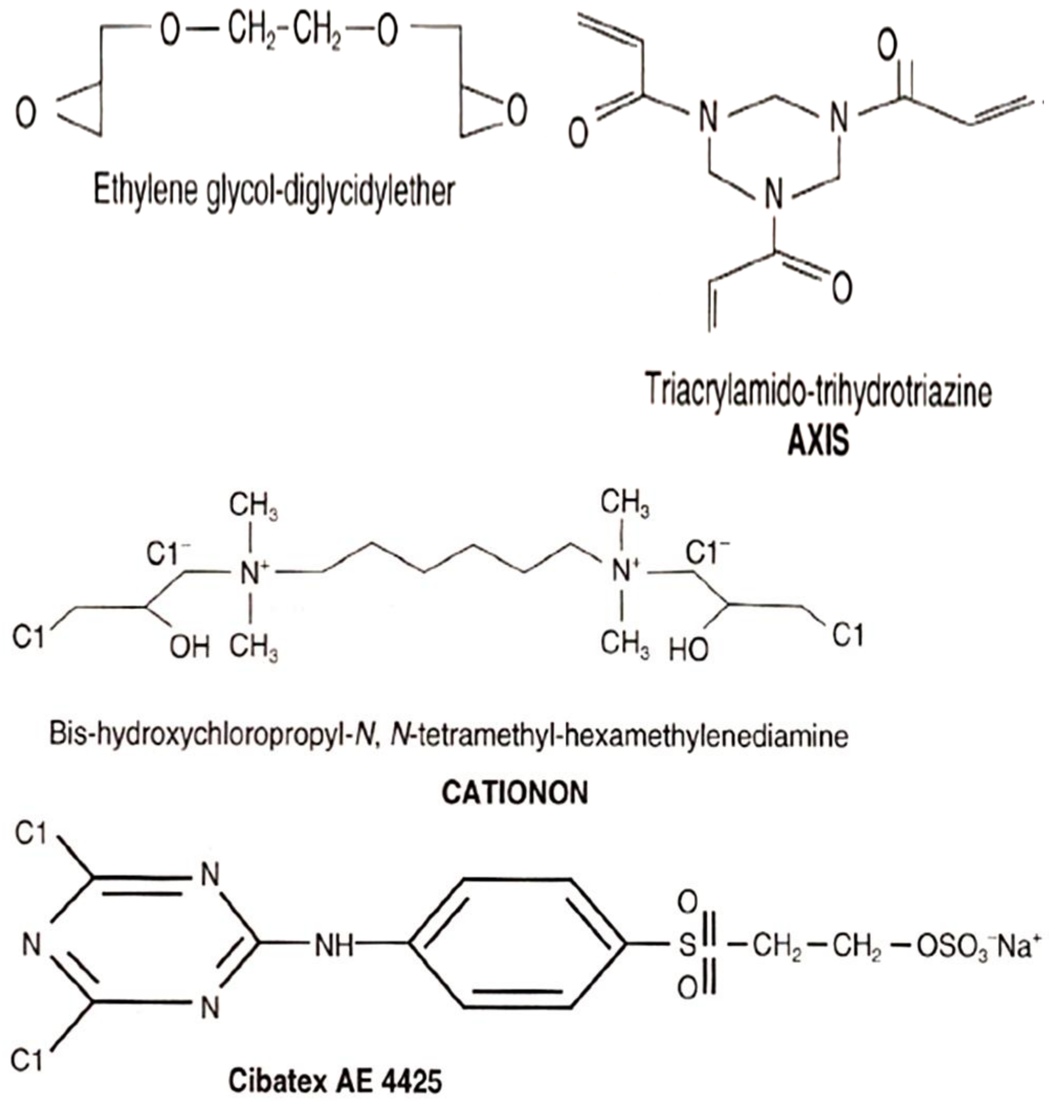
In order to get optimum quality of lyocell fibres, not only a good quality of wood pulp is required but control of manufacturing process is also necessary. Various techniques of spinning and processing were introduced for minimizing the fibrillation tendency. Mengkui Luo et al 2003 [52], introduced a centrifugal and melt blowing spinning method. The dopes were prepared by the same methods as cited above. The lyocell fibres spun by this technique were varied in diameter (1.5 - 20 μm) and had crimp compared to natural fibres, hence there was no need of texturizing. When comparing these two spinning techniques, the fibres made from melt blowing had less diameter variation. The overall morphology of the fibres made from these spinning methods has advantage of making fine and tight yarns with minor fibrillation.

Fibrillation can also be controlled by controlling the pH (greater than 8.5) during washing. Other methods, such as after-washing, treatment with swelling agents or cross-linking agents such as mono and bis-functional hydroxyl groups containing compounds as shown in Scheme 2.3 and Scheme 2.4 [32] and some reactive dyes minimize the fibrillation. Fibrillation is controlled due to the partial cross-linking between the cellulose structure units by covalent and hydrogen bonds. This leads to a better abrasion resistance in the wet state caused by reduced crystallinity and super-molecular order in the fibre material [42].

Lyocell fibres could be manufactured as dry lyocell fibres or never-dried (wet) lyocell fibres. The dry lyocell fibres has high orientation as compared to never-dried (wet) fibres because drying process causes the fibres to collapse increasing the bundle diameter and additionally merging crystallites [42]. Various exchange and drying conditions of dried cellulose material effect on the crystallinity too.



Scheme 2.3 Cross-linking with colourless dye triacrylamido-trihydrotrazine



Scheme 2.4 Cross-linking agents such as Axis, Cibatex AE and others

When comparing manufacturing process of lyocell fibres to other regenerated fibres [22], lyocell fibres manufacturing has the following advantages:

- Easy to manufacture because of fewer process steps as compared to other regenerated cellulosic fibre such as viscose, cupramonium, etc.
- The 99.5% recovery of solvent.
- Unique properties of fibre such as dry and wet strength, higher than other regenerated cellulose fibres.

- High production as compared to ordinary and organic cotton. Lisa Niedemayr [45] said that 2 – 5 % organic cotton is produce in the world wide, and Michaela Knieli said that the cultivation of cotton fibres such as pesticides, water and land are required more than with the Tencel fibres.

2.4 Types of Lyocell Fibre

Basically, Tencel fibres are of two types as listed below. However with respect to applications, they can be further subdivided into many other forms.

- Standard Tencel.
- Cross-linked Tencel (Tencel LF or A100).

2.4.1 Standard Tencel

Standard Tencel and Tencel A100 differ mainly in their fibrillation properties. Standard Tencel has more capability to fibrillate as compared to the A100. It is used for variety of purposes such as denim, menswear, women wears and home textiles. It gives soft, sued-like peach touch to smooth, clean and silky effect by controlling or manipulating fibrillation [53].

2.4.2 Cross-linked Tencel

Cross-linked Tencel; Tencel A100 and Tencel LF, introduced in 1998 [32, 53], as non-fibrillating lyocell fibres. Possessing the same softness, drape and bulk characteristics as standard Tencel. Tencel A100 has been chemically cross-linked by 1,3,5-tris(acryloyl)hexahydro-s-triazine [54, 55] during production to eradicate the fibrillating tendency. Non-fibrillated fibre such as Lyocell LF, because of difference in cross-linking agent (sodiumhydroxydichlorotriazine [55]) as compared to Tencel A100, has pronounced anionic charge than the normal lyocell which is why lyocell LF fibre has less dye uptake for direct dyes [56]. It has high pore volume (0.66 ml g^{-1}) as compared to the Lenzing lyocell fibre (0.53 ml g^{-1}) [55]. Similarly, pore volume of Tencel A-100 is 0.67 ml g^{-1} is higher than the standard Tencel 0.44 ml g^{-1}. Therefore, their processing requires less dyestuff, hence is more cost-effective. Lyocell LF is used in knitwear and woven fabric for shirting, sportswear and home furnishing textiles. Tencel A-100 type is sensitive to alkalis but type LF is sensitive to acids.

2.5 Morphology

2.5.1 Tencel Cross-sectional View

The cross-sectional view of Tencel fibre under the microscope is shown in Figure 2.13. The fibre has a circular to oval cross-section. Scanning electron microscopy [42] shows a dense cellulosic network structure of Tencel fibre with small finely distributed voids at the exits ranging in dimension 5 - 100 nm. The cross-section is uniform throughout except a small boundary layer which shows high density.

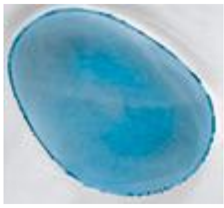


Figure 2.13 Cross-section of Tencel fibre [45]

The round, smooth and uniform cross-section [31] of Tencel fibre allows a very close packing in the yarn structure. The high strength of Tencel yarn is due to the high cohesion between the parallel fibres. The structural properties of Tencel fibre [57] are summarized in Table 2.4.

2.5.2 Tencel Longitudinal View

The rod like structure gives crisp, firm cotton like handle [31] (Figure 2.14). Tencel fibre has little striated longitudinal surface [34].

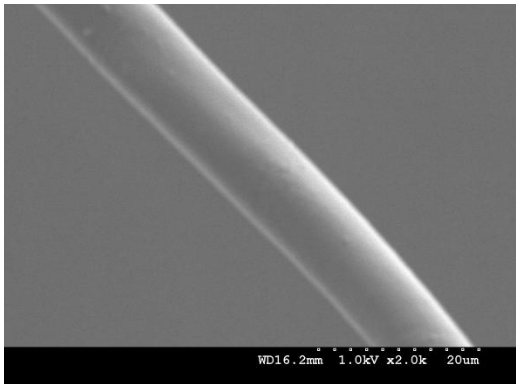


Figure 2.14 Longitudinal view of Tencel Fibre

Table 2.4 Structural characteristics of Tencel fibre

Properties	**Behaviour**
Cross-section	Round/Oval
Morphology of cross-section	Homogenous, dense
Crystallinity	High
Crystal width	Small
Crystal length	Larger
Crystalline orientation	High
Amorphous orientation	High

2.5.3 Pore Structure

It is revealed from the morphological analysis [58, 59] that lyocell fibre has a thin, nano porous skin of about 150 nm thickness with low porosity in centre of fibre. The area between the skin and core layer of fibre shows intermediate porosity. In Figure 2.15, a highly resolved image of the internal morphology of Tencel fibre, the dark random thin lines shows the pores (appear as electron dense) and the bright area shows the electron transmitted areas.

Hence, Tencel is semi-permeable with a highly porous skin [59]. The size of pores becomes more compact towards the centre of the fibre. The compact or tiny pores in the centre act as barrier for diffusion into the fibre.

The porosity of the filaments has a direct influence on the dye uptake. Due to its low or compact porosity in the centre and high cystallanity it becomes difficult to dye Tencel fabric by continuous dyeing process.

The smaller dry pores increase the uptake of fluid such as dye solution by capillary force [60]. In wet condition the large pore size reduces the uptake of fluid. However, the absorbance of dye also depends on the type of weave and its construction.

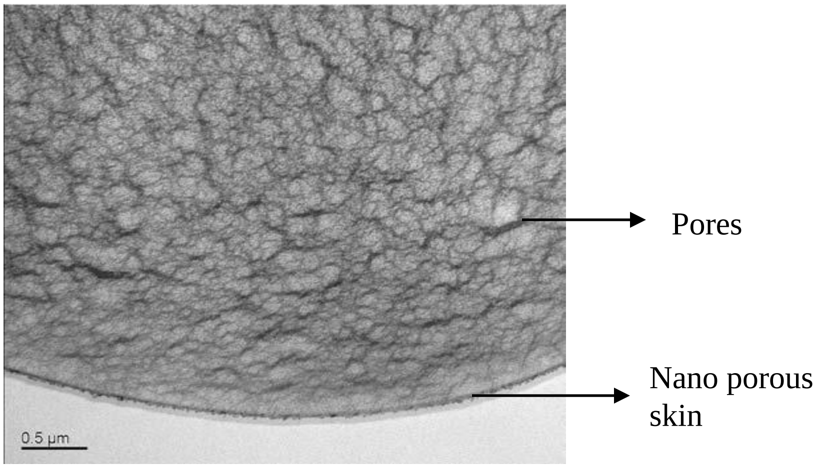


Figure 2.15 Internal morphology of Tencel Fibre [59]

2.6 Fibrillation

There are different types of lyocell fibres as discussed in Section 2.4. The standard lyocell or Tencel fibres have higher fibrillation tendency than the Tencel LF and A100 fibres.

Under wet condition lyocell fibres shows an interesting property “fibrillation” [61]. Similarly, abrasive action on lyocell also develops micro-fibrils (or tiny fibres) on the surface. Fibrillation is [8] the peeling back or splintering of the fibre ends making a view of tiny hairs on the surface of the yarn or on the fabric.

There are two types of fibrillation:

- Primary fibrillation and other is
- Secondary fibrillation.

2.6.1 Primary Fibrillation

It is the partial detachment of long fibrils or hairs from a fibre. Fabric which has primary fibrillation, exhibits an undesirable hairy appearance and after dyeing gives frosty appearance [62].

2.6.2 Secondary Fibrillation

Incomplete removal of short fibrils from the fibres is term as secondary fibrillation. It is extensively present in the structure of Tencel fabric. The secondary fibrils are different to primary fibrils because [62, 63]:

- They are generally distributed more uniformly on the fabric, as compared to a localized area.
- It gives peach-skin finish effect with no visual dye frostiness.

2.6.3 Effect of Fibrillation

Primary fibrillation gives an unpleasant frostiness dyed effect, so primary fibrils are always avoided. The fibrillations are affected by pulp type, pulp concentration [46], additional modifier to the spinning solution and the preparation of spinning dope .

The visual depth of dyed non-fibrillated Tencel fibre is higher than the fibrillated fibre even when there is no difference in percent exhaustion (%E) and percent fixation (%F) [12]. The lower visual depth of fibrillated Tencel occurs because the fibrils are usually 1 - 4 μm in diameter and the light might first be refracted in these micro fibres before being reflected from the surface.

The highly oriented lyocell fibres have greater chance to fibrillate due to the mechanical stress in the wet condition, because of the lack of lateral cohesion between the cellulose chains [64]. The lyocell fibre is swollen in alkaline solution hence, the fibrillation index (F.I) increases from 0 to 0.45 especially in highly oriented fibres where the molecules are tightly packed in the crystalline regions.

2.6.4 Methods for Controlling Fibrillation

Depending on the use of lyocell fibres and types of fibrillation there are different methods of controlling the fibrillation. Some of the methods are listed below:

- Treatment with a cross-linking agent during manufacturing process, such as Tencel A100 and Tencel LF [53, 56].
- It was observed that a warm and humid atmosphere, short air gap (distance between spinneret and precipitating liquid) and lower speed of spinning [65] minimize the propensity for fibrillation. Additionally it has been claimed that the tendency to fibrillation increases with drawing process.
- Cellulose concentration in NMMO should be in the range 1 - 15% [66]. A reduction of cellulose concentration in the spinning solution reduces both mechanical and fibrillation properties.
- Different fabric finishes, for example, cross-linking agents such as N-methylol resins [63], 1,2,3,4-butaneteracarboxylic acid [67] and etc.
- Enzymatic treatment such as cellulases dissolve the split-end hairs from the surface of lyocell fabrics [63]. Enzymes can easily remove from the surface of Tencel fabric by washing. Another method of deactivating enzymes is by increasing temperature to more than 70 ^{0}C and increasing pH using sodium carbonate. After treatment, secondary fibrillation is still left on the fabric surface which produces a suede or sand like effect. Care should be taken during enzymatic treatment because if the enzymes remain within the structure of Tencel fibre, the colour yield decreases and uneven dyeing occurs.
- Firgo et al [23] suggested the polymer solutions that have a cationic end group such as imidazole and azetidine give lower tendency of fibrillation. They also mentioned that treatment with emulsified polymer such as polyethylene, polyvinylacetate reduce fibrillation.
- Multi-functional reactive dyes minimize fibrillation propensity by cross-linking [68].
- Care labelling such as "dry clean only", prevent the fibrillation of finished textile.

2.6.5 Methods of Assessing Fibrillation

There is no standard method of measuring fibrillation on the surface of the Tencel fibre. Different analyses apply different methods of measuring it, such as fibrillation Index (F.I).

The fibrillation index, birefringence, and degree of cystallianity are decreased by 6 - 7% by the use of cross-linking agent, while viscosity is increased. These properties of fibres can be used to calculate the F.I [64] as shown in Equation 2.1.

$$FI = 1.32 - \left(1.82 * 10^{-2}\right)\eta + \left(5.894 * 10^{-3}\right)C \qquad \text{Equation 2.1}$$

where η = viscosity, and C = concentration of cross-linking agent.

Although, the degree of fibrillation can also be calculated as;

$$F.I = \frac{\sum i}{l}$$

where $\sum$ i is the sum of fibril length and l is the length of fibre.

Another method was also introduced for assessing the F.I [61], in which standard fibrillated fibres were formed and given a rating of 0 to 10, where 0 means no fibrillation and 10 means highly fibrillated. Initially the length of fibril and the number of fibrils in the fibres were measured. Arbitrary numbers were then multiplied by the number of fibrils. The fibres that have highest value were considered as highly fibrillated fibres and given a rating of 10. After that, the images of others fibres were assessed by comparing these standard and then rated. The F.I of 2 and 2.5 gives unsightly appearance in woven and knitted fabric.

An instrument Delta A100 manufactured by Lenzing AG is designed to assess the tendency of Tencel fibres to fibrillate [69]. The instrument consists of oscillated viscose coated shaft with water layer or film. Twenty fibres were selected at one time making a contact angle with shaft 0 – 100° (generally 40°). The fibres tension was adjusted using clip held at the lower end of each fibre. The sensor detected breakage of each fibre by dropping down of clip. Statistical analysis (mean, standard deviation and co-efficient of variance) was then completed the wet abrasion number (Nass-Scheuer-Festigkeit, NSF).

2.7 Properties of Lyocell Fibres

2.7.1 Physical Properties

Lyocell is popular in outfits because [1, 8]:

- It is absorbent.
- It is comfortable for wear, especially in conditions of high humidity.
- It drapes attractively and is flattering in dresses and shirts.
- It is stronger than cotton or regular viscose rayon as indicated in Table 2.5.
- It is soft, breathable and light weight because of smooth and regular nano-fibril surface.
- It is shrink resistant.
- It is durable, easy to pack, easy to care, resists wrinkling, dries quickly and is machine washable.
- It is biodegradable.
- It stretches more than cotton, but less than viscose.
- It is susceptible to mildew and damage by silver fish.
- It fibrillates under wet condition [42] but this can be controlled by the treatments discussed in Section 2.6.4.

2.7.2 Chemical Properties

The chemical properties of Tencel fibre are similar to other cellulosic or regenerated cellulosic fibres.

- Its surface acquires a net negative charge in water.
- It has resistance to alkali and to weak acids also.
- Tencel, on burning turns to grey ashes.

- It has high heat stability as compared to other regenerated cellulosic fibre such as viscose.
- Treatment with caustic soda at particular strength (more than 8% NaOH) effects its swelling behaviour and other physical properties.

2.7.3 Mechanical Properties.

Tencel fibres have excellent mechanical properties. A comparison of Tencel fibres with other cellulosic and regenerated cellulose fibres is shown in Table 2.5. The main attributes of Tencel are:

- It has high dry and wet tensile strength [42] as compared to other cellulosic fibres.
- The strength of standard lyocell is higher than the lyocell LF [56] a shown in Table 2.6.
- Tencel has lower strain at break and higher modulus in wet and dry state. The modulus of elasticity [34] of Tencel staple fibre is 50% lower than the Tencel filament fibres.
- It has high knot and loop strength [42].

Table 2.5 Comparison of fibre mechanical properties [1, 22]

Property	*Units*	*Lyocell*	*Viscose*	*Modal*	*Polynosic*	*Cotton*
Titre	dtex	1.7	1.7	1.7	1.7	-
Dry tenacity	cN/tex	40-42	22-26	34-36	36-38	20-24
Elongation at break /dry	%	14-16	20-25	13-15	11-13	7-9
Wet tenacity	cN/tex	34-38	10-15	19-21	28-30	26-30
Elongation at break/ wet	%	16-18	25-30	13-15	12-14	12-14
Water imbibition	%	65	90	75	70	50
Cellulose DP		550-600	290-320	-	450-500	2-3000
Initial wet modulus	cN/tex (5% ext)	270	50	110	210	100
Moisture regain	%	11.5	13	12.5	12.5	8

Table 2.6 Mechanical properties of Lyocell LF and standard lyocell [56]

Properties	*Lyocell LF*	*Standard lyocell*
Tenacity, cN/tex	35-37	40-42
Elongation, %	9-11	15-17
Wet tenacity, cN/tex.	27-29	34-36
Wet elongation, %	11-13	17-19

**Linear density of Lyocell LF is 1.3dtex*

2.8 Application of Lyocell Fibres

Due to their unique characteristics lyocell fibres are used in manufacturing various products, ranging from home furnishings to outwear and medical purposes. Tencel is used both as 100% Tencel fibres but is sometimes blended with other textile fibres such as cotton, viscose, polyester, wool and etc. The following are the application areas of lyocell and its blended woven fabrics.

- Home furnishings.
- Apparel.
- Sports.
- Hygienic fabric.
- Technical products.
- Fibrillated fabrics.
- Non-woven fabrics.

2.8.1 Home Furnishings

The excellent moisture absorption property of Tencel fibre make it widely used in home furnishing items such as bed covers, mattresses, etc [56].

2.8.2 Apparel

Textile apparel from causal to office wear is made of Tencel fabric [70]. Most textile apparel especially denim, knitwear and woven fabric are composed of 100% Tencel and its blended materials.

2.8.3 Non-woven Fabrics

Nonwoven fabric such as medical swabs and dressings, hygienic absorbents, wipes, coating bases, leather substitutes, filters, interlinings, diskette liners, battery separators, disposable and other semi-durable apparel are composed of Tencel fibres. It is used as raw material for non-woven fabric because of the high modulus and low shrinkage properties.

2.8.4 Technical Products

A variety of technical products are made of Tencel fibre [71] such as coating bases, abrasive substrates, printers blankets, rubber reinforcement, composites, flame retardant cloths, belting, protective clothing, work wear, tenting etc.

2.8.5 Sports

Many sport fabrics are made of the Tencel fabric. Tencel seems to be ideal for sportswear because the individual nano-fibrils regulate the absorption and release of moisture (1.8 litre of water per hour). These tiny fibrils are said to guarantee optimum moisture transportation and excellent thermal regulating properties. The space between the body and the performance textile remains dry. Moreover, pleasant coolness and smooth surface of the Tencel prevent skin irritation.

2.8.6 Hygienic Fabrics

Tencel is used nowadays for different medical purposes such as clothing for operating theatres, surgeries, and other medical fabrics. The uses of Tencel fibres are widely spread in medical areas because it prevents the skin irritation, electrostatic charges and it hinders bacterial growth.

When comparing these properties to other synthetic fibres such as polyester and polyamide fibres, these fibres have 2,000 times more risk of bacterial attack than Tencel fibre. Similarly, these synthetic fibres produce electrostatic charges when in contact to with human skin and cannot absorb moisture to the extent of Tencel fibre [45].

2.8.7 Fibrillated Fabrics

Standard Tencel is designed to produce the fibrillated fabric [70]. The fabric is made of staple fibre, 2 - 8 mm in length, and the number of fibrils on the surface of the fabric varies depending upon the type of fabric and its uses. According to the CSF (Canadian standard freeness) the level of fibrillation is from 600 to below 50 is used for making special papers, and fabrics for filtration. The fibrils give a suede-like surface, adhesive for coatings, and act as a breathable barrier.

2.9 Advantages of Tencel Fabric

The following are the advantages of Tencel fabric.

- Tencel fibres require ten times less raw material than the cotton fibres. For example, 6 m^2 of land yields ten shirts of Tencel fabric but the same area produces only one shirt of cotton fibre.
- Manufacturing of Tencel fibres, including the pulp production, consumes 100 times less water than the cotton fibres [71].
- It is completely biodegradable.
- Because of high dry and wet strength of Tencel fibres very fine filaments can be spun and very light weight fabric can be manufactured.
- It can be used for manufacturing a variety of textile and non-textile items.

CHAPTER 3: PRE-TREATMENT AND DYEING OF CELLULOSIC FIBRES

3 Pre-treatment and Dyeing of Cellulosic Fibres

3.1 Pre-treatment

Tencel and other cellulosic fabrics are pre-treated using different chemicals and methods in order to enhance the dyeability. Pre-treatment was carried out before dyeing to remove the non-cellulosic impurities and enhance the uptake of dye. Some of the common pre-treatment processes are:

- Cationic fixing agent.
- Plasma treatment.
- Enzymatic treatment
- Alkaline treatment.

3.1.1 Cationic Fixing Agent

Cationic fixing agents, such as amines, quaternary ammonium, phosphonium and tertiary sulphonium salts are used as dye fixing agents for anionic dyes. Among these most commonly used cationic fixing agent is quaternary ammonium salts [72, 73]. These fixing agents form a complex with cationic dyes and improve their fixation and fastness properties [74, 75]. Fixing agents are applied before or after dyeing depending on the type of dye [76, 77]. For example, reactive dyes give better results when cotton fabric is pre-treated with 3-chloro-2 hydroxypropyltrimethyl ammonium chloride (CMAC) or its derivatives (triethyl, tripropyl, tripentyl and tetradecyl ammonium chloride) than an after treatment [72, 78].

3.1.2 Plasma Treatment

Plasma treatment is used to enhance the wettability, flame resistance, adhesive bonding, printability, electromagnetic radiation reflection, surface hardness, hydrophilic and hydrophobic tendency, dirt-repellent and antistatic properties [79] . Plasma treatment is an ionized gas consisting of highly energetic negative (electrons) and positive (proton) ions [80]. The treatment by plasma is very energetic to break the organic bonds by using vacuum ultraviolet photons and by physical bombardment using energetic particles. Hence, it gives effect of cleaning, ablation or etching, cross-linking, and surface chemical modification at control parameters. Corona (plasma treatment operating at atmospheric pressure using air as reagent gas) forms polar groups by controlled surface oxidation with air or oxygen. These polar groups, carboxyl and hydroxyl groups, increases the surface energy of the polymer, enhancing the wettability of the textiles such as fabric, (by liquid and adhesive) and improves the bond strength and dye uptake [81, 82].

Plasma treatment of Tencel fabric using oxygen and argon imparted a negative effect, damaging the fabric [83] for both longer (60 min) and short (5 min) duration. However, 5 min duration improved the wettability.

3.1.3 Enzymatic Treatment

Treatment with enzymes such as pectinase, lipase, and cellulase remove the impurities such as waxes, pectins, and hemicelluloses hence, improved the wetting properties [84-91]. In case of Tencel fabric cellulase [92] acts as surface polishing agent by removing the primary fibrillation from the surface of fabric, but it is expensive in terms of cost and time. Further, it is not helpful in removing the rope-marks produced by jet dyeing.

3.1.4 Alkali Treatment

Alkali treatment enhance lustre, dyeability, uniformity and dimensional stability of the fabric by the swelling action within the cellulose structure, and the associated reorganization of yarn and weave geometry [93]. They cause changes in the structure, morphology, accessibility and reactivity of cellulosic fibres, depending upon the concentration, treatment temperature, physical state of the material and the degree of polymerization of cellulosic fibre [35, 94].

The change in the chemical structure and physical properties of cellulose fibre due to the caustic treatment was first introduced by Mercer in 1844. Lowe discovered the industrial use of alkali cellulose fibres, which makes it more lustrous [95].

3.1.4.1 Mechanism of Reaction of Cellulose with Alkali

Alkali treatment using sodium hydroxide on cellulose fabric produces new compound alkali cellulose; extensive swelling and partial dissolution causes a physicochemical changes and structural changes, resulting a change in the mutual position of the chain links and the cellulose macromolecules [95].

3.1.4.1.1 Chemical Changes

When sodium hydroxide reacts with cellulose, alkali cellulose is formed. The reaction of alkali on cellulose may proceed in two ways as shown in Scheme 3.1 and Scheme 3.2.

$$C_6H_7O_2(OH)_3 + NaOH \longrightarrow C_6H_7O_2(OH)_2.ONa + H_2O$$ Scheme 3.1

$$C_6H_7O_2(OH)_3 + NaOH \longrightarrow C_6H_7O_2(OH)_2.OH.NaOH$$ Scheme 3.2

The Scheme 3.1, as cited above shows that cellulose with alkali metal forms true alcoholates and replace the hydrogen ion. A medium of 17 - 18% aqueous sodium hydroxide with water are required to formed cellulose alcoholates.

In Scheme 3.2, an addition compound is formed when the molecules of NaOH are added to the hydroxyl groups of cellulose.

Rogovin [96] stated the formation of both molecular compounds and cellulose alcoholates, depend on the reactivities of hydroxyl groups in cellulose chain and concentrated aqueous NaOH solution.

The 12 - 18 % NaOH solution with cellulose formed, alkali cellulose $(C_6H_{10}O_5)_2$. NaOH (i.e $\gamma = 50$). Whereas at concentration of NaOH 20 - 40% the compound $C_6H_{10}O_5$. NaOH ($\gamma = 100$) observed. Gamma, γ, the amount or part of cellulose chain react with sodium hydroxide. The formation of new crystalline structure confirms by x-ray methods when concentrations of NaOH solutions increases by 21 % [95].

Further, the reaction between cellulose and NaOH and the formation of a new compound during caustic treatment is taken place by the hydrolysis of cellulose chain, bond between the cellulose chain and NaOH and the absorbance of NaOH in the cellulose chain.

3.1.4.1.2 Physical Changes

Most important physical changes occur in cellulosic fibres treated with alkali solution are swelling (increase in diameter) and shrinkage (reduction in length) [95]. The structure of cellulose fibre is heterogeneous and chain molecules are held into three types of bonding: van der Waal's forces, polar hydrogen bonds, and primary valence bonds. The intermolecular hydrogen bonding mainly involves in the swelling mechanism.

During intermicellar (intercrystallite) swelling the reagent solution of sodium hydroxide below 12% penetrate only into the intermicellar (intercrystallite) spaces and amorphous regions. At concentration above 12% sodium hydroxide swells the intramicellar (intracrystallite) regions which entails changes in the crystalline network, hence the swelling agent penetrates both in the amorphous spaces and in the crystallites region [97].

3.1.4.1.3 Structural changes

During mercerization process cellulose fibres form the sodium-cellulose-I when treated with 10 - 20 % sodium hydroxide at 20 ^{0}C. The native cellulose has 101 plane distances of 6.1 ^{0}A, but the incorporation of alkali causes it to widen to 15 ^{0}A. In this reaction the glucopyranose rings are dislocated and aligned into the 101 plane. The hydroxyl groups on C(2) and C(6) are free and orientate into the widening space between the 101 plane as shown in Figure 3.1[39].

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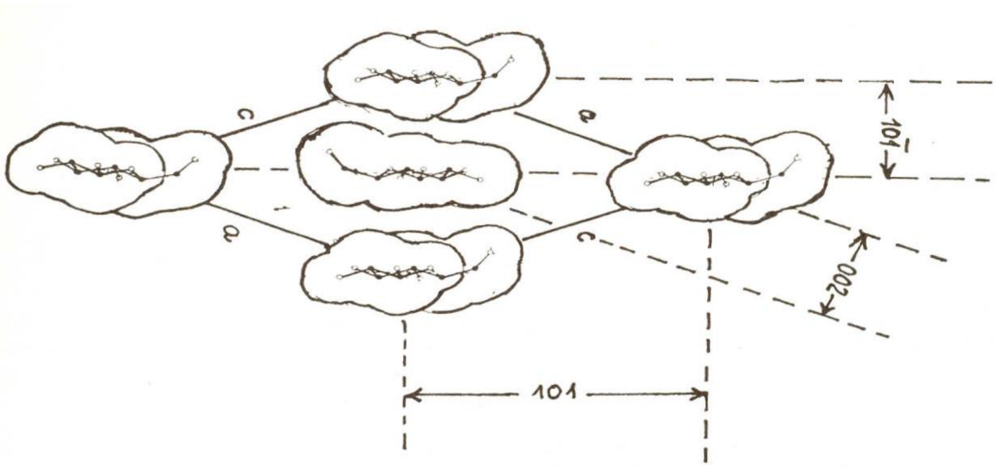


Figure 3.1 Lattice widening in the formation of Na-cellulose -I

At lower concentrations of alkali the lattice widens and etherification reactions, substitution of hydroxyl groups on the carbon atom C(2) can occur. If the reaction occurs on the surface of the fibrils and in the less order regions (amorphous), interlinking the crystallites (degree of substitution of 1.3 to 1.7) has not affected on the crystal lattice structure of cellulose. As the reaction proceeds; it opens the crystallites from both ends, increasing the molecular spacing as shown in Figure 3.2. When the degree of substitution is between 1.5 and 2.5, the reaction products show superimposed diffraction characteristics of the original cellulose-I or II. On further reaction, the cellulose is completely transformed as shown in Figure 3.2.

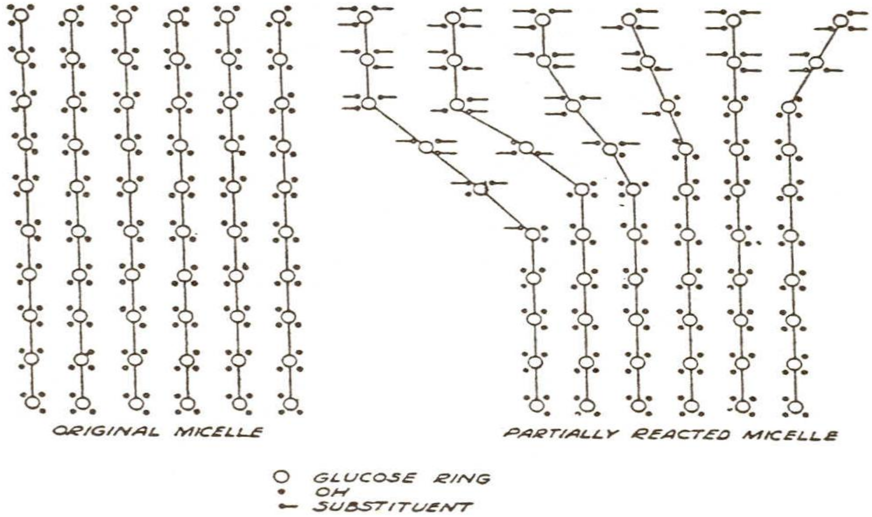


Figure 3.2 Effect of alkali reaction along the fibre axis in the crystalline structure [39]

3.1.4.2 Effect of NaOH on Tencel Fabric

Different types of alkali such as sodium hydroxide and potassium hydroxide have been applied to Tencel fabric.

Sodium hydroxide (120 g l^{-1}) and potassium hydroxide (250 g l^{-1}) were applied on plain Tencel woven fabric by pad-batch method [58]. After alkali treatment the fabric was resin finished with a dimethylol dihydroxyethyleneurea (DMDHEU) product by a pad-dry-bake process. The results showed that NaOH treatment conferred deeper diffusion within the fibres, increased the total pore volume and total pore surface, as compared to the potassium hydroxide treatment. The fibrillation tendency of alkali-swollen lyocell fibre was also higher in NaOH solution as compared to KOH solution [58], but the tendency depended on the concentration and temperature of NaOH.

It was observed that causticisation improves the dye-ability of lyocell fabric and modifies the fabric structure [92]. When Tencel fabric was pre-treated with different concentration of NaOH; applied by pad-batch process [20, 98, 99]. After pre-treatment the fabric was dyed by exhaust method using Procion and Cibacron dyes at 2 % dye conc. The lyocell fabric pre-treated up to 1.5 mol (6 %) of NaOH and more than to 2.5 moles (< 10%) of NaOH, dye was adsorbed at the periphery of the yarn. Only the 2 to 2.5 moles (8 to 10 %) of NaOH were seen to absorb the dye uniformly. The strength of colour was increased and the crystallinity was decreased as the concentration of NaOH increased due to the greater potential for hydrogen bonding between the water molecules and the fibres.

At higher concentrations of sodium hydroxide (more than 2.5 mol) [20] the degree of swelling of Tencel fibres was increased, effect on the crystalline region of the fibres and the internal voids in the twisted yarns became limited. The fibres were squeezed changed into solid unit to occupy the space and lost its circular cross-section. Even after washing they retained an angular cross-section. The change in structural and cross-section properties of Tencel fibres induce low diffusion of dye molecules in the yarn of the fabric, only surface fibres or periphery of the yarns was dyed. A fully formed Na-cellulose-II structure was formed at NaOH concentrations above 6.8 moles dm^{-3}, which caused the plasticization of lyocell fibre and breaking of intra and inter-molecular hydrogen bonds.

Depending on the concentration of alkali (NaOH), lyocell fibre undergoes reversible conversion of cellulose-II to Na–cellulose. The removal of alkali ions after washing and drying causes the irreversible conversion to cellulose-II amorphous region. In other words fibre swelling may cause drastic changes in the fabric geometry and in gross dimensions, which may become set after washing and drying [100]. The fibre bundle after treatment in 25% (w/v) NaOH solution (plot b), on washing fibre reverted initially to a hydrate crystal intermediate (plot c) termed as Na-cellulose-IV and then reverse to cellulose-II on drying (plot d) as shown in Figure 3.3 [101]. Alkali treatment slightly decreased the alignment of Na-cellulose crystallities around 15% in 10% (w/v) NaOH solution.

Sodium hydroxide 179 g l^{-1} at 40 °C increased the fabric shrinkage, flexural rigidity and reduced the crease recovery and breaking strength. Sodium hydroxide applied at room temperature, 101 g l^{-1} showed minor effect on fabric properties [102].

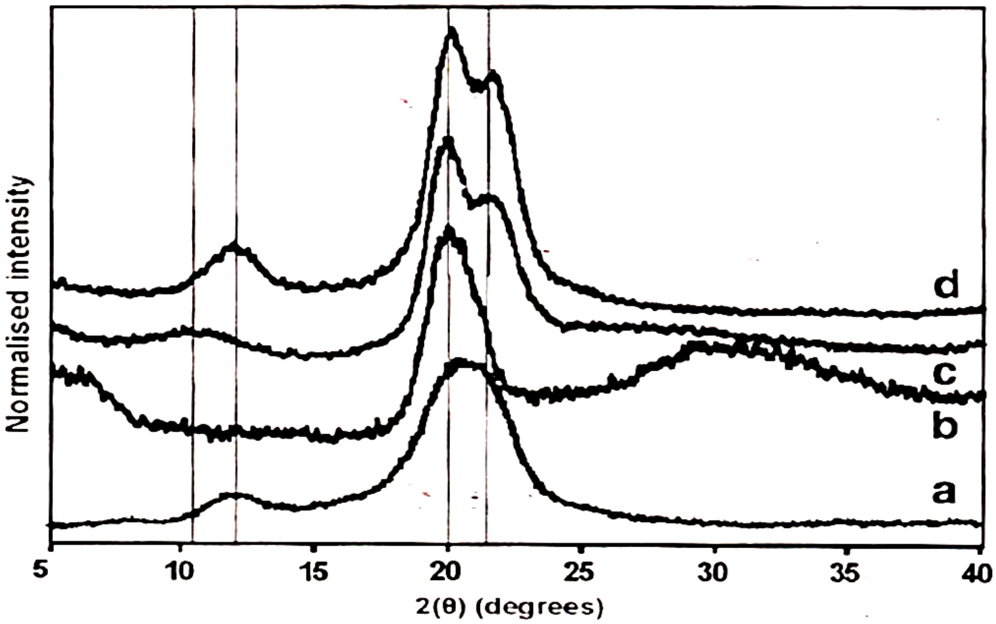


Figure 3.3 Equatorial wide angle x-ray diffractrograms of lyocell fibre, (a) original dry sample, (b) equilibrated in 25 % (w/v) NaOH (constrained), (c) same sample washed in distilled water (d) same sample re-dried [101]

It was also observed as the concentration of NaOH increased the water retention value and pilling formation resistance of lyocell knitted fabrics increased [98]. The carboxyl group of fibre responsible for fibre strength; it decreases as the concentration of NaOH increases (more than 2.5 mol/l) [98].

3.2 Dyeing

Marshall dyeing is a process of adding colorant molecules to textiles and then permanently holding these molecules inside the fabric, under certain kinds of washing conditions [103]. For dyeing textiles, dye molecules must have the desired colour, and have ability to dissolve in the water. Textile dyes are applied from an aqueous dye bath solution, therefore it is required that they are either water soluble or be capable of conversion into a water-soluble form. Secondly, dye molecules must become attached to the textile fibres. The bond between the dye and fibre is due to the force of attraction such as covalent bond, van der Waal’s, ionic, dipolar and hydrogen bonding. The force of attraction depends on the molecular interactions between dye and textile fibres. Thirdly, dye molecules must be distributed uniformly throughout the textile material to give uniform or level dyeing. Finally, dye must have suitable fastness properties, depending on the textile application [103, 104].

There are different application classes of dyes and each class of dye is further sub-classified with respect to their chemical structure, and molar mass. The class of dye applied on textiles depends on the type of fibres. Generally there are three main types of fibres: natural, regenerated natural and synthetic fibres [104]. Textiles can be dyed in a fibre form, yarn or fabric states depending on the application, cost and available equipment.

Cellulosic fibres in all forms, from loose fibre or filament to finished garments, can be dyed by the exhaust and the continuous dyeing methods on all kind of dyeing equipment designed for the substrate form to be processed.

Tencel, a regenerated cellulosic fibre is generally dyed with the dye types that are also compatible with cotton and rayon fibres, such as direct, reactive, vat, sulphur, and pre-metalized acid dyes. Direct and sulphur dyes are favoured because of their low cost. Reactive and vat dyes are favoured for high quality fabrics with excellent fastness properties.

3.2.1 Dyeing Behaviour of Different Dyes on Tencel

Burkinshaw (1994-95) compared the behaviour of direct, sulphur, and reactive dyes applied on the Tencel, cotton and viscose material by exhaust dyeing method. The results showed that when direct dyes [105] and sulphur dyes [106] were applied on all of the three different fibres, the colour depth of Tencel fibres was closer to the cotton fibres than to the regular viscose fibres. Reactive dye (red, blue, and yellow) [107] of three different manufacturers Sandoz, Sumitomo, and Nippon Kayaku, applied at 2% owf on Tencel, viscose, and cotton woven fabrics, behaved differently from the direct and sulphur dyes. Slightly higher depth of colour was obtained on the viscose fabric than the Tencel fabric and the Tencel fabric gave higher colour yields than the cotton fabric. Hence, colour depth value of Tencel fabric was closer to the viscose fabric than to the cotton fabric. Similarly, the %E (percent exhaustion) of viscose fabric was higher than the Tencel and cotton fabrics. Tencel fabric in some reactive dyes such as Drimarene Brilliant Red K-4BL, Kayacelon React Golden Yellow CN-GL, Sumifix Supra Red 3-BF and Yellow 3-RF gave higher %E than cotton fabric while in other reactive dyes such as Drimarene Blue K-2RL and Golden Yellow K-2R, Kayacelon React Red CN-3B and Blue CN-BL, Sumifix Supra Yellow 3-RF, gave lower %E than cotton fabric.

Ibbett and Duncan [108] treated lyocell fibres with a methylol-urea type resin, which incorporates cross-links, prior to applying the direct dye Direct Blue 71 by exhaust dyeing method. The cross-linking reduced the overall fibre swelling, causing a loss of both large and small pores, thereby reducing the volume accessible to large dye molecules and reducing the free energy of dye adsorption. Post-causticisation of resin-treated fibre led to a remarkable improvement in dyeability, consistent with a recovery in total pore capacity and accessible volume.

Kerze, et al compared the dye absorption properties of dried lyocell [109], viscose and modal fibres using tris-azo direct dyes and found the colour yields in the order of viscose fibres > lyocell fibres > modal fibres. Kaenthong, et al obtained similar results (viscose > lyocell > cotton) when they applied direct dyes on dried lyocell, viscose, and cotton fibres by exhaust dyeing [13].

Carrillo [110] examined the mechanical behaviour of lyocell fabric after fibrillation and defibrillation finishing treatments. Firstly Tencel fabric was fibrillated by Airtint-EVO, ATIC (jet machine) and then defibrillated with cellulase. The fabric was dyed with the direct dye Direct Blue 1 before and after fibrillation and defibrillation. It was observed that both fibrillated and defibrillated Tencel fabrics had 15 % decreased in breaking strain and 5 % in tenacity, due to the change in macro and micro-structure of Tencel treated fabric. The uptake of dye by treated Tencel fabric was higher than the untreated fabric, because of the morphological and structural changes (decreased crystallinity, extending pore size) occurring on the fibre surface.

Tencel fabric was dyed after causticisation in 2.5 mol NaOH with Direct Red 81 dye. The caustic treatment and dyeing process was applied by exhaust method. The NaOH treatment enhanced the accessibility of the fibre through internal zones of the fibres, hence increased the dye uptake. At higher concentrations of alkali (greater than 2.5 mol) there was inter-fibrillar swelling resulting in high split number (more separation between macro-fibrils) due to a lower distribution of alkali inside the fibre [111].

Collins, et al, dyed lyocell fabric with pre-metallised acid dyes. The fabric was successfully dyed and had a colour strength and wash fastness slightly higher than cotton fabric. This was because the pre-metallised acid dyes after dyeing were further solubilised with the cationic site in the cationic polymeric post-treatment agent (finishing). They concluded that the lyocell material was difficult to dye with sulphur dyes [112] because large non-reduced molecules of the solubilised sulphur dyes could not penetrate into the lyocell fibres. These dye molecules remained on the surface and were subsequently easily removed during washing.

In 2007, Avanish, et al applied vat dye (C.I Vat green 5) on cellulose pulp by exhaust dyeing process [113]. The dyed pulp was mixed with the undyed pulp at a ratio of 1:4, then dissolved in NMMO solution and spun to obtained ‘spun-dyed’ lyocell fibres. The dyeing behaviour of the pulp and the fastness properties of the spun-dyed fibres were compared with different cellulosic substrates such as cotton (woven fabric), lyocell (woven fabric, knitted fabric, yarn and undyed spun fibres). These substrates were dyed with the same vat dyes, using the same methods of dyeing. It was observed that the cellulose pulp gave the highest degree of dye exhaustion as compared to the lyocell fabrics (woven and knitted), yarns, fibres, and woven cotton fabric. The spun dyed lyocell fibres exhibited superior light fastness when compared to the conventionally dyed cotton and lyocell substrates. The spun-dyeing process was claimed to lower the costs and to be more eco-friendly. However, it is difficult to market spun dyed filaments because of the uncertainty involved in the prediction of colours in fashion.

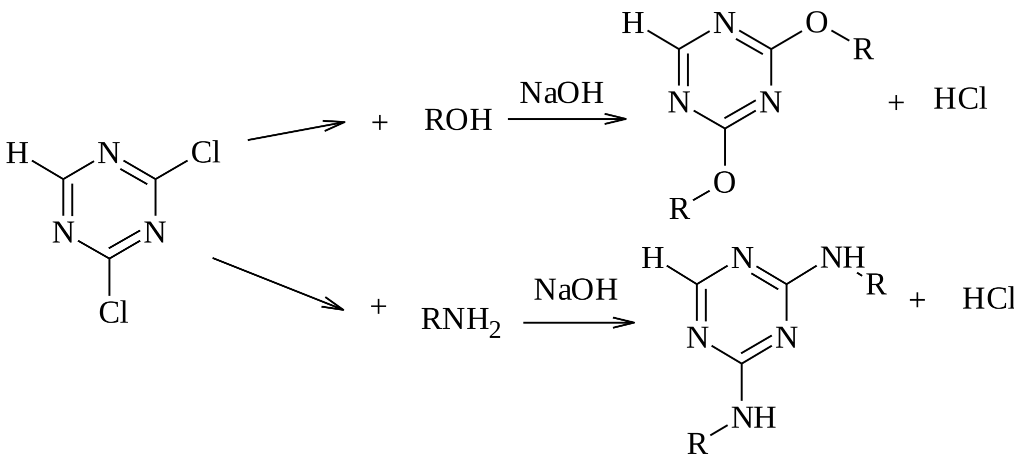
3.2.2 Reactive Dye

Reactive dyes cover a full range of bright shades, with good to excellent wash fastness, moderate to good light fastness [114]. This class of dye is mostly used to dye the cellulosic fibres, however, appropriate functional group of reactive dyes is used for wool, and man-made fibres.

It was discovered by Ratee and Stephen [115] after 1954, that dye containing a dichlorotriazinyl or 1,3,5-triazinyl [116] group could form a covalent bond with the amine and hydroxyl group of an amide and cellulose fibres respectively at suitable pH and at moderate temperature between 20 – 100 ^{0}C. Procion MX was the first reactive dye launched by ICI company [115] in 1956.

Initially, reactive dyes had many problems, such as 50% of cost was consumed on its washing-off (after dyeing) and on the treatment of resulting effluent. These problems were later overcome by the introduction of aminoflurotriazine dyes, bis-functional system and phosphonic acid reactive dyes can be fixed under hot, dry, and acidic conditions [117].

The major problem of reactive dyes is their hydrolysis. As shown in Scheme 3.3, they react with the hydroxyl groups of cellulose fibres. During dyeing process both the cellulose and dye are in contact with water. The cellulose and water both contains hydroxyl groups; if the dye reacts with the hydroxyl groups of water, then it is no longer able to form a covalent bond with the cellulose and the dye. The fibre then absorbs the dye as a direct dye with more or less affinity, which runs-off during a washing-off process. Such a type of dyeing reaction is called hydrolysis. Figure 3.4 shows the possibility of hydrolysis of reactive dyes during dyeing process with cellulose fibres and water [115].



Scheme 3.3 Reaction of dichlorotriazine with hydroxyl and amine

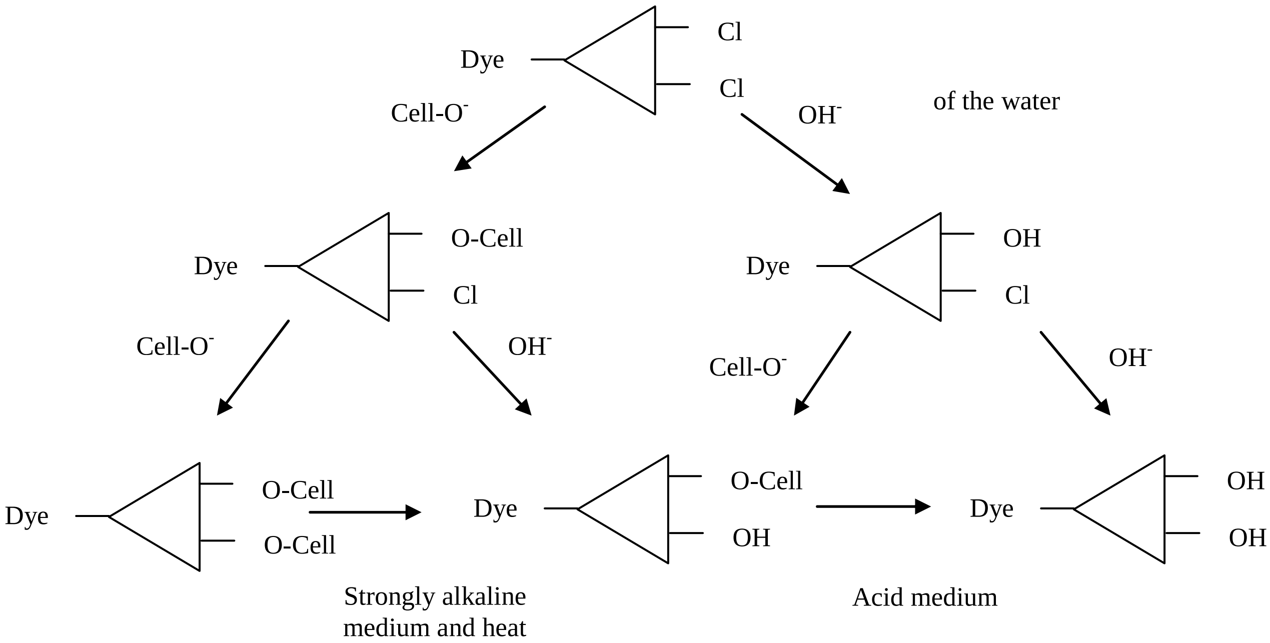


Figure 3.4 Reaction of reactive dyes with cellulose and water

An ideal or environmental friendly condition of dyeing is achieved when 75 - 90 % or even 100 % of dye molecules are fixed and less than 10 - 25 % is hydrolyzed [114]. The efficiency of fixation is not only the requirement for achieving good dyeing results; other factors such as levelness are also important. The behaviour of reactive dyes transferring from the fibre to water interface to the interior of the textile substrate depend primary on three processes, namely absorption, diffusion, and chemical reaction as shown in Figure 3.5. Absorption is the transfer of the dye from the solution phase to the fibre phase, at the fibre surface. The diffusion of the dye means movement of dye molecules from the fibre surface to the interior of the fibre. Finally, the formation of bonds between dye and fibre represent the fixation or the chemical reaction. These three phases of reactive dyeing determine the dye levelness, dye penetration (the spatial distribution of the fixed dye throughout the yarn cross-section) and dye uptake (the ratio of fixation of dye to hydrolysis) [103].

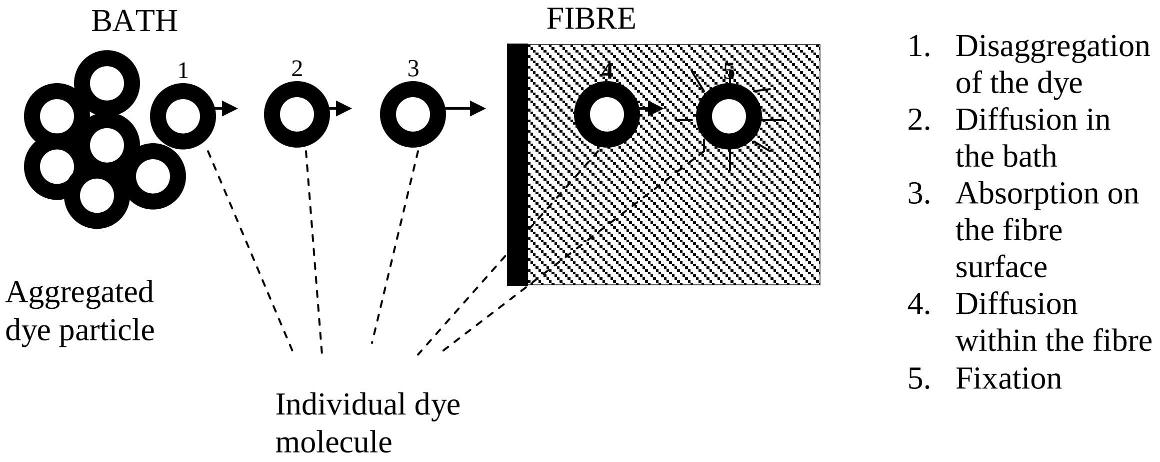
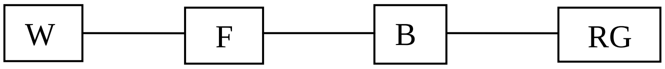


Figure 3.5 Dyeing phase

The typical reactive dye molecule consists of four components, which are as listed below [116];

- Reactive system.
- Chromogen.
- Bridging group.
- Water solubilising group.

In some case the reactive groups is attached directly i.e without a bridge, to the chromophore system as shown in Figure 3.6.



W = water solubilizing group, F = chromogens, B = bridge link, RG = reactive group.

Figure 3.6 Reactive dye molecules

3.2.2.1 Reactive Group

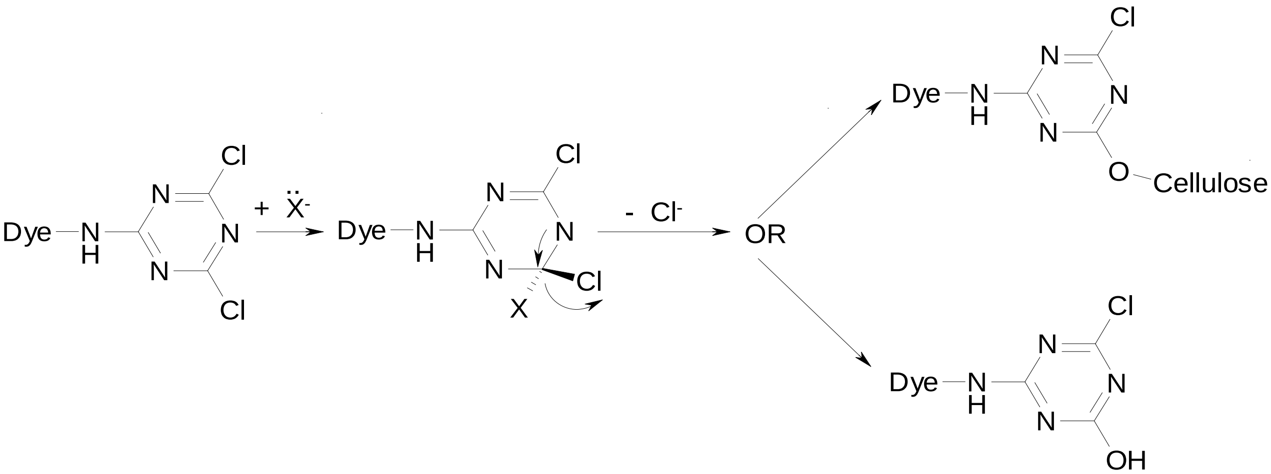
The reactive group forms a covalent bond between the dye and the fibre. There are two main types of reactive groups most commonly applied on cellulosic fibre;

- Triazine (mono or di chloro) group, which reacts by nucleophilic substitution.
- Vinylsulphone group, which reacts by nucleophilic addition.

A reactive dye molecule containing one reactive group is called mono-functional reactive dye. Dyes containing two or more reactive groups are called bis or multi-functional reactive dyes. If a bis-functional dye contains same reactive groups, it is called a homo bis-functional reactive dye otherwise it is a hetero bis-functional reactive dye. The reactivity of reactive dyes and its application procedure depends on the number and type of functional groups present in the molecule.

3.2.2.1.1 Triazine (mono and di-chloro)

In heterocyclic reactive dyes, such as dichlorotriazines the ring nitrogen atoms because of their high electronegativity provoke an electron deficiency in the adjacent carbon atoms. These carbon atoms are attacked by a nucleophilic group such as cellulosate anions [116, 118] or a hydroxide ion (X-), causing nucleophilic replacement or esterification [103, 115], as shown in Scheme 3.4.



X- is the OH- or O-Cell-

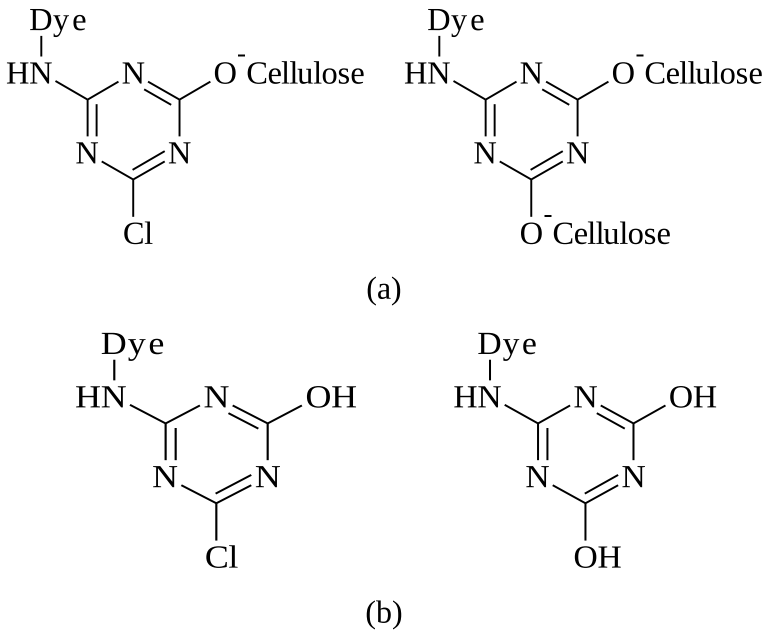
Scheme 3.4 Nucleophilic substitution reactions of s-triazine dyes

The reactive dye reacts with the dissociated hydroxyl groups (OH) of the cellulosic fibre [115]. There are three OH groups in each repeating unit of cellulose, one is a primary alcohol and the other two are secondary alcohol groups. In the presence of alkali, even dilute alkali, the cellulose acts as a weak acid and ionizes as shown in Scheme 3.5.

$$Cell - OH + OH^{-} \longleftrightarrow Cell - O^{-} + H_2O$$

Scheme 3.5 Formation of cellulose anion

The cellulosate ion and hydroxide ions are negatively charged and act as nucleophilic reagents [114]. Scheme 3.4 and Scheme 3.6 (a) shows the reaction of reactive dyes with cellulose fibres. Scheme 3.6 (b) shows the possibilities of hydrolyzed reactive dyes in which nucleophiles are lost during dyeing process.



Scheme 3.6 (a) Dye reacted with fibre, (b) Hydrolyzed reactive dye

Dicholortriazine dyes are highly reactive and can be applied at a temperature of 30-40ºC and at pH 10.5 in the exhaust dyeing process [119]. The small chromogens ensure the transformation of dye on the fibre during exhaustion stage. That is why they are suitable for bright dyeing with tertiary shades, even by using polyazo chromogens (large molecule) [118].

When a DCT dye reacts with an amine at temperature of 25 - 40 ºC one of the chlorine atoms is replaced to form a less reactive MCT dye [118]. MCT dyes are applied in the same process as DCT dyes, but at different temperature and pH. They are applied at 80 ^{0}C and at slightly higher pH 11. For textile printing MCT dyes are most commonly used, during printing, the dye-fibre bonds are formed at a temperature of 100°C by steaming.

A high exhaustion and fixation of 70 - 80% is expected using bis-functional MCT dyes because of the presence of two chlorotriazine groups. Procion H-E is the famous brand of reactive bis-functional dye.

When the K/S value of fibrillated and non-fibrillated dyed twill (2/1) lyocell woven fabric was compared using the Procion Orange H-ER (bis-MCT) showed similar K/S value [12]. This is because Procion Orange H-ER is very flexible and can rotate through its central structure, allowing geometrical u-shaped transformations in either direction. The molecule has a greater propensity to find a nucleophile in the cellulose to form covalent bonds and undergo cross-linking. Similar Procion Orange H-ER, Cibcron Navy W-B is also a bis-functional MCT. However, Cibacron Navy W-B has a rigid naphthalene ring and associated hydrogen bonding of an azo and hydrazone moieties, cause the dye to be comparatively inflexible, maintaining a planar geometry. The result [12] showed Cibacron Navy W-B gave lower K/S value as compared to Procion Orange H-ER. However, its visual depth was improved, less light scattering or greater reflection after removing the surface fibrils using enzymes.

The fibrillation tendency of lyocell fabric after dyeing by bis-MCT and bis-vinyl sulphone reactive dyes were assessed using the wet abrasion number, NSF (Nass-Scheuer-Festigkeit). The higher the mean values of NSF means more resistance to fibrillation [119]. The bis-MCT functional reactive dyes such as Procion Orange H-ER when applied on lyocell fibre at 5% owf gave NSF mean value of 73, Procion Yellow H-E4R at 8% owf gave NSF mean value of 145, Evercion Red H-E3B and Procion Navy H-ER at the same dye conc (8% owf) gave NSF mean values of 136 and 90. The NSF mean value of Remazol Black B (bis-vinyl sulphone) at 8% owf gave 371, higher than the bis-MCT functional reactive dyes. Hence, bis-MCT functional dyes, when applied on lyocell materials showed inferior cross-linking as compared to the Remazol Black B reactive dye.

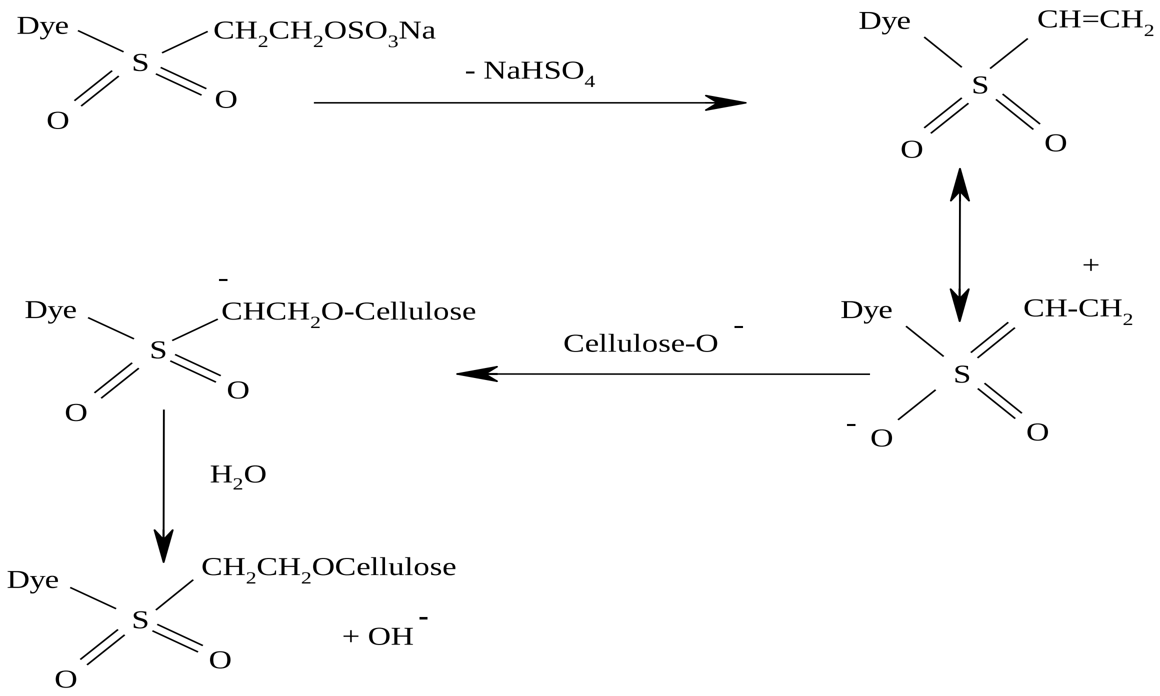
The chlorine atom is most commonly used as the leaving group in heterocyclic group systems, while some others are bromine atoms, cyano, azido and trichloromethyl groups, 2-nitro-4-sulphophenoxy and 2,4-disulphophenoxy groups, 2,4-dinitrothiophenoxy, thiocyanato and sulphonic acid groups and a variety of other sulphur, carbon and phosphorous derivatives are used. These reactive dyes are not commercialized except quaternary ammonium, sulphone and fluorine.

3.2.2.1.2 Vinyl sulphone Group

Vinylsulphone is the second major reactive group of reactive dyes. Vinylsulphones are different from halogenoheterocyclic groups because they react by a nucleophilic addition mechanism rather than nucleophilic substitution mechanism.

The ß-sulphatoethylsulphone group under alkaline conditions eliminates sodium bisulphate (sodium hydrogen sulfate) producing a vinyl sulphone group. In this group, the carbon-carbon double bond is polarized by the powerfully electron-attracting sulphone group (Scheme 3.7). This polarization imparts positive character on the terminal carbon atom, allowing nucleophilic addition of either cellulosate anion or a hydroxide ion. Addition of a proton completes the dye-fibre reaction [103, 115, 118].

The reactivity of vinyl sulphone groups is in between the mono and di-chloro-s-triazine reactive dyes. They can be applied at a temperature of 50 - 60 ^{0}C by exhaust method, depending on pH. Optimum shade reproducibility and fixation of dye in exhaust dyeing can be achieved by controlling the liquor ratio, temperature, pH, amount of salt and alkali [114].



Scheme 3.7 ß-elimination of ß-sulphatoethylsulphone to vinyl sulphone and reaction with cellulose

Bis-functional vinyl sulphone reactive dyes can act as a visible cross-linking agent. As discussed in Chapter 2, lyocell fibres are fibrillated in wet state, giving unfavourable fibre and fabric appearance, and durability. The fibrillation tendency can be controlled by cross-linking the fibrils. The bis-functional reactive dyes comprises two different reactive groups which not only develops higher wet fastness, better exhaustion and fixation percentage, but also helps to cross-link cellulose chain [68]. In this case, bis-functional reactive dyes are well-known cross-linking agents and minimize fibrillation tendency of lyocell fabrics. C.I Reactive Black 5 (bis-functional vinyl sulfone) minimize the fibrillation as compared to the other reactive groups such as MCT and bis-functional MCT reactive dyes [15, 68].

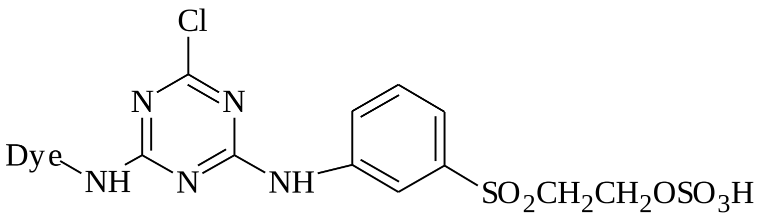
C.I Reactive Black 5 considerably increased the wet abrasion resistance of dark shade (70 g l^{-1}) compared to the medium shade (35 g l^{-1}) dyed and undyed fabric applied by cold-pad-batch (semi-continuous) dyeing method. Houng [15] believed 35 g l^{-1} medium shade of dyeing was sufficient to cross-link the lyocell fabric in order to improve the pilling resistance of lyocell fabric. Nicolai et al [68] found that higher the concentration of dye and temperature (up to 80 ^{0}C) the more cellulose fibres cross-linked. Higher dyeing temperatures favour dye diffusion into the fibres, creating better conditions for cellulose to cross-link. Bis-vinyl sulphone dyes are more efficient cross-linking agents and will make a bridge between the fibrils, causing them to ‘zip up’ [119].

Reactive dyes have the same electrophilic groups present in many effective cross-linking agents for lyocell. Sandospace R (DCT) is a colourless cross-linking agent, and with other reactive dyes such as Remazol Black B (bis-SES), Everzol Orange GR (DCT/SES), Everzol Red BS (MCT/Bis-SES), Novacron Red C-2G (MCT/bis VS) and Chloranyl Orange MX-2R (DCT) was applied by exhaust dyeing method [120]. The cross-linking tendency was measured using the wet abrasion NSF (Nass-Scheuer-Festigkeit method) on Delta 100 instrument. The Sandospace R on Tencel LF and A100 improved the cross-linking but decreased the depth of colour when applied separately from reactive dyes. However, when it was applied with reactive dyes, it improved the depth of colour. The mono-functional dyes were unable to cross-link the fibres and to improve the NSF value. The functionality of bis and tris-functional reactive dyes depends on the dye geometry, substantivity, position and molecular rigidity. The difference in dye size has an influence on their cross-linking potential. The bigger the dye size, the more is the obstruction of dyes movement within the fibres and the more are the restraining forces between dye and fibres as compared to the small dye molecule size. Dyeing at 60 ^{0}C decreased cross-linking and enhanced the hydrolysis of reactive dyes. Tri-functional reactive dyes improved the cross-linking more than bis-functional dyes such as Remazol Black B and Chloranyl Orange MX-2R [120].

In addition, cross-linking of cellulose chain depends on the internal mobility of the chromophore. For example, a polynuclear condensed aromatic system is a highly rigid structure compared to an azo group, relatively low rigidity molecule. If the second reactive group is not bonded anywhere because of steric alignment of chain or dyeing conditions, it is generally induced the hydrolyze of reactive dye [119].

3.2.2.1.3 Chlorotriazine and Vinyl Sulphone Reactive System

Chlorotriazine and vinylsulphone reactive groups (as shown in Scheme 3.8) give higher fixation. The dyes have bright shades and are easy to apply on cellulosic materials at moderate cost. The greater reactivity of the vinyl sulphone group and high substantively of tri-s-azine group gives high dye fixation with the fibres. The ß-sulphatoethylsulphone grouping can be introduced into a wide range of chromogens [118].



Scheme 3.8 Chlorotriazine and vinylsulphone reactive group

3.2.2.2 Chromogen or Chromophore Group

The chromogen is the main part of the reactive dye and responsible for colour, substantivity, and affinity and fastness properties such as light, chlorine and bleach [116]. Examples of chromophors in reactive dyes are;

- Azo (mono and di)
- Anthraquinone, and
- Phthalocyanine group.

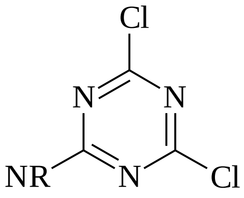
Metal-free mono azo chromophores are responsible for red, yellow and orange colours. Di-azo dyes are difficult to wash-off as compared to the mono-azo dyes but they give dark colours on fabric. Ruby, violet and navy colours are obtained with the mono and di-azo chromophores.

Anthraquinone dyes have relatively low substantivity and are easy to wash-off. The phthalocyanine group diffuses slowly and such dyes are difficult to wash-off [121]. Bright blue to turquoise colours are obtained with anthraquinone and phthalocyanine chromophores.

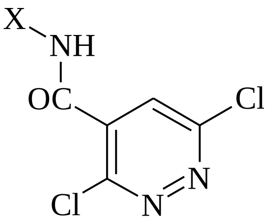
3.2.2.3 Bridge Link

The bridging group links the reactive systems to the chromophore groups. The bridging group has an influence on the reactivity and other dyeing characteristics. The influences of bridge link on the reactivity of reactive dyes are as follows:

The dissociation of amino bridge (-NH- →-N-) in the following Scheme 3.9 and Scheme 3.10 causes the reduction in the reactivity of the reactive group by power of ten, leading to lower fixation.

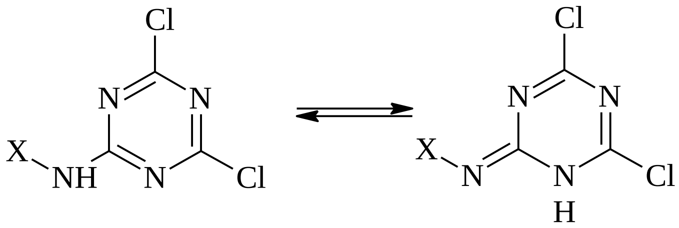


Scheme 3.9



Scheme 3.10

As shown in above Scheme 3.9 and Scheme 3.10, proton of an amino group has tendency to switch with the one or several isomers containing proton at the heterocyclic nitrogen atom (by single and adjacent double bond) as shown below (Scheme 3.11). This switching is called tautomeric form, the amino bridge links have rapid tendency to undergo tautomeric equilibrium, which lower the reactivity of cellulose and water respectively. The length and flexibility of the amino bridge such if replaced by α,ω-diaminoalkylene chain (-NH-[-CH_2-]n –NH-) link also effect the reactivity.



Scheme 3.11

The amino link has an influence on the stability of a reactive dyes because the bridge link can be broken, causing the breakage of dye-fibre bond.

3.2.2.4 Water Solubilizing Group

Reactive dyes are water soluble. They contain one or more ionic sulphonate or sulphonic acid (sodium salt) groups [111, 116, 117]. The solubilizing groups are located in the chromogen part of the dye and occasionally in the fibre reactive group.

For cellulosic and wool fibres dyeing solubilising groups are required but for nylon fibre dyeing, they are not essential [116].

3.3 Dyeing Method

For dyeing textiles materials, two methods are most commonly in used as listed below;

- Exhaust or discontinuous dyeing.
- Continuous dyeing.

Raw fibres and yarns are dyed by the exhaust dyeing method, whereas fabric can be dyed by either the exhaust or the continuous dyeing methods. The choice of dyeing method depends on the volume of the material to be dyed, particular shade, type of dye, dye reactivity and substantivity, and cost.

3.3.1 Auxiliaries used for Reactive Dyeing

For dyeing Tencel fabrics using the reactive dyes other chemicals in addition to dye are required. These chemicals are known as dye auxiliaries such as wetting agent, alkali, salt etc. A wetting agent is used to increase the wetability and penetration of dye in exhaust and continuous dyeing processes [115].

The dye-fibre covalent bond is formed in the presence of alkali. Soda Ash (98% anhydrous sodium carbonate) is most commonly and widely used alkali for reactive dyeing, while other recommended alkalis for reactive dyeing are sodium bicarbonate, sodium silicate, and sodium hydroxide. Sodium bicarbonate is a mild alkali and has maximum 4 hours stability of dye bath solution. Sodium carbonate is a stronger alkali and diminishes dye stability;

however the stability of actual dye also depends upon its chemical nature. Sodium silicate is a strong alkali used for very dark shade and requires an automatic mixer for mixing in the dye bath solution [115]. It is usually recommended for the pad-batch dyeing method.

Sodium-m-nitrobenzene sulfonate in continuous dyeing protects azo reactive dyes from reduction which may occur because of the alkali and aldehydic groups in the cellulose.

3.3.2 Exhaust Dyeing

Tencel woven and knitted fabrics can easily be dyed by exhaust methods because of the higher temperature and longer times of dyeing used [115]. However, temperature, time, pH and the amount and type of auxiliaries are varied depending on the nature of the reactive groups, chromophore groups and depth of shade. In all cases the liquor to goods ratio must be small to give high yield of colour strength.

In exhaust dyeing methods, the reaction between the dye and fibre occurs when the dye has been absorbed into the cellulose material. In case of reactive dyeing the efficiency of fixation depends on the relative concentration of dye absorbed into the substrate to the relative amount of dye left in the dye bath. In addition, the reactivity of reactive groups, substantivity, and diffusion of dye in the substrate, liquor ratio and surface area of the substrate available for absorption are also considerable factors. Tencel fabric has excellent reproducibility and has minor influences of process variables such as temperature, salt and alkali concentration, liquor ratio, in case of exhaust dyeing method [11].

In 2004 Ahmed et al [122] compared the dyeability of Tencel and Tencel alloy fabrics using Procion Crimson H-EXL, Procion Yellow H-EXL, and Navy H-EXL, Procion Rubine XL+ and Ciba reactive dyes by exhaust method of dyeing at 0.5 and 2% owf dye shade. The results showed that Tencel alloy fabrics, because of their porous structure, gave high colour yields and slightly low fibrillation, as compared to the 100% Tencel woven fabric.

The neutral-exhaustion dyeing of aminated lyocell fabrics, with low, medium and high reactivity of reactive dyes [123], in the presence of salt, was performed by exhaust method.

In this method all the dyeing were carried out at 2% owf, at a liquor-to-goods ratio of 10:1. Neutral dyeing with the high reactivity DCT dye, Procion Yellow MX-3R, showed higher colour yields than for both Remazol Yellow 3RS and Procion Yellow HE-4R, on all pre-treated lyocell fabrics.

With respect to the conditions required to control the uptake of reactive dyes, there are three categories [117]:

- Alkali-controllable reactive dye.
- Salt-controllable reactive dye.
- Temperature-controllable reactive dye.

3.3.2.1 Alkali-controllable Reactive Dye

- Optimum temperature at 40 – 60 ºC is required for fixation.
- Low exhaustion in neutral salt solution before addition of alkali.
- Care is required during alkali dosing and it has high reactivity.
- Examples: dichlorotriazine, chlorodifluoropyrimidine, dichloroquinoxaline or vinylsulphone reactive systems.

3.3.2.2 Salt-controllable Reactive Dye

- The fixation occurs at temperatures between the 80 ºC and boiling (100°C).
- High exhaustion is obtained at neutral pH, therefore electrolytes are added carefully portion wise.
- Low reactivity.
- Examples: trichloropyrimidine, aminochlorotriazine or bis(aminochlorotriazine). Aminofluorotriazine.

3.3.2.3 Temperature-controllable Reactive Dye

- In this method of dyeing the dye-fibre bond is formed at temperatures ranging from 80 ^{0}C to more than 100 ^{0}C, in the absence of alkali.

- This method has self-levelling characteristics.
- Controlled temperature is required.
- Examples: bis(aminonicotinotriazine) Kayacelon react (KYK).

3.3.3 Continuous Dyeing Methods

The short liquor ratio of exhaust method of dyeing favours the semi-fully continuous dyeing. In exhaust dyeing, slow fixation helps to improve the penetration, levelness and controlled diffusion, while rapid fixation is favourable for economy and productivity. The excellent solubility, moderate substantivity, and versatile reactivity of the various ranges of reactive dyes give great potential in continuous dyeing. Reactive dyes have all the attributes required for semi-fully continuous dyeing [117, 121].

Continuous dyeing is a simple process for dyeing textile goods, and can use either one dip and nip or double dips, and nips in the dye and chemical bath solution together or separately, with or without intermediate drying steps. The single dip and nip is preferred because it minimizes the tailing problem. Tencel fabric gives a negative tailing behaviour meaning it has a 7% shade variation [11].

In continuous dyeing methods fabric can be dyed at low liquor ratio, so there is less need of changing the trough containing dye liquor. The mangle or padder pressure is set with respect to pick-up 60 - 80%. Continuous dyeing has high productivity; because of less dwell time after impregnation of fabric and less time (few minutes) is required to fix the dye in the fabric.

Dye fixation and colour yield depends on the fixation method such as steaming, curing and batching and also on intermediate drying. Drying by infrared radiation [124], particularly of shorter wavelengths, enable the dye to penetrate into wet cellulose fibres. This effect is at least partly responsible for the suppression of dye solution migration to the yarn surfaces during the initial stages of drying. Infrared fixation produced dyeing with higher fixation yields (80 to 98%) than when using hot air alone and gave colour yields close to those obtained by cold fixation (pad-batch process) without any drying, for which migration is presumably absent. It is therefore tempting to relate the higher fixation yields obtained using infrared radiation to the suppression of the dye migration, indicated by the lower colour yields. It seems obvious that migration of the initial dye solution out of the cotton fibres pores toward the yarn surfaces, where most of the water evaporation is occurring during the constant rate drying period, would result in less dye reacting with the cotton and a higher proportion of the fixed dye at the yarn surface. In a preliminary dyeing trial with Drimarene Red X-6BN, using infrared pre-drying followed by hot air fixation, the fixation yield was 76%, intermediate between those for fixation exclusively by infrared (82%) or hot air (72%). This result suggests that migration suppression is, in fact, at least partly responsible for the higher fixation yields obtained by infrared heating [124].

The following are the advantages of continuous dyeing process:

- Low capital cost of equipment.
- Low consumption of energy and water.
- Excellent reproducibility.
- Easy to control the dye-cellulose and dye-water reaction rates.
- Can be batch 1000 - 10000 m of fabric more than the exhaust dyeing.
- More economical.

3.3.3.1 Pad-Batch

Tencel fabric when dyed by the pad-batch method of dyeing using dyes from Ciba and DyStar, had high dye uptake as compared to the modal and the viscose fabrics [11].

The pad-batch method is very simple and consists of following steps:

- Impregnate the pre-treated fabric in the dye bath liquor at certain temperature.
- Pass the fabric between the mangle nip in order to squeeze any surplus liquor.
- Wrap the wet fabric on a rod or beam and cover it with a polythene bag for a specified time, at particular temperature, depending up on the reactivity of dye.

- The prolonged exhaustion allows the dye to fix on to the fabric, the hydrolysed dye is then washed out during washing process [118].

Dyes of high reactivity are preferred, which helps to minimized the dwell time to as short as 2 - 4 hrs. The dyes are applied at low pH, they are easy to wash-off, have high stability in dye liquor, easy to mix bis-functional (chlorodifluoropyrimidines, dichloroquinoxalines [125] and aminofluorotriazine-vinylsulphone reactive dye [126]) and have excellent fixation and fastness. Dyes of low reactivity require longer dwell time (16 - 24 hrs) at higher pH. The dwell time depends on the swelling behaviour of textile fibre.

3.3.3.2 Pad-Dry-Thermosol

The pad-dry-thermosol method is used occasionally in place of pad-steam process. Intermediate drying at 110 to 120 ^{0}C for 1 - 2 min, and baking at 150 ^{0}C for 3 min is necessary for the formation of the dye-fibre bond [117]. Dichlorotriazine was the first dye type used for pad-dry-bake process with 10 g l^{-1} sodium bicarbonate. Highly substantive dyes containing highly reactive systems are preferred because it is easier to migrate the dye molecules into the fabric.

Urea is a dissolving agent, disaggregating agent and swelling agent for cellulose fibre, and is also hygroscopic agent. It enhances colour yields, speed up diffusion, and improves the levelness of dyes, particularly with viscose fabric. It is essential for pad-dry-bake process because it minimizes the migration of dye molecules during drying stage. The cheap and easily available urea has a disadvantage of being non-environmental friendly. It is being replaced by dicyandiamide [127], tri-methyl or tetramethylurea, or poly(ethyleneglycol).

3.3.3.3 Pad-Steam and Pad-Dry-Steam

Pad steam and pad-dry-steam methods of dyeing are suitable for aminofluorotriazine and selected sulfatoethylsulfone dyes. The steaming temperature and time depend on the type of reactive dyes. Steaming at 102 ^{0}C for 1 min is suitable for minimizing the migration problems and level dyeing. Pad-steam process is suitable for dyeing the light shade cellulosic fabrics.

3.3.4 Washing-off Treatment

After dyeing the substrate has unfixed hydrolyzed dye and some residual active dye. The presence of this dye causes low wet fastness properties until these are removed from the substrate. Smaller the proportion of unfixed dye and the weaker the substantivity forces, the easier it is to wash-off. Hot rinsing at 60 – 70 ^{0}C is recommended for optimal desorption of hydrolyzed dye. An initial rinsing lowers the concentration of electrolytes by progressive dilution and thus lowers the substantivity of the residual loose dye. The repeating washing process removes all hydrolyzed dye [117].

3.4 Light Fastness

The fastness of light of dyed fabric depends on the inherent resistance of the dye chromophore to photochemical attack and the chemical nature of the polymer substrate. Anionic groups (sulfo, carboxyl) confer higher light fastness. Electron donating groups (amino, methylamino, hydroxyl, methoxy) in the meta-position are highly susceptible to photo-oxidation than substituent in the 1- or 4-position.

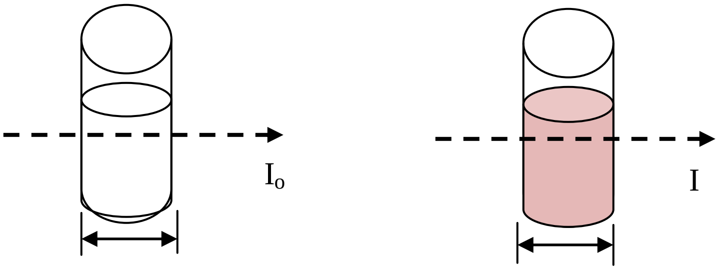
3.5 Wet Fastness

The wet fastness such as washing or perspiration is a function of diffusion and affinity effects of dye. It has an effect on the bond between the dye and fibre such as hydrogen bonding [118].

The fastness to washing according to the standard ISO CO6/C2 on Tencel fabric dyed by using dichlorotriazinyl reactive dye could be analyzed by using 2 g l^{-1} Na_2CO_3 without surfactant [128].

3.6 Absorbance

The amount of dye exhausted and fixed in the textile substrate can be determined by using UV-Visible spectroscopy. The method is based on the Beer and Lambert law. When a dye is in solution the absorption of light is determined by comparing the intensity of an incident beam of electromagnetic radiation I_o, when no dye is present, to the intensity of the transmitted beam I, when dye is present as shown in Figure 3.7 [129, 130].



(a) (b)

Figure 3.7 a) Solvent only and b) Dye in solution

The greater the absorption of the dye the bigger will be the ratio I_o/I. and the logarithm of this ratio is known as absorbance 'A' (Equation 3.1).

$$A = \log_{10} \frac{I_0}{I}$$ Equation 3.1

The Beer-Lambert law of absorption stats that "the proportion of light absorbed depend on the thickness of the absorbing layer (l) and on the concentration of the absorbing substance in the layer (c)". Mathematically, this can be defined as (Equation 3.2) [129, 130]

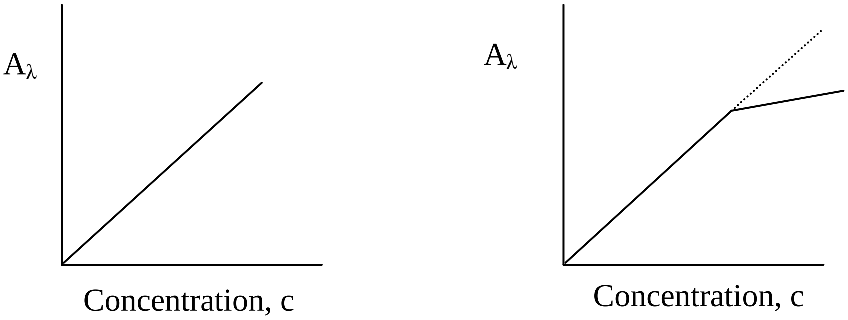
$$\begin{aligned} &A \propto l \\ &A \propto c \\ &A_\lambda = \varepsilon_\lambda c l \end{aligned}$$ Equation 3.2

The ε_λ is a constant and known as absorptivity, molar absorptivity or molar extinction co-efficient, when the concentration is measured in mole/litre and path length (l) in decimeter.

Hence, the intensity of transmitted beam I can be calculated as shown in Equation 3.3.

$$\begin{aligned} &I = I_o 10^{-A} \\ &I = I_o 10^{-\varepsilon c l} \end{aligned}$$ Equation 3.3

The concentration of dye solution can be determined by measuring the amount of light that a sample absorbs and applying Beer-Lambert law. If the absorptivity co-efficient is not known, an unknown concentration can be determined using a calibration curve of absorbance versus concentration, derived from standard of known concentration.



(a) (b)

Figure 3.8 Absorbance versus concentration

The straight line or slope in Figure 3.8 (a) is the absorptivity co-efficient at a path length l. The Figure 3.8 (b) shows deviation from a straight line. The deviation is because of the limitation of Beer-Lambert law due to chemical and instrumental factors. The following are the cause of non-linearity or limitation;

- Scattering of light due to the particulates in the sample or improper preparation of solution in the cuvette, and cracks or damage cuvette.
- Non-monochromatic radiation.
- At high concentrations (>0.01M), the absorbance value is not true because the perturbing effect of solute molecules on their neighbours affects the value of ε.
- Solutes involved in chemical equilibra that is, association, dissociation or complex formation show marked spectral changes with concentration. In extreme cases new absorption bands can occur.
- Stray light reaching the detector will cause the absorption to appear less than its true value and is independent of concentration.

3.7 Kubelka-Munk Theory K/S

K-M theory was introduced in 1930s, [131, 132] and most widely used in colour industries. The results of the analysis relate the absorption (K) and scattering (S) co-efficient in a surface to the reflectance of the surface (Equation 3.4):

$$\left(\frac{K}{S}\right)_{\lambda} = \frac{(1-R_{\lambda})^{2}}{2R_{\lambda}} \qquad \text{Equation 3.4}$$

On textile fabrics it is assumed that the absorption (K) occurs by the dye only and scattering (S) by the textile fibre. The rays of light are not only reflected at the coloured layer surface but some are refracted and internally reflected. The K/S value is proportional to the concentration of the dye and it is measured in the visible spectrum. The K/S value at maximum wavelength represents the maximum colour intensity of the dyed sample.

3.8 Integ

The perception of colour or its depth is varied by the light under which it is viewed and the visual system. Garland, 1937, introduced 'Integ' technique to measure the depth of colour of a textile substrate [5]. In this technique $(K/S)_{\lambda}$ is weighted by the product of illuminant energy (E_{λ}) and the sum of the CIE colour-matching functions $(\bar{x}_{\lambda} + \bar{y}_{\lambda} + \bar{z}_{\lambda})$at the particular wavelength. Mathematically, Integ can be defined as [133] Equation 3.5.

$$I = \sum\left[\left(\frac{K}{S}\right)_{\lambda} (\bar{x} + \bar{y} + \bar{z})_{\lambda} E_{\lambda}\right] \quad \text{Equation 3.5}$$

The integ value I is proportional to the depth of dye, it is subjective assessment of the depth of shade of dye. As shown from the equation above, this technique is based on the measurement of reflectance (% R) of dyed sample. This method is very effective and widely used for assessing the colour.

3.9 Assessment of UFC using Image Processing

Uniformity of dyeing is the most important parameter of assessing the quality of finished textile goods. There are many difficulties in communication of level or uniform dyeing among suppliers, laboratories and manufacturers. Dye evenness in the finished dyed fabric is characterised by excellent dye penetration, level and uniform dyeing. These terms are given the same sense but they are different technically. The dye penetration is a measure of relative depth dye molecules penetrate into fibres of the fabric. Level dyeing is the uniform distribution of dye molecules usually measured on the surface of the dyed fabric. The term uniformity of fibre coloration (UFC) is closely related to dye levelness and penetration. It determines the uniform distribution of dye molecules with respect to the depth of colour into the fibres or filaments of yarns of the fabric. Dyed fabrics that have high UFC also have excellent dye penetration and levelness in and on the surface of the fabric.

Previously, dye evenness was assessed visually and depended on the expert decision. Later, instrumental analysis was developed using CIELAB values, which is still in use. The present era is more focus to assess the dyeing behaviour using image processing, which has been in used since 1960s [134]. Basically, image processing is the technique of manipulating and improving images using mathematical functions.

Dyeing levelness within a sample and between samples was assessed using K/S values, measured at different areas of the dyed fabric. The results were then statistically analysed. The degree of levelness was determined using empirical constant giving rating 1 to 5, where 1 means poor levelness and 5 means excellent levelness [135].

Cardamone et al [136] investigated level dyeing of union dyed blended (wool/cotton) fabric. Fabric images were taken and converted into a two dimensional function using a grey scale. The levelness of dyeing was assessed by the shape of histogram. The high, narrow, symmetrical shapes of histogram showed level dyeing and low, board, and skewed shapes showed unlevel dyeing. The levelness index and union shade index was then calculated using Gauss-Newton iteration algorithm based on standard deviation.

Gunay [137] investigated the difference in dye levelness of knitted fabric images using Python (computer language). The fabric image was converted into a grey image. These grey images was partitioned into a different grid size and then statistically analysed with respect to the numbers of pixels in rows and columns. The levelness was then reported as irregularity index. The level dyeing of shaded cut pile carpet [138] and dyed part of silk mat were also analysed using image processing and analysis technique. Using the same technology a system was developed to measure the colour fastness testing of dyed fabric with small pattern [134].

A cross-sectional study of a dyed fabric is one of the methods of analyzing the dye evenness. The cross-sectional images were prepared by different ways. Goswami [20] embedded the dyed fabric sample and then cut 6 µm using microtone. In another method [139] yarn was first stained using osmiumtetraoxide (O_SO_4), after embedding. The sample, 60 – 90 nm thick, was cut using ultra microtone. In all methods the dye penetration and change in cross-sectional shape of dyed fibres were assessed visually.

The dye diffusion and depth of cross-sectional images of Tencel, viscose and modal fabrics were analyzed using a dye penetrant (fluorescent brightening agent). The visible width of dyed ring of each fibre were measured manually using Olympus software [99, 140].

In case of printed fabric dye penetration was instrumentally calculated from the standard deviation of K/S values of face and back. The deviation was calculated from four to five K/S values measured at different area of the dyed fabric from each side.

It is revealed from the literature most of the methods of dye penetration and levelling were based on K/S values measured using a Spectrophotometer. It is very helpful instrument in defining the depth of dyed fabric and works on the principal of light reflectance and absorbance as discussed in Section 3.6 and 3.7.

When the Integ values were calculated using a Spectrophotometer, Figure 3.9 (a) has higher Integ values than Figure 3.9 (b). As shown in Figure 3.9 (a) the peripheral fibres of the yarn are heavily dyed and the central fibres of the yarn are undyed (white) indicating it has poor dye penetration as compared to the Figure 3.9 (b) which is more evenly penetrated and does not have any undyed fibres.

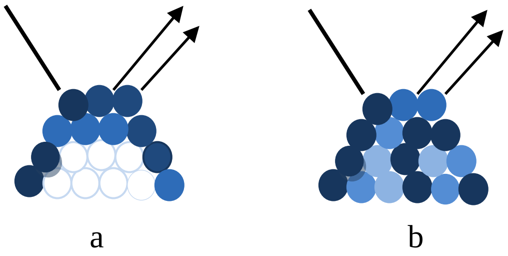


Figure 3.9 Cross-sectional image of dyed fibres

Hence, spectrophotometric methods fails to assess the dye penetration, however, it is a good representative of surface dyeing. Further, visual analysis of cross-sectional images is difficult as well as time consuming. Therefore, there is a need to develop a new method of assessment, which can measure the uniformity of the fibre coloration inside the filaments or fibres of the yarn of the fabric. In this method variation is quantitatively calculated using mean and standard deviation. The mean value defines the average intensity of the mono chrome image and standard deviation shows the variation of the depth of the fibres filaments of the yarn of the woven fabric. This method can assess the dye variation in any type of the fabric either woven or knitted.

CHAPTER 4: WOVEN FABRIC STRUCTURES AND THEIR INFLUENCE ON PROPERTIES

4 Woven Fabric Structures and their Influence on Properties

4.1 Woven Fabric

Woven fabric is produced by the interlacement of the warp and the weft yarns at right angles to each other [141] and its manufacturing process is termed weaving. The warp, a multitude of separate yarns, lies along the length of the fabric whereas the filling or weft yarns lie across the width of fabric, one length at a time [142] see Figure 4.1.

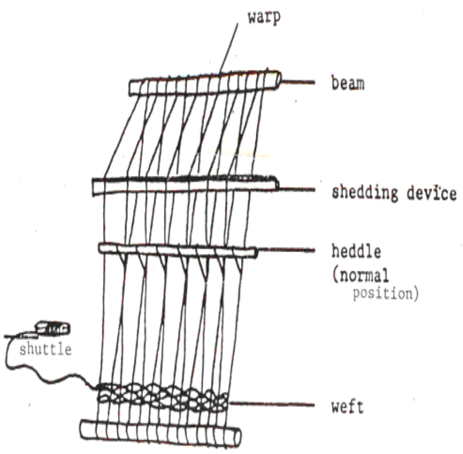


Figure 4.1 Weaving

Weave or weave repeat [141, 143] is the repetition of the small area of design in a fabric. It is usually represented by a point paper, in which vertical lines represent the warp yarns and horizontal lines represent weft yarns. Every square represents the cross-over point of one warp and one weft yarn, filled-in squares indicate warp yarn laid over the weft yarns and empty or un-filled square means weft thread is over the warp thread [141] as shown in Figure 5.1.

The manner in which warp and weft yarns are interlaced, is termed fabric structure [142]. There are several parameters which influence on woven fabric structure: raw material of warp and weft yarn, linear density of the warp and weft yarn, warp and weft yarn setting and fabric weave [144].

The fabric geometry was introduced by Peirce (1937) [145]. His theory [146] was based on two assumptions; firstly, to calculate the resistance of the fabric to mechanical deformation (in term of individual fibres) such as initial extension, bending or shear. Secondly, to determine the direct relationship of passage of air or light and also to calculate the maximum density of fabric [146]. He also analyzed the various changes taking place when the fabric was subjected to pre-determine extension or compression in given direction and even complete swelling in an aqueous medium. According to Peirce [145], the force exerted either by the warp yarns on the filling yarns or by the filling yarns on the warp yarns were equal. His theory was helpful to evaluate the fabric behaviour and properties.

Later, for ease of designers standard fabrics (the fabrics which were made of the same weave using the same yarn density [147]) were manufactured, that helped to predict the fabric properties, quality and performance with respect to their end use [147, 148]. For the reason that the fabric can be made from the same type of fibres, still different in yarn count, yarn spacing and weave but can possess the same fractional covering power [146].

Research on fabric properties has indicated that fabric weight, bending length, shear, tensile properties, dimensional stability, longitudinal compressibility are the important fabric properties in producing the suits and tailored garments with good appearance and stability [149]. It has been observed fabric lost its properties during processing (grey to finished tailored textile). Finishing process has more effect on wool fabric properties as compared to its construction, where the effect of fabric construction was pronounced in lightly finished fabrics [149]. The thickness of wet-treated Tencel fabric was decreased because of the fibrillation (splitting of fibrils into micro-fibres). In addition, the mass or weight of Tencel fabric was increased after wet finishing. This implies that the wet finishing process made the Tencel fabric heavier by enhancing its crimp formation and water absorption [150]. Weave structure with a high number of interlacing have lower shrinkage values. The lower yarn crimp values restrict the fabric shrinkage and result in better dimensional stability [151].

4.2 Fabric Parameters

For describing the fabric structure, it is necessary to describe the fabric parameters [141], which are as follows;

- The weave (plain and twill weave).
- Thread density.
- Coarseness or fineness of the yarn.
- Waviness of warp and weft.

4.2.1 The Weave

4.2.1.1 Plain Weave

Plain weave is the simplest type of weave. The interlacement of the ends and picks with each other produces a coherent structure to plain weave with maximum possible frequency of interlacing. In plain weave fabric yarns resist slippage and are not easily displaced [152]. It is the strongest fabric, and the strength of plain fabric is higher in warp direction than in weft direction [153].

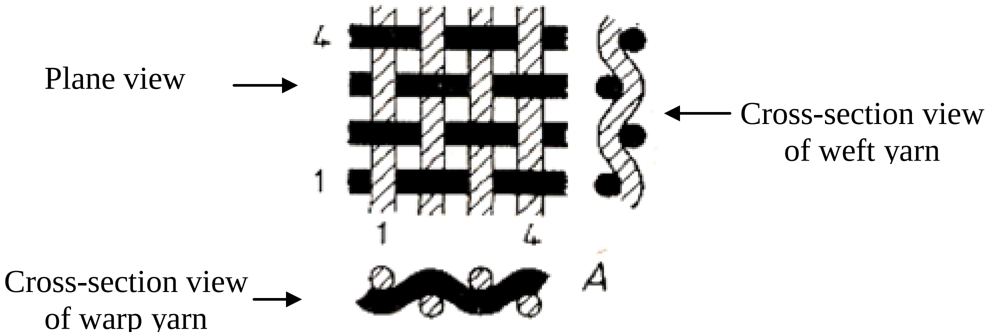


Figure 4.2 Plain weave representation

Shown in the above Figure 4.2, are four repeats of plain fabric both in the plane view and in the cross-section view. The yarns are seldom regular and the pressure between the ends and picks tends to distort the shape of the yarn cross-sections [152].

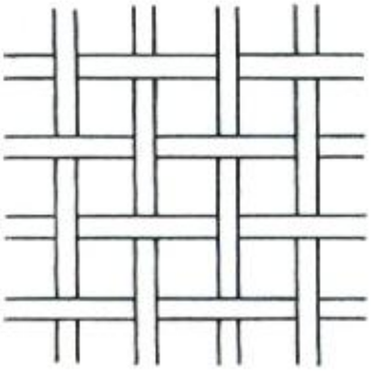


Figure 4.3 Diagrammatic representation of plain fabric structure

The plain fabric as shown in Figure 4.3, has the same number of warp and weft densities (linear and thread density) and has similar properties (cover factor, etc) depending on the type of fibres. If the warp yarn density is higher than the weft yarn or weft yarn density is higher than the warp yarn density or both yarns have different linear and thread density, all of these changes in weave structure cause the changes in geometrical and mechanical properties of fabric. Similarly, waviness of the yarn formed due to interlacement of warp and weft yarn also causes changes in fabric properties [141]. The plain fabric has higher yarn intersections points as compared to the twill fabric [149].

Seyam et al [148] found that plain weave cotton fabrics that were same in ends per cm but varied in picks per cm, were more stable in the warp direction as compared to the weft direction. A fabric which has low pick density could shrink (length side) during laundering. It is due to the space between the weft yarns caused it to swell and the fabric in warp direction to shrink as a result of the longer path needed for a warp yarn to passed under and over the swollen weft yarns. Swelling was more likely to occur in the loosely woven fabric than in tightly woven fabric [148].

There are two ways of classifying a plain weave, one is in terms of warp and weft cover factor and other is, by distinguishing the balanced and unbalanced structures. According to second way of classification plain weave is of two types [152]:

1. Balance plain weave.
2. Unbalance plain weave.

a. Difference in yarn count.
b. Difference in ends and picks per cm.
c. Difference in both a, and b.

4.2.1.1.1 Balance Plain Weave

Balance weave is also termed as square weave, in which the linear density and thread density of warp and weft yarn is the same. Hence, plain fabric has approximately the same warp and weft cover factor and crimp percentage. The square cloths have very wide range of weights and textures.

4.2.1.1.2 Unbalance Plain Weave

The unbalance cloths are further sub-divided under three headings.

- **Difference in yarn count**: The warp and weft yarn is different in cover factor due to the difference in linear density of warp and weft thread, while the ends and picks per cm are the same, such as in square sett.
- **Difference in thread density**: Again the cover factor of warp and weft of plain fabric is different because of the difference in ends and picks per cm, however, the count of both warp and weft yarn is the same.
- **Difference in yarn linear density and thread density**: When both count of warp and weft yarn and the ends and picks per cm are varied, cover factor will be varied hence this type of fabric is termed as an unbalance plain fabric.

However, in some cases warp and weft yarns have the same cover factor (K) but different linear and thread density, such as:

$$K = n / \sqrt{tex}$$

where,

n = number of ends or picks per cm.

Tex = linear density of warp and weft yarn.

$$K_1 = \frac{78}{\sqrt{36}} \qquad K_2 = \frac{52}{\sqrt{16}}$$

$$K_1 = 13 \qquad K_2 = 13$$

Both warp (K_1) and weft (K_2) has the same cover factor 13, but the ends and picks per cm is 78 and 52, similarly, count of warp and weft is 36 and 16 tex respectively. The above classification, based on balance and un-balance plain weave fabric uses all the requisite parameters such as yarn linear density, thread density and etc.

4.2.1.2 Twill Weave

Twill weave is categorized by the diagonal lines of warp and weft floats. These diagonal lines can be continuous lines such as in basic twill weave fabric, and can be broken or reversed for the derivatives of twill weave fabric. Hence they depend on the type of twill weave and its construction [154]. The smallest possible repeat of twill weave is 3*3 (ends*picks per cm). The total possible number of twill weaves is very large. The twill weave with respect to its construction can be sub divided into two types [154].

1. Balance twill weaves.
2. Unbalance twill weaves.

4.2.1.2.1 Balance Twill Weaves

The twill weaves that have the same number, size and distribution of the warp and weft floats are term as balance twill weave. The simplest twill weave is 2/2, Z or S twill (4 picks repeat), 2/2 means two ends are passing over two successive picks, under the next two picks and so on. Z or S indicate the direction of diagonal lines and differ in term of starting points or floats. Other balance twill weaves are 3/3 twill and 4/4 twill weave fabric, used for lining fabrics and in jacquard designing.

4.2.1.2.2 Unbalance Twill Weaves

When either warp or weft yarn floats predominate the weave is term as unbalance twill weave. The examples of unbalance twill weave are 2/1 twill, 1/2 twill, 3/1 twill, 1/3 twill and so on. In 2/1 twill fabric, warp yarns float dominate. Similarly in 1/2 twill, weft yarns float dominate, either in Z or S direction.

The angle of diagonals in a twill fabric is usually 45^0 and can be varied as the number of ends and picks are varied. If the number of ends per cm is higher than the picks per cm then the angle of diagonal is steeper than 45^0. An angle of twill weaves less steep than 45^0 is observed when the number of picks per cm is higher than the ends per cm. The twist of yarn also plays an important role in emphasizing the diagonal lines of twill fabric. If the direction of the fibres (twist) in either the warp or the weft yarns are opposite to the direction of twill the diagonal line of floats made by the warp or weft yarns are emphasized. When the twist direction of warp and weft yarns is the same, the twill weave is emphasized.

Fabrics made of the same linear and thread density with plain, twill and satin weave structures will differ in characteristics. The plain fabric is stiff in handle, identical on both sides of fabric, while the handle of twill fabric is intermediate between plain and satin weave and has identical face and back, mirror images of each other. Satin weave has pliable handle and one side of satin fabric seems to have entirely warp appearance and other weft appearance [141] .

When plain, twill and satin weave fabrics are composed of the same cover factor, then the rate of ultraviolet protection decreases in the order of satin < twill < plain fabric. Plain fabric has stable and uniform macro-pores as a consequence of higher thread density. While the pores of satin weave is un-stable due to the fewer thread passages or interlacing, and group together which further reduced the free space area [155].

Satin fabric had 30% more jet area and allowed fluid to pass easily as compared to the plain fabric at the same yarn density of monofilament. The plain weave has square or rectangular pores, twill 2/2 fabric has straight through pores because of diagonal pattern. In satin fabric pores are less numerous than in plain fabric, because of floating (four or five yarns per yarn is crossing over and under). As the yarn spacing increased, there was corresponding decreased in the velocity of fluid between the interstices and it increased in the size of the minimum cross-sectional area of stream tubes downstream and vice versa [156].

4.2.2 Thread Density

Warp yarns are usually referred to as ends and their density is expressed as ends per cm (ends/cm). Similarly, weft yarns are referred to as picks and their density is expressed as picks per cm [141]. The difference in thread density of warp and weft yarn causes the change in the fabric properties and behaviour, will be discussed in detail later in Section 4.3.

4.2.3 Coarseness and Fineness of yarn

In the point of view of fabric structure the coarseness and fineness of warp and weft yarn is the geometrical property. However, it is difficult to measure the cross-section of yarn. The yarn in the fabric is like a thin cylinder. Therefore, the coarseness and fineness could be determined by estimating the diameter of warp and weft yarns and by considering the weight per unit length or tex unit (weight in gm/1000 m) [141]. It indicates the size of spun yarn or linear density [157].

The selection of coarseness and fineness of yarn depends on the type of fabric to weave and its application. The fine yarn is composed of fine fibre and has more dye uptake as compared to the coarse yarn.

4.2.4 Waviness of Yarn

The waviness or crimp in the warp and weft yarn pre-requisites for the interlacing of both yarns (warp and weft). Although, it is possible to take, either warp or weft yarn which has zero crimp. In this case the crimp might transferred during interlacement in an individual or the group of yarns (high crimp) to yarns (zero crimp) [141].

In the fibre crimp is required to spin into the yarn, where as in the yarn, crimp is brought due to the interlacement of warp and weft yarns. Yarn crimp has an influence on the fabric properties such as strength, handle and extensibility of yarn in the fabric. However, the amount of crimp in the yarn depends on the type of weave, weave density and type of fibre.

4.3 Influence of Fabric Parameters

The fabric parameters mentioned in Section 4.2 effects on the following fabric properties;

- Fabric weight and thickness.
- Cover factor.
- Porosity.
- Fabric strength.
- Fabric handle.
- Abrasion resistance.
- Effect on dyeing.

4.3.1 Fabric Weight and Thickness

The weight of fabric is expressed as gram per square meter (GSM). It can be measured using three fabric parameters such as tex, crimp and ends and picks per cm and is given by [141] Equation 4.1:

$$W = \frac{end/cm t_1 (1 + C_1)}{10} + \frac{picks/cm t_2 (1 + C_2)}{10} \qquad \text{Equation 4.1}$$

where,

t is the tex unit.

C is the crimp value and the suffix 1 and 2 expressed the warp and weft yarn.

If the parameters are not known then weight of the fabric can be measured according to the BS EN 12127 ISO 3801. For the accuracy of measurement large size of samples are preferred such as an area of 10,000 m.m^2 or more [158].

The GSM range depends on the type of fabric and its application. The GSM of light fabric (loosely woven) is 30 g m^{-2}, shirting is typically about 100 g m^{-2}, sheeting is 200–250 g m^{-2} and denim is 400 g m^{-2}. A light weight suiting is about 300 g m^{-2} and heavy over coating is 600 g m^{-2} [157].

The thickness of fabric is expressed in millimeters. The yarn linear density (tex value) and yarn diameter and the crimp of warp and weft yarn has an influence on the thickness of fabric, while it is independent to the thread density. The qualitative relationships between the fabric thickness and structural parameters are difficult. Generally, even or uniform distribution of yarns crimp in the fabric minimized the fabric thickness [141]. Fabric thickness can be measured precisely using fabric thickness meter.

4.3.2 Cover Factor

Cover factor of fabric determines the appearance, handle, feel, crimp, permeability, transparency, limits of pick insertion, density, and hardness of fabric [159]. The obvious variable for fabric construction is cover factor, for any given yarn and apart from weaving [149]. Cover factor is one of the ways to compare fabrics; it is a good indication of fabric tightness [160].

Peirce (1937) [161], reported the creeping of yarn, and flattering in finishing improved the cover of fabric. However, it did not sufficiently measure the quality of fabric but it helped to predict the fabric properties and to compare fabric for experimental study. The fabrics of similar cover factors have similar behaviour such as hardness, crimp, etc. Ashenhurst in 1884 [162] gave the simplest expression of cover factor $S\sqrt{N}$, ends-plus- intersections. Newton (1995) [160] introduced a method of assessing the fabric specification of unknown comparable fabric using fabric tightness value. The fabric tightness value was measured using the maximum sett, curve designed by Peirce (1937). The direct method of measuring the cover factor of grey and finished fabric is by image analysis will be discussed in detail in Section 4.4.

Cover factor determines the area occupied by the threads in relation to the air space between the threads. For tex units [161], the cover factor (K) of warp yarn (K_1) and weft yarn (K_2) is equal to the threads per cm multiplied by the square root of tex of the yarns as shown in Equation 4.2 and Equation 4.3 [161].

$$K = 0.04126 Threadspercm \sqrt{tex}$$

and mathematically,

$$K_1 = 0.04126 n_1 \sqrt{tex_1} \qquad \text{Equation 4.2}$$

$$K_2 = 0.04126 n_2 \sqrt{tex_2} \qquad \text{Equation 4.3}$$

where,

n_1 = ends per cm.

n_2 = picks per cm.

tex_1 = linear density of warp yarn in tex.

tex_2 = linear density of weft yarn in tex.

Moreover, the cover factor indicates the degree of closing of threads in the woven fabric, or the proportional area covered by the threads. The total cover factor (K) is the sum of warp and weft cover factors [143] as shown in Equation 4.4..

$$K = K_1 + K_2 \qquad \text{Equation 4.4}$$

The above formula gives an approximate value of cover factor, but for accuracy the fraction of area covered by the warp and weft ayrns are calculated [163] by using Equation 4.5,

$$K = \frac{K_1 + K_2}{28} - \frac{K_1 K_2}{28^2}$$

Multiply by 28 for convenience, the fabric cover factor K obtained;

$$K = K_1 + K_2 - \frac{K_1 K_2}{28} \qquad \text{Equation 4.5}$$

The factor 28 is a numerical constant derived from the yarn diameter and specific volume. In a fabric that has a cover factor of 28, the yarns will be touching each other as shown in

Figure 4.4. A cover factor of lower than 28 means there is a space between the warp and the weft yarn [143].

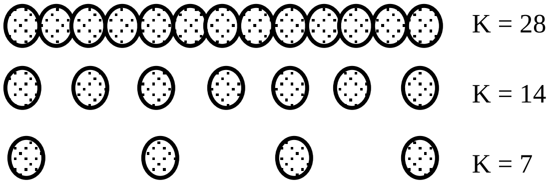


Figure 4.4 Yarn diameters relation with K.

In practice, cover factor has to be kept lower than 28 to allow space for yarns to pass over one another.

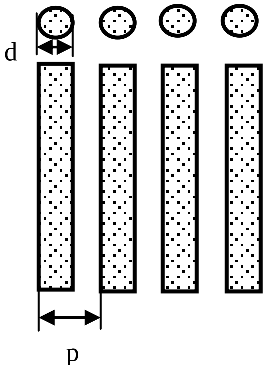


Figure 4.5 Ratio of yarn diameter and its spacing

As shown in Figure 4.5, the ratio of yarn diameter and the yarn spacing, d/p, is a measure of the relative closeness of the yarns in the warp or weft of woven fabric. This ratio expresses the fraction of the area of the cloth covered by the warp or weft yarns. It is therefore termed as fractional cover Equation 4.6:

$$K' = \frac{d}{p}$$ Equation 4.6

The fractional cover is the ratio of the projected fabric surface area covered by yarns to the total fabric surface area [164] and it is given by the following Equation 4.7 and Equation 4.8:

Fractional Cover = Cover Factor = $K' = K_1 + K_2 - K_1 K_2$ Equation 4.7

where,

$$K_1 = n_1 d_1 \text{ , } K_2 = n_2 d_2$$

Fractional Cover in percentage = $K' = 100(K_1 + K_2 - K_1 K_2)$ Equation 4.8

In terms of fractional cover factor, the maximum value of cover factor is 1 or 100% and this condition is term as jamming state (yarns are very close to each other). Air can relatively pass through interstices of woven fabric, which shows at 100% cover factor fabric is permeable. [161].

However, in slit film (very low thickness compared to its width) and other weaves as shown in Figure 4.6 [159], where the yarns can pile up, it is possible to approach 100% cover factor [161]. Weaves such as twill and satin can have high cover factor [157] . The cover factor and fractional cover factor is used to compare the relative closeness of the yarns in the different woven fabrics.

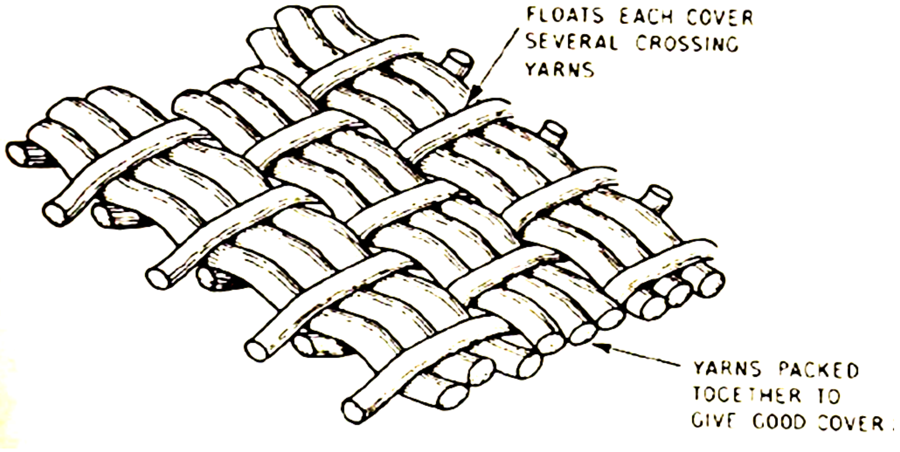


Figure 4.6 Pile up weave

The approximate practical cover factor of plain weave fabrics ranges from 0.7 to 0.8, and ranges from 0.97 to 1 for 4/4 twill weave fabrics [149]. The higher the cover factor of the woven fabric, the more close the yarns are and more tightly the fabrics are woven.

However, it is possible the fabrics of different setts, yarn count and weave structure have the same cover factor and the same fabric tightness value [160].

The number of turns (twist) in the yarns of the woven fabric induces the difference in cover factor value for a given fabric geometry. High twisted of yarns tend to give low cover factor value as compared to the less twisted yarns [159]. It has been analyzed that a tightly woven fabric was more affected by the selection of finishing treatment than a loosely woven fabric [149].

4.3.3 Porosity

The void or space in the fabric is term as porosity. It is measured as a fraction, between 0 - 1, or in percentage between 0 - 100%. Fabric porosity is facilitated to assess the fabric comfort and physical properties [165].

In a theory of a 2-D model [165], the porosity P's was defined as a complement to the woven fabric cover factor (Equation 4.8). An area of pores was calculated as a perpendicular projection of the woven fabric and can be determined using Equation 4.9 and in percentage in Equation 4.10,

$$\text{Porosity} = P = 1-\left(K_1 + K_2 - K_1K_2\right) \qquad \text{Equation 4.9}$$

$$\text{Porosity in percentage} = P = 100\left[1-\left(K_1 + K_2 - K_1K_2\right)\right] \qquad \text{Equation 4.10}$$

The classical 2-D model of porosity was insufficient for a tightly woven fabric. Neighbouring yarns were very close and the projected area of inter-yarn pores approached zero.

In a fabric, pores are situated in the fibres, between fibres in the yarns (intra-yarn zone), and between yarns in the fabric (inter-yarn zone) [166, 167]. The porosity is then the ratio of the projected geometrical area of the opening across the material to the total area of the material, as shown in Equation 4.11. This calculation was the geometrical expression of inter-yarn porosity of the woven fabric [168].

Fabric Porosity = $$P = \frac{P_1 P_2}{(P_1 + d_1)(P_2 + d_2)} \qquad \text{Equation 4.11}$$

where,

n_1 = *No of ends per cm.*

n_2 = *No of picks per cm.*

tex_1= *tex of warp yarn.*

tex_2= *tex of weft yarn.*

P_1= $1/n_1$= *warp spacing in cm.*

P_2=$1/n_2$= *weft spacing in cm.*

d_1=*diameter of warp yarn in cm.*

d_2= *diameter of weft yarn in cm.*

$$d_1 = d_2 = \frac{\sqrt{tex}}{634.3}$$

Peirce defined the yarn diameter, d in inches [161]:

$$d = \frac{1}{28\sqrt{N}} \text{ (where N was count of cotton yarn)}$$

The porosity value suggested by Peirce was 0.60 [161] and a value of 0.65 considered as a median porosity [146]. Though, it varies from 0.55 to 0.75 depending on the fibre and yarn types.

The porous material, due to the interconnected channels and voids, allows gases and liquid to flow [169]. When the fluid passes from the fabric the major part is flow under the inter yarn zone of the fabric [170]. The rate of diffusion, flow of gasses and liquid through the space or voids is called permeability. Liquid and gasses can easily pass through textile fabrics because of their construction, the space between the interlacing fibres and yarns or pores. The term porosity is different to permeability because porosity is the fraction of all the spaces or voids to the total volume. Two fabrics that have same porosity could have different permeability, because of the way the voids or space are distributed and their interconnections. For example one fabric may contain small voids in large numbers while the other has few long voids. The fabrics will have the same porosity but different permeability.

As discussed in above paragraphs fabric porosity has an influence of yarn porosity including yarn diameter [170]. As yarn twist increases, the circularity and density of yarn increases, decreasing the diameter and cover factor of the fabric and increasing the air permeability. Yarn crimp and weave influence the shape and area of interstices between the yarns and may permit yarns to extend easily. Such yarn extension would open-up the fabric; increase the free area, and increase air permeability. A high twist also allows the high-density yarns to be packed closely together in a tightly woven fabric structure, which reduces air permeability [164].

Fabric porosity or permeability is the property of fabric that allows liquid, gas or any solid material to be adsorbed or absorbed into the fabric. These types of fabric are used for various applications such as protective clothing, sportswear, laminated and coated fabrics, textiles for filtration, medical textiles, textiles for transportation, and other technical textiles [164, 165].

Depending on the type of application, fabric permeability is measured by air permeability, water permeability, and chemical (gaseous, liquid or solid chemical) permeability, related to the penetration of gas, liquid or solid material into the fabric. However, the method of testing is different for different permeability [164].

Loosely woven fabrics have high permeability [148]. In the tightly woven fabric, there are small pores or voids; therefore more force is required to penetrate the water in it. When water makes a contact, it causes hydrophilic fabrics such as cotton to swell, which increases the compactness and acts as barrier for liquid or water to flow [169]. The porosity or air permeability decreases as the woven fabric becomes denser [144].

Moisture transmission in a fabric involved both the moisture sorption by the fabric and then transmission through it. This transmission occurs through the void spaces or pores within the fabric structure [147].

Fabric construction and finishing treatment effects the air permeability by causing change in the length of air flow paths through the fabric. The difference surface texture on either side of a fabric can give variation in air permeability, depending on the direction of air flow [164].

4.3.4 Fabric Strength

The fabric strength depends on the yarn strength, yarn bending behaviour, fabric geometry, weaving conditions, fabric finishing treatments, and many other parameters [171].

The strength of fabric and yarn varies with the type of fibres and yarn manufacturing (spinning) process such as ring, rotor, compact and etc. Generally, yarn manufactured with staple fibres has strength due to the pressure (twist) between the individual fibres which prevent the slippage of fibres [143]. However, a filament yarn is a continuous strand and it is independent of fibre slippage. These all factors effect subsequently on the woven fabric.

Ring yarn cotton woven fabric has lower tensile strength both in warp and weft direction than the fabric manufactured from a compact yarn [172]. It was also observed that [171] the fabric manufactured from the ring spun yarn had higher strength than the fabric woven from rotor spun yarn at the same woven structure. This was because the cross sections of yarn of fabrics indicated higher crimp in the ring spun fabrics compared to the rotor spun fabrics.

Fabric structure also plays an important role for determining fabric strength. Additional pressure in the fabric is created when the yarn is interlaced during fabric manufacturing [143]. The breaking load (load at which the specimen breaks) in case of the warp yarns is proportionate to the ends per cm; similarly, for weft yarns is proportional to the picks per cm [141]. The fabric strength increases with the yarn densities in both directions (warp and weft) [143] because of the small voids between the neighbouring yarns and increased delay in breaking point [173]. When the strength was measured from the warp direction, number of isolated breaks and size of deformation zones was decreased as the weave texture increased (from 36* 30 to 72* 30 ends and picks per inch), due to the difference in fabric geometry . The higher number of ends and picks per inch (72* 30) in the fabric had higher percentage of original crimp, crimp interchange region and elongation to failure [171].

For maximum breaking load, the crimp of warp and weft yarns and applied force should be balanced depending on the direction of woven fabric [141].

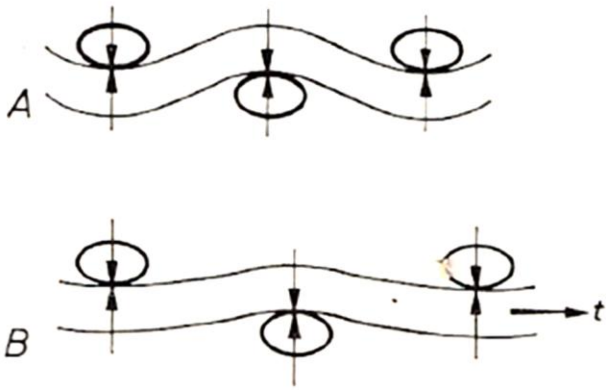


Figure 4.7 Fabric assistance

The fabric in relax position (without external force) is shown in Figure 4.7 (A) [143], The arrows shows ends and picks of the fabric at the intersection points exert pressure on each other. If ‘t’ is an external force applied on the fabric parallel to the warp yarn as shown in Figure 4.7 (B) [143, 159], the warp yarns crimp reduces, straightening the warp yarns or increasing the length of the fabric and increasing the weft yarns crimp. This reduced the woven fabric width and open-up the pores of the fabric [145]. Hence, geometrical change in the fabric was observed at the plane of the fabric and also at the cross-sections of warp and weft yarns. The loaded yarns were elongated and decreased in diameter. The extent of change depend on the percent of elongation at constant load or force on the fabric. Up to 6.6 % strain of fabric, yarn in the loading direction was straightened and became slightly more circular in cross-section. At 25 % extension flattering of cross yarns was small and at 30 % extension, the fabric sample was broken due to the cross yarn bending, increased crimp and flattened cross-section. All these factors initiate the yarns failure and then fabric [171].

The initial fabric response (increased crimp) is known as “crimp interchange”, because the crimp is decreased in the loaded direction such as warp yarn and increased in the cross direction such as weft yarn [159, 171].

The extensibility of a plain woollen fabric was much more affected by finishing treatment than by their cover factor [149]. This indicated that the fabric strength is decreased by the action of rubbing, flexing and chemical processing [174]. The wet treatment (desizing) of Tencel fabric [150] swelled the fibres of the yarns of the woven fabric. The increases of fibre diameter increase the yarns crimp and contact surface area between the fibres. Which enables the fibres to slides along each other, hence increased the fabric extension or extensibility (more than 500%) as compared to untreated Tencel fabric. After drying, extensibility was reduced because of the minimum water contents [150].

However, within a woven fabric, the strengths of warp and weft yarns are different because the fabric is not symmetrical [175]. Increase in the float length of a woven fabric decreases the warp strength. This is because of the less localization of rupture and binding effect, reducing the warp yarn strength. However, float length had not effected on the weft yarn strength. The fabric strength in warp direction increases with the picks per cm up to a certain limit and then decreasing. The limit depends on the nature of weave, number of picks per cm and elongation of yarns on maximum floats length [176].

4.3.5 Abrasion Resistance

Fabric density and handle was constantly decreased with increasing abrasion time while fabric thickness, air permeability and softness were increased inconsistently [177]. During abrasion, fibres (cotton) [148] were lost that induced increase permeability of cotton fabric. If the fibres were laid between interstices of the yarns of fabric and established an equilibrium situation (loss of fibres = gain of fibres) then there were no change of permeability. The decrease in fabric density was minimum during short periods of assessment while the change in other physical properties such as compression, relaxation and air permeability was high [177].

Cotton fabric, woven from compact yarns were reported to have less abrasion resistance with weight loss after 5000, 7500 and 10,000 of 19.3% to 43 % less than the fabric woven from the ring spun yarns [172].

4.3.6 Fabric Stiffness

Fabric stiffness depends on the direction of yarns in the fabric and on the yarns crimp [177]. Fabric cut from the warp yarns direction showed the effect of weft yarns changes, similarly, woven fabric samples cut close to weft direction showed the warp yarns changes to the bending properties [178]. For all types of weave, bending rigidity increased as the cover factor increased. The fabric density and cover factor determine the bending rigidity rather than fabric construction [149].

Bending rigidity [179] is defined as " the couple required to bend a fabric strip of unit width to unit radius of curvature under pure bending condition". Peirce [179] claimed that fabric handle is a measurable quantity and introduced the cantilever method of measuring the bending behaviour. Other methods of determining the fabric handle is Kawabata's (KES) [180, 181] and later FAST (Fabric Assurance through Simple Testing, developed by CSIRO in Australia) were introduced. The cantilever test method of bending length [182] provided the highest bending rigidity values while KES test gave lowest value particularly for stiffer or tightly woven fabric.

In the cantilever test method, fabric stiffness is measured by allowing the fabric to deform under its own weight at particular (pre-determine) deflection angle [179, 183]. Bending rigidity is the ability of a fabric to resist bending movement [150]. Woven fabric compose of small diameter of fibres have high degree of flexibility. The fibres can slip over one another due to minimum shear energy transmittance between the fibres. The tightly woven fabrics are more stiffer than the loosely woven fabric because of the considerable yarn tension at intersection points of the fabric [159]. During wet-finishing Tencel fabric exhibited smaller bending rigidity and bending moments (recovery of fabric after being bent). Hence Tencel fabric became more pliable, soft and elastic after the wet-treatment [150].

The stiffness of the fibres is proportional to the forth power of its diameter. If the diameter of fibres is doubled, its resistance to bending and twisting increased sixteen times. Fibres that has 30 - 40 micrometer diameter consider coarse and stiff and uncomfortable for wearing [184].

4.3.7 Effect of Weave on Dyeing

In the preceding Section, fabric structure and weave was discussed. All these parameters have considerable and sometimes extensive effect on the dyeing properties. McGregor [185] explained fabric dyeing on the basis of the dyeing behaviour of yarns in case of non-vigorous stirring. The geometry of fabric indicated that yarns were crossed and in contact with each other. These contact points were not dyed in the initial dyeing stage and were responsible for sorption delay compared with the dyeing of a yarn. The dye solution flowed rapidly through the inter-yarn spaces and the outermost boundary of the yarn, but penetration of the yarn itself was much slower, and flow velocities within yarn were low even in the most favourable circumstances.

Ahmet, R [186], analyzed the effect of warp and weft density variation on reactive dyeing by exhaust methods on cotton fabric. The porosity and the variation in the linear density of warp and weft yarn had an effect on the dye uptake of the cotton fabric. The high porosity and fine linear density of yarns gave high uptake of dye. However, the variation in porous dimension also leads variation in colour intensity.

The yield of colour varied as the thickness of yarn varied. Knitted fabric manufactured from single yarns showed higher colour values than the knitted fabric manufactured from plied yarns. Similarly, knitted fabric from compact yarns had higher dyeing ability than the ring spun yarns [187].

In the fabric structure yarn twist is also a considerable factor [188]. The dye liquor can readily and quickly flow in low twisted yarns fabric than the high twisted yarns fabric.

Gabrijelčič, 2009 [189] assessed the behaviour of ninety (90) different woven fabrics. The construction of fabrics was plain, twill, satin and basket weave, all varying with threads per cm. The warp yarns were dyed using a blue dye and weft yarns were dyed by six different dyes blue, red, yellow, green, black and white. After analyzing the results using linear and non-linear regression, it was observed that the fabric constructional parameters had an influence. Consequently the colour properties lightness, hue and chroma were affected. The interlacement of the yarns (warp and weft) reduced the ideal behaviour of the colour mixing on the fabric due to the reflection of light.

Further, the reflection of light by a fabric varies with fabric properties such as fibre materials, yarn thickness, weave of fabrics, yarn density and surface colour. Therefore, the characteristic properties of fabric can be determined by knowing the reflection of light such as diffusion and regular reflection at the surface layer of the fibres and diffusion and reflection between the internal fibre surface as shown in Figure 4.8 [190]:

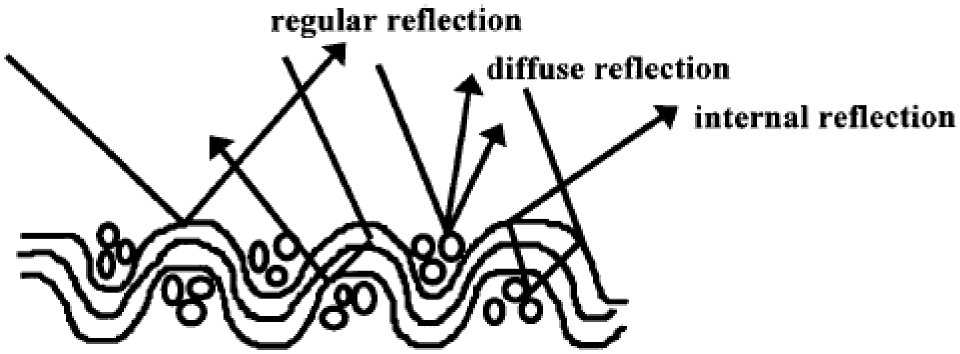


Figure 4.8 Light reflected from the textile fabric

The thickness and density of yarn has an influenced on the reflection of light. Plain fabric (high warp cover factor) and twill weave (high weft cover factor) fabrics have empty spaces between the yarns, allowing the light to pass through the space. During the colour measurement reflection of light has more chance to pass between the fabric spaces so unable to measure the actual colour. This problem can be minimized by taking several superimposed layers of fabric. Thus, the new background is the woven fabric itself. Therefore, on comparing plain and twill weave fabric, the plain weave appears less opaque than the twill weave. Backscattering made the plain fabric appear still darker (its backscattering was weaker) than if it had the same weft density as the twill weave had [191].

The appearance of colour varies with the type of fibre due to difference in reflection of light. Light refection is influenced by the size and the shape of the fibres, construction of the yarn and fabric (as discussed above). A smooth filament produces a regular reflection of light. The irregular reflection is observed in fine less uniform filaments or fibres [184].

4.4 Analysis of Fabric Properties by Image Processing

The subjective assessments of fabric properties are very time consuming and tiring job and depend on the efficiency of operator. The introduction of computerized image processing will save time and gives rapid and accurate results and performed wide range of objective assessments [134, 192].

Objective assessments based on image processing have three basic fundamentals: image-acquisition (image or sense was converted into digital image and then stored in a memory), image processing (image enhancement, analysis and coding), and image display. Image processing and analysing techniques are very helpful to blur, smooth, segmented, crop, magnify, minimize and remove distortions of the final image [134].

This precision, flexible and hustle technique is not only used in textiles but also used in medical, architecture and engineering, geography, law enforcement, archaeology and various industrial application [134].

Image processing in textiles is used to assess the raw material to finished goods. The fibre length, length distribution were assessed by image processing technique [193, 194] and then compared with manual HVI (High volume instrument) and AFIS methods [194]. Xu et al [195] were developed an image processing system based on geometric (roundness, area, and ellipticity) and Fourier (boundary and angular functions) for assessing the cross-section shape of the fibre. Using the same technology, the method of measuring fibre crimp was developed which was very reliable and an efficient [196-198]. The image processing technique was made easy to identify the blended fibre in the yarn of the fabric using neural networks [199] and algorithms [200]. The density of the yarn (width and count) was estimated using discriminate analysis [201].

Fabric properties such as cover factor and porosity are very important in terms of assessing behaviour of flow of dyeing in between the yarns (inter-yarn pores) and between the individual filaments of the yarns of the fabric (intra-yarn pores) [185]. These properties were assessed by geometrical formulas (as discussed in Section 4.3.2 and 4.3.3) and can also be assessed by image processing and analysis techniques.

Ravandi et al [202] evaluated fabric appearance and directionality, thread density, density of yarn protruding on the surface of the fabric using image processing. They introduced VSIP (video system image processing) to measure the fabric properties using Fourier transfer technique of angular power spectrum (APS) peak. Similarly, Xu and others [203, 204] used Fourier transform techniques (APS) to analyze the weave pattern, fabric count, yarn skewness and for correcting the uneven background.

The weave of the fabrics were analyzed using an iteration function. The protruding fibres on the surface were first removed by burning, and clipping the fabric images. Pixels of the fabric image in both x and y-axis were counted and added. Then, using an iteration programmes warp and weft float was identified. After digitalizing images, weave diagrams including weave repeat, harness draft and chain draft of relative weave structure were drawn [192].

Kang et al [205] measured the count, cover factor, yarn crimp, fabric thickness and weight per unit area automatically from the cross-sectional and planer images of the woven fabric. Tapias et al [206] introduced the method of measuring the fabric cover factor (CF) of different weave density using Fourier transform techniques. The digital fabric images were converted into binary images using SSQ (sum square residuals) function. Then the number of pixels was counted. The ratio of the number of pixels covered by the yarn to the total number of pixels measured the CF. Cay et al [168] calculated the average illuminate and average percentage illuminate to assessed the fabric porosity using Matlab software.

The fabric density, cover factor, and thread density of six knitted fabrics were also evaluated using image processing. On comparing the digital image with manual assessment, the digital image showed 5 - 12 % higher values, the difference was because of the image processing ignore the quite a few loop stitches [207].

The image processing technique is better method of estimating the fabric cover factor as compared to determined by the yarn count and yarn size [208]. However, there are still some limitations of image analysis of fabric cover factor and porosity such as difficult to analyse the highly slub or fancy yarn woven fabric.

CHAPTER 5: EXPERIMENTAL WORK

5 Experimental Work

5.1 Material

5.1.1 Fabric

Pre-treated (scoured) 100% Tencel woven fabric of Plain, Twill 2/1, Twill 3/1, and Twill 5/1 as shown in Figure 5.1 and plain fabric comprised of nine different weave densities were kindly supplied by Lenzing, AG (Austria).

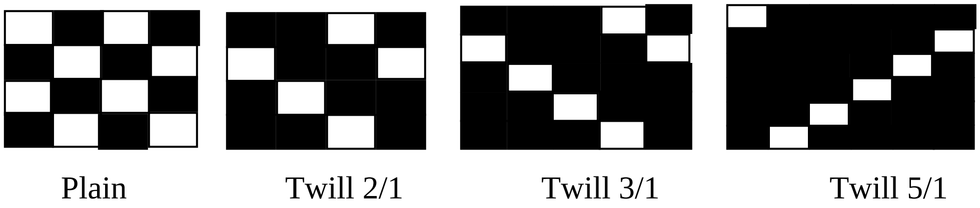


Figure 5.1 Fabric weaves structures

The results obtained on the plain, Twill 2/1, Twill 3/1 and Twill 5/1 fabrics are discussed in Chapter 6. The results and discussion of the experiments on the plain weave fabrics of varying warp and weft densities and number of ends and picks, are in Chapter 7.

5.1.2 Dyes and Auxiliaries

Three different types of exhaust dyeing dyes and two different types of continuous dyeing dyes were selected for use. The dyes used, and their characteristics, are shown in Table 5.1 [209]. The dye auxiliaries ALBAflow FFC (slightly anionic, penetration, and accelerant), ALBAflow UNI (non-ionic, penetration, and accelerant) and ALBAflow PAD (penetrating, anti-foaming, and accelerant) were kindly supplied by Huntsman Chemical (Switzerland).

All these dyes [209, 210] are bi-reactive in nature, with the potential to reduce the fibrillation effect. Novacron FN dyes require less water, less time and low temperature, having high fixation, penetration and are suitable for very dark shades. Novacron LS dyes [209] have high fixation and require little salt, hence have a lower cost of production. They have high fastness properties. LS and H dyes have optimum fixation at a temperature between 70 ºC to 80 ºC. For level dyeing, salt should be added carefully, and alkali portion wise.

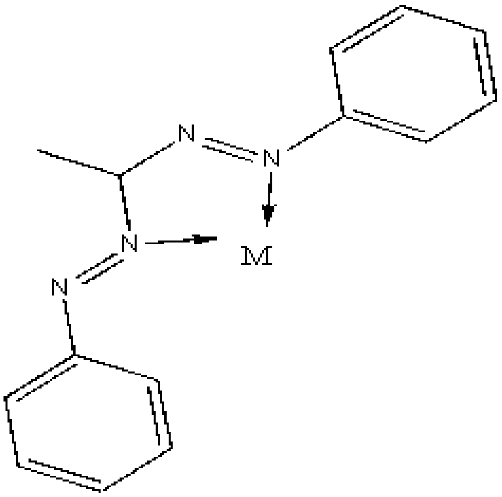
Samples of Levafix Red CA, Levafix Blue CA, Levafix Yellow CA and Remazol Balck B-A for continuous dyeing were kindly supplied by DyStar (Germany). Sodium silicate (Alkali) and sodium-m-nitrobenzenesulphonate (mild oxidizing agent), were supplied by Alfa Aesar (U.K) and Synperonic BD (non-ionic surfactant) were supplied by Clariant (U.K).

Table 5.1 Novacron [209, 211] and Levafix CA dyes [210] and their characteristics

S.No	Dye Type	Colour Index	Characteristics
1.	Novacron FN 1. Brilliant Red FN- 3GL. 2. Red FN-R. 3. Yellow FN-2R. 4. Black C-NN.	1. C.I Reactive Red 282. 2. C.I Reactive Red 238. 3. C.I Reactive Yellow 206. 4. Not disclosed.	Bi-reactive, low water consumption, less time and low temperature dyes, having high fixation, penetration and suitable for very dark shade
2.	Novacron LS 1. Red LS –B. 2. Blue LS-3R. 3. Yellow LS-R. 4. Black LS-N.	1. C.I Reactive Red 270. 2. C.I Reactive Blue 263. 3. C.I Reactive Yellow 208. 4. Not disclosed.	Bi-reactive, high fixation and fastness properties and low salt consumption hence lower the cost of production.
3.	Novacron H 1. Turquoise H-GN. 2. Brilliant Blue H-GR. 3. Brilliant Yellow H-4G.	1. Not disclosed. 2. C.I Reactive Blue 269. 3. C.I Reactive Yellow 207.	High fixation and fastness properties. Low salt consumption hence lowers the cost of production. Bi-reactive in nature.

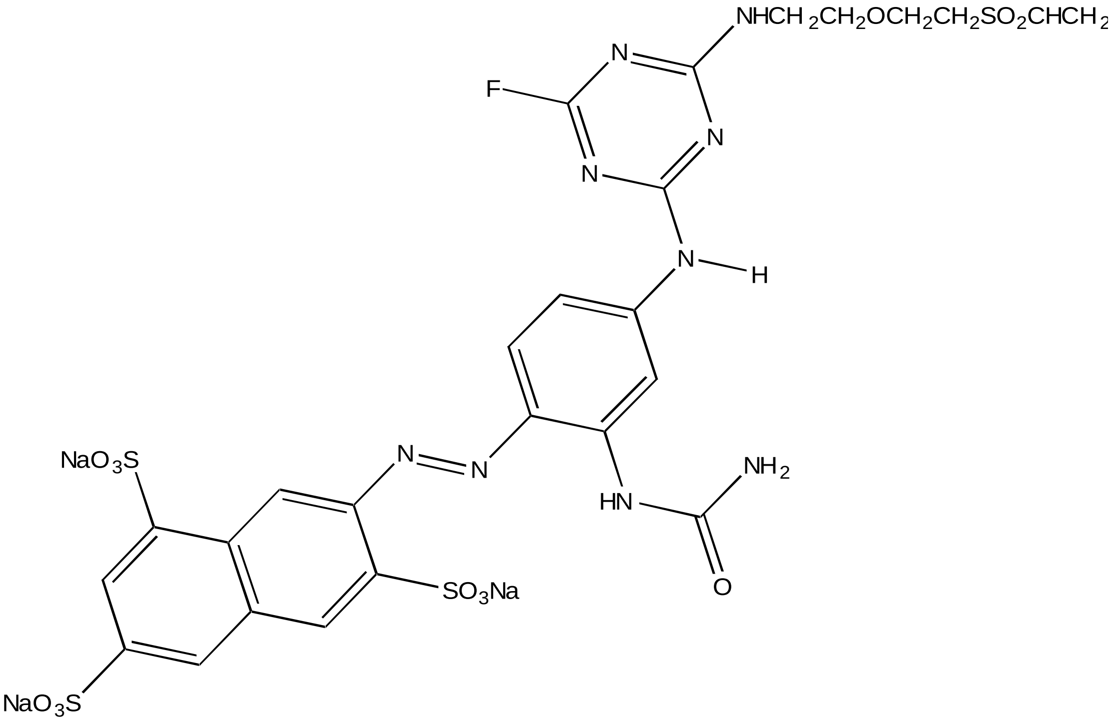
4.	Novacron C 1. Red C-2G. 2. Blue C-R. 3. Yellow C-RG. 4. Black C-NN. 5. Turquoise C-GN.	1. C.I Reactive Red 228. 2. C.I Reactive Blue 235 3. C.I Reactive Yellow 174. 4. Not disclosed. 5. Not disclosed.	Suitable for cold pad batch and continuous application. Low dusting powder form, high fixation, excellent washing-off, and fastness, very good reproducibility and dependability of results.
5.	Levafix CA 1. Red CA. 2. Blue CA. 3. Yellow CA. 4. Remazol Black B-A.	1. Not disclosed. 2. Not disclosed. 3. Not disclosed. 4. C.I Reactive Black 5	Levafix dyes suitable for cold pad-batch and continuous application. Medium reactivity, good leveling and fastness. • Blue CA: Copper formazan dye with a heterobifunctional, 1000 MW. • Red CA: H-acid red azo chromophore with two reactive groups, 900 MW. • Yellow CA: Golden yellow azo chromophore with a heterobifunctional reactive group,1000 MW. • Black B-A: Bifunctional azo. 991.824 MW. *MW is the Molecular weight*

The chemical structures of some of these listed dyes are shown below:



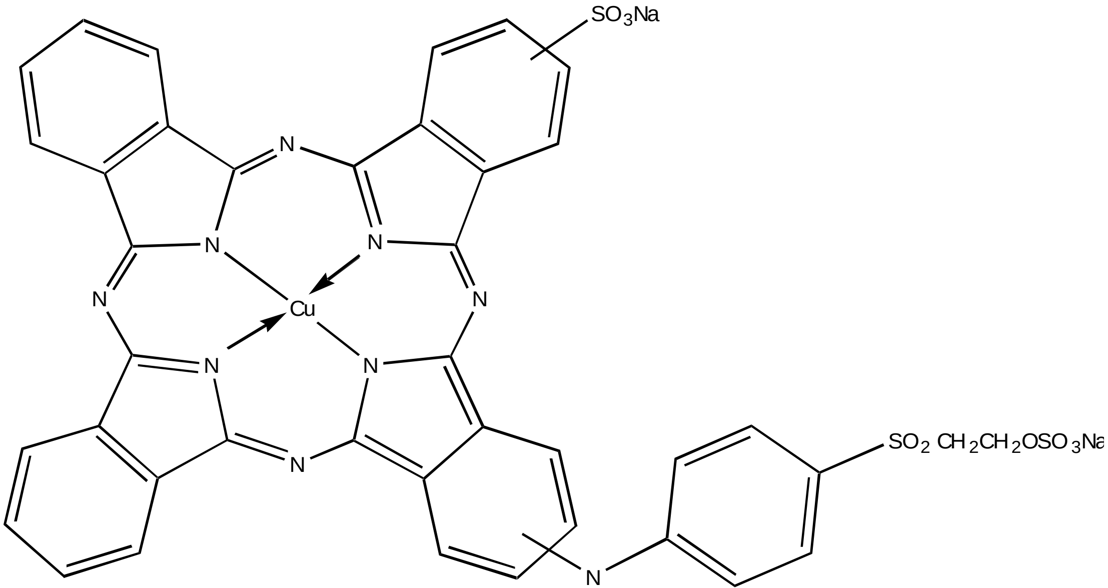
Scheme 5.1 Novacron Blue C-R.

- Formazane metal complex



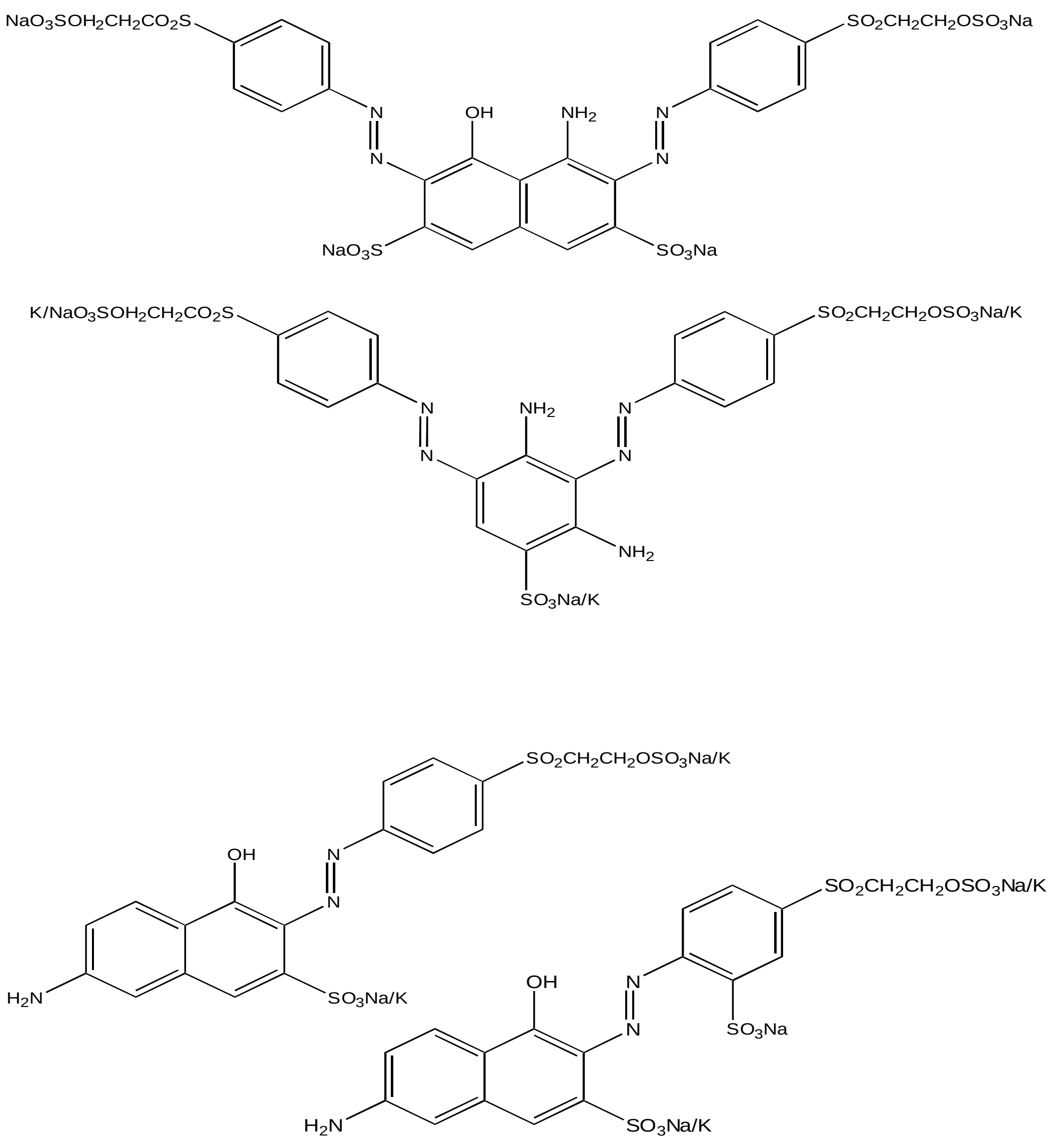
Scheme 5.2 Novacron Yellow C-RG

- Trisodium 7-(4-(6-fluoro-4-(2-(2-vinylsulphonylethoxy)ethylamino)-1,3,5-triazine-2-ylamino)-2-ureidophenylazo)naphthalene-1,3,6-trisulphonate.



Scheme 5.3 Novacron Turquoise H-GN/C-GN

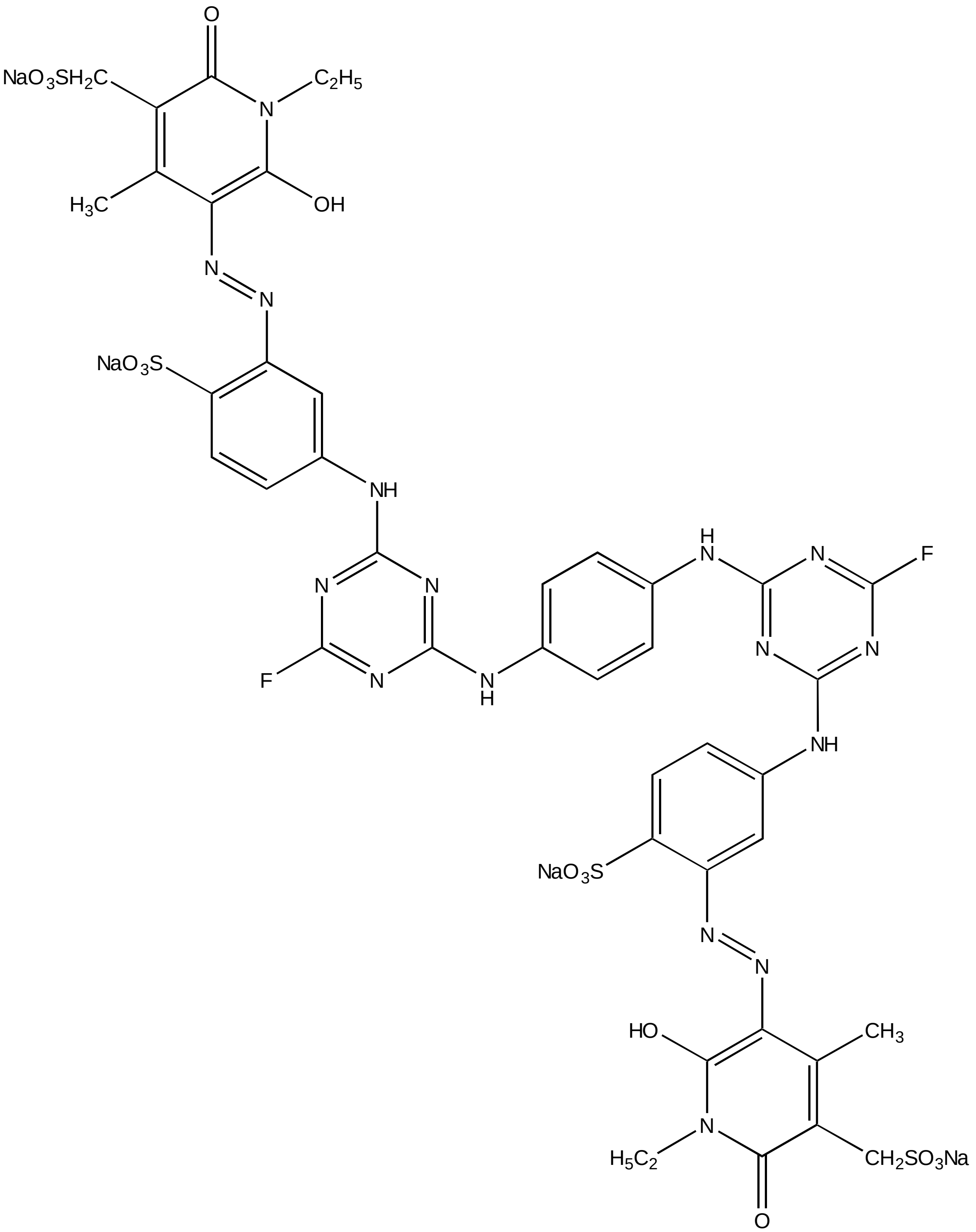
- Copper,[29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-,sulfo[[4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]amino]sulfonyl derivatives (60-70%).



Scheme 5.4 Novacron Black C-NN

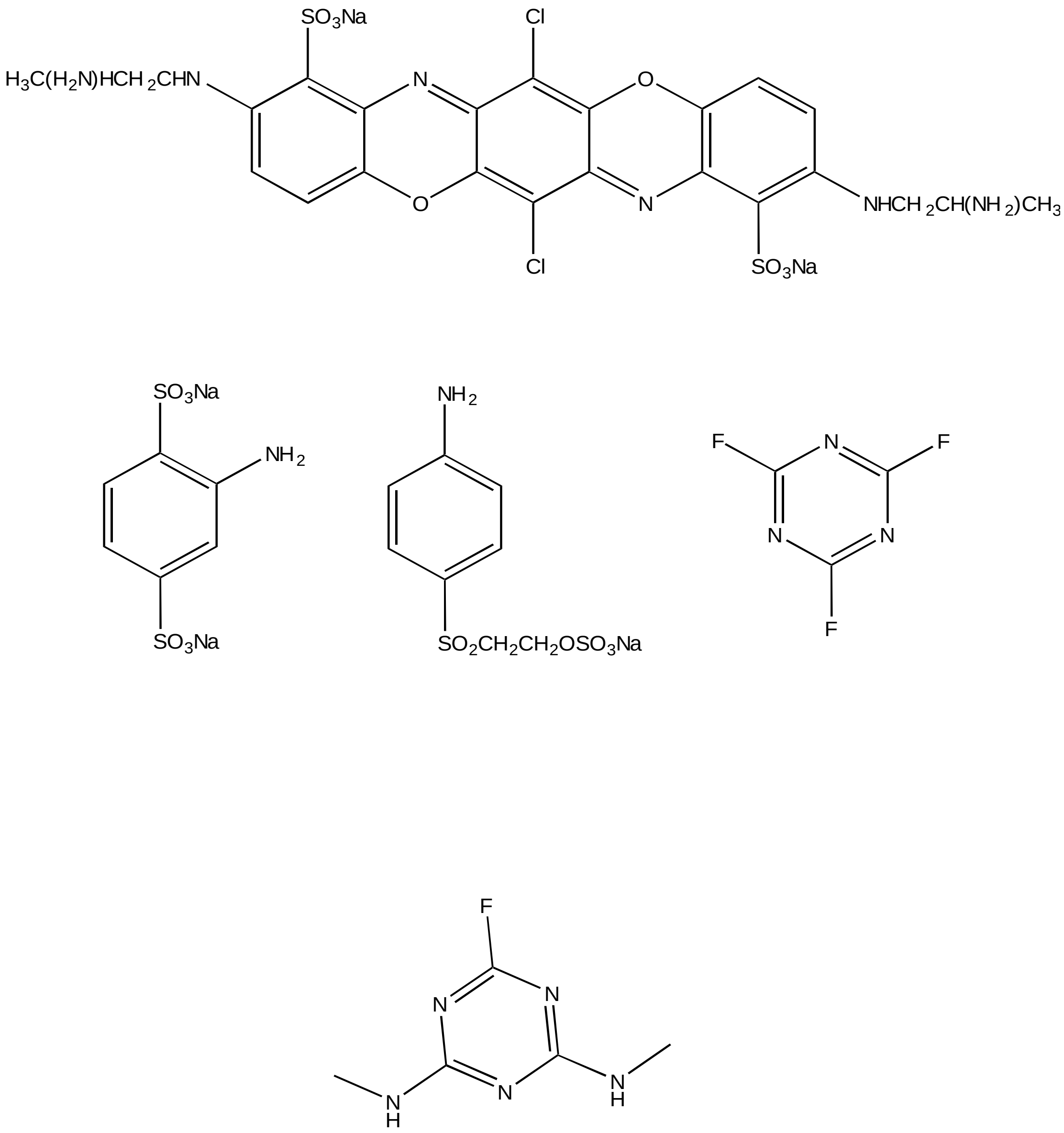
Novacron Black C-NN is the combination of the structures showing in Scheme 5.4.

- Sodium4-amino-5-hydroxy-3,6-bis[[4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]azo]-2,7- naphthalenedisulfonate (50 - 60%)
- Sodium, potassium 2,4-diamino-3-[[4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]azo]-5-[[2-sulfo-4-[[2-(sulfoxy)ethyl]sulfonyl] phenyl]azo]-benzenesulfonate (12 - 15%).
- 7-amino-4-hydroxy-2-naphthalenesulfonic acid, coupled with diazotized 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate and diazotized 2-amino-5-[[2-(sulfoxy)ethyl]sulfonyl]benzenesulfonic acid, potassium sodium salts (12 - 15%).



Scheme 5.5 Novacron Yellow H-4GN.

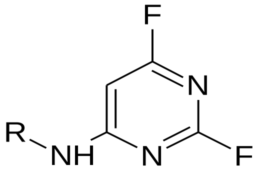
- N,N’-bis(6-fluoro-4-[3-(N-ethyl-6-hydroxy-4-methyl-3-sulfomethylpyride-2-one-5-ylazo)-4-sulfophenylamino]-[1,3,5]triazine-2-yl)-1,4-phenylenediamine sodium salt.



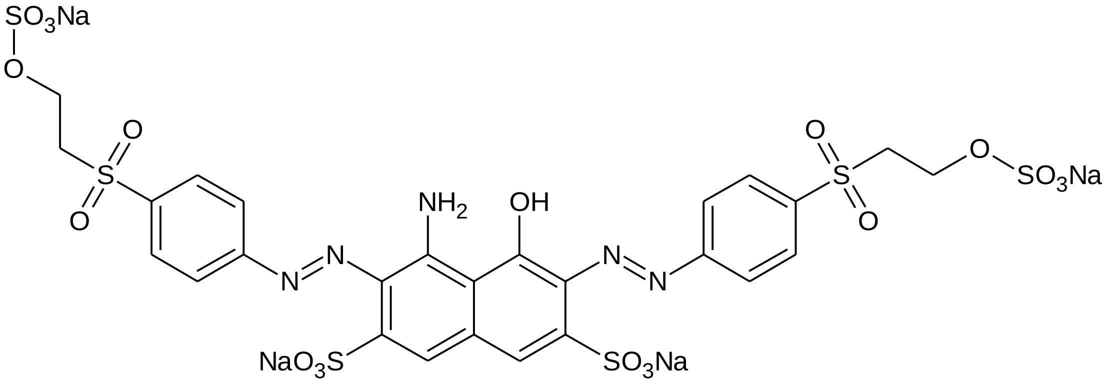
Scheme 5.6 Novacron Brilliant Blue H-GR.

Scheme 5.6 shows the possible intermediates of make-up structure of Novacron Blue H-R

- -3,10-bis[(2-aminopyopyl)amino]-6,13-dichloro-4,11-triphenodioxazine disulfonic acid, reaction products with 2-amino-1,4-benzenedisulfonic acid, 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate and 2,4,6-trifluoro-1,3,5-triazine, sodium salts.



Scheme 5.7 Reactive group of Levafix CA dyes



Scheme 5.8 Remazol Black B-A

5.2 *Method*

5.2.1 *Fabric Assessment*

A solution of iodine in potassium iodide (I_2 solution) was used to confirm the Tencel fabrics had been pre-treated and that no size remained. The following were the tests carried on Tencel woven fabric for assessing the behaviour of fabric before dyeing in textile testing laboratory of school of textiles and design.

- Weave density.
- Linear density.
- Gram per square meter.
- Cover factor.
- Porosity.

5.2.1.1 *Thread Density*

Thread density, ends and picks per cm has been already discussed in Section 4.2.2. The ends and picks per cm of Tencel woven fabric were assessed visually by using a pick glass, after conditioning the fabric in standard atmospheric condition. The weave density was measured from five different areas of woven fabric; the average of five reading was then calculated.

5.2.1.2 Linear Density

The linear density of plain fabrics was calculated according to standard BS ISO 7211-5:1984 [212]. From each plain fabric, five different strips, two from warp side and three from weft side were taken; the length of each strip was 50 cm and width 1 to 2 cm. From each strip, fifty yarns were taken out and each yarn was then un-crimped using a Shirley crimp tester, the increased of length was measured. The linear density of yarn of the woven fabric in tex was calculated using Equation 5.1.

$$Lineardensity, tex = \frac{1000w}{l} \qquad \text{Equation 5.1}$$

where,

w = mass of yarns taken from fabric (fifty yarns), in gms.

*l= total length of yarn in meter = means straightened length * number of thread weighted.*

After calculating the linear density of each individual strip of plain fabrics, an average linear density of two warp strips was calculated. Similarly, an average of three strips of weft was used to determine the count of weft yarn.

5.2.1.3 Gram per square meter

The GSM of fabric was calculated directly according to the BS EN 12127 ISO 3801 standard. A circular piece of woven fabric; having a diameter of 11.3 cm was cut and then weighed. The weight (in gm) of fabric sample was then multiplied by 100.

5.2.1.4 Cover Factor and Porosity

The cover factor and fraction of cover factor in percentage was assessed by using Equation 5.2 and Equation 5.3.

$$Cover factor = K_1 + K_2 - \frac{K_1 K_2}{28}$$ Equation 5.2

$$Cover, C, \% = 100(K_1 + K_2 - K_1 K_2)$$ Equation 5.3

The porosity and porosity in percentage of Tencel woven fabrics was assessed using the Equation 5.4 and Equation 5.5.

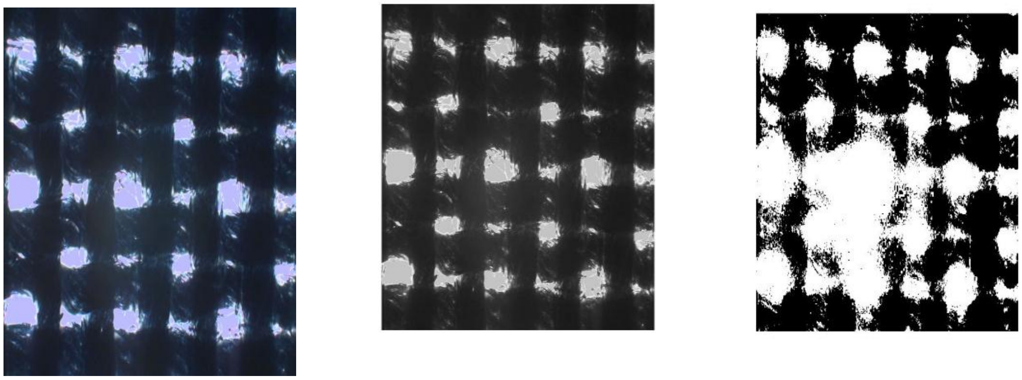
$$P = \frac{P_1 P_2}{(P_1 + d_1)(P_2 + d_2)}$$ Equation 5.4

$$P, \% = 100[1 - (K_1 + K_2 - K_1 K_2)]$$ Equation 5.5

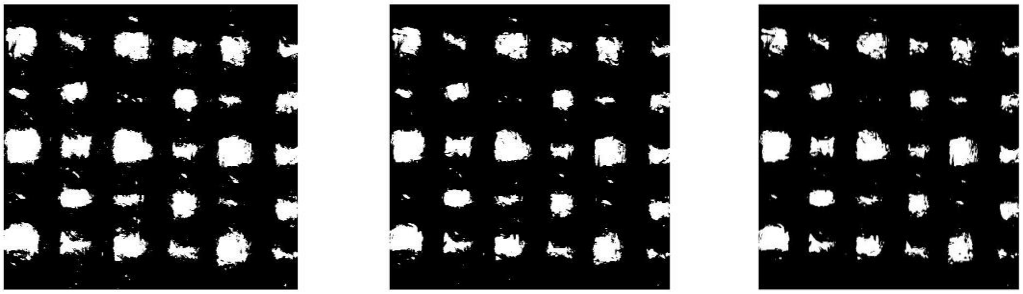
The cover factor and porosity are inversely proportional, higher porosity means lower cover factor. However, the cover factor and porosity values varied as the ends and picks per cm or weave density and linear density are varied.

Image processing software was also used to assess the cover factor and porosity of the Tencel plain weave fabric. The software programme was designed using Matlab 2009a version (see appendix A). The images were taken using optical microscope Leitz Diaplan microscope at a magnification of 160x and constant transmission light intensity (3). Twenty images were taken from each fabric side by side, before and after dyeing, in order to avoid weaving variations.

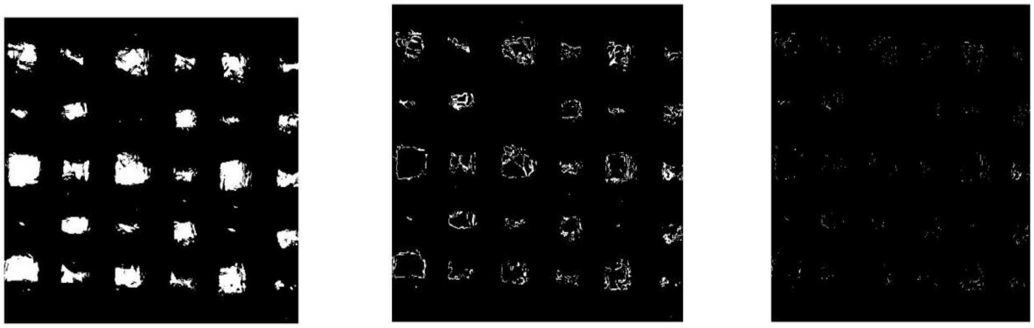
The coloured image of the fabrics was first converted into monochrome and then the average illuminate value was calculated. The grey scale covers the range 0 - 256, where 0 is black and 256 is white. As shown in Figure 5.2 (b), the pore areas are given a greying effect. This is due to the light of the microscope; the pore areas in the original fabric are coloured rather than white, and on grey image these colour areas are included in the average illuminate value, resulting in low and incorrect values for the porosity of the fabric.



(a) Original 115 GSM (b) Grey 115 GSM (c) 40 Threshold



(d) 70 Threshold (e) 140 Threshold (f) 150 Threshold



(g) 160 Threshold (h) 200 Threshold (i) 220 Threshold

Figure 5.2 Fabric images at different threshold (threshold values are intensity values on 0 – 256 scale)

Therefore, in order to minimize the error caused by the greying effect, in this program, loops were used to convert the grey image into a binary image (black and white) according to a pre-decided threshold value (150). The software calculated the average illuminate, and converted all the pixels that had a value of more than or equal to 150 into white pixels and less than to 150 threshold value into black (0). The percentage of white pixels gave the porosity of the fabric.

The threshold value of 150 was decided after studying the fabric images at different threshold values ranging from 40- 220 as shown in Figure 5.2 (c – i). It was observed visually that at 140, 150 and 160 threshold values, binary image were similar to the original fabric image. Therefore, the threshold value of 150 was selected because it is in the middle of this range. The selection of threshold value was further confirmed by two different assessors.

5.2.2 Pre-treatment

5.2.2.1 Cationic fixing agent

The Tencel plain weave fabric was pre-treated using 1 g l^{-1} of 3-chloro 2-hydroxytripropylmethylammonium chloride (CMAC), by pad-bake process. The fabric was padded at 78 % pick-up and then cure at 100 ^{0}C for 10 min. The fixing agent (CMAC) of 1 g l^{-1} was also applied by exhaust method at 40 ^{0}C for 30 min.

5.2.2.2 Causticisation

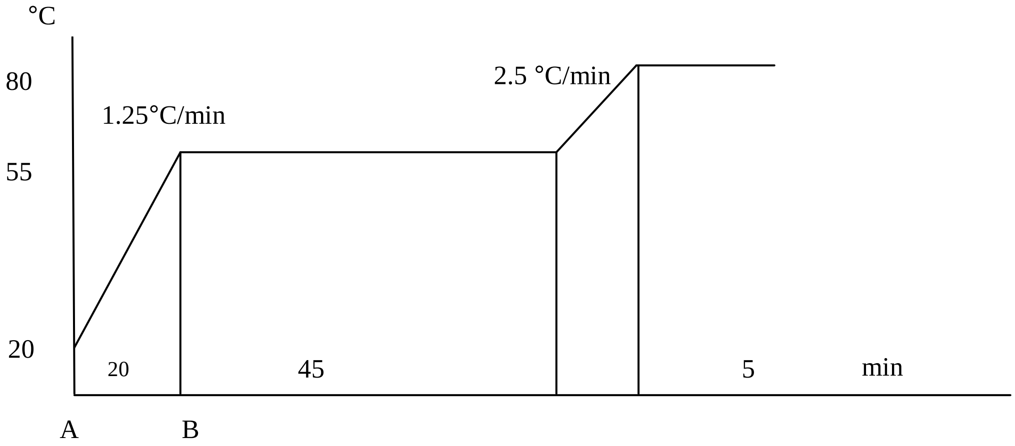
The caustic treatment using sodium hydroxide was applied on Tencel plain fabric by the following methods;

- The treatment was carried out by immersing the fabric in liquor to goods ratio of 100:1 at 5 °C for 5 min [213]. The concentration of caustic (NaOH) in the bath was 10% (w/v) and 15% (w/v). After immersing the fabric was dipped into the de-ionized water at 80 ^{0}C for 10 min and then neutralized with 0.1% acetic acid at 25 ^{0}C (room temperature) for 10 min. Rinsed at 25 ^{0}C using de-ionized water for 10 min and then dried in an oven at 40 ^{0}C for 24 hrs.
- The Tencel woven fabrics were causticised using sodium hydroxide (NaOH) 0.5 mol dm^{-3} and 2 mol dm^{-3}; by pad-batch process at room temperature [20]. For causticisation, fabric was padded at 80 to 92 % pick-up after passing from the NaOH and water solution and then rolled on a glass rod and covered with plastic

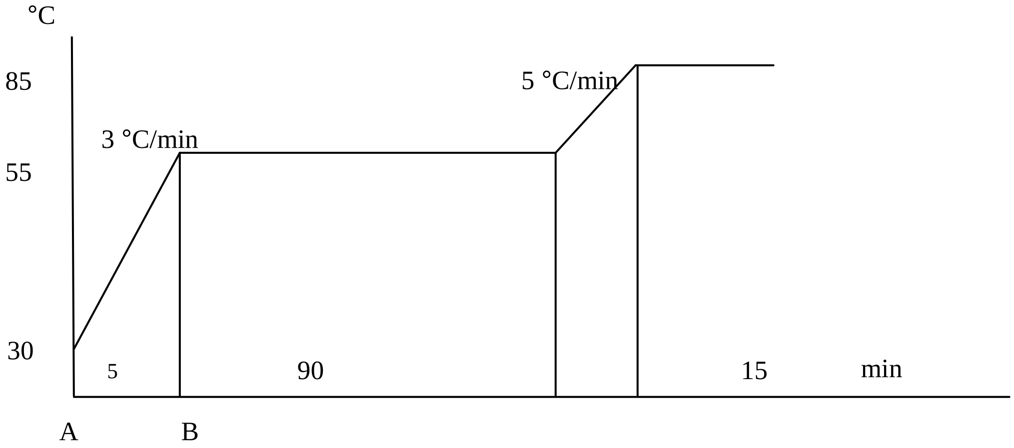
bag. After 30 min at room temperature, fabric was washed with hot water for 5 min then treated with 5% acetic acid solution for 60 min. It was then washed with cold water for 5 min and then dried in an oven.

5.2.2.3 Enzymatic Treatment

The cellulase enzymes, Cellusoft CR and Cellusoft L were kindly supplied by Novazymes (Denmark) [214]. Both CR and L were applied by exhaust as well as by pad-batch method. The method of enzymatic treatment by the exhaust methods is shown in Figure 5.3.



A = water. B = Cellusoft CR 0.5% or 2% owf at 6 pH.



A = water. B = Cellusoft L 0.5% or 2 % owf at 5.5 pH.

Figure 5.3 Enzymatic treatment by exhaust method

The pH (6 and 5.5) was adjusted using acetic acid and sodium acetate. The fabric after treating with enzymes was then rinsed with cold water for 10 min and then dried in an oven.

By pad-batch method; fabric was treated with Cellusoft CR (0.6 % and 0.75 %) and Cellusoft L (0.5%) at 80 % pick-up. The Cellusoft CR was applied at 60 ± 3 °C and 6 - 8 pH, where Cellusoft L was applied at 55 ± 3 °C, and pH at 5. The fabric was then batch on the glass rod and covered with plastic bag and under rotated slightly and left for 4 - 6 hrs in case of Cellusoft CR and 2 hrs for Cellusoft L. The fabric was then hot rinsed at a temperature of 90 – 100 °C for 20 min and then dried in an oven.

Enzymes with caustic treatment (2 mol dm^{-3}) were applied by the following methods as shown Figure 5.4. Enzymes as discussed above were applied on fabric by both exhaust and continuous method while caustic was applied on Tencel fabric by pad-batch method. The pre-treated fabrics were then dyed by pad-dry-thermosol process at 40°C liquor temperature with a 1 min dwell time using Levafix Blue CA (0.5% dye conc) on 163 GSM fabrics.

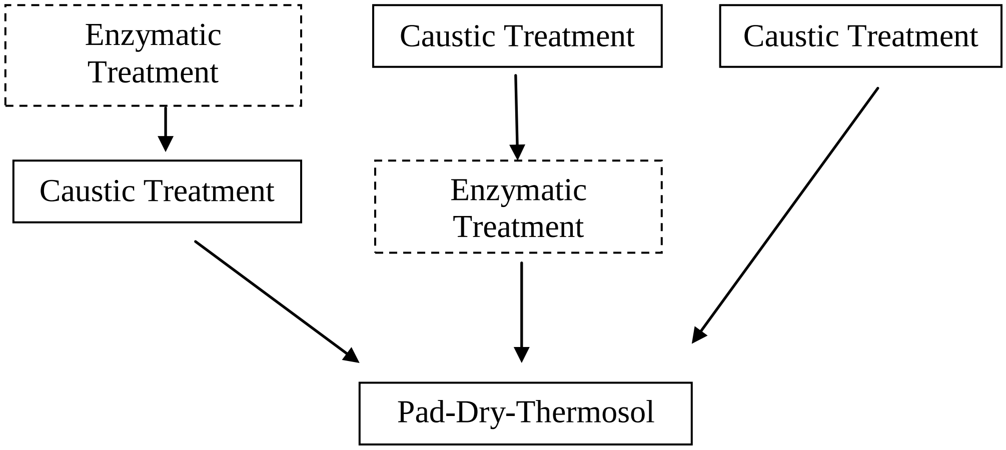


Figure 5.4 Enzymes with caustic pre-treatment

5.2.2.4 Weight Loss

The weight loss assessment is very simple method of assessing the loss of weight after causticisation. The fabric was taken and its area, (length * width in m.m) and weight (gm) were measured before and after causticisation. The loss of weight or density (WL) was calculated using Equation 5.6.

$$WL = \frac{W_1 - W_2}{W_1}$$

Equation 5.6

where,

W_1 = weight/area of fabric before causticisation.

W_2 = weight/area of fabric after causticisation.

*Area = length * width of fabric*.

5.2.3 Dyeing

Two different dyeing methods were used. The first method (method A) was used to dye the Plain, Twill 2/1, Twill 3/1 and Twill 5/1 Tencel fabrics and the second method (method B) to dye the nine different Tencel plain weave fabrics.

5.2.3.1 Exhaust Dyeing

5.2.3.1.1 Method A

The dyeing process was carried out at two different concentrations 0.5% and 2% using a Roaches Infrared dyeing machine. For exhaust dyeing the weight of plain Tencel woven fabric was 5 gm, while the weight of twill fabrics used was 2.5 gm.

The Novacron FN dyes were applied using low liquor- to- goods ratio of 10:1. The dyeing process [209] started with dye, water and auxiliaries at 80 ^{0}C. After 10 min salt solution (10% w/v) was added to the dye bath then the temperature was reduced to 60 ^{0}C at a rate of 1.5 ^{0}C min^{-1} within 15 min. Alkali solution (10% w/v) was added and treated for up to 45 min at the same temperature. The dyeing recipe is presented in Table 5.2 and dyeing procedure is shown in Figure 5.5.

Table 5.2 Recipe of Novacron FN dyes

Dye %	0.5	2.0
Albaflow FFC (ml/l)	0.5	1
Sodium Chloride (g/l)	20	40
Soda Ash (g/l)	10	12.5

In order to remove the unfixed dyes, alkali and electrolytes after dyeing, the dyed samples were rinsed in deionised water for 10 min at 50 ^{0}C, then neutralized with 0.7-1.0 % acetic acid (80%) for 10 min. They were then soaped for 15 min at 90 ^{0}C using 1-2 g l^{-1} Synperonic BD using a liquor-to-goods ratio of 10:1. The samples were further rinsed for 10 min at 50 ^{0}C and finally dried in an oven.

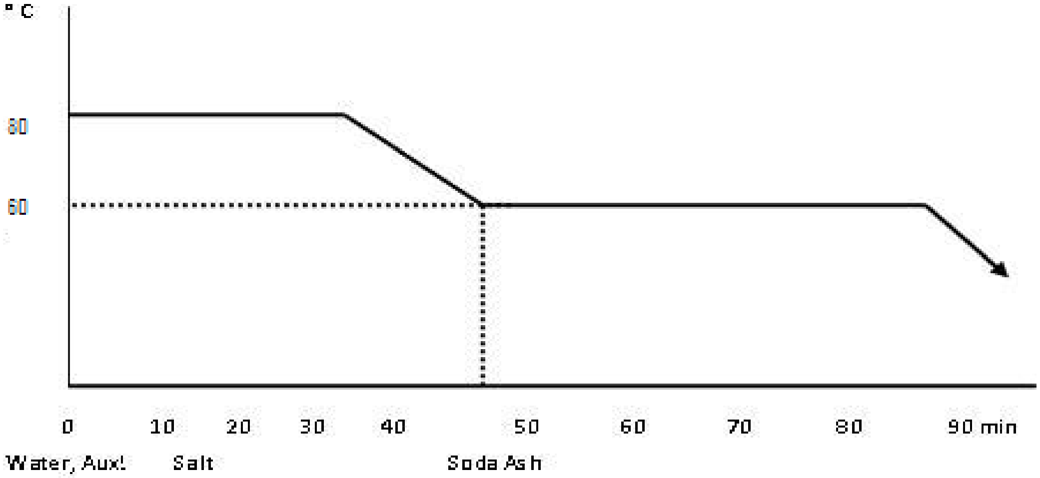


Figure 5.5 Novacron FN dyeing method

The dyeing procedures for applying Novacron LS and Novacron H dyes are shown in Figure 5.6 and Figure 5.7 and the recipes are presented in Table 5.3 [209] . Both processes of dyeing were carried out using a liquor-to-goods ratio of 15:1 at 50 ^{0}C using water and auxiliaries only. The temperature was increased to 90 ºC at a rate of 2^{0}C min^{-1} within 20 min and then dye was added. After 30 min salt solution (10% w/v) was added and the samples were treated at the same temperature for 40 min. After that, the temperature was reduced to 70 ^{0}C at a rate of 2^{0}C min^{-1} in case of using LS dyes and to 80 ºC at a rate of 1^{0}C min^{-1} for the H dyes for 10 min. Soda ash solution was then added portion wise as shown schematically in Figure 5.6 and Figure 5.7. After dyeing the fabrics were rinsed for 10 min at 50 ^{0}C and 70 ^{0}C, and then neutralized with 0.7 - 1.0 % acetic acid (80%) for 10 min. They were then soaped for 10 min at 95 ^{0}C using 1 - 2 g l^{-1} Synperonic BD at a liquor ratio of 15:1, before drying the fabric samples; they were rinsed further for 10 min at 70 ^{0}C and 50 ^{0}C.

Table 5.3 Recipe of Novacron LS and H dyes

Dye %	0.5	2.0
Albaflow UNI (g/l)	0.5	1
Sodium Chloride (g/l)	10	20
Soda Ash (g/l)	3	4
Soda Ash (g/l)	7	8

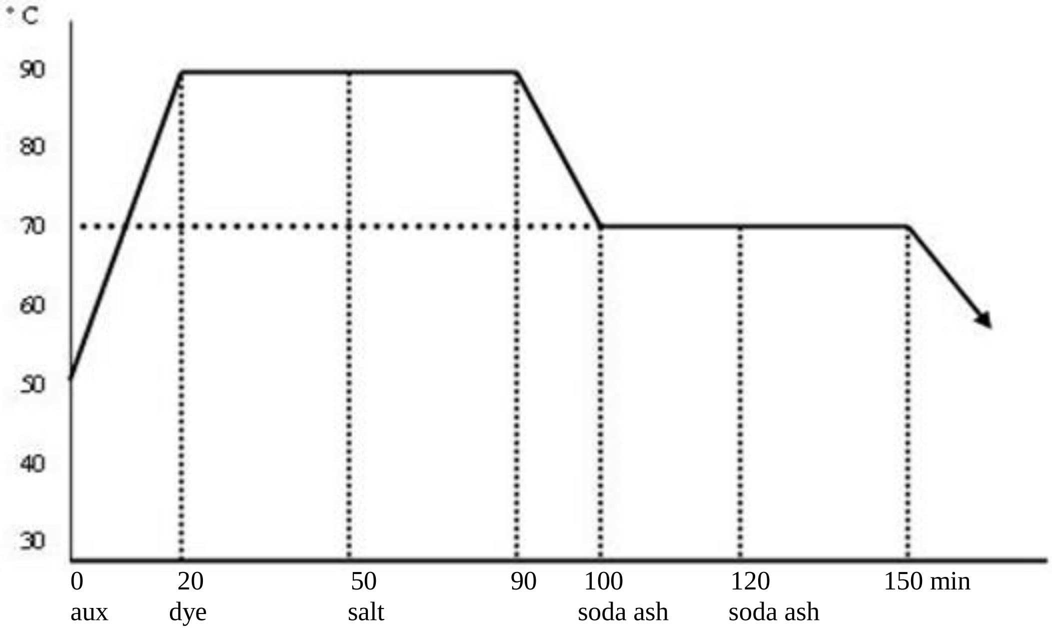


Figure 5.6 Dyeing procedure of Novacron LS

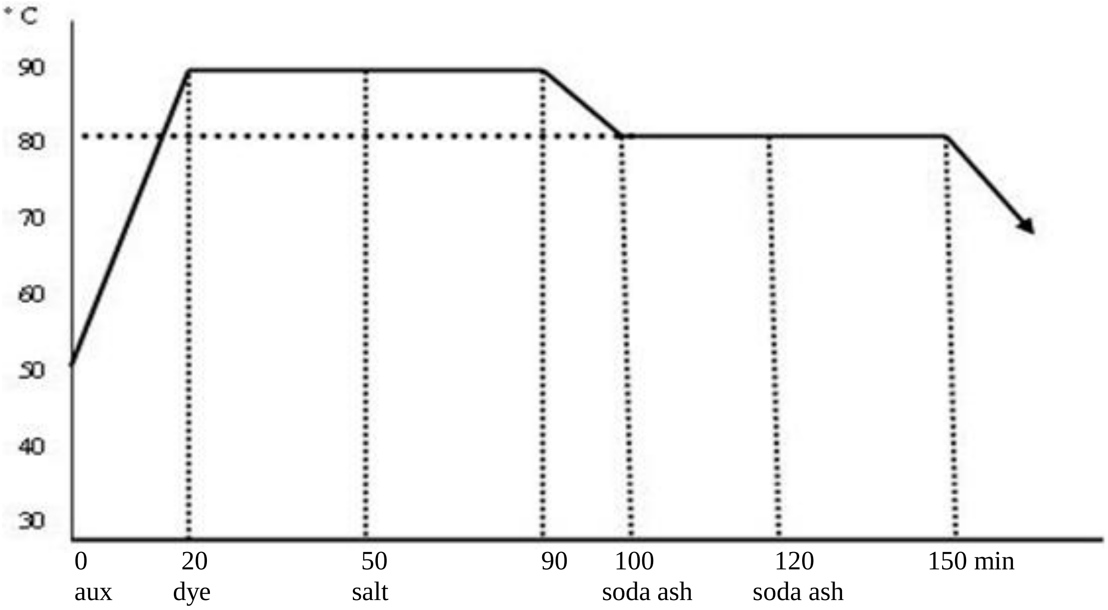


Figure 5.7 Dyeing procedure of Novacron H

5.2.3.1.2 Method B

The difference between method A and B was dyeing procedure while the recipes of Novacron FN and LS were the same (Table 5.2 and Table 5.3). The highest GSM of fabric (163 GSM) 5 gm of fabric weight was taken and dyed at a dyeing conc of 0.5% owf.

For Novacron FN/C-R dyes, the dyeing process was started at 110 ^{0}C with water, AlbaFLOW UNI (0.5 g l^{-1}) and dye (0.5% conc) at liquor to goods ratio of 10:1. After 10 min salt solution (20 g l^{-1}) was added and fabric was treated for further 50 min at the same temperature. Then the temperature was decreased to 70 ^{0}C and soda ash solution was added and processed for 45 min. The washing was carried out at the same methods as recommended by the Huntsman [209].

For Novacron LS dyes; the dyeing was started at 110 ^{0}C with water and AlbaFLOW UNI (0.5 g l^{-1}), after 20 min dye solution (0.5% owf) was added and fabric was treated for 50 min. Then salt solution (10 g l^{-1}) was added, after 40 min the temperature was decreased to 70 ^{0}C with in 10 min and then soda ash solution (7 g l^{-1}) was added. After 20 min remaining quantity of soda ash solution (3 g l^{-1}) was added and further processed for 30 min. The washing was carried out by the method recommended by the Huntsman [209].

5.2.3.2 Continuous Dyeing

5.2.3.2.1 Method A

Continuous dyeing processes were carried out in three different ways for each of the Novacron C and Levafix CA dyes at 0.5% and 2% owf.

- Pad-steam.
- Pad-batch.
- Pad-dry-thermosol.

The recipe for applying Novacron C dyes is presented in Table 5.4 [209] and for Levafix CA dyes in Table 5.5 [210]. The weight of fabric was 2.50 gm (Plain) and 1.60 gm (Twill) and a pick-up of 80% was used. For pad-steam, after padding the fabric was steamed at 102 ^{0}C for 2 min for Novacron C dyes but for 90 sec for Levafix CA dyes.

For application of both classes of dyes by pad-batch, after padding the padded fabric was rolled around glass test tubes and covered with a plastic bag for 20 hrs at 20 – 25 ^{0}C. For pad–dry-thermosol, after padding the substrate was first dried in an oven at a temperature 100-120 ^{0}C for 1-2 min, and then cured in an oven for 3 min at 150 ^{0}C.

The washing –off of dyed fabrics using Novacron C dyes was carried out using the same methods as described for Novacron FN dyes. In case of Levafix CA dyes the substrate was rinsed for 10 min at 30 – 50 ^{0}C, and 50 – 80 ^{0}C, then neutralized with 0.7 - 1.0 % acetic acid (80%) for 10 min. They were then soaped for 10 min at 90 ^{0}C using 1 - 2 g/l Synperonic BD. Finally, the fabric was rinsed further for 10 min at 80 ^{0}C, then 50 ^{0}C and dried in an oven.

Table 5.4 Dyeing recipe of Novacron C dyes

	0.5%	*2%*
Novacron C (g/l)	5	20
ALBA Flow PAD (ml/l)	1	2
Na-Silicate 72^{0}Tw (ml/l)	70	70
Caustic Soda 66^{0}Tw (ml/l)	6	9
Urea (g/l) *In case of Pad-dry-cure*	50	100

Table 5.5 Dyeing recipe of Levafix CA and Remazol B-A dyes

	0.5%	*2%*
Levafix CA (g/l)	5	20
ALBA Flow PAD (ml/l)	4	4
Sodium m-nitrobenzenesulphonate (ml/l)	10	10
Sodium bicarbonate (ml/l)	10	10
Sodium carbonate (ml/l)	10	10
Urea (g/l) *In case of Pad-dry-cure*	50	100

5.2.3.2.2 Method B

The nine different GSM of Tencel plain weave fabrics were dyed using different dyeing methods as shown in Figure 5.8. Dyeing was carried using the same dyeing recipe (Table 5.5) of Levafix Red, Yellow and Blue CA and Remazol Black B-A at 0.5% dye conc. The causticised and non-causticised fabrics were dyed as shown in the flow chart (Figure 5.8). In both cases the fabric was padded at 80% pick-up, with the following liquor temperature and dwell time (duration of impregnated fabric in padding liquor):

1. 40 ^{0}C liquor temperature, with a 5 min dwell time
2. 40 ^{0}C liquor temperature with a 1 min dwell time.
3. Liquor at room temperature with no dwell time.

Then the fabric was processed by:

- Pad-steam
- Pad-dry-steam.
- Pad-dry-thermosol/pad-dry-cure.

In the pad-steam process the fabric was steamed at 102 ^{0}C for 90 sec. In pad-dry-steam the fabric was dried after padding at 110 - 120 ^{0}C for 1 - 2 min, and then steamed at 102 ^{0}C for 90 sec. For the pad-dry-thermosol process the padded fabric was dried at 110 - 120 ^{0}C for 1 - 2 min and baked at 150 ^{0}C for 3 min. In the pad-batch method the fabric was batched for 20 hrs. After dyeing, washing was carried out by the methods recommended by DyStar.

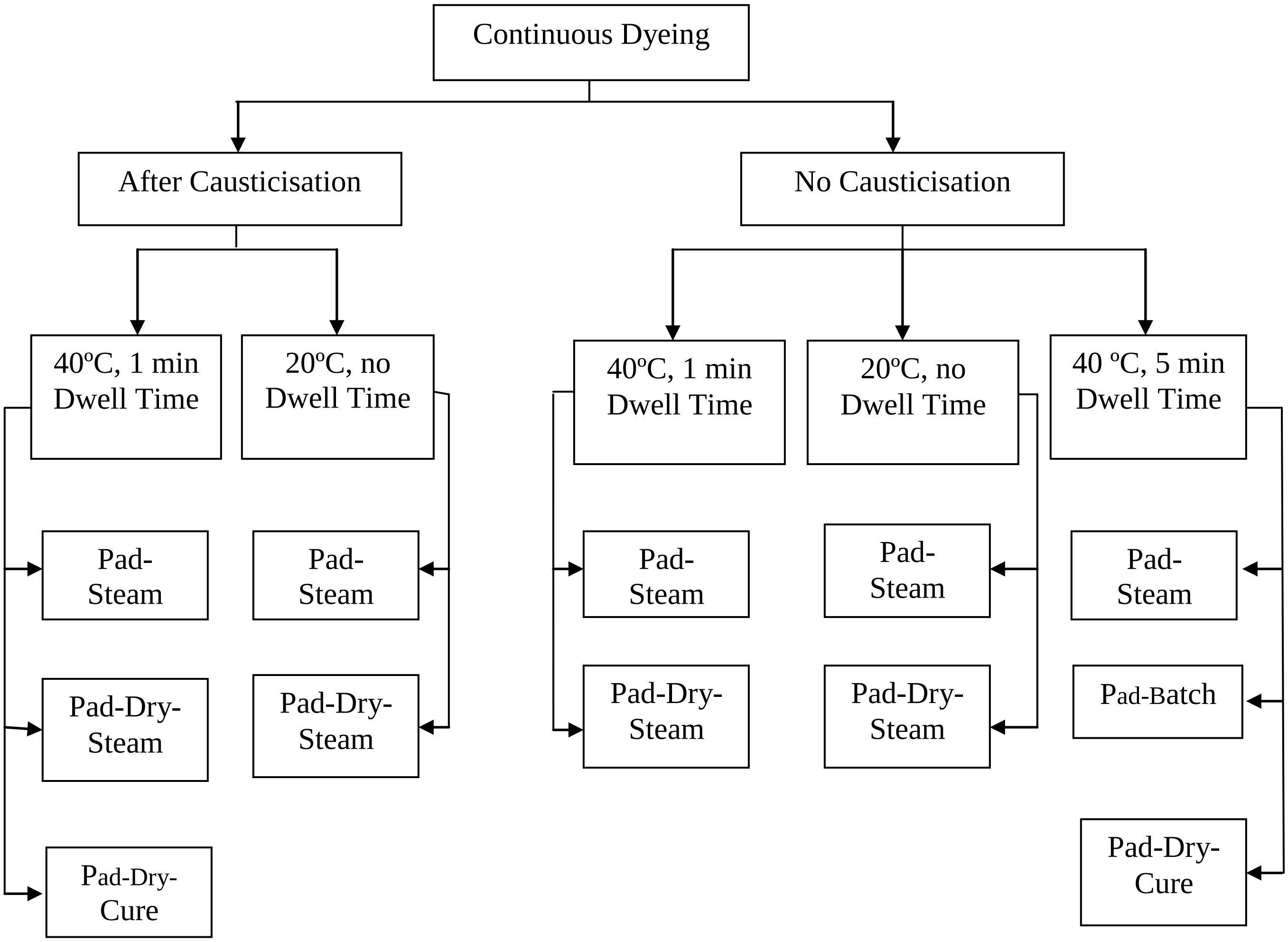


Figure 5.8 Flow chart of continuous dyeing methods

5.2.4 *Assessment of Visual Depth*

The spectral reflectance values (400-700 nm) were measured using a Spectra Flash SF600 spectrophotometer (Datacolor International) using the 9.00 mm aperture for plain and twill weaves of fabrics and 38.00 mm aperture for plain fabrics (nine different weave density). For each sample, readings were taken four times, each at a different position. The percentage reflectance values 'R' were converted to K/S values, using the formula shown in Equation 5.7.

$$K/S = \frac{(100 - R)^2}{200R}$$ Equation 5.7

The K/S values were used to calculate the visual depth by using Equation 5.8, which gives the Integ value ‘I’ [133]. The average of the four values was taken to express the visual depth of the dyed fabric.

$$I = \sum \left[\left(\frac{K}{S} \right)_{\lambda} \left(\bar{x} + \bar{y} + \bar{z} \right)_{\lambda} E_{\lambda} \right]$$

Equation 5.8

5.2.5 *Dye Exhaustion and Fixation*

A Perkin Elmer UV/VIS Lambda 2 spectrometer was used to measure the absorbance (A) in the visible region of the spectrum (400-700nm) of dye bath liquors before and after dyeing and after washing. Concentrations were calculated from the calibration graphs at the wavelength of maximum absorption (λ_{max}). The absorbance, A, of the dye solution both before and after dyeing were measured at λ_{max} for the dye. It was necessary to dilute the dye solutions prior to measurement in order to obtain absorbance reading between 0-2 units. In converting the absorbance to concentration, the dilution factors used were taken into account. The dye exhaustion was calculated from the differences absorbance of dye liquors before and after dyeing as shown in Equation 5.9 below;

Dye Exhaustion in percentage, $E = 100\left(\frac{A_1 - A_2}{A_1} \right)$ Equation 5.9

In case of exhaust dyeing, the fixation of dyes was calculated from the difference of before dyeing, after dyeing and after number of washing as shown in Equation 5.10.

Dye Fixation in percentage, $F = 100\left(\frac{A_1 - A_2 - A_3 - A_4 - A_5}{A_1} \right)$ Equation 5.10

A_1= Absorbance of dye liquor before dyeing,

A_2= Absorbance of dye liquor after dyeing,

A_3, A_4, & A_5 = Absorbance of first, second and third wash liquors.

For continuous dyeing application, the percentage pick-up of dye from the dye bath is an additional variable and the weight (in gm) of dye padded on to the fabric has to be determined. The fixation was calculated from the difference of amount of dyes in gm (M) in the dye bath and after number of washings as shown in Equation 5.11. The amount of dye in the washing liquors in gm was determined from the calibration graph of absorbance versus concentration for the dye in water at the λ $_{\max}$ for the dye.

$$\text{Dye Fixation in Percentage}=100\left(\frac{M_1-M_2-M_3-M_4}{M_1}\right) \qquad \text{Equation 5.11}$$

where,

M_1= Mass of dye in gm before washing.

M_2, M_3, M_4 = Mass of dye in gm after number of washing liquor.

For measuring the overall dye uptake of Tencel plain weave fabrics, the amount of dye in the fibres ‘E’ was first calculated using calibration graphs of K/S values versus dye uptake at different dye concentration (0.1%, 0.5%, 1%, 2%, 3% and 5%). The K/S values were calculated using a Spectra Flash SF600 spectrophotometer and the dye uptake % was calculated from the difference of absorbance value of before and after washing using Perkin Elmer UV/VIS Lambda 2 Spectrometer as shown in Equation 5.12.

$$\%D=100\left(\frac{A_1-A_2-A_3-A_4}{A_1}\right) \qquad \text{Equation 5.12}$$

where,

A_1= Absorbance of dye liquor before dyeing.

A_2= Absorbance of dye liquor after dyeing.

A_3, & A_4= Absorbance of first and second washing liquors.

The amount of the dye fixed in the samples was measured by assessing the K/S value after dyeing (before washing). After washing the dyed fabric was treated with 25% (w/w) pyridine and water solution at 100 °C and liquor-to-goods ratio 10:1 for 2 min each time until no dye molecules was runoff. Every time fresh pyridine solution was taken. The dyed and pyridine treated fabric was then dried in an open air for whole night and after drying the K/S value of the fabric was again measured. The dye fixation (F) was then calculated by using below Equation 5.13 [215]:

$$F = \frac{(K/S)_2}{(K/S)_1} \qquad \text{Equation 5.13}$$

where,

$(K/S)_1$= K/S value after dyeing.

$(K/S)_2$=K/S value after pyridine treatment.

The overall dye uptake, T (g $100g^{-1}$) was calculated by using the below Equation 5.14:

$$T = EF \qquad \text{Equation 5.14}$$

5.2.6 Uniformity of Fibre Coloration

The uniformity of dyeing throughout the cross-section of yarn was assessed using Leitz Diaplan microscope at a magnification of 160x. Between 10 - 12 yarns were taken randomly from the dyed samples and arranged in a parallel fashion [216]. In order to pass the bunch of yarns into the hole of the cross-sectional plate, a carrier yarn was used. It was knotted with a bunch of yarns and then threaded through the hole of the plate. After threading, the extra length of yarn (more than about 0.64 cm) was cut with sharp scissors at both front and back sides. The cross-sectional plate was then positioned in such a way that the edges of yarn were touching the edge of a block (wooden or hard board). The remaining 0.64 cm of yarn was trimmed by a sharp razor from one side and then the plate was turned on the back side and the remaining yarn trimmed. The plate was ready to view under the microscope and images were automatically captured by a digital camera. The sharpness of the images depended on the sharpness of the razor.

Images were taken and statistically analyzed for uniformity of fibre coloration (UFC) in two ways:

- Subjective assessment.
- Objective assessment.

5.2.6.1 *Subjective Assessment*

In this method ten yarns were selected and the uniformity of fibre colouration was calculated by counting the number of fibres according to a rating 1 to 5 as shown in Figure 5.9 and Figure 5.10.

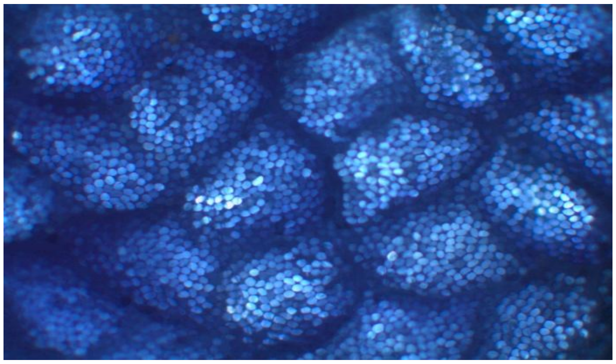


Figure 5.9 Novacron Blue C-R 0.5% Twill 2/1

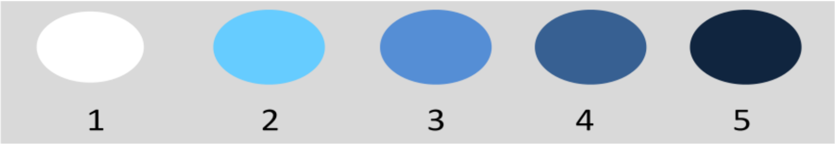


Figure 5.10 Rating for assessing the UFC

After counting and rating the number of fibres in the yarn of woven fabric, the standard deviation (SD) was then calculated as shown in Equation 5.15.

$$\text{Standard Deviation} = S.D = \sqrt{\frac{\sum FR^2 - \left(\frac{\left(\sum FR\right)^2}{N}\right)}{N-1}} \qquad \text{Equation 5.15}$$

where,

R= Rating.

F= Fraction of sample population given rating, R.

N= Population=∑F (normalize to 100).

5.2.6.2 Objective Assessment

The UFC of yarns of the woven fabrics were also analyzed by objective assessment. A programme was designed using Matlab version 2009a (see appendix B). In this programme, the RGB yarn cross-sectional images were first converted into monochrome (0 – 255). For defining the threshold values, the grey neutral density Lee filters (209, 210, 211, 298, 299) as shown in Figure 5.11 were purchased from Lee filters, U.K. The percentage transmittance (%T) of Lee filters was measured on Perkin Elmer lambda 35 UV/Visible spectrophotometer. At least five readings were taken from each filter. The average of five %T values were multiplied by $E_\lambda Y_\lambda$ [217] along the visible wavelength (360 – 780 nm) and converted to Y value. Using Y value of each filter, lightness L* values were calculated using the Equation 5. 16.

$$L^* = 116\left(\frac{Y}{100}\right)^{1/3} - 16 \qquad \text{Equation 5.16}$$

For measuring the grey intensity of the Lee filters, each filter was scanned using a HP scanner (300 dpi) and then the intensity of filter images was measured using Matlab version 2009a. The calibrated graph of grey intensity (0 – 255) versus lightness (0 – 100) was drawn as shown in appendix C, a polynomial equation was used to fit the graph. The L* values were taken as visually uniform scale and divided into 5 different ratings. Using the calibration graph (see appendix C), the grey values were taken from the L* values. These grey values are shown below and represent the threshold values with respect to the rating of depth of the fibre filament.

Threshold	**Rating**
160 ≥ 256	1 (White)
86 ≥ 160	2
35 ≥ 86	3
7 ≥ 35	4
0 ≥7	5 (Dark)

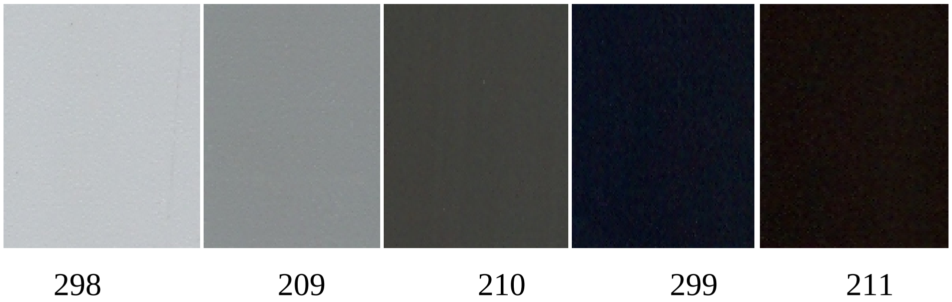


Figure 5.11 Lee filters

The Matlab programme counts the grey level of the cross-sectional images pixel by pixel, with respect to its rating (threshold values) and then standard deviation (Equation 5.15) and average (Equation 5.17) were calculated.

$$Mean = \frac{\sum FR}{N}$$

Equation 5.17

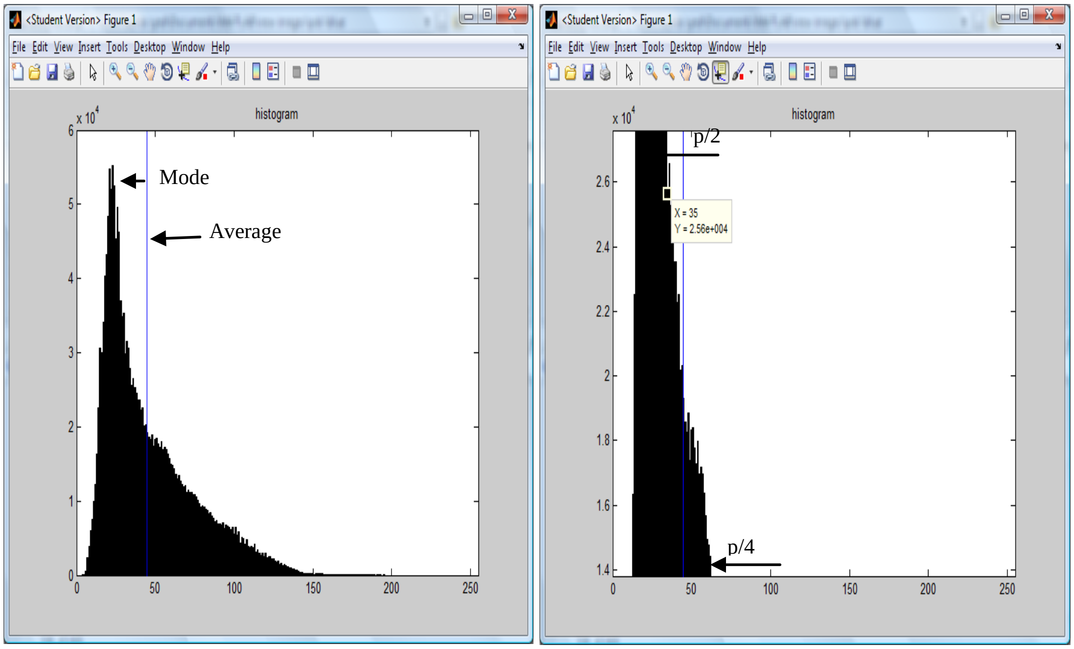
The software was also designed to draw histogram using the same monochrome image (Figure 5.12). The maximum number of pixel (p) versus grey level was calculated which corresponds to mode in the histogram. The maximum peak was then divided into mid (p/2) and quarter point (p/4). The grey values were measured relative to the pixel at midpoint and quarter point manually both from the right and left side of histogram using data courser option (Figure 5.12 b). The ratio of difference of mode values to the right and left side of the histogram determine the dispersion of histogram or grey values in the image (see Equation 5.18). The dispersion at the midpoint (D_1) and quarter point (D_2) of mode was used to determine the symmetrical shape of histogram. The range of dispersion 0 to 1 was obtained by subtracting 1 to D_1 and D_2 values.

$$D_1 = \frac{ac}{ab} or - \frac{ab}{ac}$$
$$D_2 = \frac{ac'}{ab'} or - \frac{ab'}{ac'}$$

Equation 5.18

where, $ac = c - a$ and $ab = a - b$

$ac' = c' - a$ and $ab' = a - b'$



a.Histogram b. Midpoint and Quarter point

Figure 5.12 Histogram (mode and average)

0 = symmetrical histogram.
-0.5 — +0.5 = moderately symmetrical.
-1 — +1 = not symmetrical or highly skewed.

A negative sign shows the tail of histogram is more towards the darker (0 grey value) while the positive tail shows the lighter (255 grey value).

Histogram could have either high peak (red colour) or flat-topped curve (blue colour) (Figure 5.13). The bandwidth of histogram indicates the distribution of set of data or distribution of depth of fibres coloration. When compare two or more images, can have same SD values and almost similar dispersion but can be different in bandwidth. However, images which have uniform distribution of colour have zero SD value and symmetrical bell-shape.

The bandwidth is measured by dividing the maximum pixel value (p) to the difference of mode value (grey level) at midpoint (p/2) of each left (L) and right side (R) of the histogram (see Figure 5.14). Mathematically can be define as

Bandwidth at right hand side = BR = ac/p

Bandwidth at left hand side = BL = -(ab/p)

where

ac = c – a and ab = a – b

Right hand side tail have positive sign and tail is towards the lighter side (255 grey value) and left hand side tail have negative sign and tail is towards the darker side (0 grey value). The high values of bandwidth either right or left side indicate the flat-topped curve with long and heavy tails. Similarly, lower values of bandwidth in each side indicate sharp thin peak of histogram with short and narrow tail as shown in appendix F. The interpretation of dispersion and bandwidth gives quick indication of distribution of depth of fibres or filaments whether distribution is lighter side (right hand side) or darker side (left hand side).

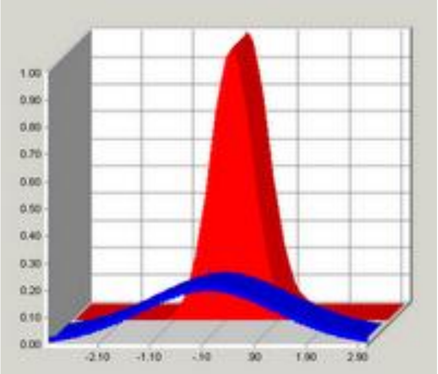


Figure 5.13 Bandwidth of histogram

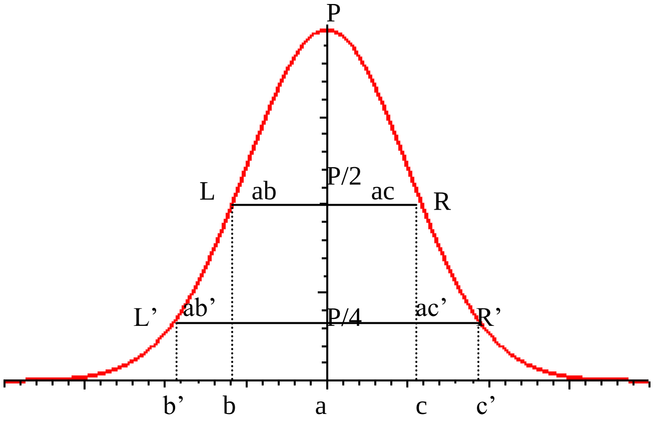


Figure 5.14 Histogram

In order to measure the dye uniformity more accurately three cross-sectional images were taken from each dyed fabrics. Each image contains approximately ten yarns of the woven fabric. All images were taken at the same light intensity of the microscope. The accuracy of the objective assessment depends on the accuracy of images; therefore, correct preparation of images is necessary.

5.2.7 Microspectrophotometry (MSP)

The colour depth of single fibre filament of Tencel four weave fabric (plain, 2/1, 3/1 and 5/1 twill) was measured on MSP AX10, Imager DIM Zeiss. The fibre images were captured (see Figure 5.15) using J and M Tidas vision and Panorama A 1.1 software under the transmittance TL and light source of 32,00 K. Two fibres one from the warp side and other from the weft side were selected. Ten points of each fibre were then measured along their length at a magnification 40x/0.75. The standard deviation of absorbance value at λ_{max} of individual fibre was then calculated.

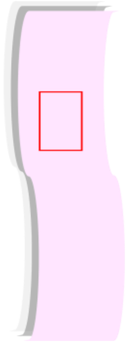


Figure 5.15 Fibre image on MSP

5.2.8 Additional Assessments

The additional assessments (listed below) were carried out on the Tencel plain weave fabric dyed by pad-steam process using Levafix Red CA dyes, after caustic treatment at 40 °C liquor temperature with a 1 min dwell time except fastness to rubbing. The rubbing fastness test was performed on all dyeing methods (Figure 5.8) using Levafix Red CA dyes. For comparing the behaviour of Tencel fabric after dyeing, some tests such as tensile strength, and fabric handle were carried out before dyeing (scoured and causticised fabric).

- Fastness to rubbing.
- Fastness to washing.
- Fibrillation.
- Tensile strength.
- Fabric handle.
- Abrasion resistance.

5.2.8.1 Fastness to Rubbing

Rubbing fastness was performed according to the BS EN ISO 105-X12:2002 [218] on crock meter. The dyed fabric was measured in both warp and weft directions separately. The test specimen of 14 * 2 inch was taken both from warp and weft yarn of the woven fabric and held on the crock tester. Cotton bleached fabric of 5 *5 cm was taken and gripped with the help of wire on the finger having a size 1.4 cm. The cotton fabric was rubbed 10 times to and fro against the test specimen. The bleached fabric was rubbed both in dry and wet state separately.

5.2.8.2 Fastness to Washing

Washing fastness tests were performed on a Wash Tec-P, Roaches International according to the BS EN 20105-C03:1993, ISO 105-C03:1989 [219]. The dyed sample was cut to 4 * 10 cm, and the same size of multifibre (secondary cellulose acetate, bleached un-mercerized cotton, nylon 6.6, polyester, acrylic, wool worsted) society of dyers and colourists (SDC) standard specimen was taken. The dyed sample and standard was then stitched together from the face (one side). The washing liquor was prepared at liquor to goods ratio 50:1, containing SDC standard soap 5 g l^{-1} and soda ash 2 g l^{-1}. The dyed and standard samples were immersed in the washing bath at a temperature of 60 ^{0}C for 30 min. After washing the specimens were taken out, un-stitched and washed with cold water for 5 min and then running tap water for further 5 min and then dried in an open air or oven. After drying the fabric was rated by using grey scale (1 to 5) and staining scale (1 to 5). Each multi-fibre was rated separately.

5.2.8.3 *Fibrillation*

There is no standard method of measuring the fibrillation of Tencel woven fabric. Therefore, for assessing the number and length of fibril in the fabric, twenty (20) fibre images from each woven fabric were taken on the Scanning Electron Microscope (SEM) at 600x magnification. The Olympus image analysis software was used to measure the length and the number of fibrils as shown in Figure 5.16 below. The software automatically transferred the data into an excel sheet but from the fibres the fibrils were selected manually. However, the software calculated the length of the manually selected fibrils automatically, in µm.

The lengths of fibrils in each fibre were then arranged in descending order. Similarly, fibril lengths of approximately twenty fibres were arranged and the frequency distribution was calculated by defining the range of fibril lengths. The range was 5 µm apart between 1 and 150 µm.

In order to know approximately how many fibrils were in the fabric and which lengths of the fibrils were most common. The sum of each fibre was calculated with respect to the distribution of the fibril. These data are very helpful to know whether the fabric had primary fibrillation or secondary fibrillation and the behaviour of fabric towards the dyeing and other physical properties. For analyzing the proportional length of fibrils, the frequency distribution of each fibre was individually multiplied with the median of the frequency distribution range and then sum of each value was calculated. The sum was then divided by the total number of fibrils.

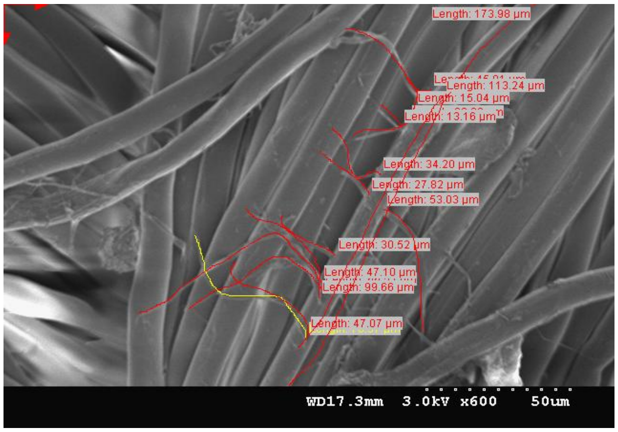


Figure 5.16 Assessment of fibrillation

5.2.8.4 Tensile Strength

The strength of Tencel woven fabric was measured on an Instron 3345-K7484 tester, according to the standard BS EN ISO 13934 [220]. The following parameters were set for the test.

Gauge length = 100 m.m.

Sample size = 200 *50 m.m.

Jaws width = 50 m.m.

Jaws pressure = 40 psi.

Pre-tension = 2N.

Elongation rate = 100 m.m/ min.

State of specimen = dry state.

Five samples were taken from the warp and other five from the weft yarn side, from each of the nine plain woven fabrics. The test was performed on Tencel woven fabric at three different stages of processing - before causticisation, after causticisation and after dyeing. The fabric was left for 24 hrs for conditioning in the standard atmosphere. The samples were then cut and fringed in such a way the yarns were laid parallel depending on the direction of warp or weft yarns and then clamped between the jaws. The pressure on the jaws was set in such a way no jaw break or slippage occurred. The test result including the tenacity N/tex, load at break N, and extensibility % were calculated and then statistically analyzed.

5.2.8.5 Fabric Handle

The fabric handle was measured by assessing the bending length and flexural rigidity. The test was carried out according to standard BS 3356:1990 standard [221], The size of rectangular sample was (length*width) 200+- 1*25+-1 mm. At least three samples were taken from both warp and weft yarns of the woven fabrics. The samples were first conditioned at standard conditions (20 ± 2 ^{0}C and 65 % humidity) for twenty four (24) hrs. Then the samples were laid on the smooth horizontal surface of the Shirley Stiffness Tester. The specimen was moved lengthwise over the edge at a uniform rate of an approximately 25 mm in 5 sec, until the tip of specimen viewed in the mirror cuts both index lines. The bending length C, cm was immediately read off from the scale mark opposite a zero line engraved on the side of the platform. The flexural rigidity G, gm cm^{-3} was then calculated using Equation 5.19. A fabric that has high flexural rigidity means stiffer. Each specimen was tested by twice, once from the face and the second from the back of the same end of specimen uppermost.

Flexural Rigidity, $G = 0.10\ MC^3$ Equation 5.19

where, *M = fabric weight or GSM.*

5.2.8.6 Abrasion Resistance

Abrasion resistance test was performed on Nu-Martindale abrasion and pilling tester, James H Heal and co ltd, according to the BS EN ISO 12947-3:1999 "determination of the abrasion resistance of fabrics by the Martindale method part 3: determination of mass loss" [222]. Three samples (38 mm diameter) of each woven fabric were taken and abraded against the woollen standard abraded fabric. The mass loss was determined after every 1,000 number of cycles up to 5,000 cycles and then after every 2,000 cycles until the specimen (two yarns) were broken. Each woven fabric was abraded by using two different pressures 9 kpascal (for apparel) and 12 kpascal (for technical textiles).

5.2.9 Mathematical Modelling

In order to predict the visual depth and uniformity of fibre colouration (mean and SD) of Tencel plain weave fabrics dyed by continuous dyeing methods, numerical equations were determined using Microsoft Excel 2007. The model developed gave a relationship between the dyeing behaviour and the fabric density. Visual depth values were calculated using numerical equations. The errors between the actual and calculated visual depth values were minimized using "Solver" in Excel. Other dyeing behaviours, such as UFC standard deviation and mean values, were calculated and fitted in a similar way.

CHAPTER 6: RESULTS AND DISCUSSIONS OF DIFFERENT WEAVE STRUCTURE

6 Results and Discussions of Different Weave Structure

6.1 Fabric Assessment

The physical properties of Tencel Plain, Twill 2/1, Twill 3/1 and Twill 5/1 woven fabrics are shown in Table 6.1. The value of the physical properties of GSM, cover factor and porosity vary in all (four) Tencel woven fabrics because of the variation in ends and picks per cm and weave.

The Twill 2/1 fabric has the highest porosity and lowest cover factor as compared to the other Twill weave fabrics. The Twill 3/1 weave fabric has the highest cover factor and the lowest porosity. The Twill 5/1 weave has tight weave because of the higher number of picks per cm as compared to ends per cm; therefore, it has a highest GSM. These differences in physical properties lead to the variation in dyeing behaviour as discussed later.

Table 6.1 Physical properties of Tencel woven fabric

	Plain	Twill 2/1	Twill 3/1	Twill 5/1
Fabric	100% Tencel	100% Tencel	100% Tencel	100% Tencel
End/cm * Picks /cm	38 * 30	36* 32	38* 33	35 * 36
Linear Density of Warp (tex)	20	20	20	20
Linear Density of Weft (tex)	21	20	20	20
G.S.M	138	143	140	148
Cover Factor	11.26	11.14	11.57	11.56
Cover Factor in %	85.7	84.8	86.9	86.7
Porosity	0.38	0.39	0.37	0.372
Porosity in %	14.3	15.15	13.05	13.24

6.2 Exhaust Dyeing

6.2.1 Visual Depth

The trends of average of visual depth obtained with Novacron dyes in Figure 6.1 show that Novacron FN dyes (0.5% and 2% dye conc) give higher Integ values as compared to the Novacron LS and H dyes. As discuss in Section 5.1.2 Novacron FN dyes required lower liquor ratio; hence promote the dye uptake. The Integ values of Novacron LS dyes are higher than the Novacron H dyes, although the recipe of both Novacron LS and H dyes were the same. The reason of the lowest Integ values of Novacron H dyes is because of their bigger molecular size.

The Integ value of Novacron Brilliant Red FN-3GL, Red FN-R, Black C-NN and Yellow-FN-2R are shown in Figure 6.2. Novacron Red FN-R (monoazo) because of less substantivity shows the lowest Integ value as compared to other dye shades of FN dyes. Further, the Twill 2/1 fabrics appear more deeply dyed than the other Twill weave and plain weave fabrics (see Figure 6.2). The reason for this is that the Twill 2/1 fabric has a high porosity which enables dye liquor to flow easily throughout the fabric structure [18]. The Twill 3/1 and Twill 5/1 fabrics have low porosity and high cover factor, which does not allow the dye liquor to flow as easily through in the Twill 2/1 fabrics.

The trends of visual depth using Novacron LS dyes at 2% dye conc (Figure 6.3) descends in order Plain > Twill2/1>Twill3/1>Twill5/1 fabrics. The trend in Novacron H (Figure 6.4) and LS (0.5% dye conc) dyes shows that Integ value of plain < Twill 2/1 fabrics, except Novacron Brilliant Blue H-GR 2%, where the trend is same as other Novacron LS (2% dye conc).

Overall in exhaust dyeing using Novacron FN, LS and H dyes, the Twill 3/1 and Twill 5/1 fabrics have lowest visual depth. It has been observed that the plain fabric shows the highest visual depth except for Novacron FN and LS 0.5% dye conc. The plain fabric surface is flat, and when light comes into contact on its surface, less is scattered; hence there is greater absorbance and it appears deeper visual depth. Additionally, low weight and fewer picks per cm as compared to ends per cm of the plain fabric would also allow dye to easily flow through it.

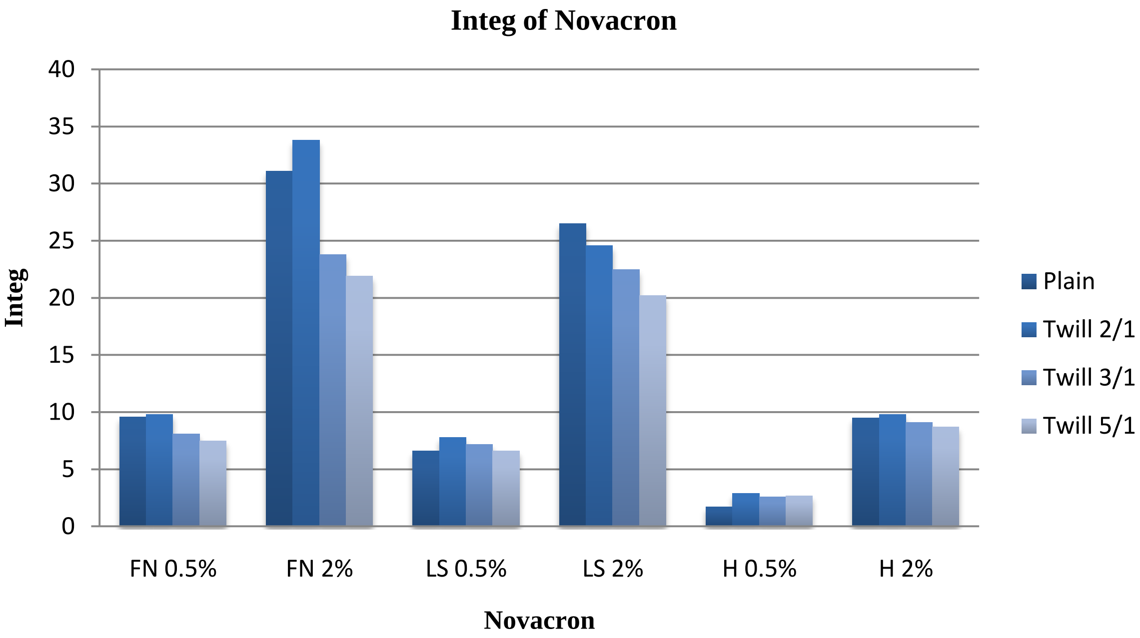


Figure 6.1 Visual depth of Novacron dyes

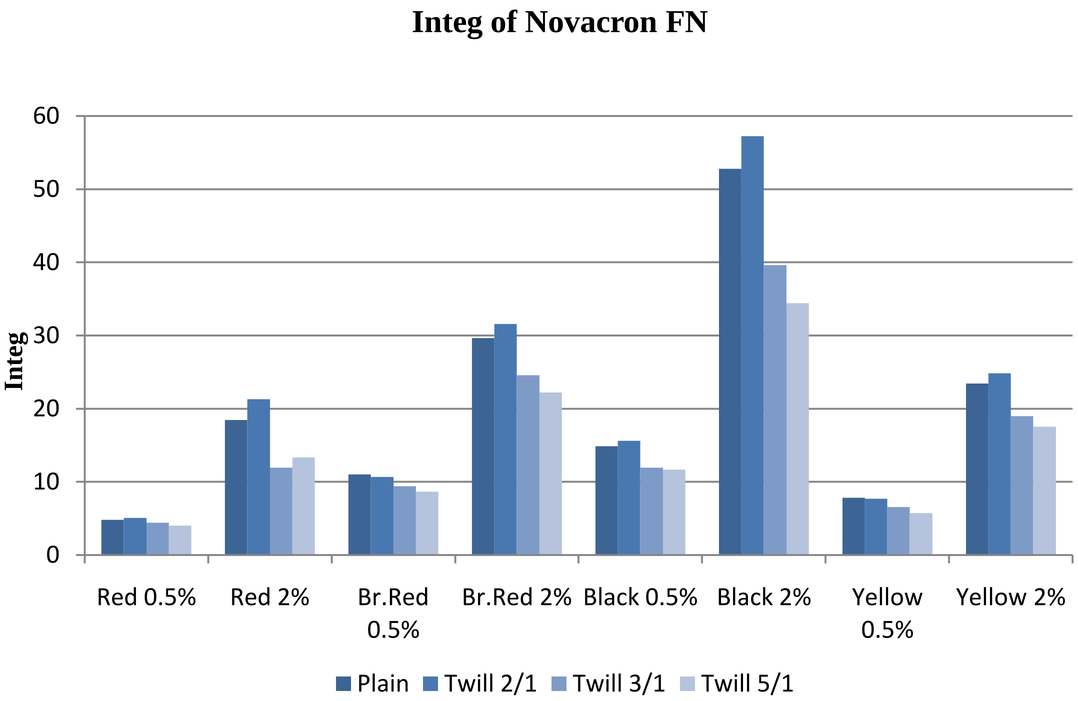


Figure 6.2 Visual depth of Novacron FN dyes

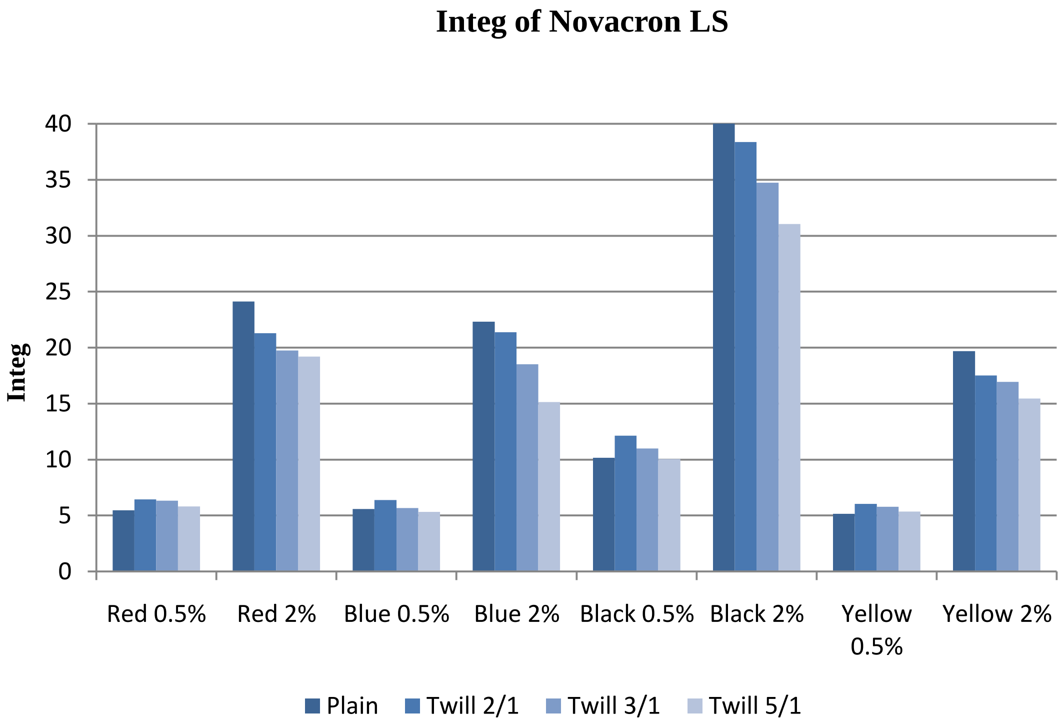


Figure 6.3 Visual depth of Novacron LS dyes

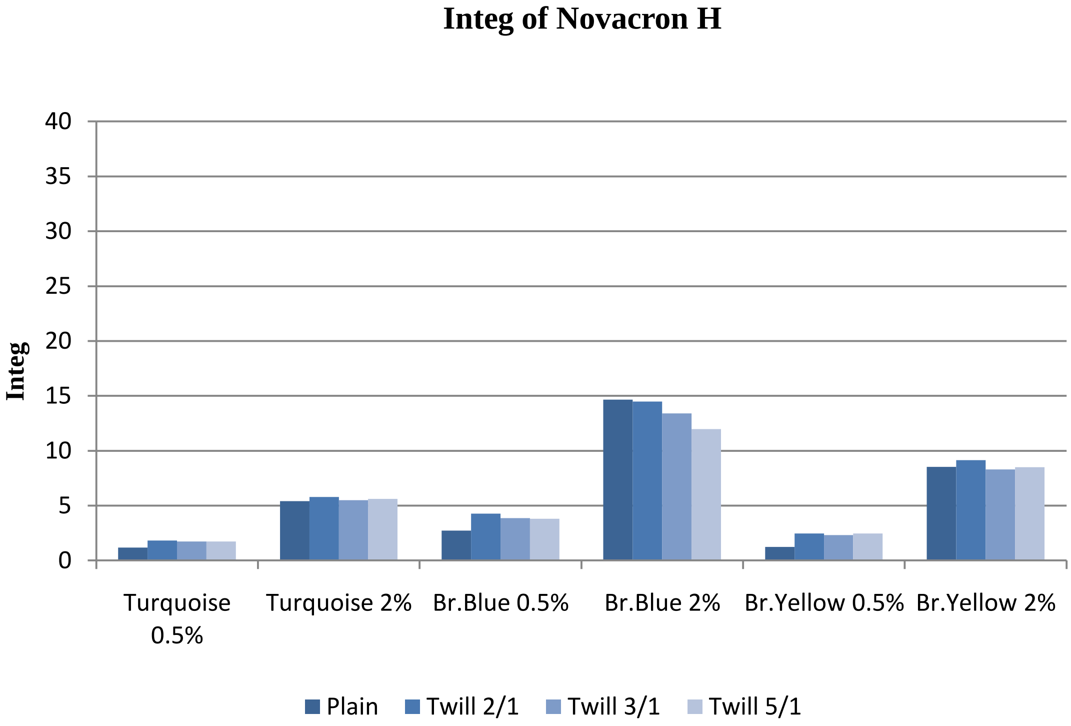


Figure 6.4 Visual depth of Novarocn H dyes

6.2.2 Exhaustion and Fixation

The average of exhaustion (%E) and fixation (%F) of dyeing using Novacron FN, LS and H dyes are shown in Figure 6.5. The results show that %E and % F behaviour of Novacron FN and LS dyes are very similar at each application concentration. Novacron H dyes show lower dye exhaustion and fixation (20 - 60%) as compared to the other exhaust dyeing process (Novacron FN and LS).

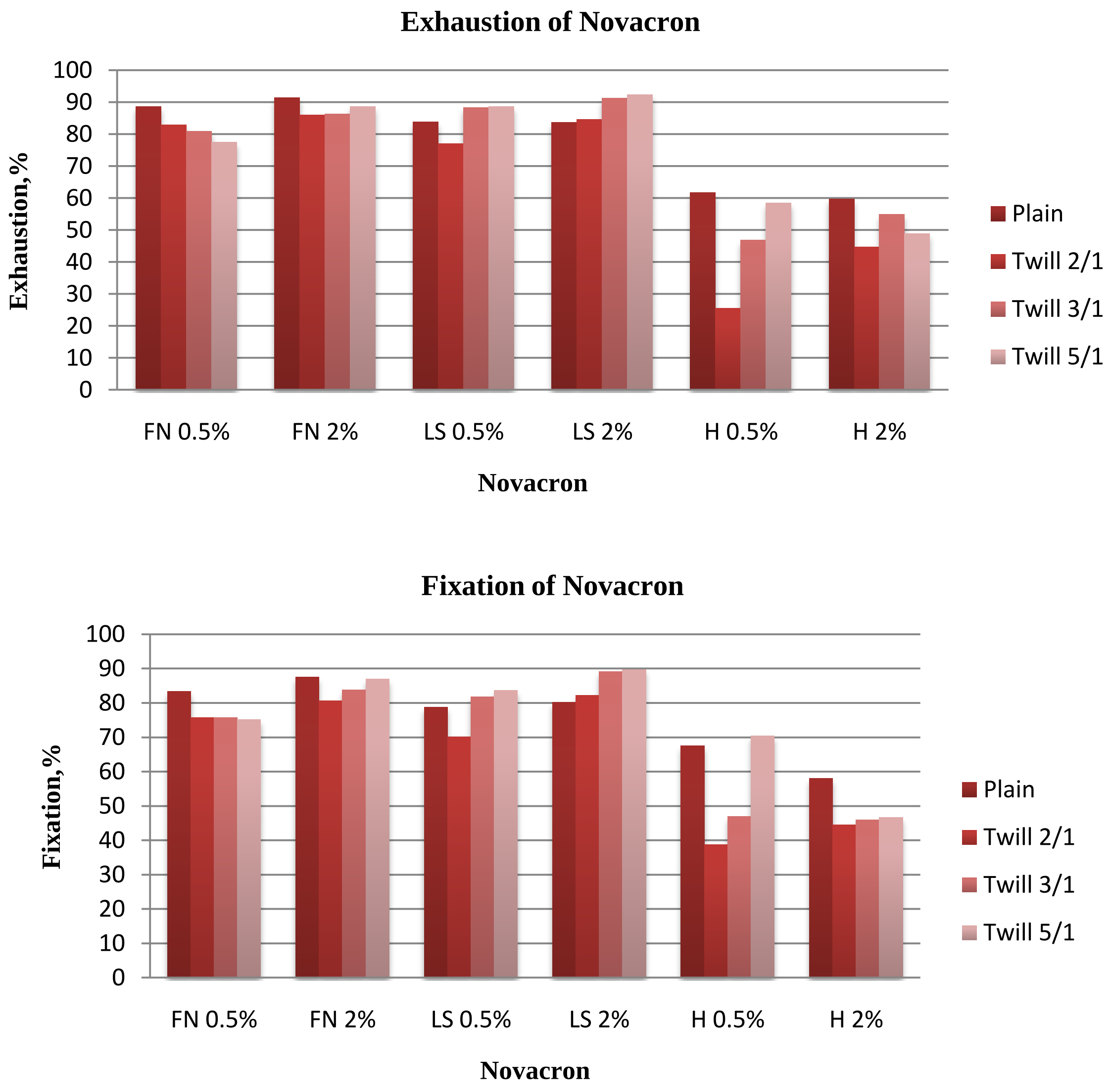


Figure 6.5 Exhaustion and fixation of Novacron dyes

Furthermore, the Twill 3/1 and Twill 5/1 fabrics show low visual depth but high %E and %F. It is because twill fabrics have irregular surface (due to yarn floats) and when light comes into contact it is reflected in a manner giving glossy effects, hence low visual depth. On the contrary, because of the floating of yarns (three up and one down, and five up and one down) dyes can penetrate easily into the fabric with resultant high %E and %F and uniform dye penetration.

6.3 Continuous Dyeing

6.3.1 Visual Depth

6.3.1.1 Novacron C Dyes

The results of pad-steam dyeing by using Novacron C dyes shows that the plain fabric has the highest visual depth values except Novacron Red C-2G 2% as shown in Figure 6.6 and Figure 6.8. Figure 6.6 shows the average values of Novacron C dyes applied on three different continuous dyeing methods.

The pad-batch dyeing (Figure 6.6 and Figure 6.7) shows the lowest visual depth as compared to the pad-steam and pad-dry-thermosol processes. This is because Tencel fabric is highly crystalline in nature and comprises interlayers of less order between the crystallites in the elementary fibrils [211]. This is why Tencel woven fabric requires certain temperature or heat treatment, rather than time only, to allow dye molecules to penetrate in the fibres.

It has observed in Figure 6.9, the visual depths obtained using Novacron C dyes by pad-dry-thermosol dyeing process is higher than the other continuous dyeing process and are almost equal to the visual depth obtained by the exhaust dyeing. Overall, the plain Tencel woven fabrics have higher visual depth than the other twill fabrics and in some instances the Twill 2/1 fabric and the plain fabric appeared the same depth of colour.

In order to compare the colour depth on the different fabrics the plain fabric was taken as standard and from that the percentage difference in colour depth of the other twill weave fabrics were calculated. It is shown in Figure 6.10, except pad-batch (PB) dyeing in all other dyeing process, the visual depth of Twill 5/1 fabric is lowest. The pad-dry-thermosol (PDT) dyeing process shows very consistence visual depth both in 0.5% and 2% dye conc.

However, the visual depth obtained by the continuous dyeing using Novacron C, is more than to 60% (2% dye conc) and more than to 50% (0.5% dye conc) lower than the exhaust dyeing.

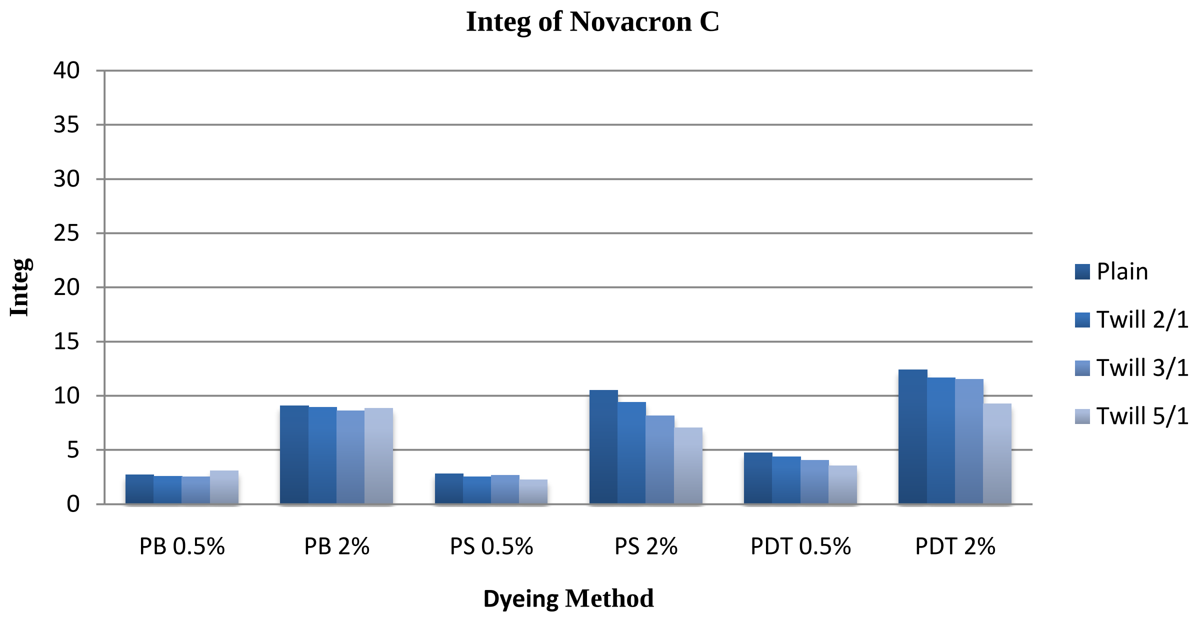


Figure 6.6 Visual depth of Novacron C dyes

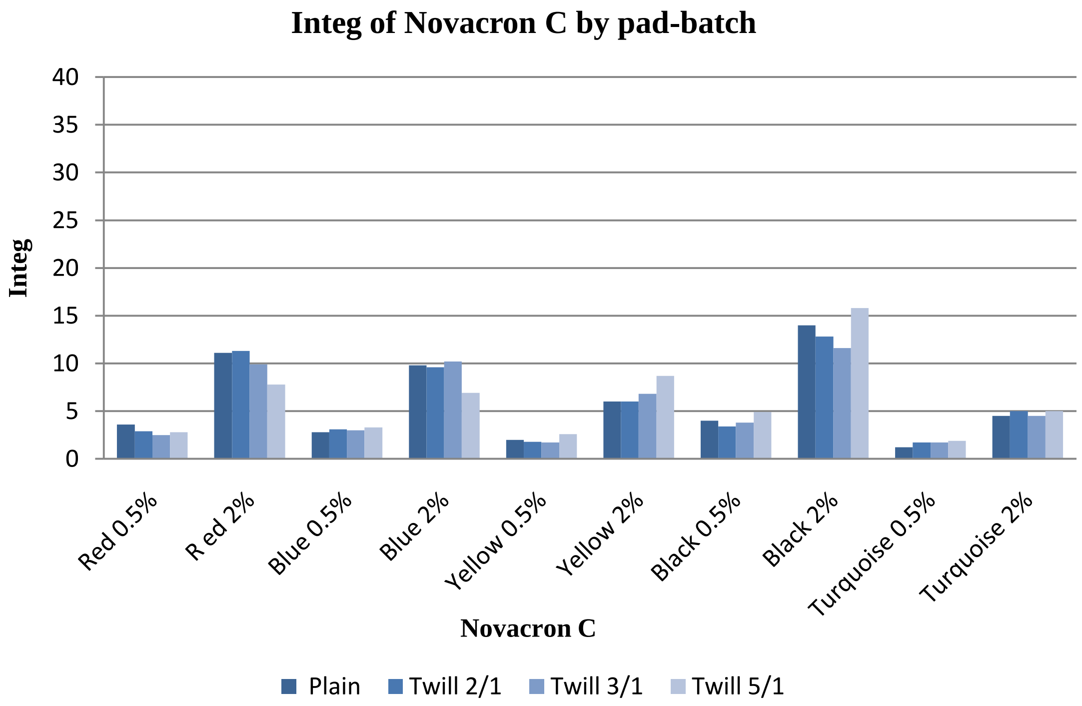


Figure 6.7 Visual depth of Novacron C dyes by pad- batch process

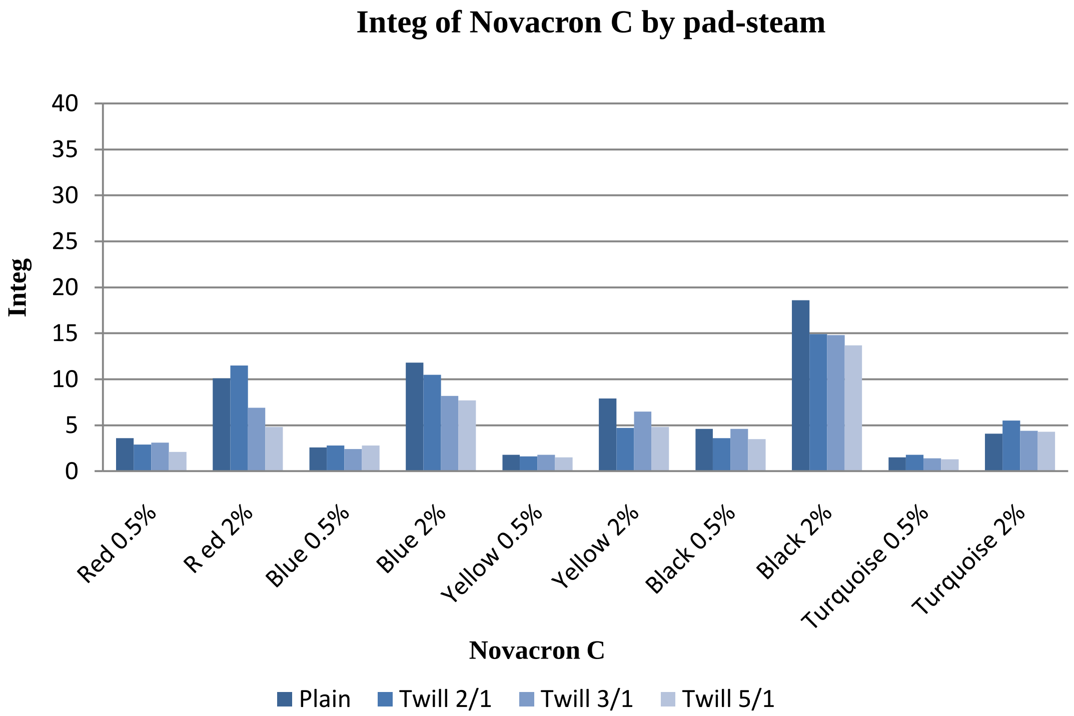


Figure 6.8 Visual depth of Novacron C dyes by pad-steam process

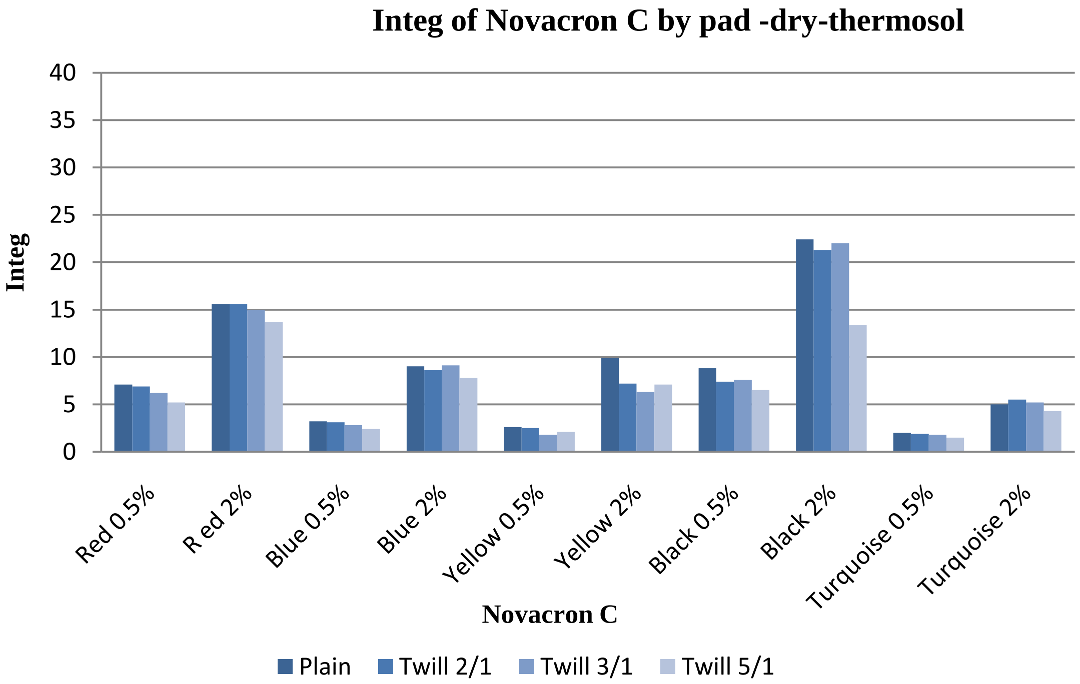


Figure 6.9 Visual depth of Novacron C dyes by pad-dry-thermosol process

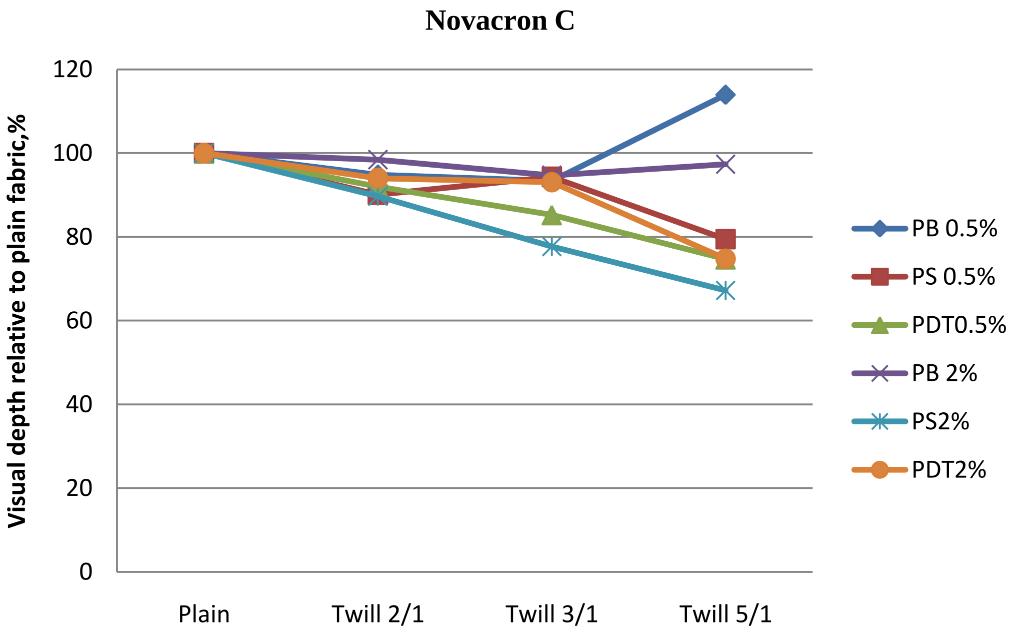


Figure 6.10 The difference in visual depth of Novacron C dyes

6.3.1.2 Levafix CA

It is apparent from Figure 6.11 that the methods of dyeing, as well as types of weave and their structure, extensively affect the colour intensity of the dyed samples. The order of visual depth among three continuous dyeing processes using Levafix CA dyes are same as obtained by using Novacron C dyes, that is pad-dry-thermosol > pad-steam > pad-batch.

Tencel fabrics when dyed using Levafix CA dyes by pad-batch process (Figure 6.12) and pad-steam process (Figure 6.13) show varying trends except Levafix Blue CA 2% (dye conc) and Yellow CA 0.5% (dye conc). This is because more than 50% lower Integ values are obtained by pad-batch and pad-steam processes as compared to the exhaust dyeing using Novacron FN and LS dyes. However, in both dyeing processes, plain fabric gives the highest visual depth. The visual depth of Twill 2/1 fabric is higher than the Twill 3/1 fabric except for the Levafix Red CA 2% (dye conc) is obtained by pad-steam process. Twill 5/1 fabric in some dyes shows higher visual depth and in some dyes shows lower visual depth as compared to Twill 3/1 fabric (Figure 6.12 and Figure 6.13).

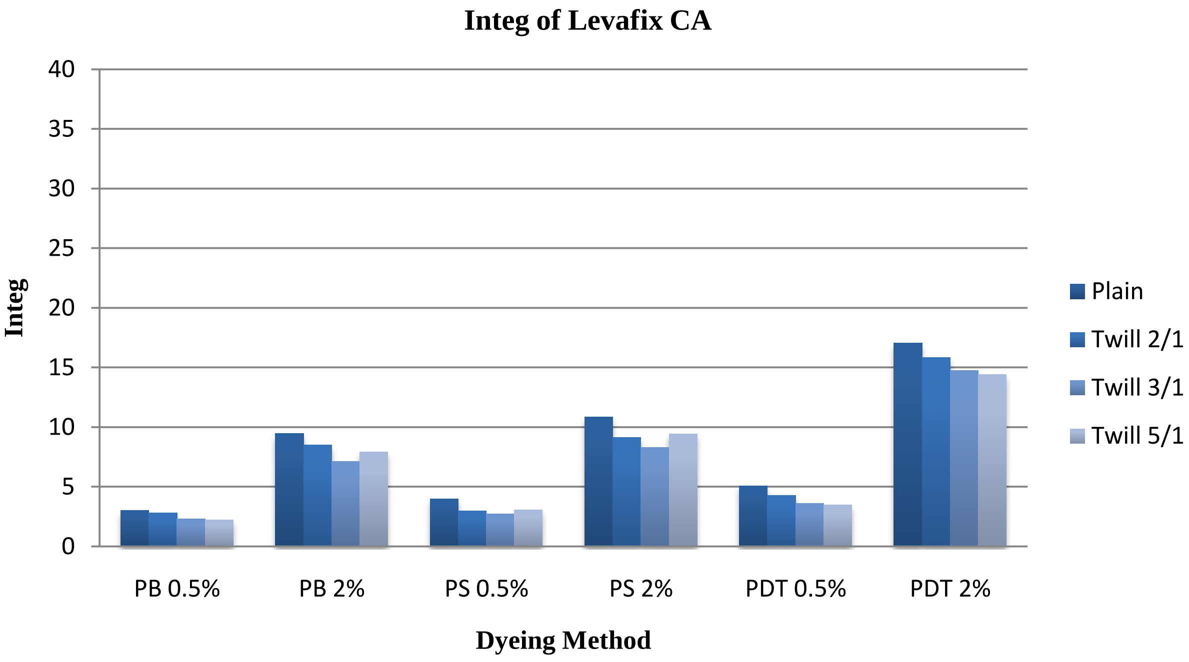


Figure 6.11 Visual depth of Levafix CA dyes

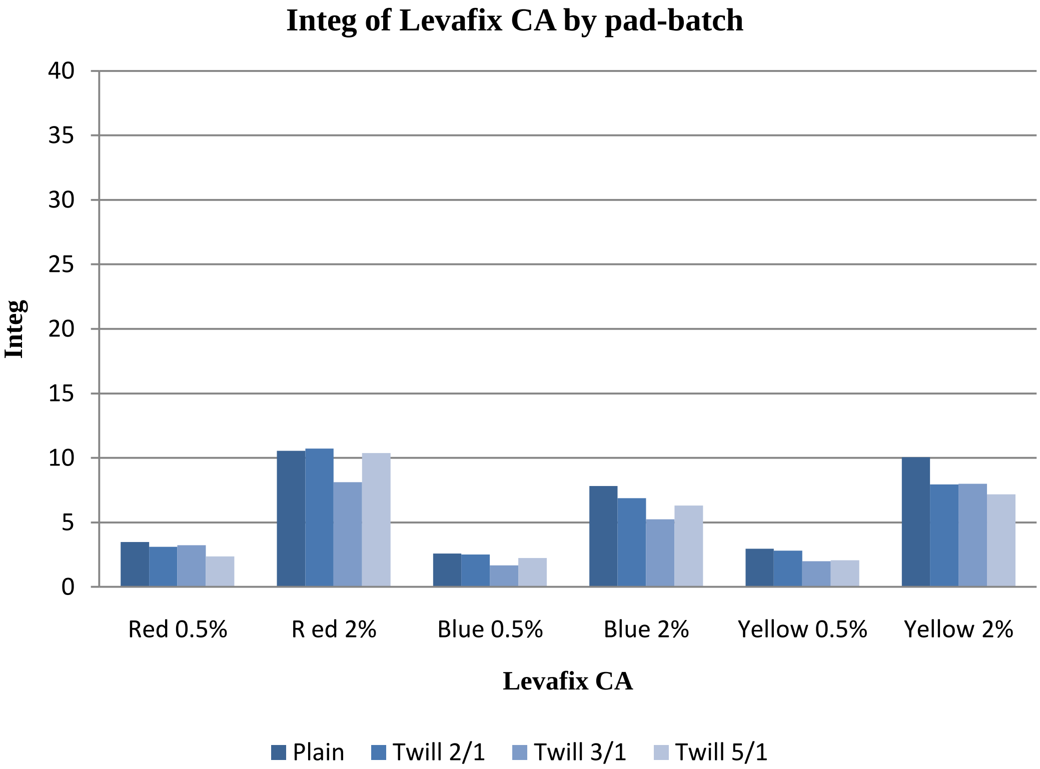


Figure 6.12 Visual depth of Levafix CA dyes by pad-batch process

The trends obtained from the pad-dry-thermosol dyeing processes with Levafix CA dyes (Figure 6.14) are same as those obtained using Novacron LS dyes at 2% dye conc (Figure 6.13), except Levafix Yellow CA 2%. The visual depth values of fabrics using Levafix CA dyes are higher than the Novacron C dyes applied by all continuous dyeing methods. Moreover, the visual depth values obtained from pad-dry-thermosol (PDT) dyeing process at 2% dye conc are 50% lower than the exhaust dyeing method (Novacron FN and LS) where the difference in rest of the dyeing process at both 0.5% and 2% dye conc are more than to 50%.

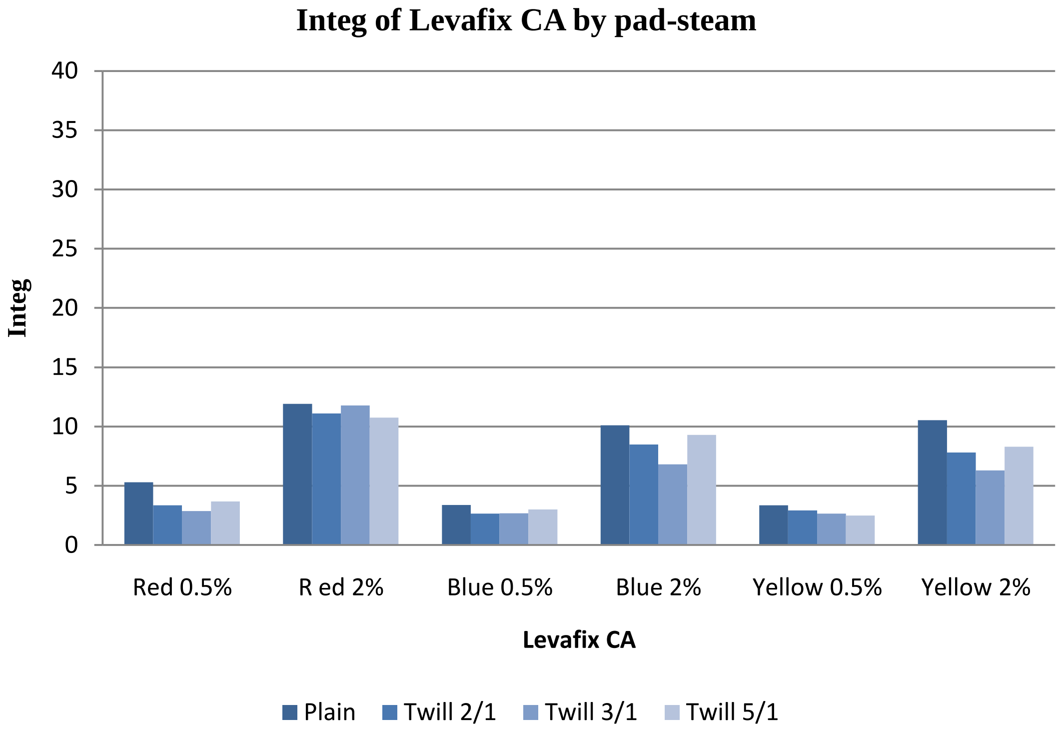


Figure 6.13 Visual depth of Levafix CA dyes by pad-steam process

The difference in Integ value of different weave structure by considering the plain fabric as a standard is show in Figure 6.15. The plain fabric has highest visual depth as compared to the twill fabrics. The Twill 2/1 is having a high visual depth to the Twill 3/1 fabric while the trend of Twill 3/1 fabric has high visual depth in pad-dry-thermosol (0.5% and 2% dye conc) and pad-steam and pad-batch at 0.5% dye conc only. This is due to the difference in the fabric porosity and dye chemistry. The pad-dry-thermosol dyeing is carried out at higher temperature as compared to the pad-steam dyeing; therefore, it allowed the dyes molecules to reacts with the accessible sites of the Tencel fibre and become fixed.

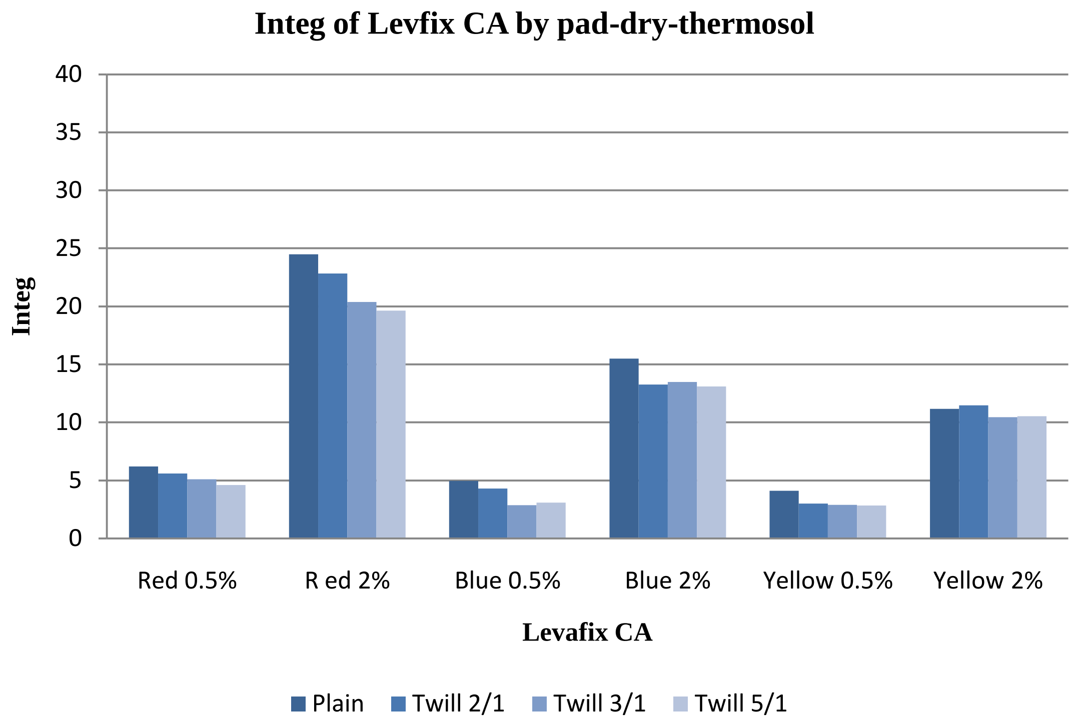


Figure 6.14 Visual depth of Levafix CA dyes by pad-dry-thermosol process

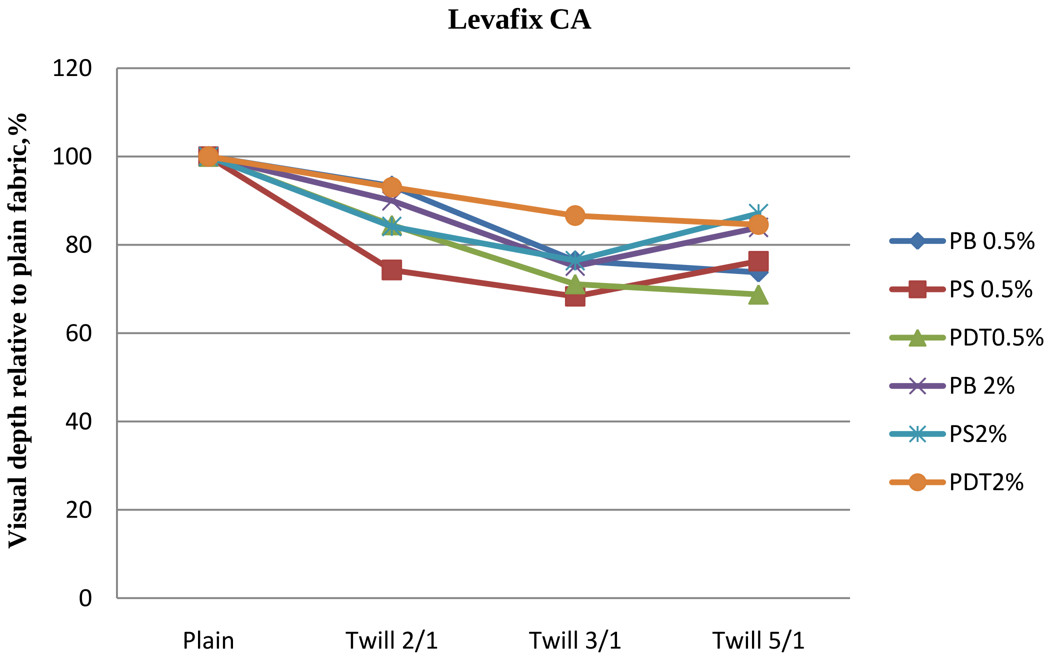


Figure 6.15 The difference in visual depth of Levafix CA dyes

6.3.2 Fixation

6.3.2.1 Novacron C

The results using Novacron C dyes by continuous methods show that the fixation on the various fabrics varies between 65 – 82 % (Figure 6.16).

For comparison the plain fabric was taken as standard and from that the percentage of other Twill weave fabrics was taken as shown in Figure 6.17. The fixation percentage obtained by the continuous dyeing methods using Novacron C dyes is almost similar to the exhaust dyeing methods (Novacron FN and LS). It is due the difference in measuring the dye uptake, in continuous dyeing the dye uptake was calculated by the % pick-up of dye during padding process and the percentage of dye has been fixed after padding. The plain fabric which shows highest visual depth also have highest % fixation in all continuous dyeing process. The Twill 5/1 fabric shows the lowest % fixation (maximum 20% compared to plain fabric) except in pad-batch 0.5% dye conc.

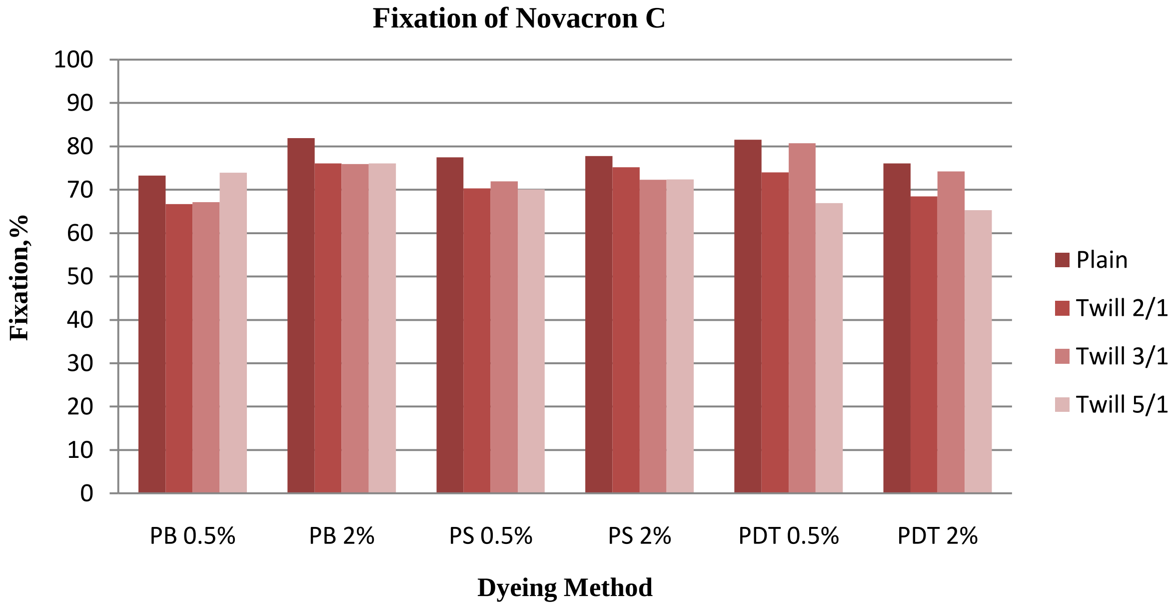


Figure 6.16 Fixation of Novacron C dyes

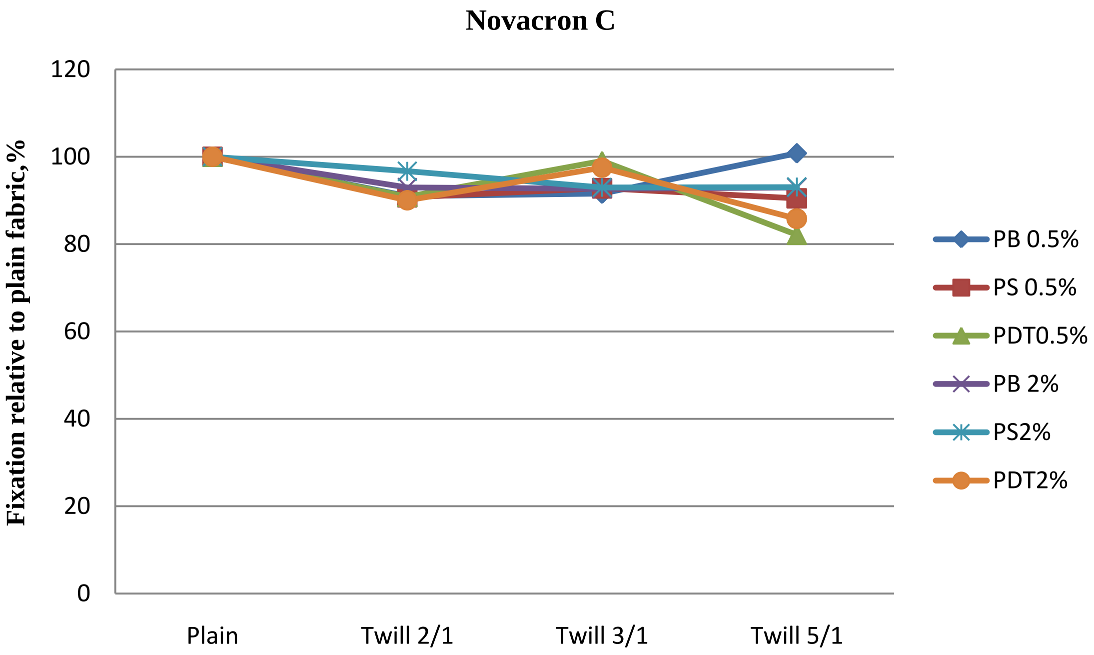


Figure 6.17 The difference in fixation of Novacron C dyes

6.3.2.2 Levafix CA

The average of fixation percentage of Levafix CA dyes are shown in the Figure 6.18 . The plain fabrics that show the highest visual depth also have highest fixation percentage 80 > 100%. The fixation on the Twill 2/1, Twill 3/1, and Twill 5/1 fabrics varies between 65 > 100%.

The comparison of dye uptake on different weave structure by considering the plain fabric standard is show in Figure 6.19. The trends of % fixation using Levafix CA is similar to its visual depth except in pad-dry-thermosol process. The Twill fabrics shows more than to 20% lower fixation percentage as compared to the plain fabric, while in certain dyeing methods such as pad-batch and pad-dry-thermosol 0.5% dye conc, Twill 2/1 fabric shows the same percent fixation to plain fabric.

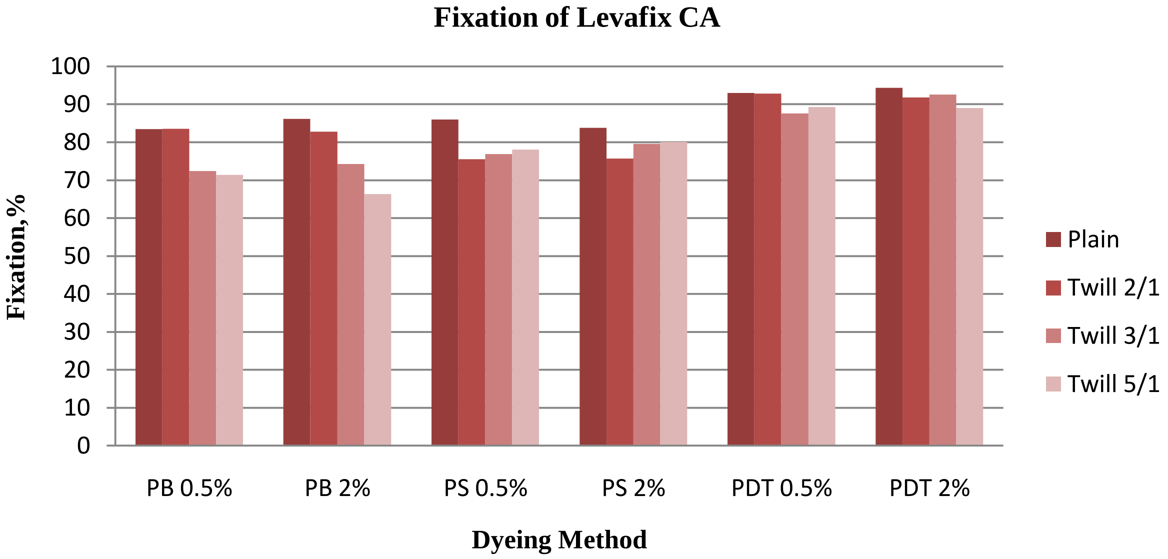


Figure 6.18 Fixation of Levafix CA dyes

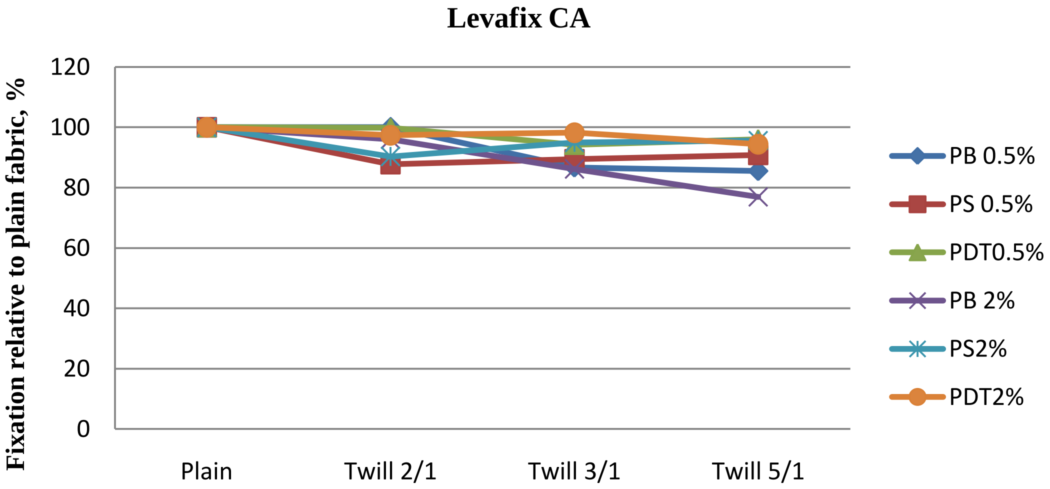


Figure 6.19 The difference in fixation of Levafix CA dyes

6.4 Uniformity of Fibre Coloration (UFC)

6.4.1 Subjective Assessment

The UFC was assessed by selecting two yarns in the woven fabric. The average of standard deviation (SD) is show in Table 6.2 for the exhaust methods, Table 6.3, Table 6.4 and table 6.5 for the continuous methods.

It is apparent from the Table 6.2 to Table 6.5, Twill 2/1 fabric exhibits greater variation in dye penetration as compared to the rest of the woven fabrics, in all dyeing methods and dye classes except Novacron LS and Levafix CA by pad-batch (PB) and pad-dry-thermosol (PDT) process, where Twill 3/1 fabric shows high variation. For the Novacron FN, LS, and H dyes the standard deviation (SD) values range from 0.8 - 1.16 while the Novacron C dyes have values ranging from 0.63 - 1.19 and Levafix CA from 0.66 - 1.05. The mean values show the average rating (1 to 5, 1 means white filament and 5 means very dark filament). In the case of exhaust dyeing methods (Novacron FN, LS and H) and continuous dyeing methods (Novacron C and Levafix CA) the mean values are higher than for rating 3 but less than to rating 5. Levafix CA dyes applied on plain Tencel fabric by pad steam (Red CA) and pad-batch (Yellow CA) gives the highest mean value as compared to Novacron dyes.

As shown in the Table 6.2 to Table 6.5, the SD and mean values of Plain, Twill 2/1, Twill 3/1 and Twill 5/1 fabrics are not proportional to their visual depth trends. The Twill 5/1 fabric shows less deviation (SD) because there are fewer points of yarn intersection in the fabric.

Table 6.2 UFC values of Novacron FN,LS and H dyes by exhaust method

Dyes		**Plain**		**Twill 2/1**		**Twill 3/1**		**Twill 5/1**	
		SD	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**
Novacron FN	**B.Red FN-3GL***	0.89	4.17	0.92	3.80	0.92	4.06	0.84	3.85
	Red FN-R	0.81	3.80	0.96	3.80	0.95	3.90	0.85	3.80
	Yellow FN-2R	1.01	3.89	1.16	3.77	0.93	3.98	0.90	4.14
Novacron LS	**Red LS-B**	1.01	3.82	0.96	3.88	1.02	3.84	1.01	4.02
	Yellow LS-R	0.93	3.78	0.97	3.81	1.00	3.87	0.83	3.92
Novacron H	**B.Yellow H-4G`**	0.81	3.84	0.96	3.81	0.95	3.92	0.84	3.81
	B.Blue H-GR¬	0.99	4.30	0.99	3.90	1.02	3.80	0.96	4.14
	Turquoise H-GN	0.91	4.24	0.92	3.94	0.88	4.04	0.87	3.99

**B.Red FN-3GL =Brilliant Red FN-3GL*
`B.Yellow H-4G= Brilliant YellowH-4G
¬B.Blue H-GR = Brilliant Blue H-GR

Table 6.3 UFC values of Novacron C and Levafix CA dyes by pad-batch process

		Plain		**Twill 2/1**		**Twill 3/1**		**Twill 5/1**	
Dyes		**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**
Novacron	**Red C-2G**	0.94	4.00	0.83	4.22	0.83	4.23	0.9	4.06
	Yellow C-RG	0.68	4.23	0.91	3.07	0.78	4.15	0.82	3.99
	Blue C-R	0.87	3.93	0.88	4.29	0.96	4.06	0.91	4.1.4
	Turquoise C-GN	0.86	4.28	0.82	4.18	1.12	3.89	0.82	4.24
Levafix	**Red CA**	0.91	4.15	0.92	4.18	0.91	4.26	0.92	4.19
	Yellow CA	0.66	4.29	0.84	4.14	0.8	4.13	0.84	4.20
	Blue CA	0.84	4.21	0.98	4.05	0.97	4.06	0.89	4.05

Table 6.4 UFC values of Novacron C and Levafix CA dyes by pad-steam process

		Plain		**Twill 2/1**		**Twill 3/1**		**Twill 5/1**	
Dyes		**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**
Novacron	**Red C-2G**	0.90	4.12	1.01	3.87	0.97	4.03	0.91	4.07
	Yellow C-RG	0.90	3.77	0.90	3.99	0.76	4.09	0.81	4.05
	Blue C-R	1.03	3.92	1.17	4.07	1.19	3.77	1.16	3.96
	Turquoise C-GN	0.96	3.8	1.17	3.74	0.91	4.06	0.78	4.18
Levafix	**Red CA**	0.81	4.29	0.89	4.24	0.86	4.18	0.86	4.17
	Yellow CA	0.82	4.21	0.89	4.18	0.85	3.99	0.84	4.18
	Blue CA	0.69	4.18	0.93	4.09	0.89	4.12	0.87	4.24

Table 6.5 UFC values of Novacron C and Levafix CA dyes by pad-dry-thermosol process

		Plain		**Twill 2/1**		**Twill 3/1**		**Twill 5/1**	
Dyes		**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**
Novacron	**Red C-2G**	0.75	4.20	0.88	4.00	0.88	4.00	0.80	4.10
	Yellow C-RG	0.63	4.07	0.82	4.05	0.76	4.06	0.75	4.05
	Blue C-R	0.92	4.01	0.92	4.23	1.14	3.84	1.06	4.16
	Turquoise C-GN	0.95	4.11	0.92	4.13	0.92	4.13	0.84	4.25
Levafix	**Red CA**	0.68	4.19	0.93	4.03	0.93	4.02	1.05	3.96
	Yellow CA	0.70	4.10	0.86	4.04	0.85	4.03	0.81	4.00
	Blue CA	0.91	4.20	0.92	4.10	0.82	4.00	0.82	4.00

6.4.2 Objective Assessment

The objective assessment is a more accurate method of measuring dye uniformity as compared to the subjective assessment. In this method the whole image, containing approximately ten yarns were selected as compared to two yarns from an image of the woven fabric used for subjective assessment.

In case of exhaust dyeing methods (Figure 6.20) the trends of standard deviation are in the order of Plain >Twill 2/1≥Twill 3/1> Twill 5/1 fabrics, except in Novacron H, where SD value of Plain = Twill 2/1 fabric. Pad-dry-thermosol process using Novacron C dyes and Levafix CA dyes as shown in Figure 6.21 and Figure 6.22 have similar trends to exhaust dyeing methods using Novacron FN and LS dyes.

In pad-batch and pad-steam process of Levafix CA dyes standard deviation are in the order of Plain> Twill 2/1 < Twill 3/1 > Twill 5/1 fabric. Pad-steam process using Novacron C dyes behave different and Twill 3/1 fabric has low SD values as compared to other dyeing methods. Although in all dyeing process the UFC (SD) trend of objective assessment are different and gives lower standard deviation values as compared to the subjective assessment.

The exhaust dyeing method shows SD values from 0.18 – 0.22 except Novacron H dyes, which have lower visual depth, % E and %F and have high SD (0.42 – 0.50). The continuous dyeing processes using Novacron C dyes have SD values ranging from 0.42 to 0.55. The Levafix CA dyes shows excellent dye uniformity and have depth variation in the range from 0.38 – 0.43.

The UFC shows uniformity of the dye molecules inside the filaments of yarn of woven fabric and it is not always proportional to the visual depth and fixation percentage. However, correspondence with Integ and dye uptake values is observed when the SD value is zero, which means dye molecules are uniformly distributed. The calculation also depends on the size of the sample, in case of subjective assessment, the sample size is very small (2 yarn from an image per fabric per dyeing process), where as in objective assessment the sample size is large and the SD values are accurate.

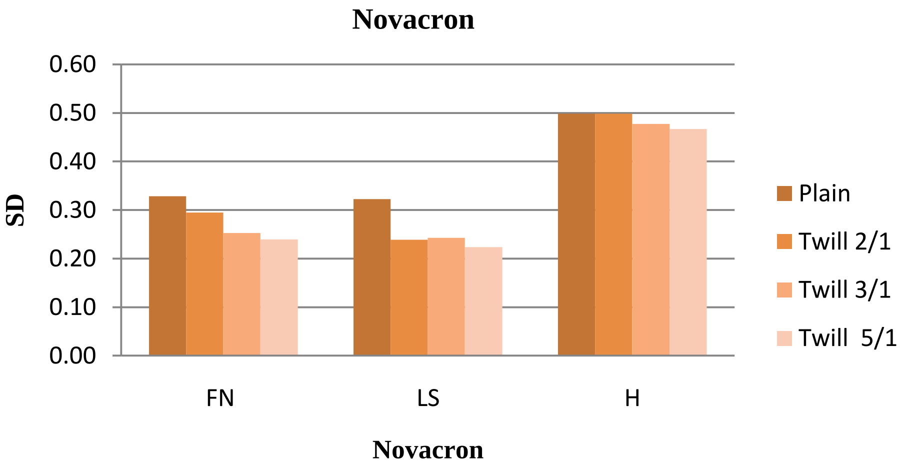


Figure 6.20 SD trends of exhaust dyeing (Novacron)

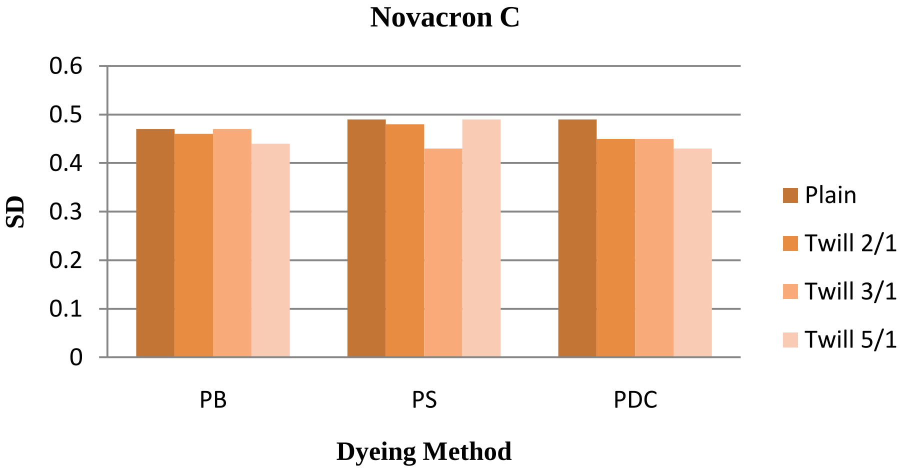


Figure 6.21 SD trends of continuous dyeing using Novacron C dyes

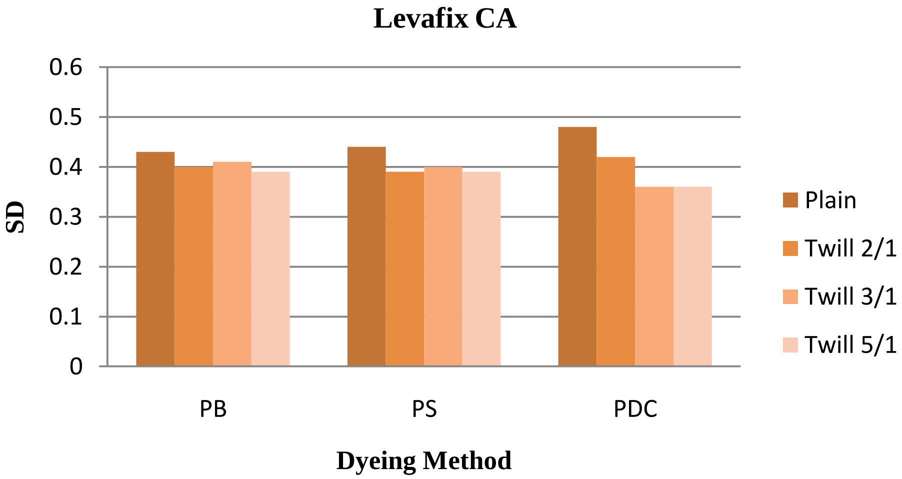


Figure 6.22 SD trends of continuous dyeing using Levafix CA dyes

Table 6.6 Mean

	Exhaust			Novacron C			Levafix CA		
	FN	**LS**	**H**	**PB**	**PS**	**PDC**	**PB**	**PS**	**PDC**
Plain	2.6	2.4	2.1	2.3	2.2	2.3	2.4	2.4	2.6
Twill 2/1	2.6	2.4	2.2	2.6	2.4	2.5	2.5	2.5	2.7
Twill 3/1	2.6	2.4	2.2	2.6	2.4	2.4	2.4	2.6	2.5
Twill 5/1	2.7	2.4	2.3	2.7	2.4	2.4	2.5	2.6	2.6

Table 6.7 Dispersion of histogram at midpoint of mode value (D_1)

	Exhaust			Novacron C			Levafix CA		
	FN	**LS**	**H**	**PB**	**PS**	**PDC**	**PB**	**PS**	**PDC**
Plain	0.57	0.58	0.52	0.63	0.55	0.62	0.63	-0.43	0.63
Twill 2/1	-0.27	0.62	0.63	0.58	0.60	0.54	0.61	0.49	0.45
Twill 3/1	-0.56	-0.47	0.55	0.58	0.55	0.54	0.52	0.58	0.54
Twill 5/1	-0.41	-0.51	-0.53	0.55	0.60	-0.46	0.56	0.59	-0.47

Table 6.8 Dispersion of histogram at quarter point of mode value (D_2)

	Exhaust			Novacron C			Levafix CA		
	FN	**LS**	**H**	**PB**	**PS**	**PDC**	**PB**	**PS**	**PDC**
Plain	0.67	0.55	0.61	0.68	0.59	0.69	0.68	-0.59	0.73
Twill 2/1	-0.53	0.62	0.68	0.65	0.67	0.64	0.65	0.62	0.57
Twill 3/1	-0.58	-0.46	0.62	0.67	0.67	0.63	0.62	0.64	0.58
Twill 5/1	-0.54	-0.46	-0.63	0.66	0.69	0.54	0.63	0.69	0.57

The mean value of Novacron FN dyes are highest and comparable to the Levafix CA dyes, dyed by pad-dry-thermosol process. As shown in Table 6.6 the average rating of Tencel fabrics is higher than 2 (35 – 86 grey value). The Twill 2/1 fabric dyed using Novacron FN dyes have almost symmetrical shape towards the darker (0) grey value. It is observed from the Table 6.7 and Table 6.8 Tencel fabrics composed of different structure shows uniform dyeing behaviour because in all the dyeing methods dispersion value is less than 1.

The bandwidth value (Table 6.9) of Novacron FN and LS is lower which shows peak of the histogram is towards the mode value and have thin and short tail. The Novacron H and C and levafix CA dyes have shorter peak and wider tail. The bandwidth value of different weave structure is in the order of Plain > Twill 2/1 < Twill 3/1 > Twill 5/1 fabric. The plain weave fabric which shows high visual depth but have more deviation in dye penetration as compared to twill weaves fabrics. In all dyeing methods the tail of the histogram is towards the lighter side.

Table 6.9 Bandwidth of Novacron and Levafix dyes (×10^{-4})

		Plain		Twill 2/1		Twill 3/1		Twill 5/1	
		BR	**BL**	**BR**	**BL**	**BR**	**BL**	**BR**	**BL**
Novacron	**FN**	4.83	-1.65	3.17	-2.04	3.42	-1.22	3.44	-1.53
	LS	5.79	-2.48	4.78	-1.89	3.58	-1.60	3.60	-1.46
	H	9.44	-4.06	8.31	-2.87	6.26	-2.97	6.38	-2.96
Novacron C	**Pad-batch**	8.52	-3.11	5.31	-2.14	5.11	-1.87	3.53	-1.65
	Pad-steam	8.65	-3.36	6.11	-2.44	5.02	-2.17	5.71	-2.26
	Pad-dry-thermosol	8.60	-3.28	6.29	-2.77	5.98	-2.74	5.73	-2.76
Levafix CA	**Pad-batch**	7.43	-2.43	6.24	-2.09	6.37	-3.16	5.07	-1.94
	Pad-steam	6.39	-3.31	4.99	-2.29	5.24	-2.06	4.23	-1.81
	Pad-dry-thermosol	5.93	-2.72	3.81	-2.01	5.25	-2.27	3.73	-2.18

6.5 Microspectrophotometry

The uniformity of colour inside a filament of the yarns in the woven fabric was assessed using microspectrophotometry (MSP), for selected dyeing as shown in Figure 6.23. In case of exhaust dyeing of Novacron FN dyes, the results are in relation to the UFC results (Figure 6.23), while in case of continuous dyeing the trends are ambiguous. Dyeing by the exhaust method shows more variation (SD) as compared to the continuous pad-steam dyeing. Similarly, the pad-dry-thermosol dyeing process has higher SD than the pad-steam dyeing process. Hence, the overall trend of graphs are exhaust = pad-dry-thermosol > pad-steam process.

The MSP measured the absorbance (λ_{max}) in an individual fibre filament and measurements were taken along the length of each fibre. Generally fibres from the Twill 5/1 fabric had greater SD than fibres from the Plain, Twill 2/1 and Twill 3/1 fabrics, except Novacron Red C-2G (pad-steam) and Novacron Blue C-R and Levafix Red CA (pad-dry-thermosol). The variation in results of UFC and MSP might be because the UFC was measured using 0.5% dye conc dyed samples but the MSP measurement were made on the 2 % dye conc dyed samples.

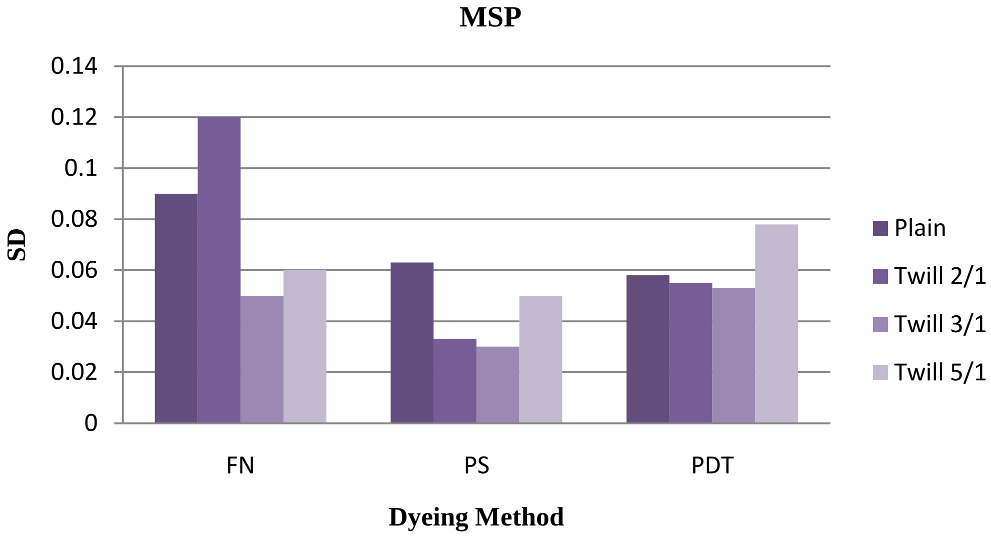


Figure 6.23 SD by Microspectrophotometry

6.6 Effect of Fabric Properties on Dyed Samples

Fabric properties such as GSM, porosity and weave structure effects their dyeing behaviour, as discussed in Section 4.3. The fabrics of varying weave and construction, dyed with different classes of dyes and methods, showed greater variation in visual depth. A further analysis to investigate the influences of weave and structure were carried out using the results of 2% red shades dyed by exhaust and continuous methods. The results are shown in Figure 6.24.

It is believed that twill fabrics; because of the floating of yarns have good penetration of dyes as compared to the plain woven fabric. Twill 2/1 fabric has high visual depth among other twill weave fabrics because of its high porosity percentage and low GSM, as compared to twill 5/1 fabric. The low weight and high porosity of Twill 2/1 fabric allows the dye to flow inside the fabric structure and penetrate in the fibres. Twill 3/1 fabric has the lowest GSM and gives low visual depth and in some cases better dye penetration as compared to Twill 2/1 fabric.

Overall, the plain fabric gave high visual depth. Firstly, the plain fabric has low GSM, therefore enables greater uptake of dye during dyeing process. Secondly, the weave type (one up and one down), gives square and regular pores [156] and also a flat surface and regular reflection of light.

There are fewer pores in the Twill 2/1, Twill 3/1 and Twill 5/1 fabrics because of the floating. In a twill weave, each weft yarn crosses a specific number of warp yarns, so that one yarn floats above two, three and five others yarns in the fabric, in the perpendicular direction. The increase yarn spacing correspondingly decreases the velocity of dye liquor [156]. While yarn floating in the twill weaves fabric promote even distribution of dye molecules.

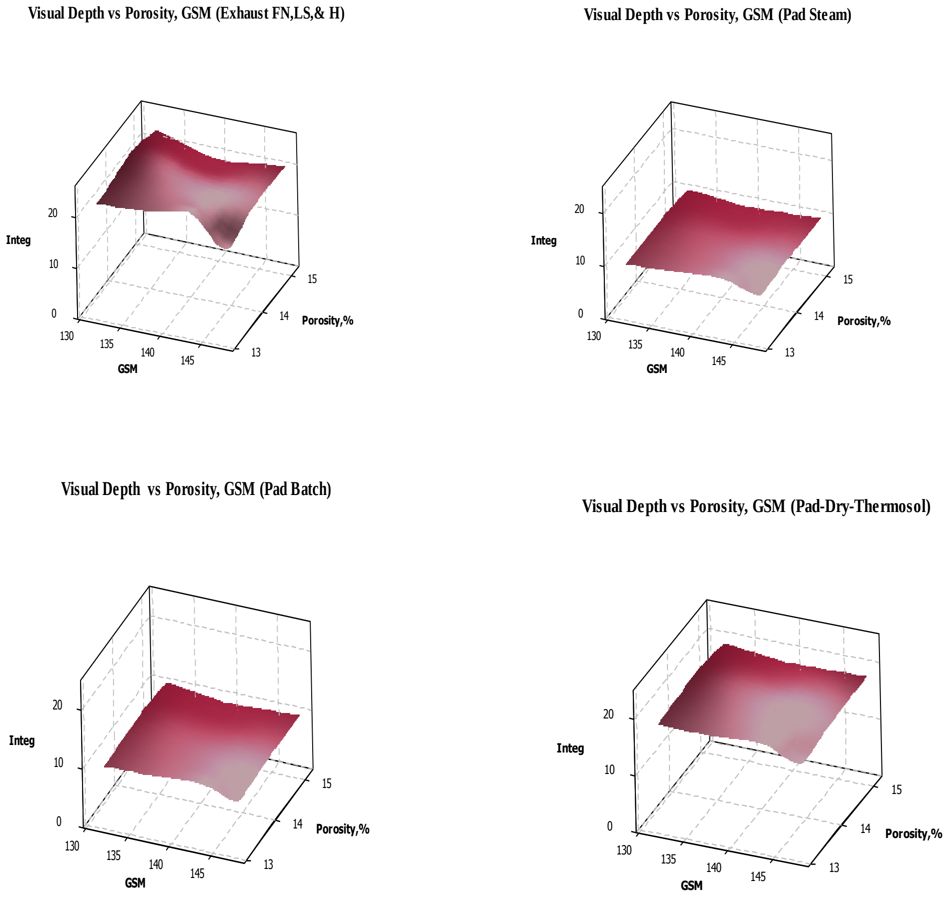


Figure 6.24 Visual depth versus GSM and porosity

CHAPTER 7: RESULTS AND DISCUSSIONS OF PLAIN WOVEN FABRIC

7 Results and Discussions of Plain Woven fabric

7.1 Plain fabric Construction

The plain Tencel woven fabrics are composed of different warp and weft linear and thread densities (Table 7.1). The fabric parameters, such as linear and thread density, cause variation in fabric cover factor and porosity. The following fabric parameters were calculated according to the methods mentioned in Section 5.2.1.

Table 7.1 Construction of Tencel plain fabric

Samples	warp*weft in tex	End*Picks per cm	GSM	Cover Factor	Cover Factor, %	Porosity	Porosity, %
1	14.3*14.7	43*25	110	9.7	78.5	0.44	21.5
2	14.5*14.6	43*28	115	10.1	80.3	0.42	19.7
3	14.4*14.8	43*36	132	11.1	84.6	0.39	15.4
4	14.4*14.4	43*40	140	11.5	86.4	0.38	13.6
5	14.4*14.4	43*44	145	12.0	88.5	0.36	11.5
6	14.3*20.4	43*24	124	10.1	80.3	0.42	19.7
7	14.4*20.6	43*28	135	10.7	83.0	0.40	17.0
8	14.4*20.8	43*36	157	11.9	88.1	0.36	11.9
9	14.2*20.7	43*40	163	12.4	90.5	0.35	9.5

🟥 Group A 🟪 Group B

All the plain Tencel woven fabrics have same warp linear density; but the linear density of weft yarns of four woven samples (6 to 9) is different.

For further assessment the above samples are categorized into two groups A and B, with respect to the difference in linear density of weft yarn. The group A comprises of 110, 115, 132, 140 and 145 GSM and the fabrics having the same warp and weft linear density. The group B fabrics have, 124, 135, 157, and 163 GSM and are different in warp and weft linear density. In the both group A and B, the number of ends and picks per cm are varied at particular difference.

It can be observed in the values in Table 7.1 that fabrics which have the same thread density such as samples 2 and 7, 3 and 8, 4 and 9, can differ in cover factor and porosity values, because of the difference in the yarn linear density. The porosity of the woven fabric depends on the diameter of the yarn and is inversely proportional to the cover factor [170], therefore the difference in yarn thickness (yarn diameter) causes the difference in fabric porosity.

To check the accuracy of the values in Table 7.1 they were further analyzed using Matlab programming as shown in appendix A. It is apparent from the graphs (Figure 7.1) the loosely woven fabrics have high porosity as compared to tightly woven fabrics in both group A and B. The geometrical porosity percentage (% P) is very high in both groups; this is due to the % P values being derived from the formulas. These geometrical formulas are very useful for estimating the % P, but current research shows they do not give exact porosity percentages (inter-yarn zone). The % P of the fabric decreases with processing such as scoured fabric has slightly higher than the causticised and dyed fabric. The difference in % porosity after processing seems to be slightly higher in loosely woven fabric (110 GSM), where porosity is decreased by more than 3% in group A. It is observed from the images that fabric of 110 GSM has very irregular and large pores. The tightly woven fabrics show minor differences in %P values both in group A and B. On the contrary, the porosity of group A’s fabrics are higher than the group B’s fabrics due to the difference of linear density as discussed in the above paragraphs.

The method of assessing the percentage porosity of fabric at constant intensity of light source is very helpful to investigate the dyeing behaviour in terms of liquor flow inside the fabric. The fabric images were taken with light source of constant intensity which behaves the same dye liquor flow for all the woven fabrics. As the % white pixels or porosity decreases with density of the fabrics, similarly the behaviour of liquid flow is being changed or decreased with fabric density. Therefore, amount of dye in the fabric is inversely proportion to the fabric density. For example: in the group A, where all the warp and weft yarns have the same linear density, their differ in ends and picks per cm causes change in the flow of liquid or light in between the yarns and at the intersection points of the fabric, resulting in the variation of dyeing properties.

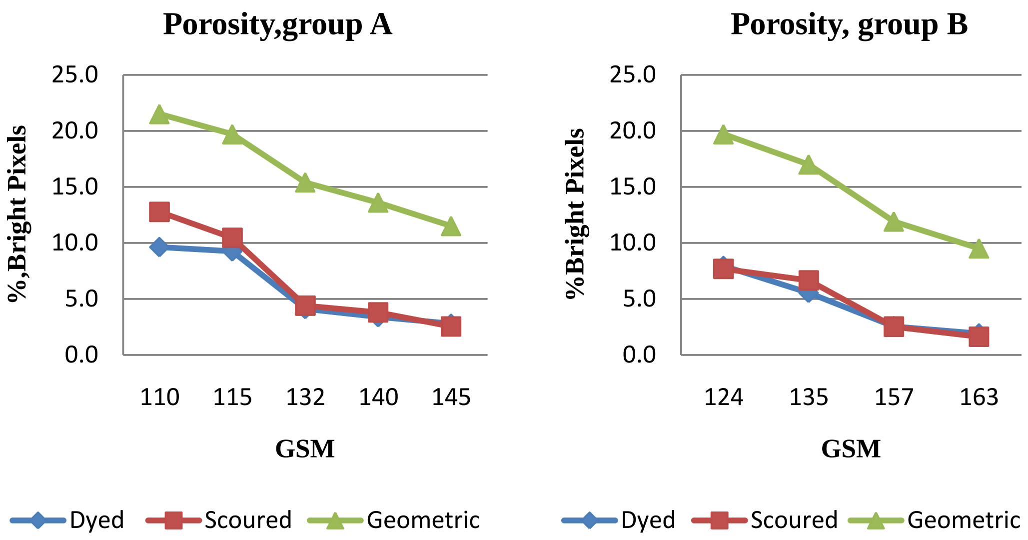


Figure 7.1 Percentage bright pixels of plain woven fabrics

The data in Table 7.1 and Figure 7.1 are very helpful to describe the behaviour of dyeing on the Tencel woven fabrics with respect to the fabric density and other fabric construction parameters. The dye molecules vary in size, geometry, and reactivity within the same class of dye. Some dyes are very small in size and can easily penetrate inside the filaments of the yarns of the woven fabric but others are not because of their structure. Similarly, all three Levafix CA dyes and a Remazol B-A dyes are composed of bis-functinal reactive groups, the molecular weight of Levefix Blue CA and Levafix Yellow CA are same. Therefore, the behaviour of these dyes is almost very similar depending on the dyeing methods and fabric density.

The woven fabric is a homogeneous material, the two parallel regions (warp and weft), account for the intra-yarn and inter-yarn pores [170]. The smaller the pores in the fabric the more difficult it is for the dye to diffuse inside the fabric, more force is required to penetrate the fabric, especially in continuous dyeing processes, because of short dyeing time. When a tight weave cotton fabric such as ventile, absorbs water or dye liquor it swells, increases the compactness and provides a virtually solid barrier to the passage of liquor or water. However, on drying ventile sufficiently opens and gives comfort for wearing.

As compared to loosely woven fabrics, tightly woven fabrics are stiff when wetted and are expensive to weave, therefore, they are not suitable for everyday use [169]. This type of fabric is most commonly used for home furnishing, and other technical purposes. However, the proportion of highly sett (high cover factor) fabrics is more effected by finishing treatment than those of lightly (low cover factor) fabrics and an effect of construction is more pronounced in lightly finished fabrics [149].

For dyeing fabrics not only is the correct recipe and procedure required, but knowledge of fabric parameters is also necessary, so that the dyers can get right-first-time and uniform shade.

7.2 Preliminary Dyeing

The plain Tencel woven fabrics is shown in Table 7.1, were dyed using Novacron Red FN, Blue C-R/ FN and Yellow FN at 0.5% (dye conc), by exhaust method as shown in Section 5.2.3.1.1.

It is shown in Figure 7.2; the Novacron Blue C-R/FN has the highest Integ value as compared to the Novacron Red and Yellow FN. Moreover, the Integ values using Novacron Blue C-R/FN is high at tightly woven fabric (163 GSM) in both groups A and B, as compared to the loosely woven fabrics. The trends of Integ values vary similarly in all three Novacron FN dyes.

The Novacron FN dyed samples are not uniformly dyed inside the yarns of the fabrics, as shown in Figure 7.3 and Figure 7.4, especially at tight weave fabric (163 GSM). The lowest GSM fabric (110) shows good or uniform distribution of dye molecules. The variation in dyeing is increased from 132 GSM in group A and 135 GSM fabrics in group B. The highest GSM fabric (163) shows a dark colour at yarn periphery and light or different hue in the centre, such as the red colour shows yellower to orange hue, yellow colour shows pale yellow hue and blue colour shows white colour.

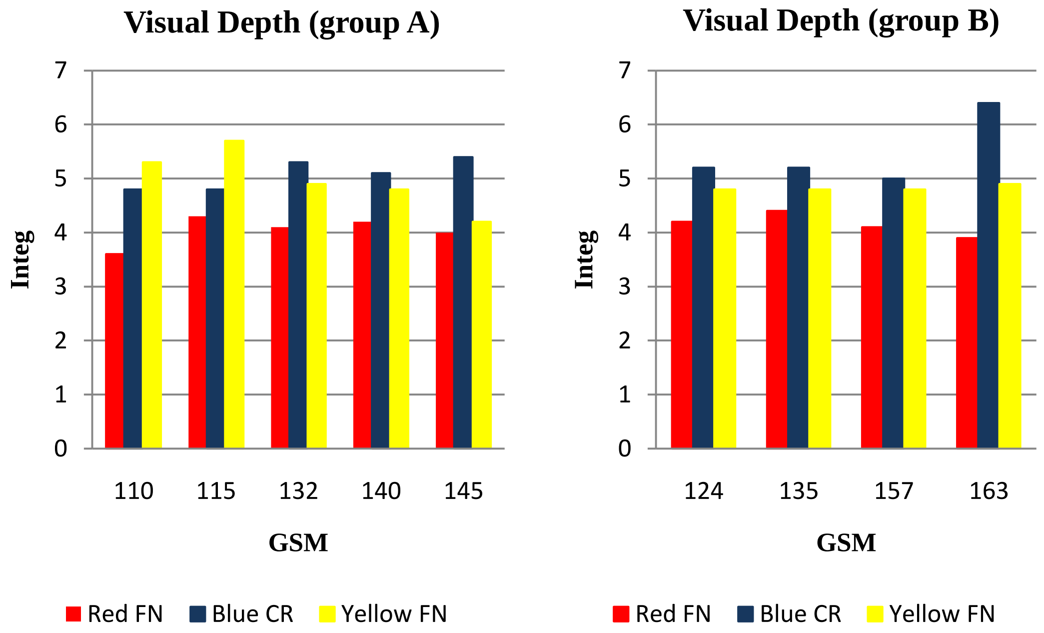


Figure 7.2 Visual depth of Novacron FN dyes

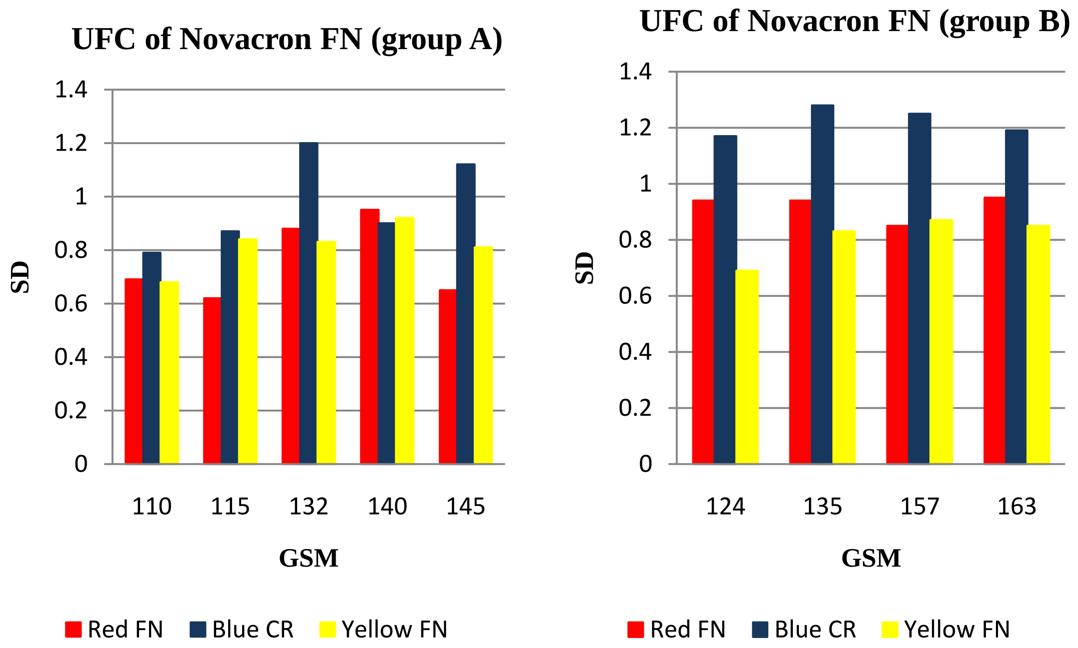
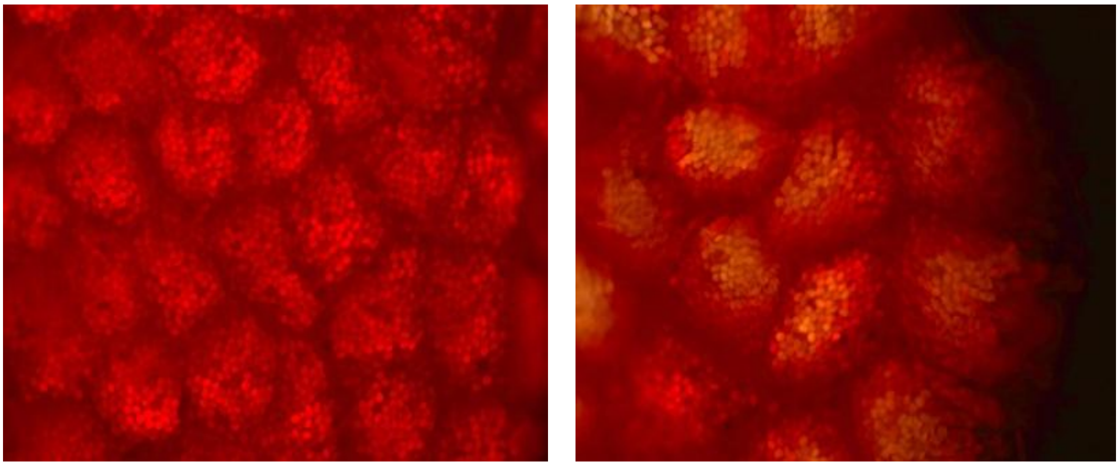
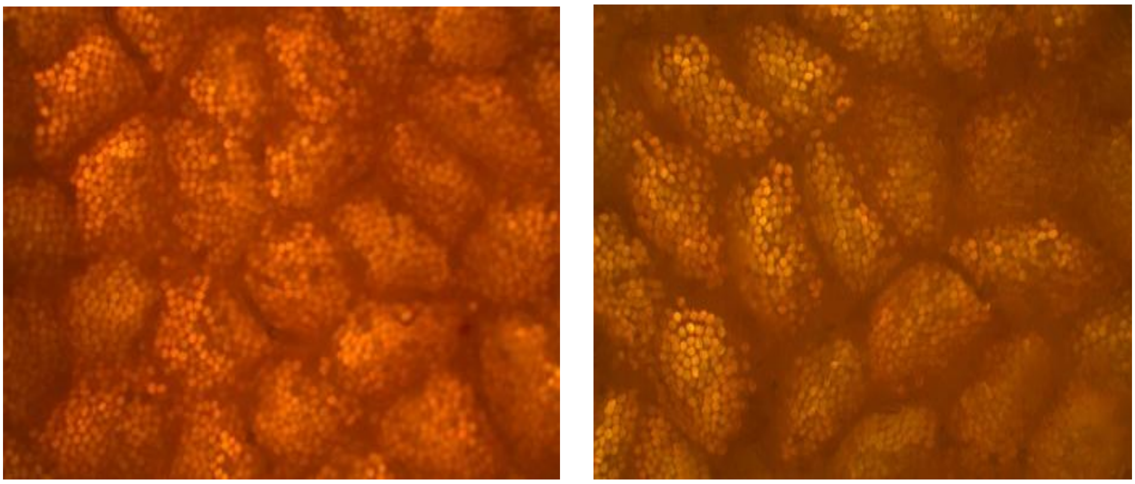


Figure 7.3 UFC of Novacron FN dyes

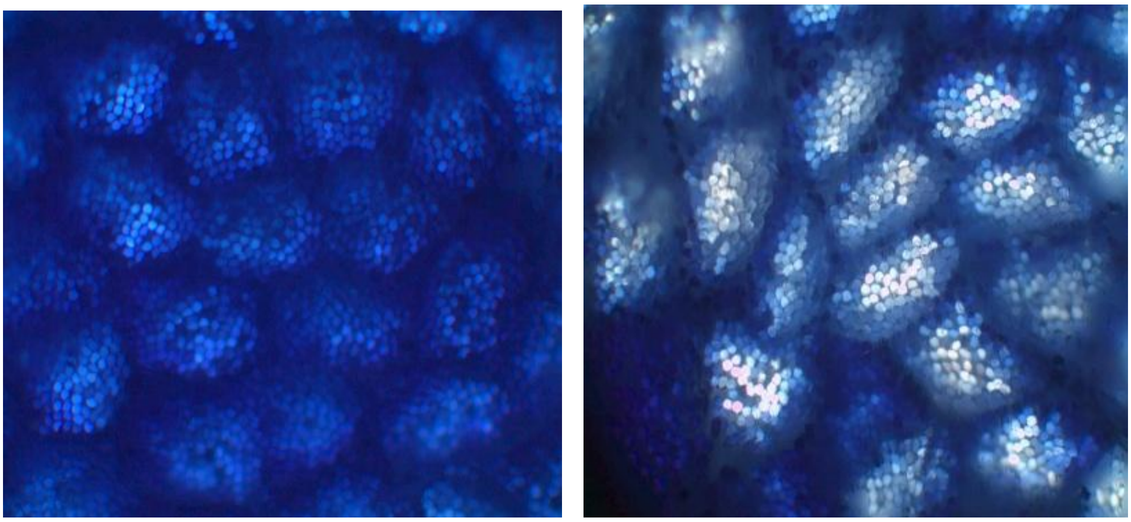
Hence, non-uniformity of dyeing is observed, due to the partially diffusion of dye molecules into the interior of fibres of the yarn, and most of it is remain on the yarn surface and form a layer of dyes. Thus cross-sectional views making a ring like appearance of dye and have poor fastness.



Novacron Red FN-R (110 GSM) Novacron Red FN-R (163 GSM)



Novacron Yellow FN-2R (110 GSM) Novacron Yellow FN-2R(163 GSM)



Novacron Blue C-R/FN (110 GSM) Novacron Blue C-R/FN (163 GSM)

Figure 7.4 Cross-sectional views of Novacron FN dyes

Similar results as discussed in the above paragraph are observed when Tencel plain fabrics (composed of different weave density) were dyed by a continuous dyeing method (pad-steam process) are shown in Figure 7.5.

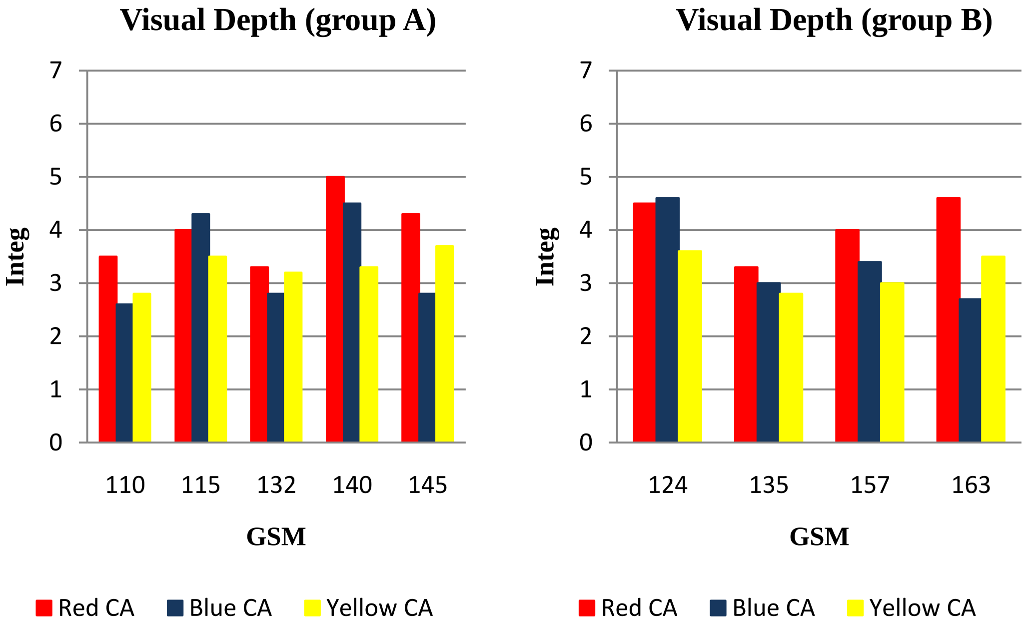


Figure 7.5 Visual depth of Levafix CA dyes

When comparing the results of exhaust and continuous dyeing methods on Tencel Plain, Twill 2/1, Twill 3/1 and Twill 5/1 weave fabrics, the visual depths obtained by continuous dyeing processes are lower than by exhaust process. For improving the dye penetration and increasing the visual depth various steps were taken.

Initially, fabric was pre-treated using cationic fixing agents (3-chloro 2-hydroxypropyltrimethylammonium chloride, CMAC) by both exhaust and continuous methods (pad-bake process). Then, the fabric was dyed using Novacron Blue C-R/FN (0.5% dye conc) by an exhaust method recommended by the Huntsman. Another method of improving the dye penetration and uniformity was to extend the dyeing temperature and time as mentioned in method (B) of exhaust dyeing (Section 5.2.3.1.2). However, high temperature with more reactive dyes was recommended for heavy fabric and highly twisted yarns, to obtain even dye penetration [115].

When comparing the results of yarn cross-section images (UFC) of cationic pre-treated and method (B) exhaust dyeing, the dye molecules were much more uniformly distributed in the method (B) exhaust dyed samples (Novacron Blue CR/FN and LS) than the pre-treated with cationic fixing agent and exhaust dyed samples (Table 7.2 and Figure 7.6). Similarly, the visual depth of pre-treated dyed fabrics was also lower than the method (B) exhaust dyed fabrics. Hence, pre-treatment by cationic fixing agent was not helpful to improve the dye penetration. Cationic fixing agents form cationic charges on the surface of the fabric, which attract reactive dye molecules, facilitating formation of covalent bond between the dye and the fibre and become fixed, rather than to increase penetration or diffusion of the dye molecules inside the filaments of the fabric. The dye molecules were fixed at the surface of the yarns only and giving a ring dyeing effect, while the centre of the yarn of the woven fabric remained un-dyed.

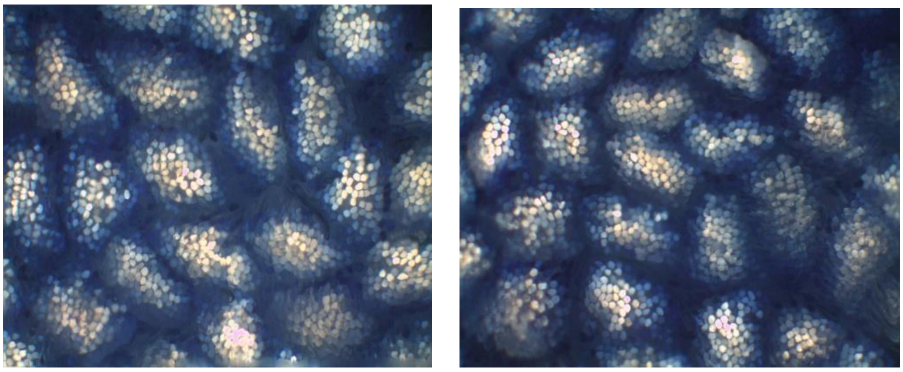
Table 7.2 Exhaust dyeing with and without pre-treatment.

Methods	Integ	*SD
CMAC$_1$	5	1.24
CMAC$_2$	4.9	1.26
Novacron Blue FN/C-R	5.4	0.89
Novacron Blue LS.	6.2	0.74

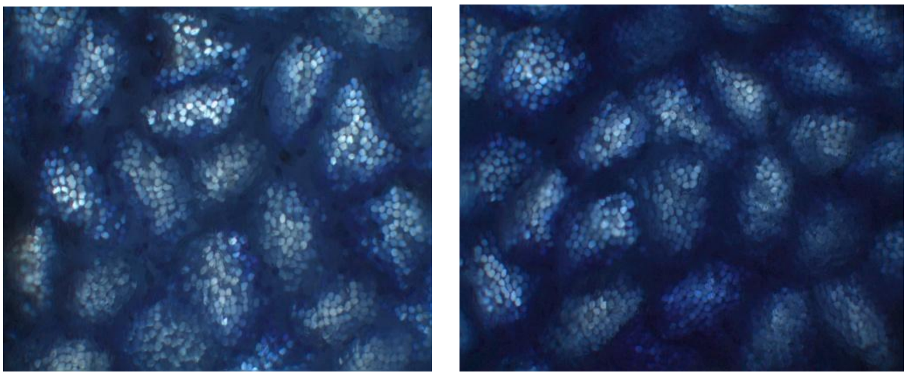
*****SD = Standard Deviation measured by subjective assessment of UFC.*

CMAC$_1$ = CMAC applied by pad-bake method.

CMAC$_2$ = CMAC applied by exhaust method.



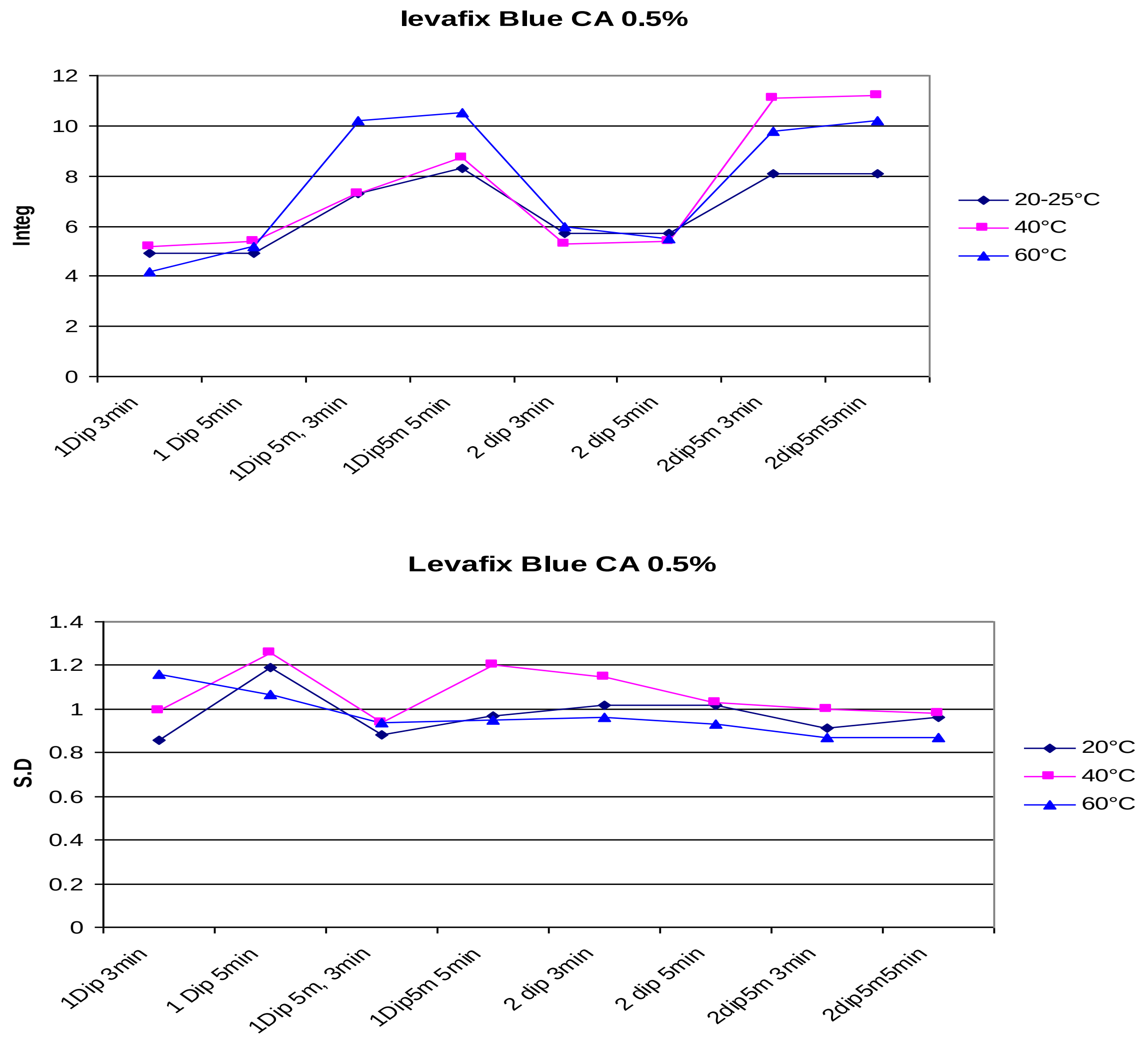
CMAC (Pad-bake) and Blue FN CMAC (Exhaust) and Blue FN



Novacron Blue C-R/FN Novacron Blue LS

Figure 7.6 Comparison of pre-treatment and without pre-treatment process.

To improve the ring dyeing problem and low visual depth, in case of continuous dyeing processes, 163 GSM fabrics was dyed by pad-dry-thermosol dyeing process at 78% pick-up using Levafix Blue CA dye (0.5 % dye conc) according to the recommended method. The fabric was padded at different liquor temperature such as 20 - 25^{0}C, 40 ^{0}C and 60 ^{0}C, with no dwell time and 5 min dwell time, single and double nip and baking at 150 ^{0}C for 3 min and 5 min as shown in Figure 7.7.



**1Dip 3 min = one dip 3 min baking time, no dwell time.*
1 Dip 5 min = one dip 5 min baking time, no dwell time.
1 Dip 5m 3 min = one dip 3 min baking time, 5 min dwell time.
1 Dip 5 m 5 min = one dip 5 min baking time, 5 min dwell time.
2 Dip 3 min = two dip and two nip 3 min baking time, no dwell time.
2 Dip 5 min = two dip and two nip 5 min baking time, no dwell time.
2 Dip 5m 3 min = two dip and two nip 3 min baking time, 5 min dwell time.
2 Dip 5 m 5 min = two dip and two nip 5 min baking time, 5 min dwell time.

Figure 7.7 Integ and UFC of Levafix Blue CA 0.5% , at different dyeing conditions

Whilst 60°C liquor temperature gave high visual depth and UFC values it was very difficult to dye the fabric on a large scale because of the instability of dyeing at this temperature. Further, reactive dyeing at 60°C increased the fibrillation tendency of Tencel fibre [120]. Similarly, double dip and nip is also difficult practically and depends on the flexibility of the continuous dyeing machine.

Hence, after number of experiments it was decided to dye the Tencel fabric, using the recommended dye recipe at liquor temperature of 40 °C, with a five min dwell time. The fabric after padding, was fixed by the same methods (temperature and time) as recommended by DyStar. The results of 40 °C with a 5 min dwell time will be discussed later.

The higher temperature of 40 °C promotes the diffusion of dye molecules within the fibre of yarn of the woven fabric, even these of tight weave structure. On the other hand, a five min dwell time is difficult to implement on a large scale, one of the easiest ways is to reduce the speed of the padding machine, but that decreases the production. Therefore, work is focuses on designing the dyeing method that can minimized the dwell time. It has been already mentioned, pre-treatment with cationic fixing agents did not improve dye penetration. Therefore, the fabric was later pre-treated with caustic soda (10 % (w/v), 15 % (w/v), 0.5 mol dm^{-3} and 2 mol dm^{-3}) using the method described in Section 5.2.2.2 and then dyed by pad-dry-thermosol process using Levafix Blue CA dye. The test results are shown in Table 7.3.

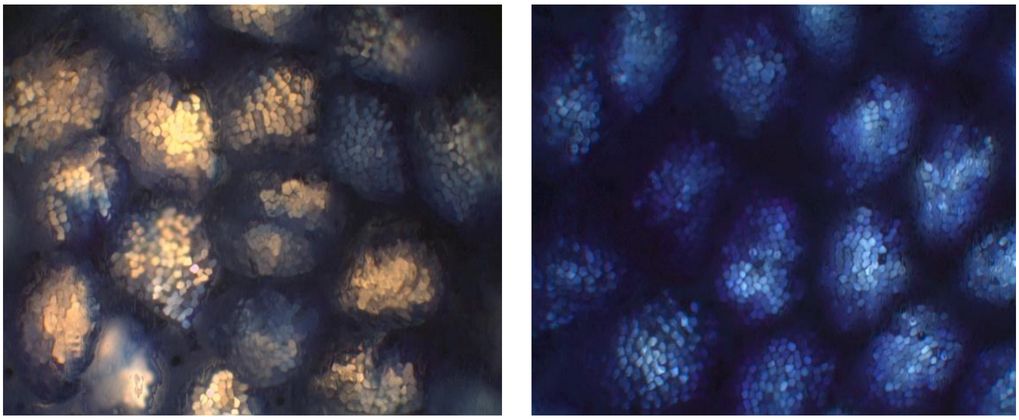
Table 7.3 Integ value after NaOH treatment

NaOH	**Integ**
10 % NaOH `	15.76
15% NaOH `	19.99
0.5 mol dm^{-3} NaOH*	10.69
2 mol dm^{-3} NaOH*	16.68

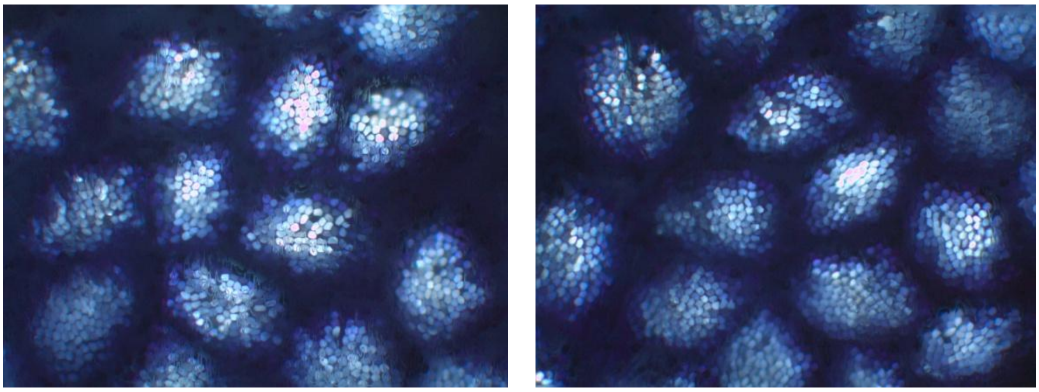
`Pad-dry-thermosol process at 40 ℃ liquor temperature with a 5 min dwell time.

**Pad-dry-thermosol process at 40 ℃ liquor temperature with a 2 min dwell time.*

The Integ values of dyed samples; using 10 % (w/v) and 15% (w/v) NaOH at 5 °C are much higher than those obtained using the other quantities of NaOH because of the 5 min dwell time. However, causticisation using 10 - 15 % (w/v) NaOH changes the Tencel fabric properties, especially handle and it became very stiff.



15 % NaOH PDT, Blue CA 0.5% 10 % NaOH PDT, Blue CA 0.5%



0.5 mol dm^{-3} NaOH PDT, Blue CA 0.5% 2 mol dm^{-3} NaOH PDT, Blue CA 0.5%

Figure 7.8 Cross-sectional view of yarns after NaOH treatment and dyeing

The results are further confirmed by assessing the UFC (Figure 7.8) at 15 % (w/v) NaOH pre-treated dyed samples are ring dyed.

However, a 2 mol dm^{-3} NaOH pre-treatment shows uniform dye penetration as well as high Integ value, even at 2 min dwell time and there was no effect, especially on fabric handle. The same concentration of caustic (2 mol dm^{-3}) was applied with enzymes (Cellusoft CR and Cellusoft L). The results are shown in Table 7.4.

It has been observed that a high visual depth could be obtained by caustic treatment only. Enzymes (Cellusoft CR and L), removes the fibrils on the surface of the fabric but did not increase the visual depth. The results were further confirmed by cross-sectional images, where Cellusoft CR, 2% and caustic pre-treated fabric showed ring dyeing. The cellulase enzyme treatments were used only to remove the long fibre ends, primary fibrils from the surface of the fabric [92].

From the results shown in Table 7.3 and Table 7.4, it was concluded that caustic treatment with 2 mol dm^{-3} applied by pad-batch method improves the dye uptake as well as the UFC.

Table 7.4 Integ value of after caustic and enzymatic (CR & L) treatment

	Procedure	**%, Enzymes**	**Integ**
CR & L, Exhaust process	CRC[1]	0.5	13.3
	CRC	2.0	15.6
	CCR[2]	0.5	13.1
	CCR	2.0	7.3
	LC[3]	0.5	14.4
	LC	2.0	14.8
	CL[4]	0.5	13.4
	CL	2.0	13.0
CR & L, Pad-batch process	CRC	0.60	14.9
	CRC	0.75	16.3
	CCR	0.60	12.0
	CCR	0.75	11.9
	LC	0.50	14.2
	CL	0.50	12.0
	C[5]		16.3

1.CRC=Cellosoft CR-Caustic.

2.CCR=Caustic-Cellusoft CR.

3.LC=Cellusoft L-Caustic.

4.CL= Caustic-Cellusoft L.

5. C=Caustic.

7.3 Continuous Dyeing

The fabric was dyed by different dyeing methods using Levafix Red, Yellow, Blue CA and Remazol Black B-A at 0.5% dye conc. The dyeing methods used were:

- After causticisation.
  - Dye liquor at 40 °C with a 1 min dwell time.
  - Dye liquor at room temperature with no dwell time.
- Without causticisation.
  - Dye liquor at 40 °C with a 1 min dwell time.
  - Dye liquor at room temperature with no dwell time.
  - Dye liquor at 40 °C with a 5 min dwell time.

The behaviour of reactive dyes on Tencel woven fabrics are assessed by measuring the visual depth or Integ values, dye uptake and uniformity of fibre coloration.

7.3.1 Visual Depth

7.3.1.1 After Causticisation

The plain weave Tencel fabrics were dyed using Levafix CA and Remazol B-A dyes by the pad-steam process. The results are shown in Figure 7.9. The visual depth of the lowest GSM (110) fabric is less than the 115 GSM fabric. This is because 110 GSM has very big and irregular pore sizes, giving more space in between the yarns. It was observed that if porosity is very high it becomes difficult for the dye molecules to react. The very large and irregular pore size, not only effects the dyeing of woven fabrics but it effects yarn package dyeing as well. Very loosely wound yarn packages also give low visual depth.

The other fabrics, from 115 GSM to 145 GSM, and similarly in group B (124 to 163 GSM) visual depth decreases as the fabric density increases. The highest GSM (163 GSM) most tight weave fabric, has lowest Integ value, as compared to the light weight fabric (115 GSM). The reason for the lower Integ value, particularly at 163 GSM of fabric, is the coarse linear density of weft yarn and the tighter weave. Like cotton, in the Tencel filaments, the finer the filament the more will be the uptake of dye molecules [1].

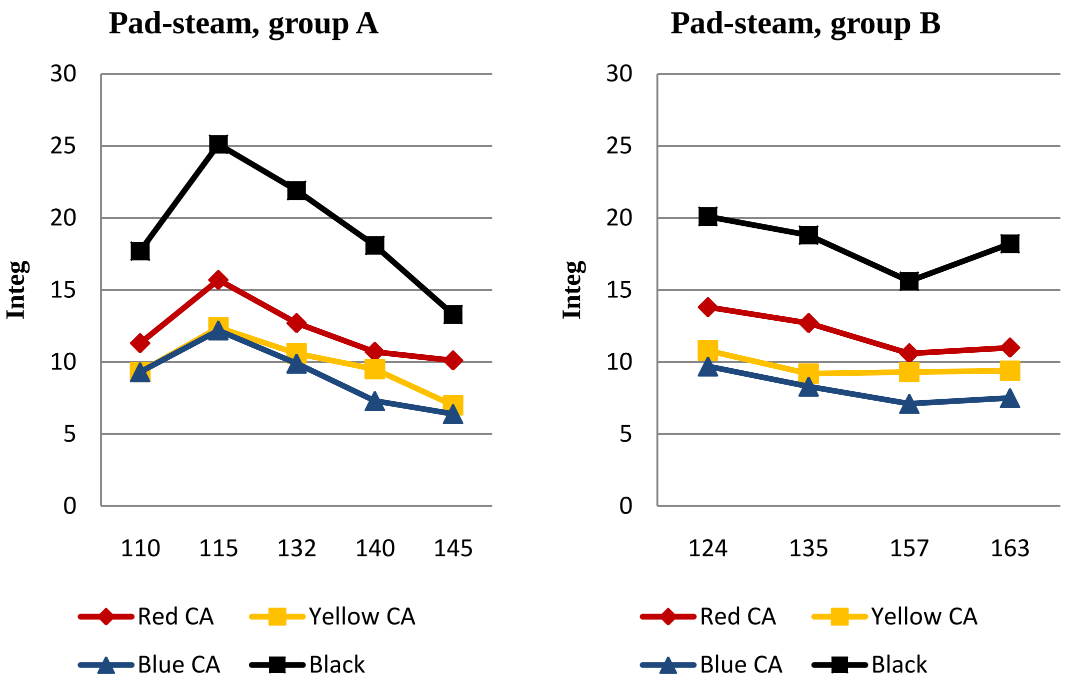


Figure 7.9 Pad-steam at 40°C with a 1 min dwell time

The averages of Integ values of Levafix Red CA and Blue CA are shown in Figure 7.10 and Figure 7.11. The Integ values obtained from the pad-dry-thermosol process are higher than by the pad-dry-steam and pad-steam processes. Similarly, the Integ value of the pad-dry-steam process is higher than by the pad-steam process but lower than the pad-dry-thermosol process. The same trends of visual depth are observed at 40 ^{0}C liquor temperature with a 1 min dwell time and room temperature liquor with no dwell time, after causticisation.

The caustic treatment using 2 mol dm^{-3} swells the interfibrillar structure of the filaments of the Tencel fabric. The interfibrillar swelling increased the dye accessibility by breaking the hydrogen bond in the 101 direction, hence increase the dye accessibility. The dye molecules are not absorbed within the crystallites of fibre but might be adsorbed on the accessible surface of the crystallites and absorbed more readily in the amorphous region of the fibre. The caustic treatment increases the reactive sites on the Tencel fibres; therefore, reactive dyes can easily penetrate inside the filaments of Tencel fabric.

The caustic soda is usually applied at room temperature because the reaction is exothermic. At high temperature swelling of the cellulosic fabric is decreased.

Furthermore, temperature and dwell time imparts a vital role in continuous dyeing. As discussed in Section 6.3.1, the Integ values obtained by continuous dyeing process are lower than by an exhaust dyeing method. The visual depth values at 40 ^{0}C liquor temperature with a 1 min dwell time after causticisation are more than 50 % higher than the room temperature dyeing.

It was observed that the yarn can be dyed at a faster rate as compared to the fabric dyeing. This is because the dyeing on the fabric is slow at the yarn cross and in contact points or point of interaction of yarns. It was assumed that the yarn in the fabric is an impermeable cylinder and the major part of the dye liquor is passed through the inter-yarn zone of the fabric [170]. The fabric is not initially dyed at these intersection points. Dyeing at 40 ^{0}C promotes the movement of liquid in the space between pores of the fabric. According to the pore diffusion model, at 40 ^{0}C dye diffuses at inter-filament at short dyeing time [223]. The 40 ^{0}C dyeing temperature enables the dye molecules to diffuse inside yarn intersection and cross-over points. Additionally, the caustic pre-treatment creates more accessible sites for the dye molecules and the higher temperature helps the dyes to diffuse within the fabric geometry. The 1 min dwell time also allows dye liquor to penetrate inside the yarns of the fabric; however the rate of diffusion and penetration is dependent on the temperature. Hence, both causticisation and temperature improved the Integ and penetration especially in tightly woven fabrics.

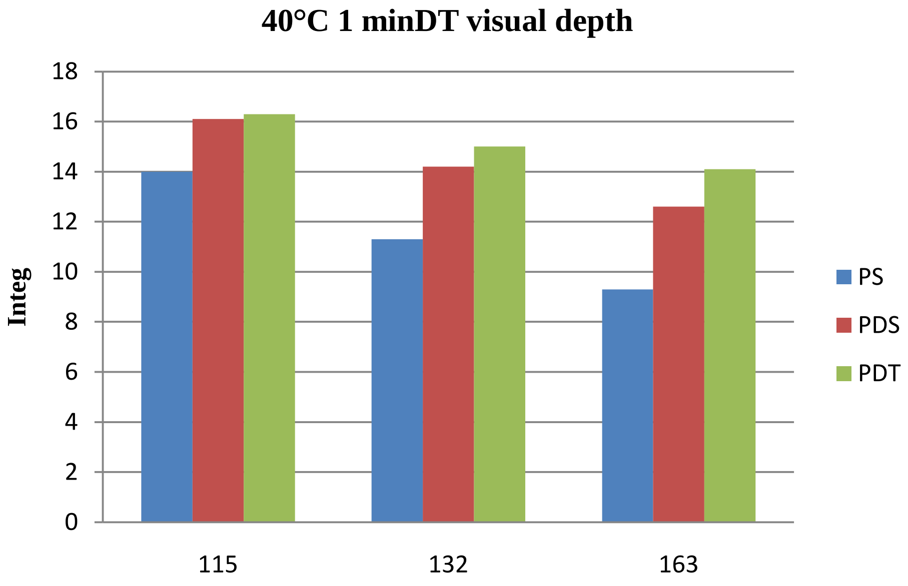


Figure 7.10 After causticisation 40 ^{0}C with a 1 min dwell time

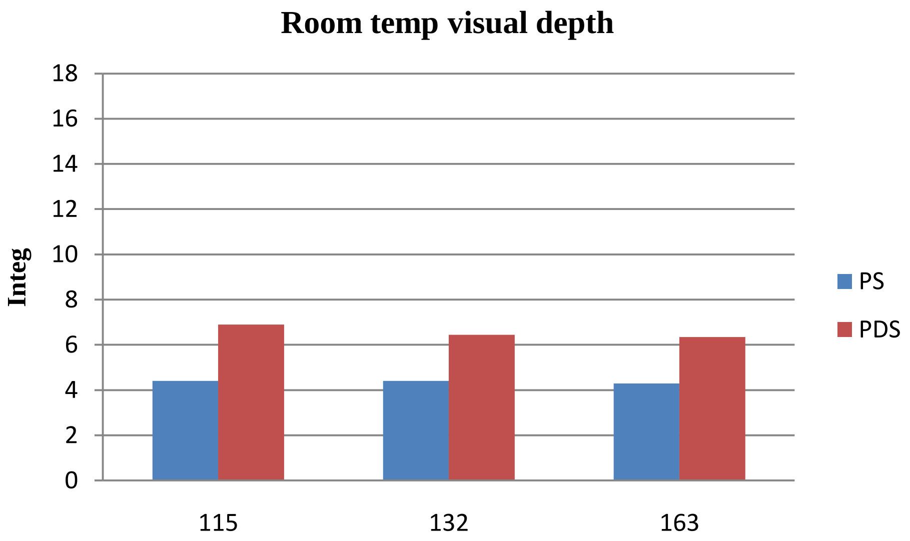


Figure 7.11 After causticisation room temp with no dwell time

7.3.1.2 *Without Causticisation*

The visual depth values of the Tencel woven fabrics without causticisation are lower than after the caustic treatment (see Figure 7.12 and Figure 7.13). However, minor differences are observed between the trends of Integ value (average of Levafix Red and Blue CA) of padding at room temperature liquor bath with no dwell time after causticisation, and without causticisation. The 40 ^{0}C liquor temperature with 1 min dwell time dyeing gives good visual depth without causticisation as compared to the room temperature dyeing even after causticisation. But it is lower than the after causticised dyed fabric at the same temperature and dwell time. This is because the sodium hydroxide (2 mol dm^{-3}) can swell the fibres, disturb the molecular alignments on the surface of the fibre hence, increase the accessibility for the dye molecules [224].

Dyeing of Levafix CA dyes (0.5% dye conc) at 40 ^{0}C liquor temperature with a 5 min dwell time yielded higher Integ values than exhaust method of dyeing (Figure 7.14 (a) and Figure 7.14 (b)) and comparable to dyeing at 40 ^{0}C with 1 min dwell time after causticisation. On the other hand, dyeing method (40 ^{0}C liquor temperature with a 5 min dwell time) can have drawbacks, such as a tailing effect and low production because of the long dwell time as already been discussed. The temperature of 40 ^{0}C can easily be achieved, especially in those countries where ambient temperature is more than 40 ^{0}C, while in other countries by applying very small amount of heat.

The trends of visual depth are pad-dry-thermosol > pad-steam > pad-batch process. On the other hand, 40 ^{0}C liquor temperatures with a 5 min dwell time visual depth trends are ambiguous, as shown in Figure 7.14. In all three dyeing methods (pad-steam, pad-dry-thermosol and pad-batch process) 132 and 135 GSM of Tencel woven fabrics showed the highest visual depth as compared to the other fabrics except by pad-steam process.

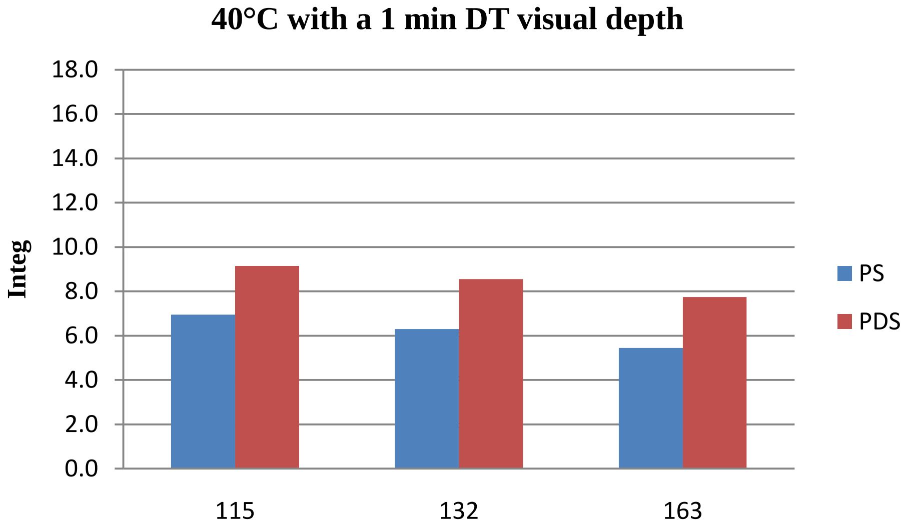


Figure 7.12 Without causticisation 40 ^{0}C with a 1 min dwell time

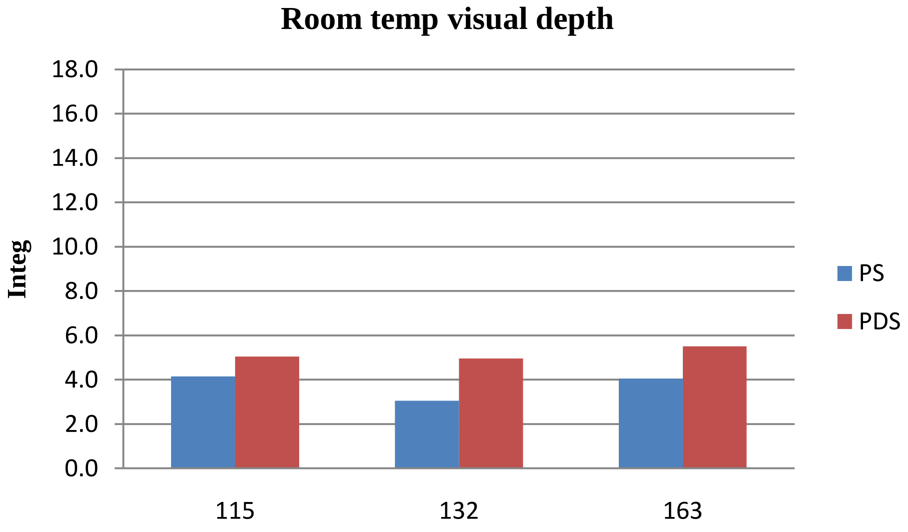


Figure 7.13 Without causticisation room temp with no dwell time.

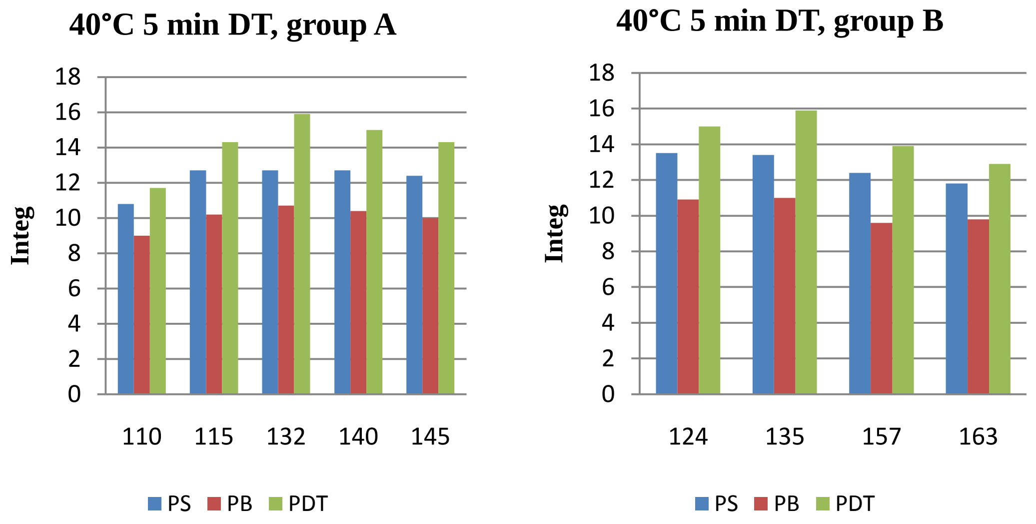


Figure 7.14 Novacron visual depth 40 ^{0}C with a 5 min dwell time group A and B

The reactive dyeing behaviour is further confirmed by dyeing the Tencel fabrics using Novacron C dyes by pad-dry-thermosol process. The fabrics were dyed at a liquor temperature of 40 °C with a 1 min dwell time after caustic treatment and room temperature liquor without dwell time and causticisation. The Novacron Red C-2G and Blue C-R was dyed using the recipe as shown in Table 5.4, has shown very low visual depth as shown in Figure 6.6. That is why Novacron C was then dyed according to the recipe mention in Table 5.5. The results shows (see Figure 7.15) average of Red and Blue C dyes, liquor at 40 °C temperature with a1 min dwell time after causticisation (AC 40C 1 min DT) gives 50 % high Integ values as compared to the standard condition (room temperature dyeing without dwell time). Hence, reactive dyeing at 40 °C liquor temperature with a 1 min dwell times when applied by continuous dyeing process on standard Tencel fabric gives highest visual depth.

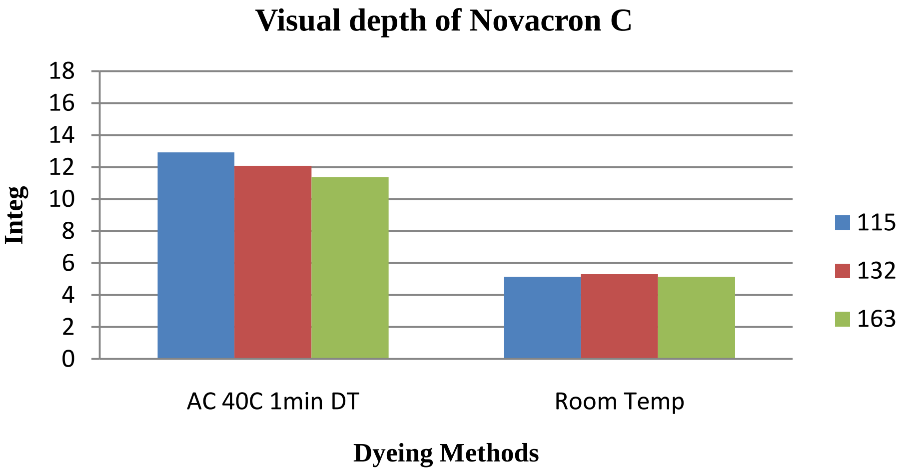


Figure 7.15 Visual depth of Novacron C dyes

7.3.2 Fixation

The fixation or dye uptake trends shown in Table 7.5 and Table 7.6 are the averages values of Levafix Red CA and Blue CA. High fixation values means dye molecules are efficiently exhausted towards the fabric and have been fixed in the fabric. Conversely, similarly, low fixation means low dye exhaustion in the fabric. The trends of fixation are similar to the trends of visual depth in both after and without causticisation treatment. The fixation (g/100g of fibre) of the Tencel fabrics when dyed by using Levafix CA decreases as the weight of the fabric increases.

After caustic pre-treatment and dyeing of 40 °C with a 1 min dwell time Tencel fabrics shows 1.40 – 0.93 dye uptake, while without causticsation at the same condition is 0.70 – 0.55 dye uptake. The F value without causticisation at room temperature liquor with no dwell time, is very low and in the range of 0.39 - 0.33 and after causticisation in the range of 0.56 - 0.43. In the case of 40 °C with a 5 min dwell time the F value is 1.22 to 0.86. The 0.50 – 0.75 fixation means 0.50 and 0.75 g/100g of fibres are covalently bonded to the dyes molecules and remaining are hydrolyzed [114].

Table 7.5 Fixation of Levafix CA by pad-steam and pad-dry-steam (g/100g fibre)

GSM	**Pad-steam**				**Pad-dry-steam**			
	After Causticisation		**Without Causticisation**		**After Causticisation**		**Without Causticisation**	
	40°C, 1 min DT	**Room temp, no DT**	**40°C, 1 min DT**	**Room temp, no DT**	**40°C, 1 min DT**	**Room temp, no DT**	**40°C, 1 min DT**	**Room temp, no DT**
115	1.28	0.48	0.70	0.39	1.40	0.56	0.68	0.37
132	1.01	0.45	0.62	0.33	1.13	0.48	0.61	0.36
163	0.93	0.43	0.57	0.33	0.98	0.47	0.55	0.34

Table 7.6 Fixation of 40 °C with a 5 min dwell time no causticisation (g/100g fibre)

GSM	**PS**	**PB**	**PDT**
115	1.22	1.09	1.18
132	0.88	0.70	1.11
163	1.00	0.86	1.14

7.3.3 Uniformity of Fibre Coloration (UFC)

7.3.3.1 Subjective Assessment

The subjective assessment results are shown in the Figure 7.16 (after causticisation) and Figure 7.17 (no causticisation). The standard deviation is increased with the density of woven fabric. At very high weave density, the yarns are very close to each other and have very low porosity; therefore, it is very difficult for dye liquor to flow between the fibres of the yarn of the woven fabric. Whereas, in the loosely woven fabric the spaces between the yarns allow the dye liquor to flow easily hence, there is a high diffusion of dye molecules and more uniform dye uptake.

A small difference of standard deviation is observed when comparing the standard deviation after caustic treatment and without caustic treatment in all dyeing methods. The pad-dry-thermosol process shows higher SD values than the pad-steam. The pad-dry-steam shows highest deviation. The pad-steam process shows more uniformity of fibre coloration and lowest deviation.

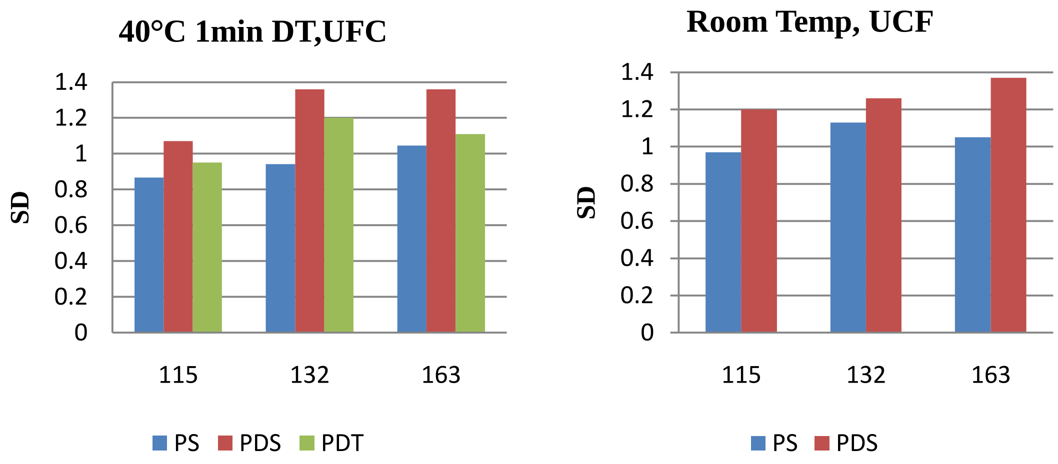


Figure 7.16 UFC of dyed fabrics after caustic treatment

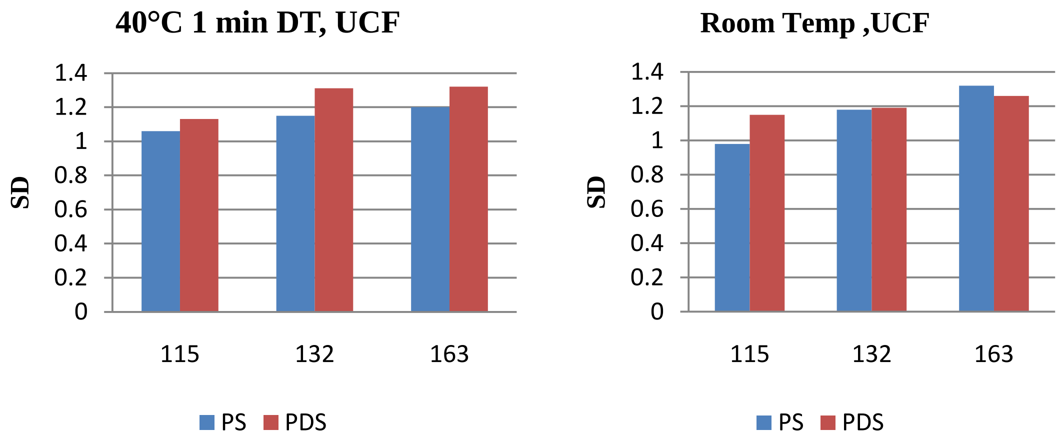


Figure 7.17 UFC of dyed fabrics without caustic pre-treatment

7.3.3.2 Objective Assessment

Objective assessment (see Table 7.7) gives similar trends to those obtained with visual assessment. The loosely woven fabric shows lower deviation in dye penetration. The deviation increases with the density of the fabric. When comparing the dyeing methods, the pad-steam process shows uniform dye penetration usually at lower GSM but shows high deviation in tightly woven fabric. The pad-dry-steam process shows non-uniform dyeing by subjective assessment but behaves differently in objective assessment, which might be because of difference of sample and its size.

Padding at 40 °C liquor temperature with a 1 min dwell time after caustic treatment gives SD values 0.20 to 0.51, while at the same liquor temperature with a 5min dwell time without caustic treatment has SD values 0.2 to 0.50. Similarly, both dyeing methods as shown in Table 7.7 (after caustic treatment 40 °C liquor temperature with a 1 min dwell time and 40 °C liquor temperature with 5 min dwell time without caustic treatment) have an average rating of 3 or more up to rating 5 (very dark or 0 grey value). While other dyeing methods have average rating close to 3 and the deviation are in the range of 0.42 to 0.50. In the case of 40 °C liquor temperature with a 5 min dwell time, pad-batch dyed fabric shows uniform dye penetration as compared to the other dyeing process; on the other hand it shows lower visual depth as compared to PS and PDT process.

The histogram analysis shows that 40°C liquor temperature with a 1 min dwell time after caustic treatment and at the same temperature with a 5 min dwell time without caustic treatment have dispersion on the negative side (Table 7.9 and Table 7.10). Hence, the fibres were heavily dyed and have uniform dye penetration. The high temperature dyeing without caustic treatment also has negative dispersion especially dyed by pad-dry-steam process.

Table 7.7 Standard deviation of UFC by objective assessment

GSM	**After Causticisation**					**No Causticisation**						
	40 °C 1 min D T			**Room Temp**		**40 °C 1 min DT**		**Room Temp**		**40 °C 5 min DT**		
	PS	**PDS**	**PDT**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PB**	**PDT**
115	0.2	0.27	0.27	0.42	0.47	0.41	0.39	0.46	0.47	0.2	0.18	0.24
132	0.31	0.39	0.38	0.44	0.5	0.52	0.51	0.47	0.48	0.31	0.15	0.33
163	0.58	0.55	0.51	0.53	0.5	0.56	0.56	0.52	0.53	0.45	0.31	0.5

Table 7.8 Mean of UFC by objective assessment

	After Causticisation					No Causticisation						
	40 °C 1 min D T			Room Temp		40 °C 1 min DT		Room Temp		40 °C 5 min DT		
GSM	**PS**	**PDS**	**PDT**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PB**	**PDT**
115	3.5	3.4	3.5	2.8	3.0	3.3	3.3	3.2	3.0	3.5	3.5	3.4
132	3.4	3.3	3.4	2.7	2.9	2.9	3.2	2.7	2.9	3.4	3.5	3.4
163	2.9	3.1	3.1	2.5	2.9	2.7	2.9	2.5	2.7	3.2	3.4	3.2

Table 7.9 Dispersion of histogram at midpoint of mode value (D_1)

	After Causticisation					No Causticisation						
	40 °C 1 min DT			Room Temp		40 °C 1 min DT		Room Temp		40 °C 5 min DT		
GSM	**PS**	**PDS**	**PDT**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PB**	**PDT**
115	-0.49	-0.67	-0.51	0.45	0.62	-0.36	-0.52	0.53	0.44	-0.42	-0.61	-0.61
132	-0.37	-0.48	-0.40	0.58	0.59	0.53	-0.42	0.65	0.44	-0.49	-0.43	-0.52
163	0.69	-0.59	-0.34	0.58	0.64	0.51	0.66	0.61	0.68	-0.50	-0.33	-0.47

Table 7.10 Dispersion of histogram at quarter point of mode value (D_2)

	After Causticisation					No Causticisation						
	40 °C 1 min D T			Room Temp		40 °C 1 min DT		Room Temp		40 °C 5 min DT		
GSM	**PS**	**PDS**	**PDT**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PDS**	**PS**	**PB**	**PDT**
115	0.48	-0.68	-0.51	0.66	0.76	0.56	-0.69	0.71	0.68	-0.66	0.61	-0.59
132	0.55	-0.63	0.48	0.70	0.73	0.70	0.73	0.71	0.67	-0.49	0.48	0.45
163	0.81	-0.78	0.67	0.67	0.72	0.76	0.81	0.66	0.73	-0.61	0.41	0.70

Table 7.11 Bandwidth at midpoint of mode value (× 10^{-4})

			115		132		163	
			BR	**BL**	**BR**	**BL**	**BR**	**BL**
After Causticisation	**40 °C 1 min DT**	**PS**	1.21	-0.62	1.36	-0.94	4.01	-1.08
		PDS	0.85	-0.38	1.25	-0.53	3.70	-1.14
		PDT	1.29	-0.51	1.16	-0.69	1.87	-1.18
	Room Temp	**PS**	3.96	-1.88	6.85	-2.34	13.79	-5.05
		PDS	4.41	-1.56	5.46	-2.08	6.02	-1.88
No Causticisation	**40 °C 1min DT**	**PS**	1.35	-0.80	2.83	-1.13	5.46	-3.01
		PDS	1.19	-0.40	2.73	-0.83	4.91	-1.59
	Room Temp	**PS**	2.39	-1.03	6.68	-2.25	12.94	-3.92
		PDS	2.57	-1.47	3.95	-2.20	8.36	-2.65
	40 °C 5min DT	**PS**	0.70	-0.89	1.13	-0.49	1.37	-0.75
		PB	0.86	-0.96	1.03	-0.58	1.74	-0.39
		PDT	1.44	-0.42	1.25	-0.49	0.85	-0.80

Padding at room temperature with and without caustic treatment has wider width of histogram with long tail towards the right hand side (see Table 7.11). The dyeing at 40 °C liquor temperature with 1 min dwell time and 5 min dwell time have thin long peak with short tail towards lighter side and darker side. The peak of the histogram is decreases with the fabric density increases. When comparing SD, mean, dispersion and bandwidth values shows Tencel fabrics have high UFC value dyed at 40 °C liquor temperature with a 1 min dwell time after caustic treatment and at 40 °C liquor temperature with a 5 min dwell time without caustic treatment in all continuous dyeing methods. Hence, Tencel fabrics are heavily and uniformly dyed at 40 °C liquor temperature.

The UFC results of Novacron C dyes shows SD values of dye liquor at room temperature without dwell time and at 40 °C liquor temperature with a 1 min dwell time after caustic treatment have minor difference while the mean grey intensity of 40 °C liquor temperature with a 1 min dwell time after caustic treatment (≤ 3) is higher than the dye liquor at room temperature without dwell time. The negative dispersion of mode value at midpoint (D_1) further shows 40 °C liquor temperature with a 1 min dwell time after caustic treatment dyed fabrics have heavily dyed. The smaller value of bandwidth both right-hand side (BR) and left-hand side (BL) at midpoint of mode value also in favour of dyeing at 40°C liquor temperature with a 1 min dwell time.

Table 7.12 UFC value of Novacron C dyes

		115	**132**	**163**
SD	AC* 40 °C 1min DT\`	0.43	0.47	0.58
	Room Temp	0.47	0.48	0.51
Mean	AC 40 °C 1min DT	3.5	3.4	3.0
	Room Temp	2.3	2.9	2.7
D_1	AC 40 °C 1min DT	-0.87	-0.84	-0.73
	Room Temp	0.53	0.67	0.71
D_2	AC 40 °C 1min DT	0.68	0.64	0.81
	Room Temp	0.76	0.78	0.73
BR	AC 40 °C 1min DT	1.66	1.61	2.34
	Room Temp	3.77	4.55	13.79
BL	AC 40 °C 1min DT	-0.31	-0.39	-1.41
	Room Temp	-1.55	-1.47	-2.92

**AC = After causticisation*

\`DT = Dwell time

Tencel fabrics at room temperature liquor without dwell time not only shows lower value of Integ and also gives non-uniformity of colour depth of fibre filament especially at tightly woven fabric, where histogram is very wide with shorter peak.

7.3.3.3 UFC Assessment Validity

In order to verify the uniformity of dye penetration assessment, the visual assessment of cross-sectional images of plain weave dyed fabrics by pad-dry-steam at 40°C liquor temperature with a 1 min dwell time without caustic treatment using Levafix Red CA (163 GSM) and after caustic treatment using Levafix Blue CA (115 GSM) were selected. The assessment was carried out by two assessors A1 and A2 and the author (U1). The graph shows there is not as much difference in visual assessment of rating 1 to 5 (Figure 7.18). The A2 assessment shows difference in rating 5 only.

The assessments were further verified by the author by measuring the UFC of the same images at three different times as shown in Figure 7.19. It has been concluded that the variation in the manual counting could be possible. For this reason, results of subjective assessment were further compared with the objective assessment. The fabric cross-sectional images dyed with Levafix Red, Blue and Yellow CA dyes were assessed using Matlab programming and by author (subjectively). Figure 7.20 shows subjective and objective assessments are very close and have same deviation.

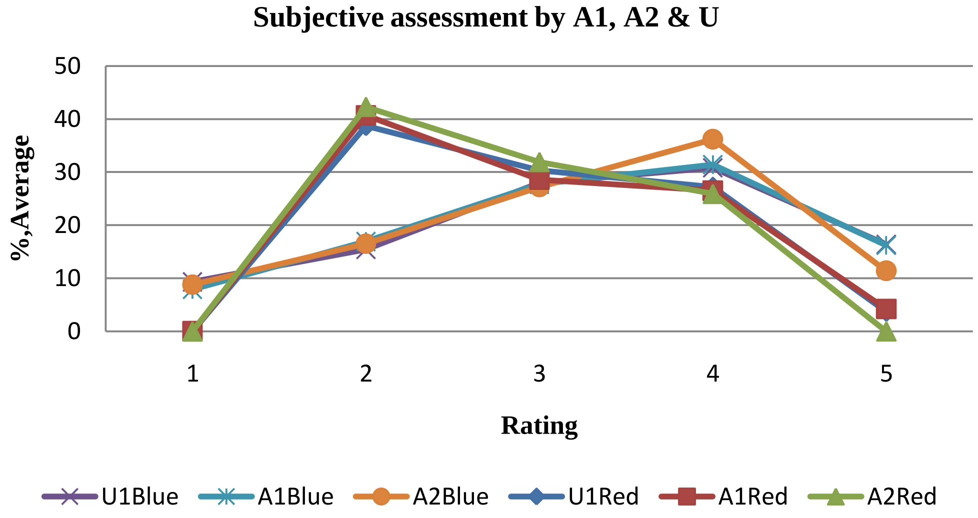


Figure 7.18 Subjective assessment by A1, A2, and U1

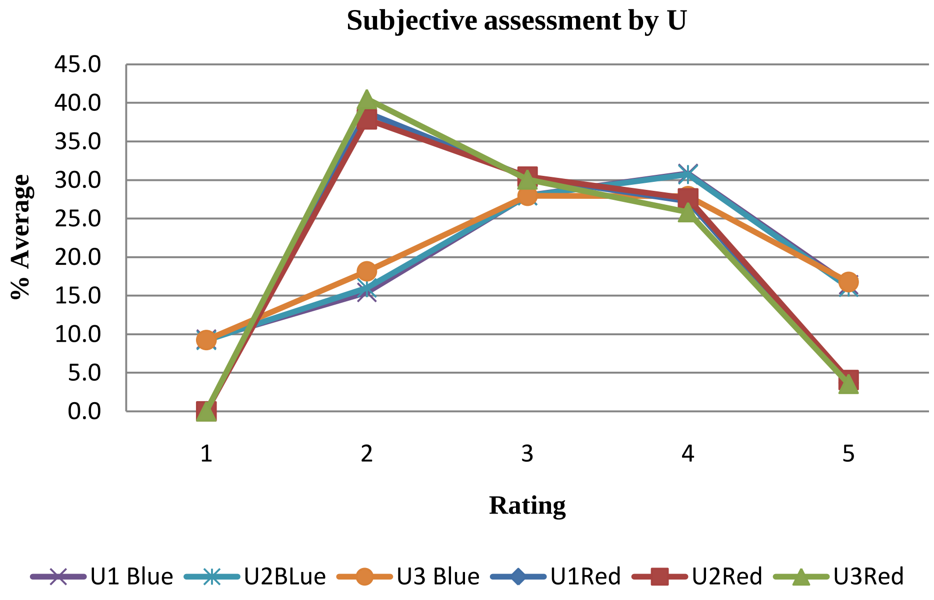


Figure 7.19 Subjective assessment by U

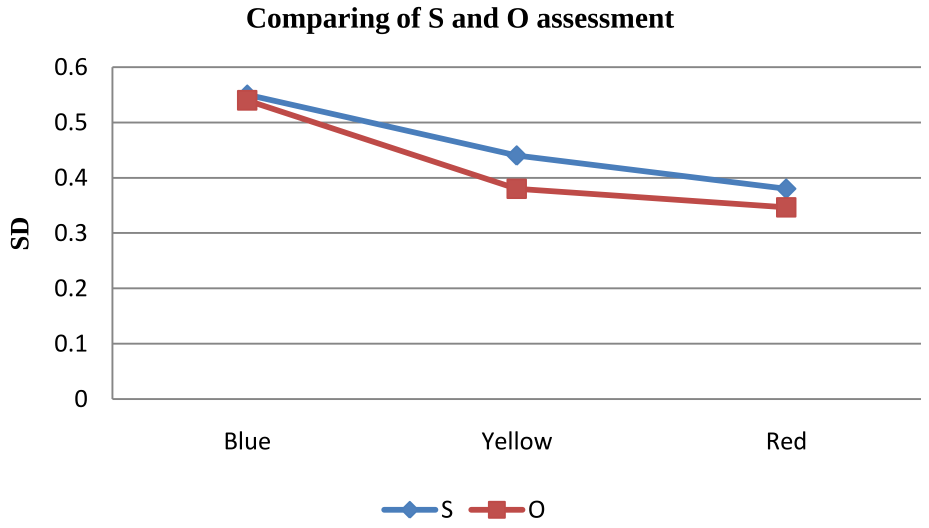


Figure 7.20 Comparison of subjective and objective assessment

S = Subjective assessment.

O = Objective assessment.

7.3.4 Washing Fastness

This was assessed by using Levafix Red CA dye, when applied by pad-steam process after causticisation at 40 ^{0}C liquor temperature with a 1 min dwell time. All nine fabrics ranging from 110 to 163 GSM showed excellent wash fastness, as shown in Table 7.13. The fabrics had zero staining and fading of colour in all multifibre scale. From the results it is observed that the fastness, especially washing depends more on the dye type rather than type of woven fabric, if the dye is evenly penetrated. Fastness rating could be varied due to the difference in reactive dye type and dyeing method.

Table 7.13 Washing fastness

GSM	Dyed Fabric	Multifibres*
110	5	5
115	5	5
132	5	5
140	5	5
145	5	5
124	5	5
135	5	5
157	5	5
163	5	5

**Multifibres are secondary cellulose acetate, bleached unmercerized cotton, nylon 6.6, polyester, acrylic, wool worsted.*

7.3.5 Rubbing Fastness

The rubbing fastness of Tencel fabrics is very good to excellent when dyed by using Levafix Red CA dye. The fastness of 115 GSM fabrics is always higher than the 163 GSM fabrics. The overall trends of rubbing fastness is pad-steam (5 to 5-4) > pad-dry-steam (5 to 4) > pad-dry-thermosol (5 to 4-3). Further, the rubbing fastness of dyed fabric after causticisation is higher than the dyed sample without causticisation because of the uniformity of dyeing after caustic treatment. The non-uniformity of dyeing leads to lower rubbing fastness. It was assessed that dye could be transferred from the fine fibrils to the rubbing cloth when assessing by wet fabric, giving the impression of lower rub fastness. Inherently, the dry rub fastness on Tencel is identical to the other fibres such as viscose and cotton [11].

7.3.6 Tensile Strength

The tensile strength is expressed in tenacity, cN/tex. This property of fabric is varied as the density of fabric is varied; however, type of fibre also has an effect on tenacity value. The strength of Tencel fabric is comparable to the other synthetic fibres such as polyester and nylon. Tencel fibres do not loose their strength as much after wet treatment as compared to the other cellulosic and regenerated cellulosic fibres.

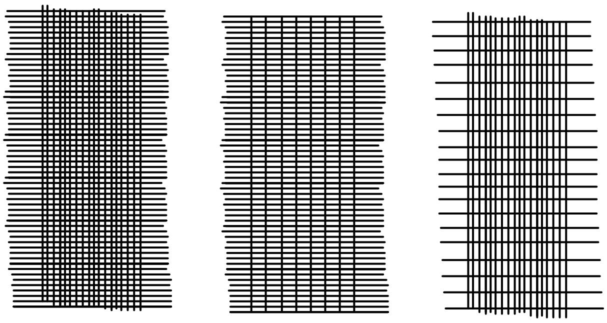
The tenacity of Tencel fabrics increases or decreases after causticisation but drops after dyeing see Figure 7.22 and Figure 7.23. The percent difference of tenacity is calculated between scoured fabric and pre-treated fabric, and also between scoured fabric and dyed fabric is shown in Table 7.14 while Table 7.15 shows the difference in elongation before and after-treatment and dyeing.

In the group A (Table 7.14), warp direction, the lowest GSM 110 decreases 14.7% strength while 115 GSM decreases 17.9% after dyeing when compared to the scoured fabric. The reason 110 GSM shows less loss of tenacity is because of the high elongation percentage (appendix D), even after dyeing. However, the decrease in tenacity percent is observed as GSM of the fabric increases while reversed trend is observed in weft direction in both group A and B fabrics. Similar trend of percent elongation (%E) is observed when comparing the dyed and scoured fabric. The negative value shows (Table 7.15) the fabric increased its elongation more after pre-treatment and then after dyeing. The results are further confirmed by measuring the weight loss of the fabric after causticisation, will be discussed in Section 7.3.10.

The increase in tenacity after causticisation is because of the shrinkage of the fabric. The causticisation causes the fabric to shrink, increases the thickness of the fabric and decreases the gap between the adjacent yarns. The effect is more apparent in the loosely woven fabric as compared to tightly woven fabric. The reduction in fabric strength after causticisation is because the fibres become more amorphous [139].

After dyeing usually all the fibres decrease in strength because of the interaction of chemicals and heat, cause decrease in the DP (degree of polymerization) effecting the structure of the fibre. Overall, causticisation treatment using 2 mol dm^{-3} has very minor influence on the strength of Tencel fabric; in contrast it increases the percent elongation as discussed in the above paragraph

The behaviour of tenacity, load at break and maximum load are opposite in the warp and weft directions (appendix D) because of the difference of number of ends and picks per cm as shown in Figure 7.21. Generally, plain weave fabric is considered to be the strongest fabric, and the strength of plain fabric is higher in warp direction than in the weft direction [144]. As the thread density increases, in the warp direction the strength is decreased because there is less space in between the yarns to move or crimp interchanges to be developed. In the weft direction the reverse trend is observed because there are fewer ends and picks as shown in Figure 7.21 (b). The lower the number of yarns, easier it is for them to break at minimum load. Similarly with fewer picks, as compared to ends as shown Figure 7.21 (c), more load is required to beak the yarns, delay in breakdown results in increase in the fabric strength. Tightly woven fabrics are found to be the strongest [173]. The fabric extension in the warp directions is thus mainly due to bending and compression rather than extension of the yarns [225].



(a) (b) (c)

Figure 7.21 Possibilities of ends and picks per cm in the fabric

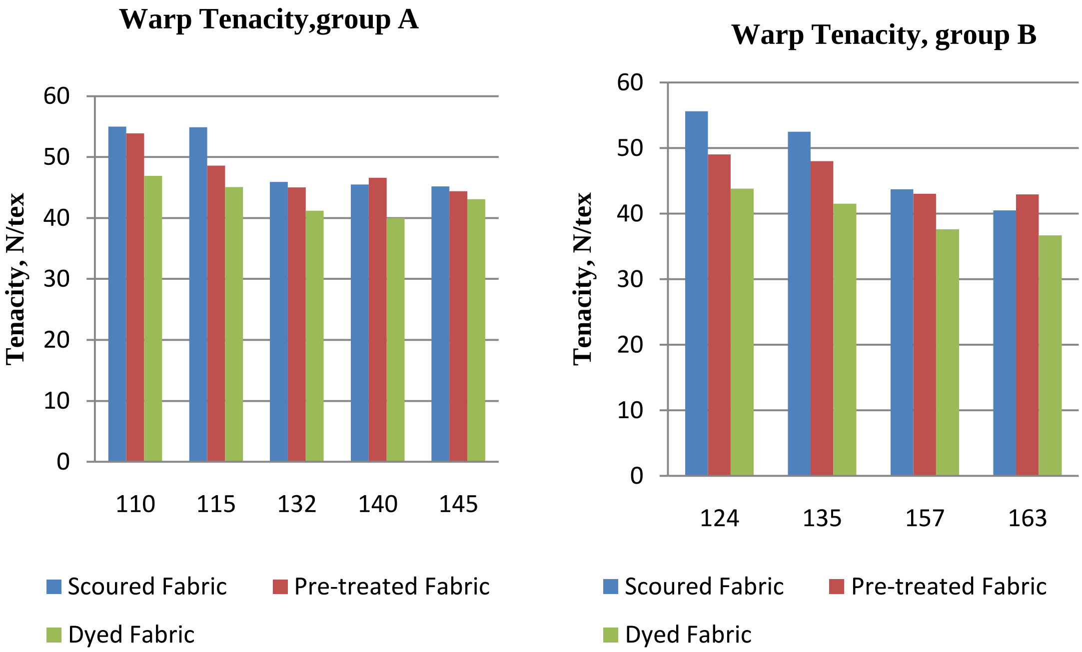


Figure 7.22 Tencel fabrics tenacity in warp direction (group A &B)

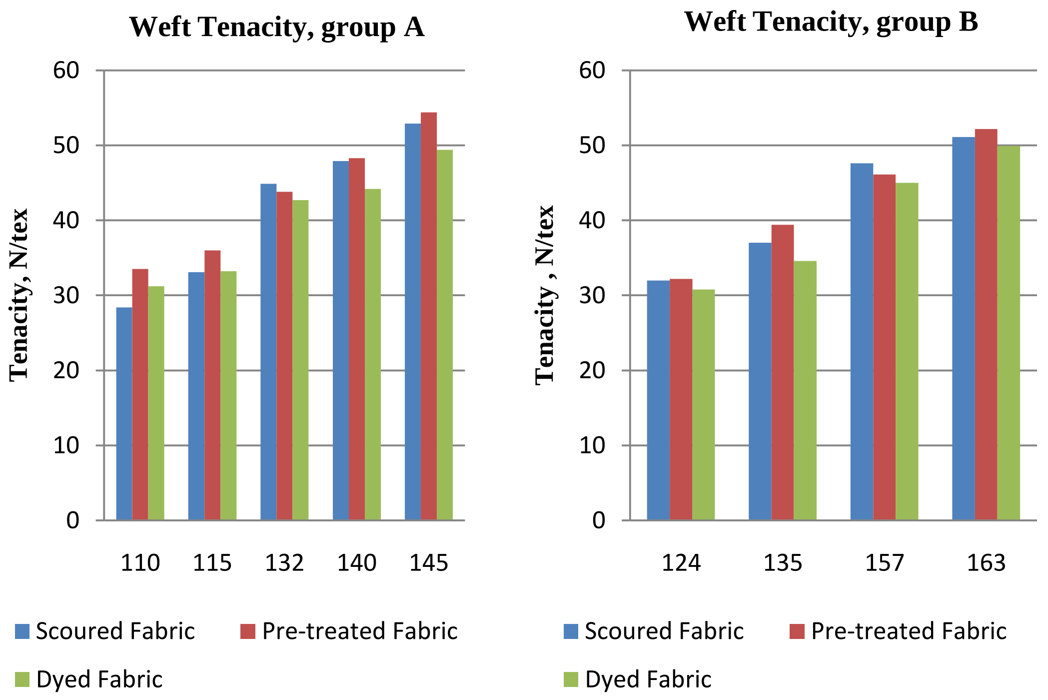


Figure 7.23 Tencel fabrics tenacity in weft direction (group A &B)

Table 7.14 The percent difference of tenacity (N/tex)

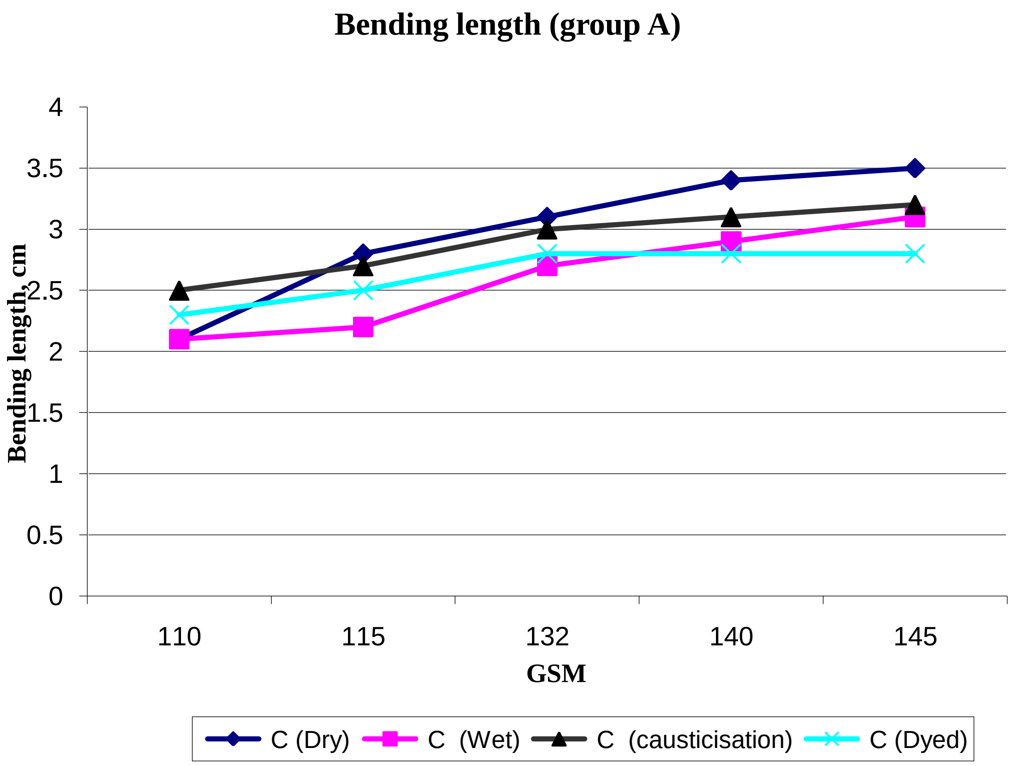
	GSM	Warp		Weft	
		Pre-treated,%	Dyed,%	Pre-treated,%	Dyed,%
Group A	110	2	14.7	-18	-9.9
	115	11.5	17.9	-8.8	-0.3
	132	2	10.2	2.4	4.9
	140	-2.4	12.1	-0.8	7.7
	145	1.8	4.6	-2.8	6.6
Group B	124	11.9	21.2	-0.6	3.8
	135	8.6	21	-6.5	6.5
	157	1.6	14	3.2	5.5
	163	-5.9	9.4	-2.2	2.3

Table 7.15 The percent difference of elongation (%)

	GSM	Warp		Weft	
		Pre-treated,%	Dyed,%	Pre-treated,%	Dyed,%
Group A	110	-89	-79.1	-88.4	-19.7
	115	-88.8	-66.5	-10.2	-4.5
	132	-68	-50	-21.2	-17.5
	140	-55.7	-34.4	-23.1	-24.6
	145	-49.5	-44.2	-29.5	-22.7
Group B	124	-89.6	-70.9	-5.2	-7.4
	135	-74.9	-55.4	-8.4	-9.2
	157	-47	-34.7	-20.7	-21.1
	163	-45.5	-40.7	-23.3	-26.9

7.3.7 Fabric Stiffness

The stiffness of fabric was measured using cantilever method at four different stages of fabric dry scoured, 50 % wetted scoured fabric, after caustic treatment and after dyeing (Section 5.2.8). Figure 7.24 and Figure 7.25, is the average of three samples of each fabric taken from the warp and weft directions, where within the fabric samples, stiffness was measured from each back side and face side. It was observed that as the thread density and GSM of the fabrics increases stiffness of the fabrics also increases. This is because at tight weave density the gap between the yarns is less and it is difficult to the yarns to move hence the yarns are less soft. The fabric stiffness is more effected by the finishing treatment as compared to the fabric construction, however, it heavily depends on fabric cover factor and fabric weight [149]. The trends of bending length is in the order of dry scoured > causticisation > 50 % wet scoured < > dyed fabrics. The flexural rigidity was calculated from the bending length that is why both are proportional to each other (Figure 7.24 and Figure 7.25).



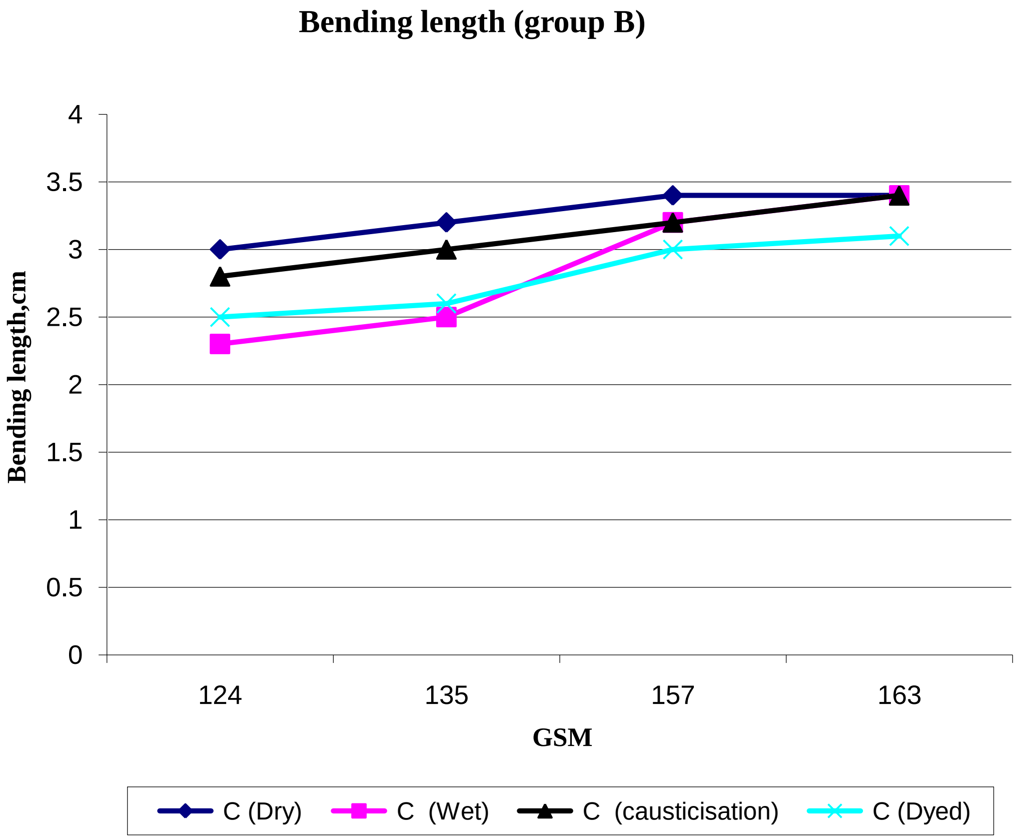


Figure 7.24 Bending length of group A and B

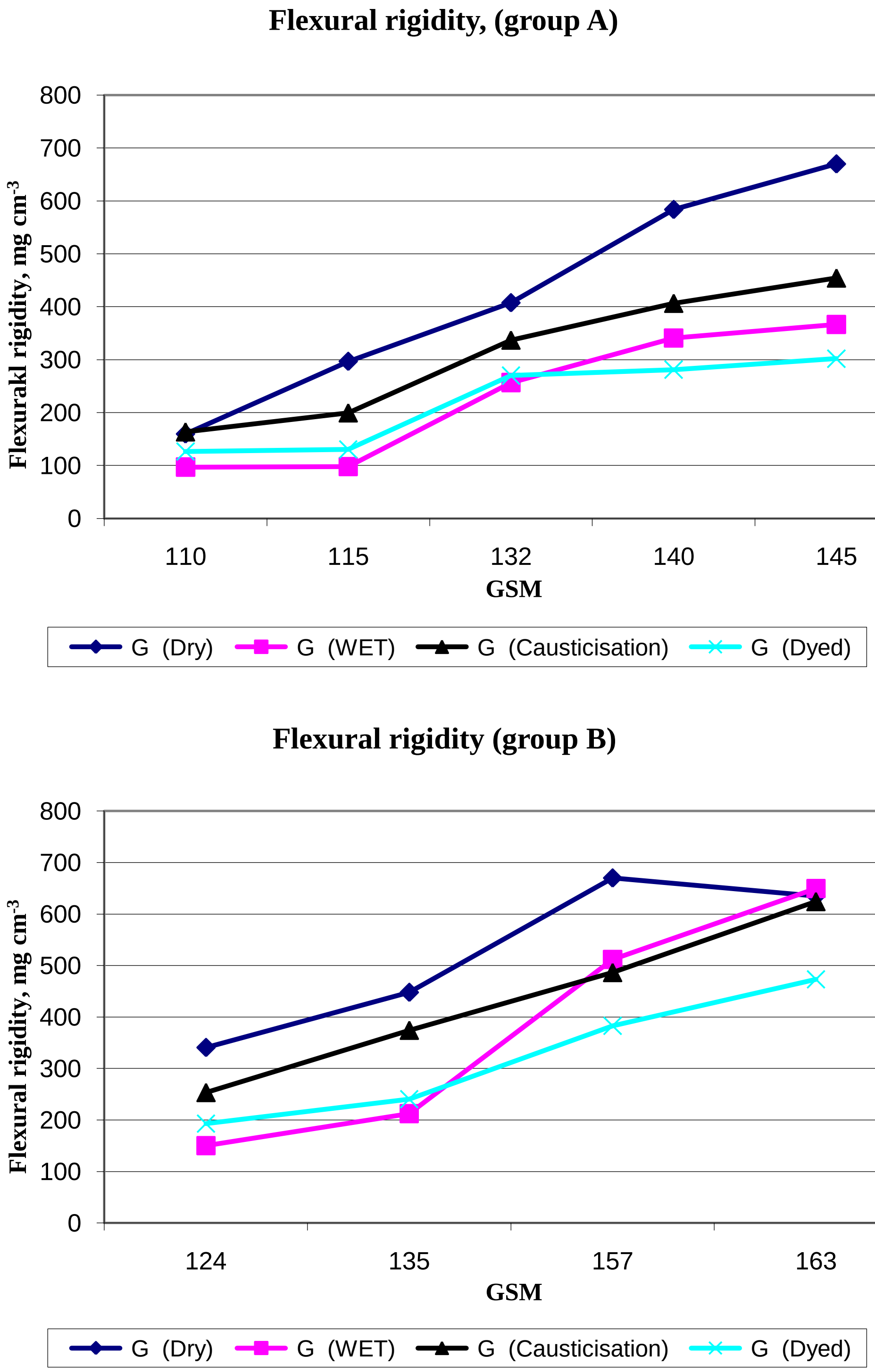


Figure 7.25 Flexural rigidity of group A and B

7.3.8 Abrasion Resistance

Fabric abrasion represents the ability of fabric to be used for specific purpose. The percentage difference of fabric weight loss in gm, before and after abrasion resistance is shown in Table 7.16. It has been observed from the Table 7.16 that tightly woven fabrics have more resistance to abrasion as compared to the loosely woven plain Tencel fabrics. Moreover, Tencel woven fabric can be used for apparel because it has high resistance to abrasion.

Table 7.16 Percentage difference before and after abrasion

GSM/Pressure	9 Kpascal	12 Kpascal
	Group A	
110	86.8	79.7
115	89.9	85.6
132	88.4	90.8
140	94.4	92.8
145	90.8	91
	Group B	
124	88.3	89.7
135	89.8	88.9
157	92.9	94.1
163	92.5	93

7.3.9 Fibrillation

Tencel fibres have a tendency to fibrillate during wet treatments, discussed in Chapter 2. The fibrillation can be reduced by using cross-linking agents such as bis-functional reactive dyes (two chromophores and at least two reactive groups [15]), enzymes and etc.

The fibrillation of Tencel fibres occurs because it contains large pores, the longitudinal exhibits of pores between the microfibrils is relatively high, which facilitates the diffusion of dye molecules, and promotes fibrillation [16].

The results of fibrillation are shown in Table 7.17. It is observed that after dyeing, using Levafix Red CA dyes (0.5% dye conc) by pad-steam process the fibres have number of fibrils ranging from 156 to 229. Most of the Tencel fibres fibrils length is in the range of 10 - 15 µm except 124 and 163 GSM fabrics.

Table 7.17 Fibrillation assessment

Range	110		115		132		140		145		124		135		157		163	
	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent	Sum	Percent
5	10	4.6	7	4.2	16	7	2	1.2	12	7.6	8	3.6	3	1.6	5	2.7	7	4.5
10	27	12.3	16	9.7	41	17.9	23	13.3	27	17.2	33	14.7	26	14.3	35	18.6	26	16.7
15	43	19.6	23	13.9	42	18.3	31	17.9	31	19.7	29	12.9	34	18.7	45	23.9	24	15.4
20	36	16.4	18	10.9	35	15.3	24	13.9	23	14.6	30	13.3	20	11	23	12.2	33	21.2
25	24	11	16	9.7	30	13.1	25	14.5	25	15.9	27	12	22	12.1	18	9.6	19	12.2
30	19	8.7	16	9.7	19	8.3	14	8.1	15	9.6	28	12.4	11	6	20	10.6	9	5.8
35	10	4.6	8	4.8	14	6.1	15	8.7	8	5.1	10	4.4	12	6.6	10	5.3	14	9
40	12	5.5	15	9.1	7	3.1	9	5.2	5	3.2	12	5.3	10	5.5	8	4.3	4	2.6
45	9	4.1	7	4.2	7	3.1	8	4.6	2	1.3	8	3.6	7	3.8	6	3.2	3	1.9
50	4	1.8	8	4.8	4	1.7	7	4	1	0.6	5	2.2	8	4.4	3	1.6	4	2.6
55	9	4.1	10	6.1	3	1.3	4	2.3	4	2.5	2	0.9	8	4.4	4	2.1	5	3.2
60	8	3.7	6	3.6	2	0.9	1	0.6	1	0.6	5	2.2	1	0.5	4	2.1	3	1.9
65	1	0.5	5	3	1	0.4	2	1.2	1	0.6	5	2.2	7	3.8	2	1.1	2	1.3
70	1	0.5	0	0	2	0.9	1	0.6	2	1.3	4	1.8	5	2.7	0	0	0	0
75	1	0.5	2	1.2	1	0.4	1	0.6	0	0	6	2.7	0	0	0	0	1	0.6
80	1	0.5	2	1.2	2	0.9	2	1.2	0	0	4	1.8	0	0	0	0	1	0.6
85	2	0.9	1	0.6	0	0	1	0.6	0	0	0	0	2	1.1	1	0.5	0	0
90	0	0	1	0.6	0	0	0	0	0	0	1	0.4	0	0	2	1.1	0	0
95	2	0.9	2	1.2	0	0	1	0.6	0	0	2	0.9	1	0.5	0	0	1	0.6
100	0	0	2	1.2	1	0.4	0	0	0	0	3	1.3	2	1.1	1	0.5	0	0
150	0	0	0	0	2	0.9	2	1.2	0	0	3	1.3	3	1.6	1	0.5	0	0
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sum	219		165		229		173		157		225		182		188		156	
∑ (RD*FD)	5367.5		5073		4932.5		4600		3042.5		6545		5297.5		4262.5		3490	
Mean	24.5		30.74		21.54		26.6		19.4		29.1		29.1		22.7		22.4	

7.3.10 Causticisation

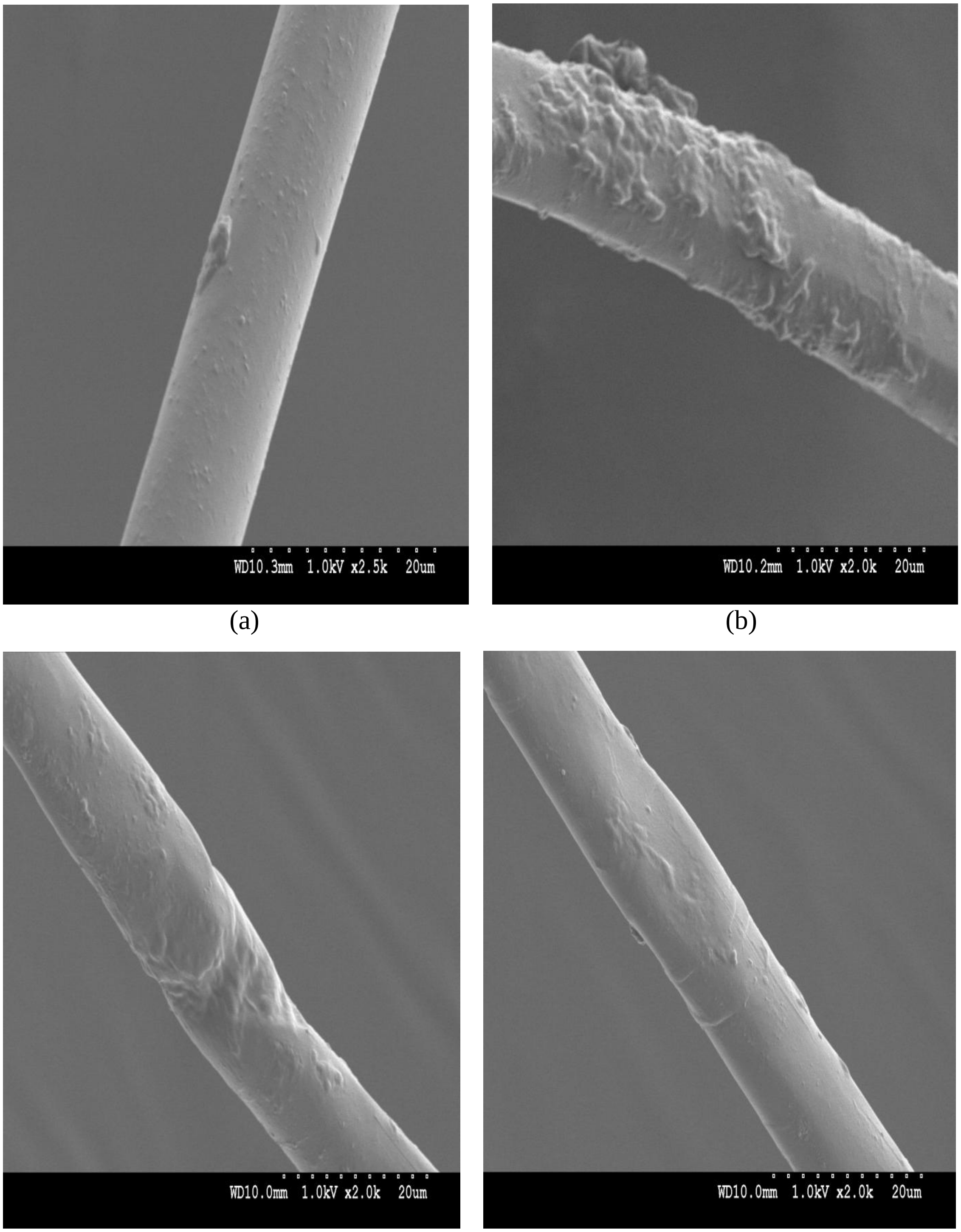
Sodium hydroxide pre-treatment (2 mole dm^{-3} by pad-batch process) had no apparent effect on Tencel fabrics. The cross-sectional images of yarns after causticisation and without causticisation had the same diameter (60 μm), while the shape of filament cross-section was also the same.

The longitudinal views of Tencel fibres before causticisation are shown in Figure 7.26. SEM images show that before causticisation the filament has dirt particles on its surface. As the fabric is already scoured, it might be possible the trace of some chemicals is still on the surface of the filaments as shown in Figure 7.26 (b). The fibre (Figure 7.26 (c)) has an irregular surface in the centre of the image, which might be because of the yarns twist causes the filaments to bend. Another possible reason might be due to the pressure of yarn at the intersection point of the fabric.

After causticisation the Tencel filament has cracks and bends (Figure 7.27 (a)). Surface defects such as cracks enhances the wettability of the filaments and increases dye uptake, especially in pad dyeing process [226]. However, this feature has been observed extensively in the Tencel fabrics. Another suggestion is that it might be because of primary fibrillation [11]. Figure 7.27 (b) shows the presence of dirt particles while the splitting of filament or fibrillation is shown in Figure 7.27 (c). Figure 7.27 (d) shows a fibril shaped like a leaf, but it is actually a small layer of filament which has come out of the surface of the fibre due to the causticisation process. The skin of Tencel fibre has small crystallites compared to the core of the fibre. The core has a less oriented structure which enables it to react easily with chemicals. Swelling using sodium hydroxide opens the accessible sites for the dye molecules.

The images taken after dyeing are almost similar to those taken before dyeing. Figure 7.27 (d) shows a layer is separated from the surface of the fibre give the image of Figure 7.28 (d). In this figure diameter of a filament decreases from the top to the bottom, and imparted effect on the fabric strength. The Figure 7.28 (c) has dirt particle, (b) shows the fibrillation and cracks on the fibre surface.

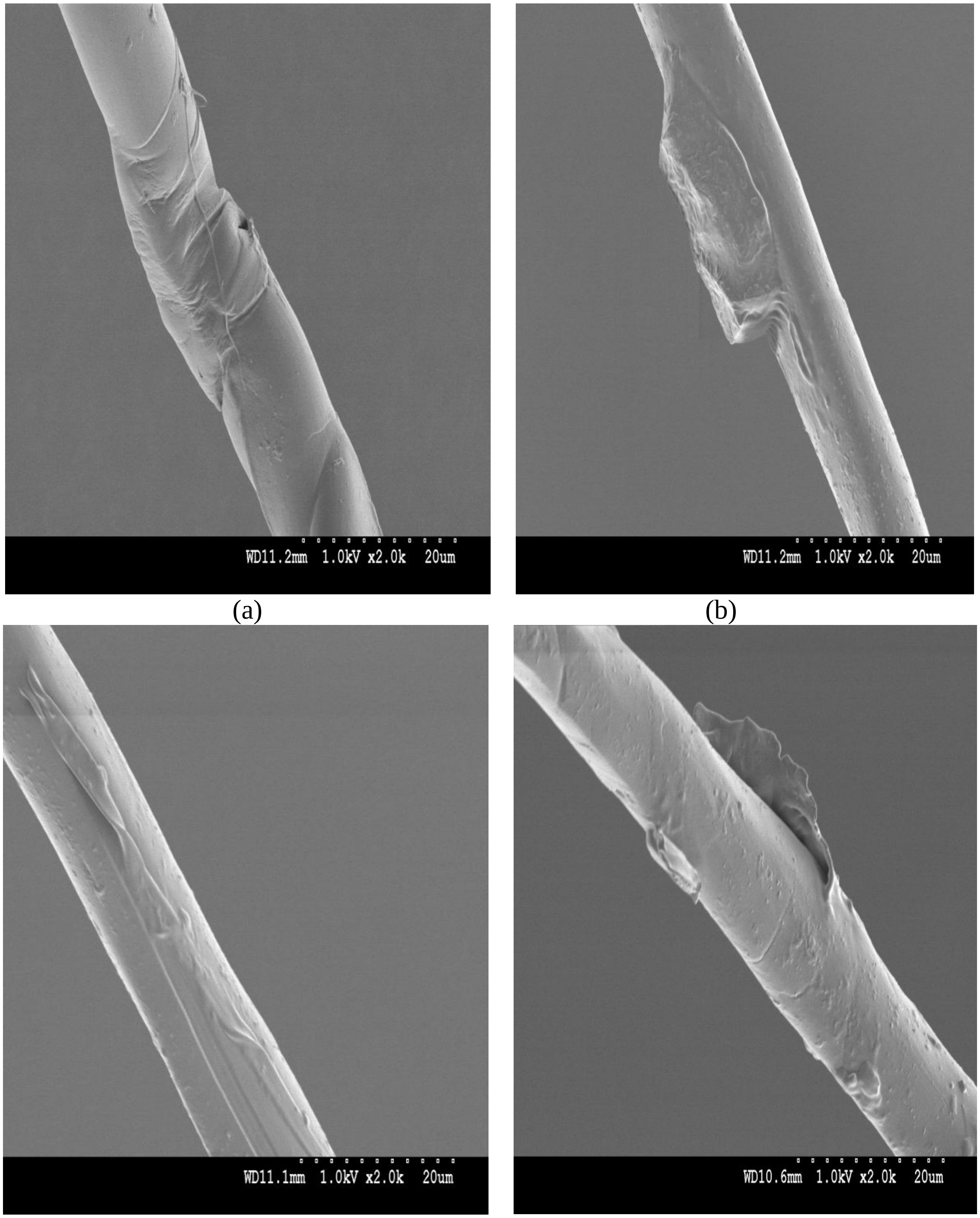
The lower concentration of sodium hydroxide has no effect on the weight loss of the fabric while it causes the fabric to shrink, especially loosely woven fabrics, as shown in Figure 7.29 and actually increased the weight of the fabric. Hence, number of ends and picks has an influence on the shrinkage and increases the weight of the fabric. Further, if the density of the fabrics are not as much decreased it means there is no loss of carboxyl content of the Tencel fibres. However, the number of carboxyl groups decreases with increases the concentration of NaOH (2.5 mol or higher) [143].



(a) (b)

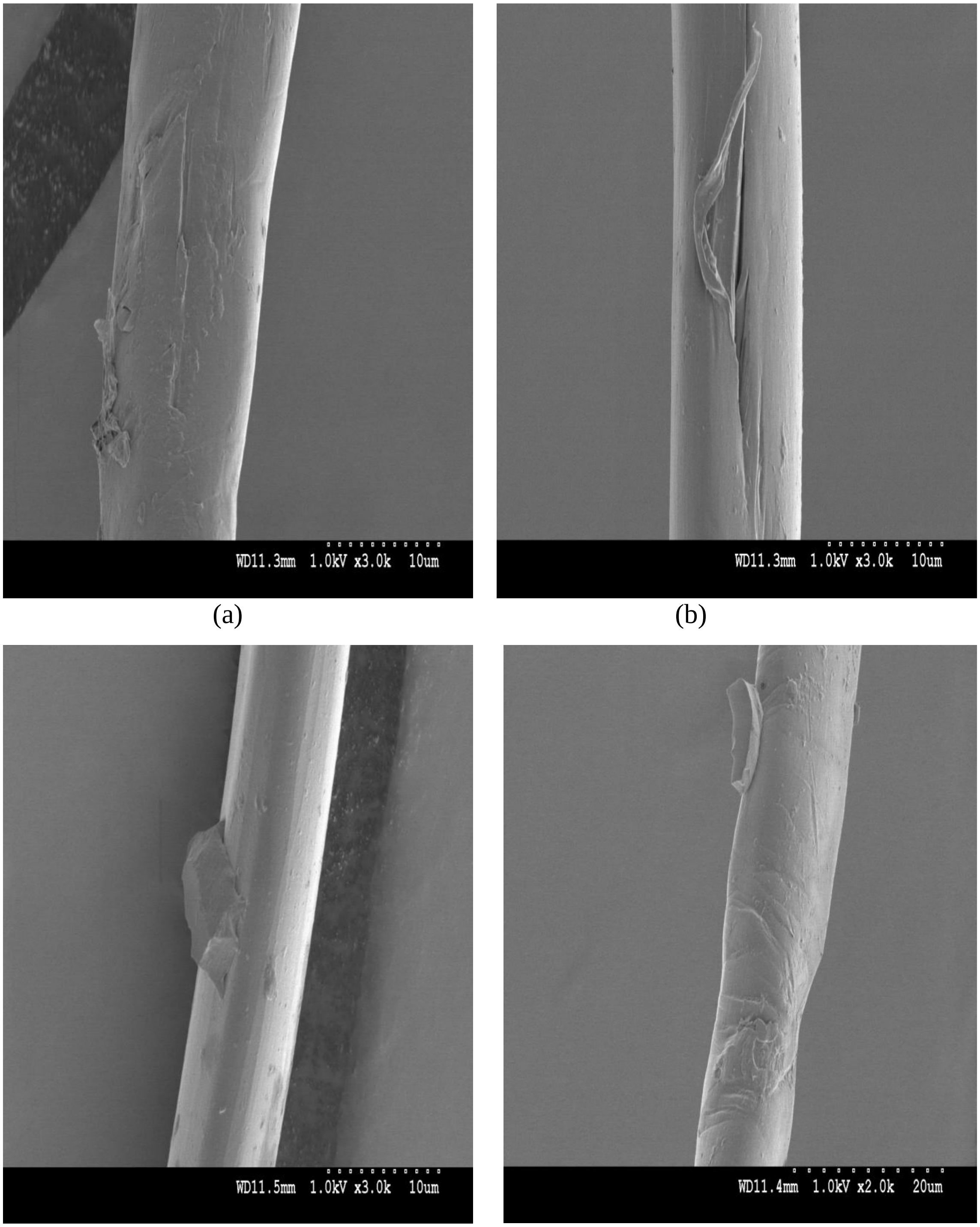
(c) (d)

Figure 7.26 Longitudinal view of Tencel fibre without causticisation (110 GSM)



(a) (b) (c) (d)

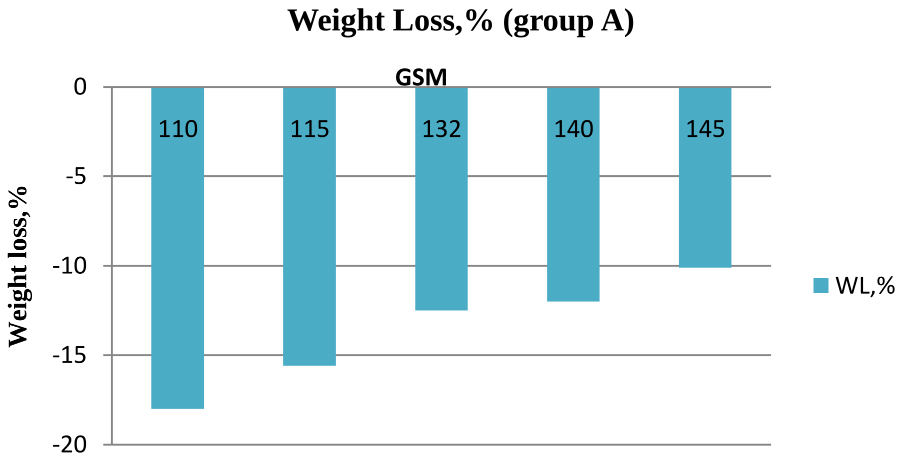
Figure 7.27 Longitudinal view of Tencel fibre after causticisation (110 GSM)



(a) (b)

(c) (d)

Figure 7.28 Longitudinal view of Tencel fibre after dyeing and causticisation (110 GSM, Pad-Steam, Levafix Red CA 0.5%)



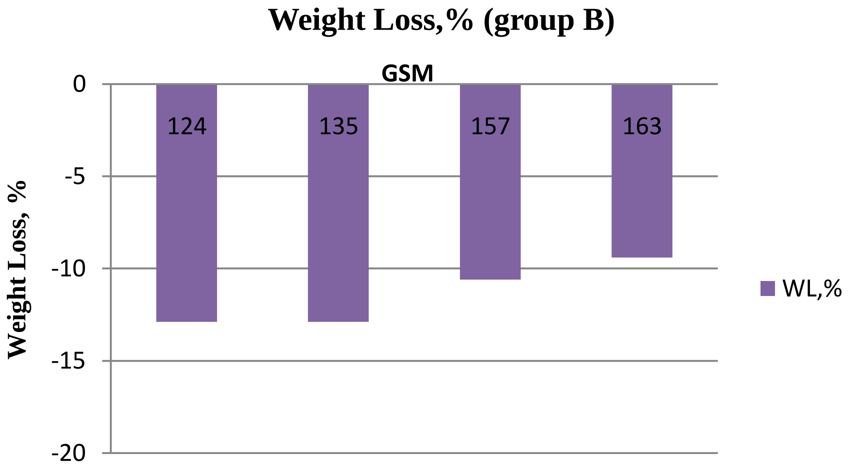


Figure 7.29 Weight loss after caustic treatment

7.3.11 Mathematical Modelling

The dyeing properties results such as visual depth and uniformity of fibre colouration have already been discussed in preceding sections of Chapter 7. These dyeing assessments are very useful to predict the dyeing behaviour such as dye uniformity, dye penetration and depth of colour. The visual depth or Integ value depicts the actual depth of colour in the fabric. The UFC standard deviation and mean value assess the dye penetration in the fibre filaments of the yarns of the woven fabric. It also assesses the variation in the dye penetration. The mean value based on the rating scale (1 to 5) gives the average colour intensity of the dyed fabric.

It has been argued that variation in fabric properties induces the variation in dyeing properties. In order to predict the influence of fabric density on the dyeing behaviour using the same results (Section 7.3.1 and 7.3.3.2) a mathematical model was designed as discussed in Section 5.2.15. Tencel plain weave fabrics were dyed using selected reactive dyes by continuous dyeing methods (see Section 5.2.3.2.2).

The model is based on numerical equations with derived constants. Using the model dyers are able to predict the dyeing properties of the Tencel plain weave fabrics that have the same yarn linear densities as mentioned in this research but can vary in thread densities (ends and picks per cm) or fabric density.

Dyers can predict:

- Integ and UFC values for fabrics of varying GSM of linear density 14.4*14.5 tex.
- Integ and UFC values for fabrics of varying GSM of linear density 14.4 * 20.6 tex.

The model was designed for Tencel plain weave fabrics comprised of the same warp and weft linear density (average 14.4 * 14.5 tex), group A, varying in fabric densities (110, 115, 132, 140 and145 GSM). Second group (group B) comprised of different warp and weft linear density (average 14.4 * 20.6 tex) and fabric densities, (124, 135, 157 and 163 GSM). Third group comprised of three samples two from group A (115, 132 GSM) and one from group B (163 GSM) (loose to tight woven fabric). The actual visual depth and UFC values were taken relative percentage of dyeing behaviour of loosely woven fabric or lowest GSM in the relevant group such as in group A 110 GSM, group B 124 GSM and group C 115 GSM.

Dyeing behaviour trends versus fabric density of group C are shown in Figure 7.30 to Figure 7.35. Table 7.18 to Table 7.27 shows the equations of visual depth and UFC value of Tencel plain weave fabrics of varying fabric densities. All are based on two degree or three degree polynomial quadratic equations of varying constants. The model has been applied to all continuous dyeing methods using Levafix Red and Blue CA dyes.

The visual depth trends of group A and B fabrics versus fabric density are shown in Figure 7.36 and Figure 7.40, whereas Table 7.28 to Table 7.33 shows the equation of Tencel plain weave fabrics dyed by pad-steam process (after causticisation 40°C liquor temperature with a 1 min dwell time and liquor at room temperature without dwell time and 40 °C liquor temperature with a 5 min dwell time without causticisation), pad-batch (40°C liquor temperature with a 5 min dwell time without causticisation) and pad-dry-thermosol process (after causticisation 40°C liquor temperature with a 1 min dwell time and without causticisation 40 °C liquor temperature with a 5 min dwell time). In all these dyeing methods, equations are based on three degree polynomial quadratic and in some cases four degree polynomial quadratic equations. The reason of difference in equations within the same group and method is because of the difference in dye chemistry and fabric density.

The calculated and predicted trends of the dyeing behaviour graphs are similar to the trends obtained in actual results. Equations in this model were derived for individual reactive dyes in each continuous dyeing method so that dyers can predict an appropriate behaviour of selected reactive dyes. The average of dye results could predict the behaviour of a mixture of dyes hence; predict the correct value of visual depth and UFC with respect to the fabric density. The model can be used to predict the dyeing behaviour of trichromatic dyes.

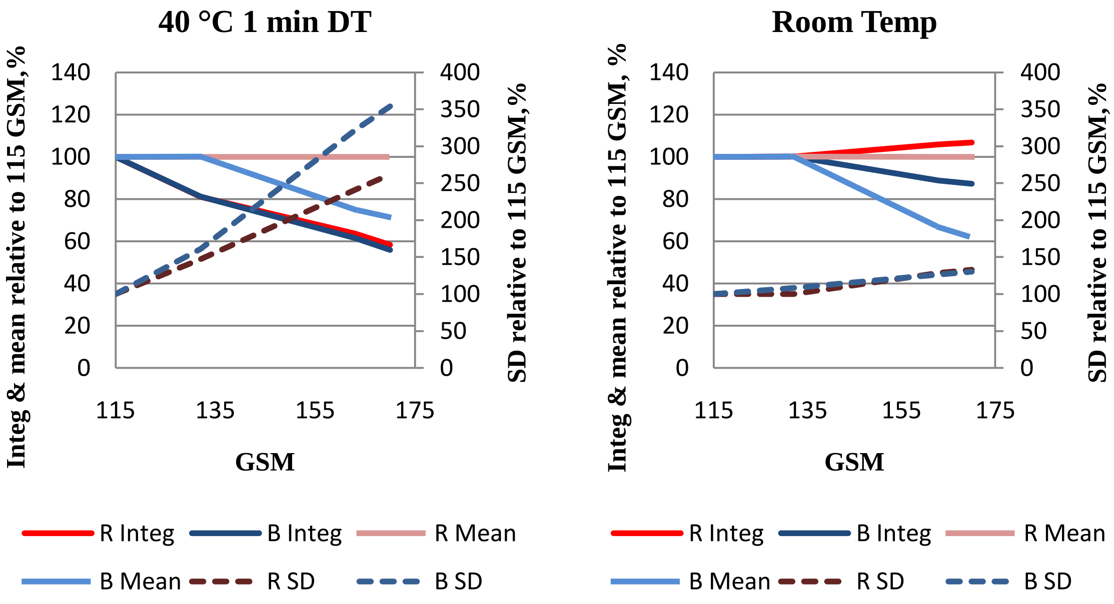


Figure 7.30 Dyeing behaviour trends of pad-steam process after causticisation

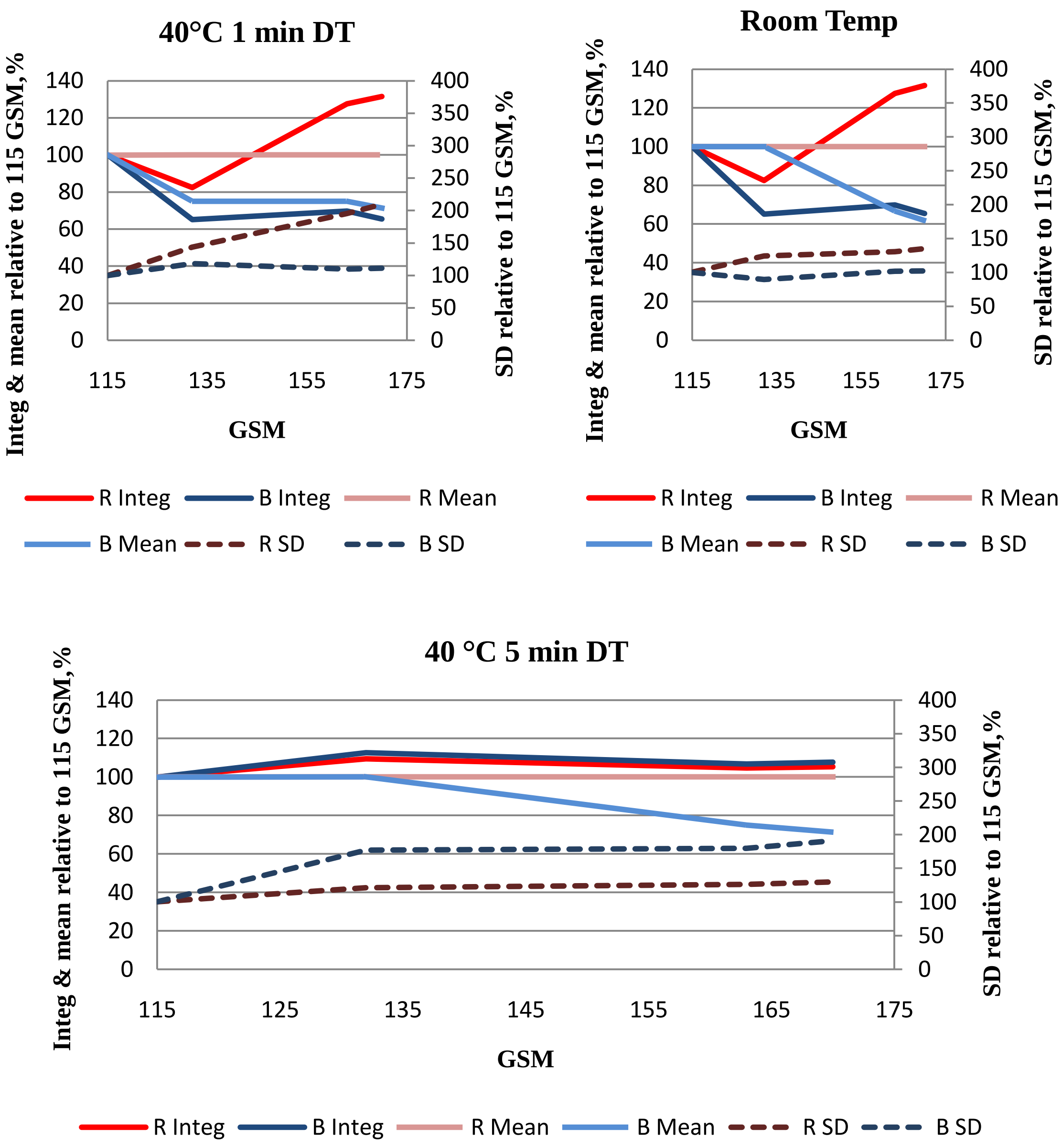


Figure 7.31 Dyeing behaviour trends of pad-steam process without causticisation

-R Integ = Red CA Integ value.
-B Integ = Blue CA Integ value.
-R Mean = Red CA mean value.
-B Mean = Blue CA mean value.
-R SD = Red CA standard deviation.
-B SD = Blue CA standard deviation.

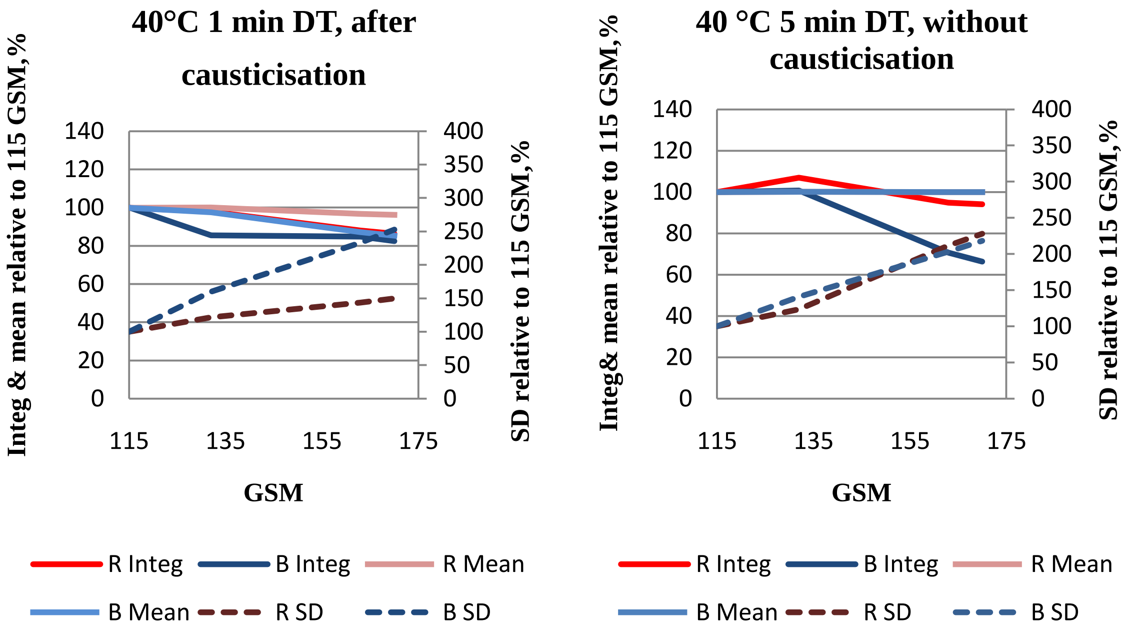


Figure 7.32 Dyeing behaviour trends of pad-dry-thermosol process

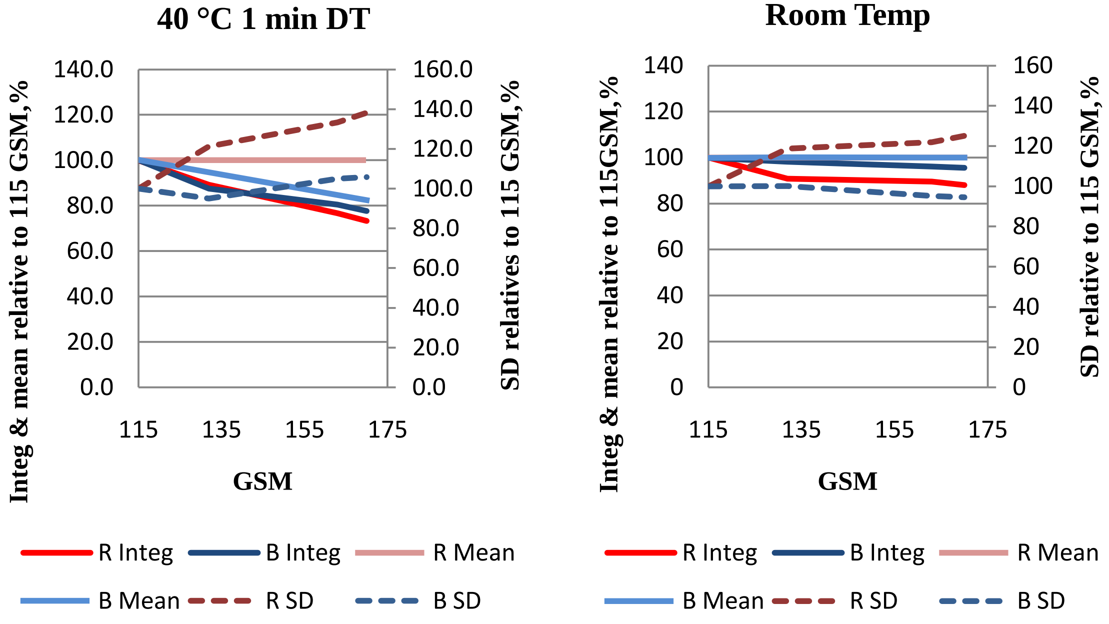


Figure 7.33 Dyeing behaviour trends of pad-dry-steam process after causticisation

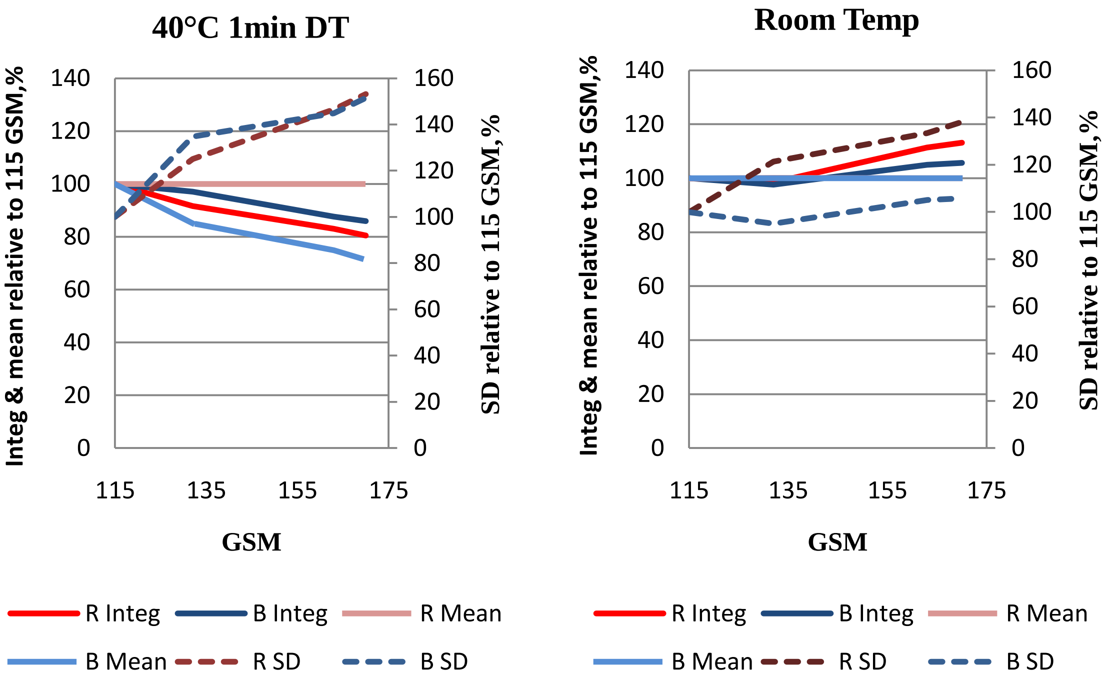


Figure 7.34 Dyeing behaviour trends of pad-dry-steam process without causticisation

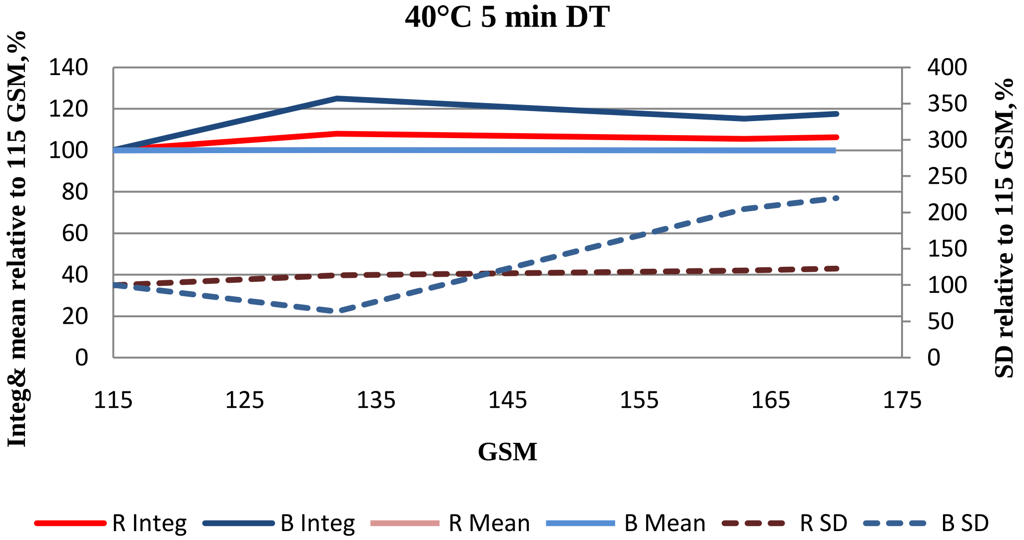


Figure 7.35 Dyeing behaviour trends of pad-batch process without causticisation

Table 7.18 Table of equations for predicting visual depth of pad-steam

Dyeing Method		Dyes	Equations	Constant
After cauticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+ K_3GSM^3$	K_0 = 405.4
				K_1 = -3.99
				K_2 = 0.0116
				K_3 = 6.13E-09
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2+ K_3GSM^3$	K_0 = 373.3
				K_1 = -3.5
				K_2 = 0.0097
				K_3 = 4.94E-08
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 154.01
				K_1 = -0.89
				K_2 = 0.0036
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -18.51
				K_1 = 1.921
				K_2 = -0.0078
Without caustic treatment	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 1005.39
				K_1 = -13.84
				K_2 = 0.052
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 1033.69
				K_1 = -13.4
				K_2 = 0.0456
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 1004.77
				K_1 = -13.83
				K_2 = 0.052
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 1033.69
				K_1 = -13.40
				K_2 = 0.046
	40°C 5min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -187.65
				K_1 = 4.20
				K_2 = -0.015
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -281.99
				K_1 = 5.56
				K_2 = -0.019

Table 7.19 Table of equations for predicting visual depth of pad-dry-thermosol process

Dyeing Method		**Dyes**	**Equations**	**Constant**
After causticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = 29.37
				K_1 = 1.41
				K_2 = -0.00807
				K_3 = 0.00001
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 459.68
				K_1 = -5.12
				K_2 = 0.017
Without causticisation	40°C 5 min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = -445.47
				K_1 = 10.040
				K_2 = -0.058
				K_3 = 0.0001
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = -470.25
				K_1 = 10.76
				K_2 = -0.062
				K_3 = 0.0001

Table 7.20 Table of equations for predicting visual depth of pad-dry-steam process

Dyeing Method		**Dyes**	**Equations**	**Constant**
After caucticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 247.47
				K_1 = -1.85
				K_2 = 0.0049
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 341.51
				K_1 = -3.29
				K_2 = 0.011
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 320.37
				K_1 = -3.11
				K_2 = 0.011
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 122.74
				K_1 = -0.283
				K_2 = 0.00073
Without caucticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 223.13
				K_1 = -1.58
				K_2 = 0.0044
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 77.83
				K_1 = 0.51
				K_2 = -0.0027
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 271.39
				K_1 = -2.72
				K_2 = 0.011
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 234.75
				K_1 = -2.074
				K_2 = 0.0078

Table 7.21 Table of equations for predicting standard deviation of UFC by pad-steam process

Dyeing Method		Dyes	Equations	Constant
After cauticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -139.11
				K_1 = 1.47
				K_2 = 0.0053
		Levafix Blue CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3$	K_0 = -0.282
				K_1 = 0.00087
				K_2 = 7.96E-05
				K_3 = -0.069
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 387.99
				K_1 = -4.69
				K_2 = 0.019
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 73.87
				K_1 = -0.0043
				K_2 = 0.0021
Without cauticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -470.68
				K_1 = 7.058
				K_2 = -0.0182
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = 9.724
				K_1 = -2.30
				K_2 = 0.048
				K_3 = -0.00019
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = -217.77
				K_1 = 2.59
				K_2 = 0.0119
				K_3 = -9E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 482.65
				K_1 = -5.71
				K_2 = 0.021
	40°C 5min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = 76.23
				K_1 = -3.50
				K_2 = 0.053
				K_3 = -0.00019
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -1827.22
				K_1 = 27.42
				K_2 = -0.093

Table 7.22 Table of equations for predicting mean value of UFC by pad-steam process

Dyeing Method		Dyes	Equations	Constant
After cauticisation	40°C 1min DT	Levafix Red CA	K_0+K_1GSM	K_0 = 99.99
				K_1 = 5.02E-08
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -157.97
				K_1 = 4.19
				K_2 = -0.0167
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 93.47
				K_1 = 0.0948
				K_2 = -0.00034
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -242.143
				K_1 = 5.563
				K_2 = -0.02251
Without cauticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 94.075
				K_1 = 0.086
				K_2 = -0.00031
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 733.58
				K_1 = -9.029
				K_2 = 0.031
	Room temp no dwell time	Levafix Red CA	K_0+K_1GSM	K_0 = 99.998
				K_1 = 1.35E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -241.17
				K_1 = 5.550
				K_2 = -0.022
	40°C 5min DT	Levafix Red CA	K_0+K_1GSM	K_0 = 99.999
				K_1 = 8.48E-07
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -158.25
				K_1 = 4.20
				K_2 = -0.017

Table 7.23 Table of equations for predicting standard deviation of UFC by pad-dry-thermosol

Dyeing Method		Dyes	Equations	Constant
After causticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -232.68
				K_1 = 4.30
				K_2 = -0.012
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -673.99
				K_1 = 9.52
				K_2 = -0.024
Without causticisation	40°C 5 min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 401.50
				K_1 = -6.11
				K_2 = 0.031
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -296.37
				K_1 = 4.36
				K_2 = -0.0080

Table 7.24 Table of equations for predicting mean value of UFC by pad-dry-thermosol process

Dyeing Method		Dyes	Equations	Constant
After causticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 60.85
				K_1 = 0.63
				K_2 = -0.0025
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 54.76
				K_1 = 0.86
				K_2 = -0.0040
Without causticisation	40°C 5 min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 60.08
				K_1 = 0.64
				K_2 = -0.0025
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -77.72
				K_1 = 2.75
				K_2 = -0.01048

Table 7.25 Table of equations for predicting standard deviation of UFC by pad-dry-steam process

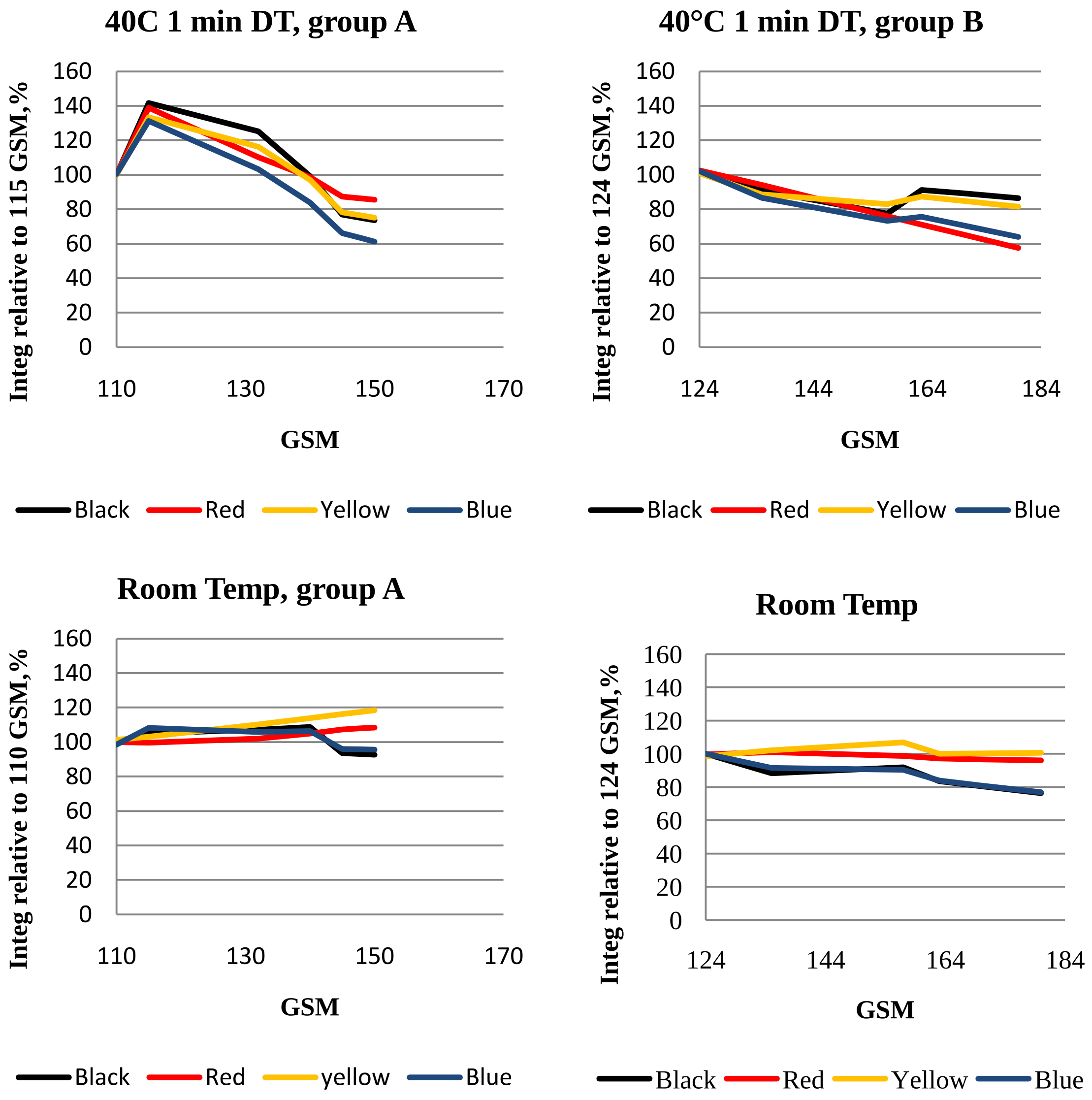
Dyeing Method		Dyes	Equations	Constant
After caucticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -1133.36
				K_1 = 16.66
				K_2 = -0.0516
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -190.55
				K_1 = 2.67
				K_2 = -0.00125
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -344.68
				K_1 = 6.27
				K_2 = -0.021
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 47.49
				K_1 = 0.846
				K_2 = -0.00339
Without caucticisation	40°C 1min DT	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -317.42
				K_1 = 5.507
				K_2 = -0.0163
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -676.01
				K_1 = 10.85
				K_2 = -0.036
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -316.85
				K_1 = 5.69
				K_2 = -0.018
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 324.68
				K_1 = -3.41
				K_2 = 0.0126

Table 7.26 Table of equations for predicting mean value of UFC by pad-dry-steam

Dyeing Method		Dyes	Equations	Constant
After caucticisation	40°C 1min DT	Levafix Red CA	K_0+K_1GSM	K_0 = 99.99
				K_1 = 4.38E-07
		Levafix Blue CA	K_0+K_1GSM	K_0 = 137.19
				K_1 = -0.322
	Room temp no dwell time	Levafix Red CA	K_0+K_1GSM	K_0 = 99.997
				K_1 = 1.41E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 93.48
				K_1 = 0.0948
				K_2 = -0.00034
Without caucticisation	40°C 1min DT	Levafix Red CA	K_0+K_1GSM	K_0 = 99.999
				K_1 = 1.4E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 375.04
				K_1 = -3.711
				K_2 = 0.0115
	Room temp no dwell time	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 94.31
				K_1 = 0.083
				K_2 = -0.00029
		Levafix Blue CA	K_0+K_1GSM	K_0 = 99.999
				K_1 = 1.24E-05

Table 7.27 Table of equations for predicting visual depth by pad-batch

Dyeing Method		Dyes	Equations	Constant
Without causticisation 40°C 5 min DT	Integ	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -124.15
				K_1 = 3.24
				K_2 = -0.011
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2 + K_3GSM^3$	K_0 = 9.92
				K_1 = -3.76
				K_2 = 0.069
				K_3 = -0.00026
	Standard deviation	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -173.85
				K_1 = 3.77
				K_2 = -0.012
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 2474.98
				K_1 = -36.75
				K_2 = 0.140
	Mean	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 94.41
				K_1 = 0.081
				K_2 = -0.00029
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 93.68
				K_1 = 0.092
				K_2 = -0.00033



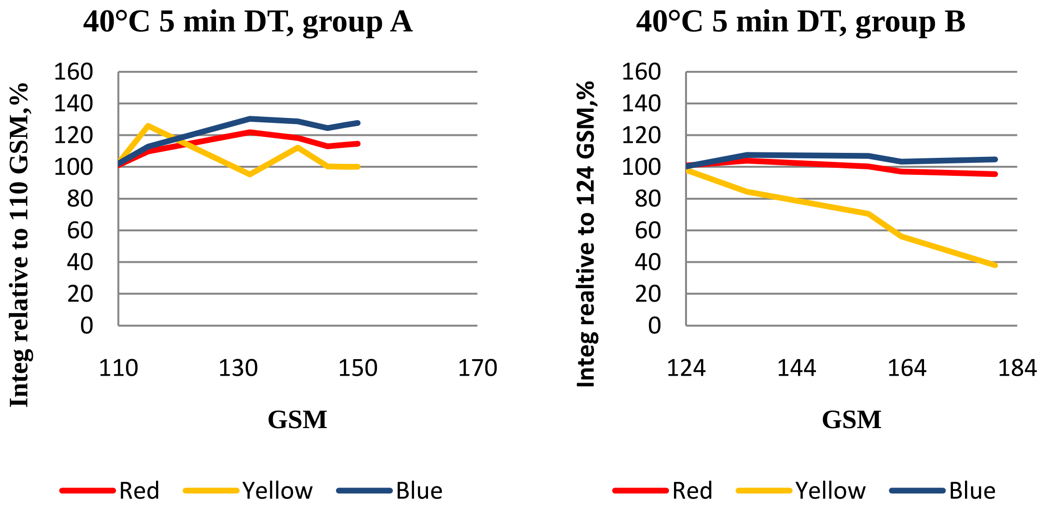
40C 1 min DT, group A

40°C 1 min DT, group B

Room Temp, group A

Room Temp

Figure 7.36 Visual depth of pad-steam process after caustic treatment (group A & B)



40°C 5 min DT, group A

40°C 5 min DT, group B

Figure 7.37 Visual depth of pad-steam process without caustic treatment (group A & B)

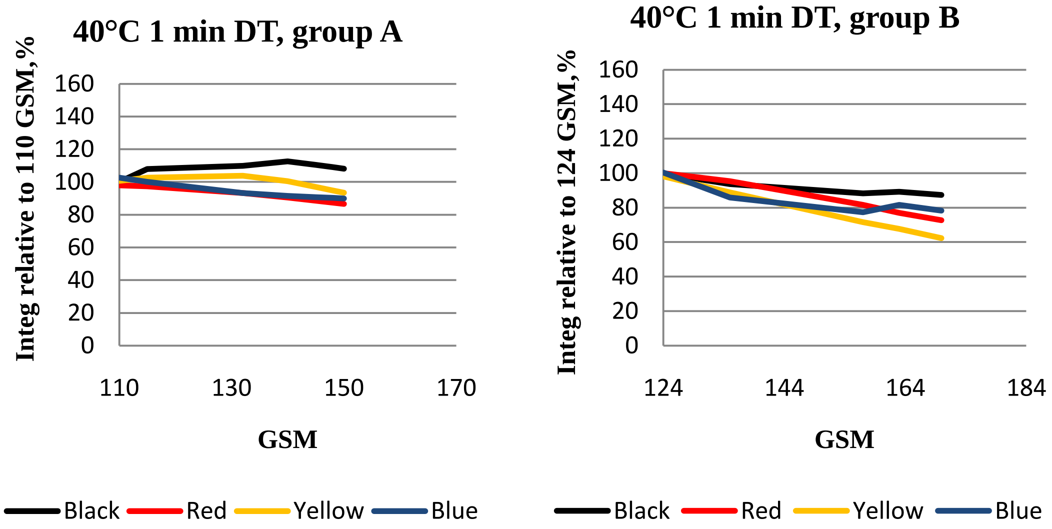


Figure 7.38 Visual depth of pad-dry-thermosol after caustic treatment (group A&B)

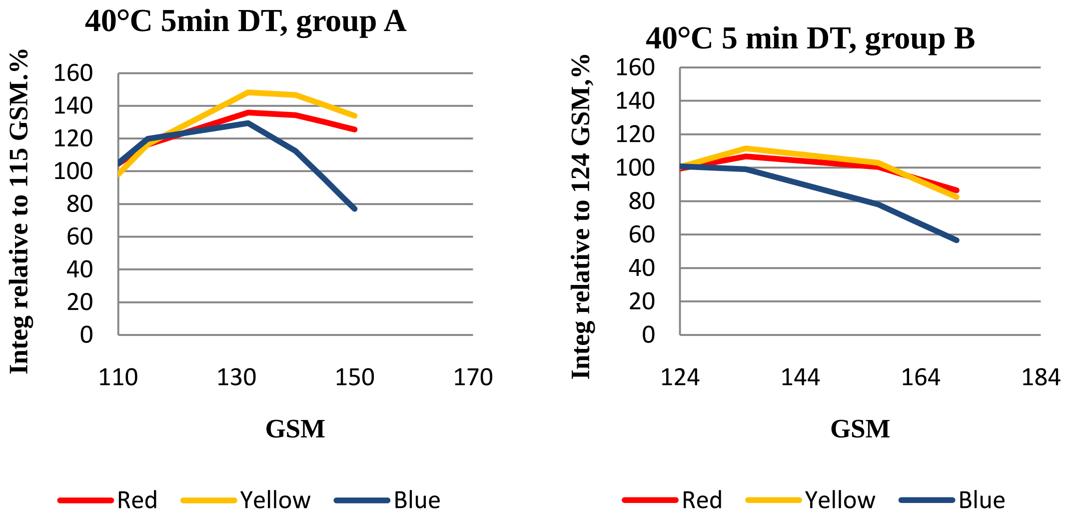


Figure 7.39 Visual depth of pad-dry-thermosol without causticisation (group A&B)

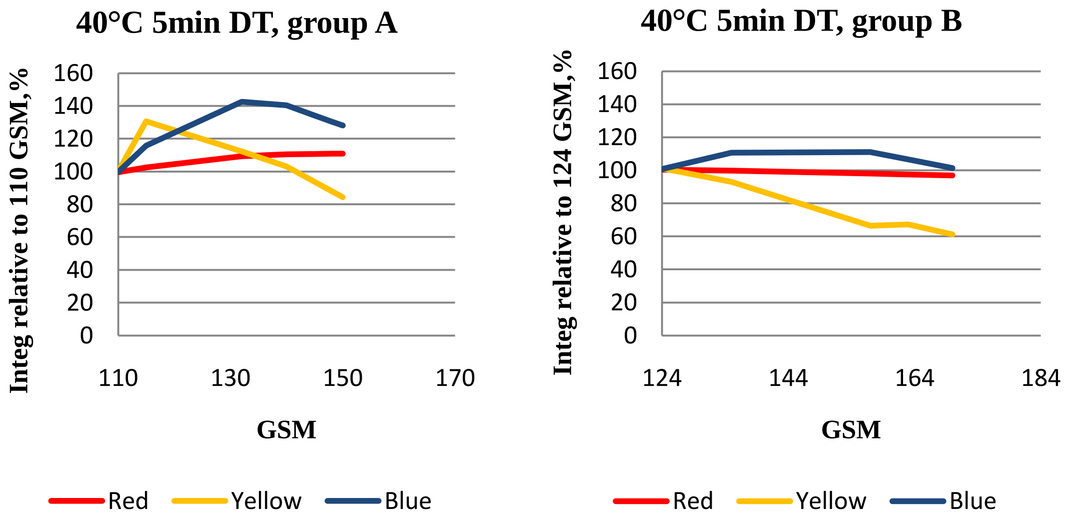


Figure 7.40 Visual depth of pad-batch without caustic treatment (group A&B)

Table 7.28 Table of equations for predicting visual depth of pad-steam

Dyeing Method		Dyes	Equations	Constant
After cauticisation, 40°C 1min dwell time	Group A	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 =-1140.48
				K_1 =21.71
				K_2 = -0.092
				K_3 = -2.7E-05
		Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (115 GSM only)	K_0 = -861.82
				K_1 = 15.66
				K_2 = -0.063
				K_3 = 2.04E-05
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (115 GSM only)	K_0 = -1498.5
				K_1 = 26.03
				K_2 = -0.1045
				K_3 = 1.37E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (115 GSM only)	K_0 = -1152.97
				K_1 = 20.78
				K_2 = -0.085
				K_3 = 1.5E-05
	Group B	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (157 GSM only)	K_0= 664.95
				K_1= -7.781
				K_2 = 0.0261
				K_3 = -5.3E-06
		Levafix Red CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3$	K_0= 2.817644
				K_1= -0.0242
				K_2 = 5.36E-05
				K_3 = 23.37
		Levafix Yellow CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3$	K_0 = 6.529
				K_1 = -0.078
				K_2 = 0.000251
				K_3 = 17.57
		Levafix Blue CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3$	K_0 = 6.958
				K_1 = -0.083
				K_2 = 0.00026
				K_3 = 17.59

Table 7.29 Table of equations for predicting visual depth of pad-steam

Dyeing Method		Dyes	Equations	Constant
After cauticisation, Room temp no dwell time	Group A	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (135 GSM only)	K_0 = -496.97
				K_1 = 9.70
				K_2 = -0.039
				K_3 = 3.1E-06
		Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 224.72
				K_1 = -2.15
				K_2 = 0.0093
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = 75.89
				K_1 = 0.0783
				K_2 = 0.0014

				K_3 = -2.2E-08
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -499.94
				K_1 = 9.66
				K_2 = -0.038
	Group B	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2$ + K_3GSM^3 or $K_0+K_1GSM+K_2GSM^2$ (157 GSM only)	K_0 = 622.18
				K_1 = -7.14792
				K_2 = 0.024
				K_3 =-2.7E-06
		Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -18.04
				K_1 = 1.722
				K_2 = -0.00623
		Levafix Yellow CA	$K_0GSM+K_1GSM^2+K_2$ or $K_0GSM+K_1GSM^2+K_2GSM^3$(163 GSM only)	K_0 = 1.22
				K_1 = -0.00343
				K_2 = -1.8E-06
		Levafix Blue CA	$K_0GSM+K_1GSM^2+K_2GSM^3- K_3$	K_0 = -821.83
				K_1 = 13.48
				K_2 = -0.055
				K_3 = 4.05E-05

Table 7.30 Table of equations for predicting visual depth of pad-steam

Dyeing Method		**Dyes**	**Equations**	**Constant**
Without causticisation 40°C 5 min DT	Group A	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -684.20
				K_1 = 12.30
				K_2 = -0.047
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (115 GSM only)	K_0 = -816.94
				K_1 = 15.59
				K_2 = -0.066
				K_3 = 1.28E-05
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -753.75
				K_1 = 13.20
				K_2 = -0.049
	Group B	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = -93.99
				K_1 = 2.42
				K_2 = -0.0042
				K_3 = -2.1E-05
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$ K_3GSM^3or $K_0+K_1GSM+K_2GSM^2$ (157 GSM only)	K_0 = 357.88
				K_1 = -2.88
				K_2 = 0.0063
				K_3 = 2.31E-06
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -328.95
				K_1 = 6.036
				K_2 = -0.021

Table 7.31 Table of equations for predicting visual depth of pad-dry-thermosol

Dyeing Method		Dyes	Equations	Constant
After cauticisation, 40°C 1min DT	Group A	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ (132 GSM only)	K_0 = -888.87
				K_1 = 15.73
				K_2 = -0.06107
				K_3= -0.00001
		Levafix Red CA	$K_0+K_1GSM+K_2\ GSM^2$	K_0 = 56.51
				K_1 = 0.867
				K_2 = -0.0045
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$	K_0 = 75.86
				K_1 = -1.548
				K_2 = 0.0301
				K_3= -0.00013
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ or $K_0+K_1GSM+K_2GSM^2$(132 GSM only)	K_0 = 148.4
				K_1 = -0.45
				K_2 = 2.72E-06
				K_3= 0.0001
	Group B	Remazol Black B-A	$K_0+K_1GSM+K_2GSM^2+K_3GSM^3$ or $K_0+K_1GSM+K_2GSM^2$(135 GSM only)	K_0 = 73.96
				K_1 = 0.66
				K_2 = -0.00398
				K_3= 2.79E-06
		Levafix Red CA	$K_0+K_1GSM+K_2GSM^2+K_3$	K_0 = 29.04
				K_1 = 1.068
				K_2 = -0.0058
				K_3 = 27.55
		Levafix Yellow CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3$	K_0 = 3.778
				K_1 = -0.0351
				K_2 = 8.87E-05
				K_3 = -0.00011
		Levafix Blue CA	$K_0GSM+K_1GSM^2+K_2GSM^3+K_3GSM^4$	K_0 = 7.451
				K_1 = -0.0883
				K_2 = 0.00028
				K_3 = 1.85E-09

Table 7.32 Table of equations for predicting visual depth of pad-dry-thermosol

Dyeing Method		Dyes	Equations	Constant
Without causticisation, 40°C 5 min DT	Group A	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -825.36
				K_1 = 14.32
				K_2 = -0.053
		Levafix Yellow CA	$K_0GSM+K_1GSM^2+K_2$	K_0 = 22.28
				K_1 = -0.0826
				K_2 = -1352.38
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3 GSM^3$(115 GSM only)	K_0 = -1585.54
				K_1 = 27.04
				K_2 = -0.11
				K_3 = 7.89E-06
	Group B	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -454.39
				K_1 = 7.97
				K_2 = -0.028
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -734.75
				K_1 = 11.997
				K_2 = -0.042
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -293.67
				K_1 = 6.24
				K_2 = -0.025

Table 7.33 Table of equations for predicting dyeing behaviour by pad-batch process

Dyeing Method		Dyes	Equations	Constant
Without causticisation, 40°C 5 min DT	Integ (group A)	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -87.79
				K_1 = 2.75
				K_2 = -0.0095
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -1181.9
				K_1 = 19.75
				K_2 = -0.073
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3 GSM^3$ (115 GSM only)	K_0 = -784.19
				K_1 = 14.27
				K_2 = -0.057
				K_3 = 1.5E-05
	Integ (group B)	Levafix Red CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = 90.39
				K_1 = 0.197
				K_2 = -0.00095
		Levafix Blue CA	$K_0+K_1GSM+K_2GSM^2$	K_0 = -461.05
				K_1 = 7.87
				K_2 = -0.027
		Levafix Yellow CA	$K_0+K_1GSM+K_2GSM^2$ or $K_0+K_1GSM+K_2GSM^2+K_3 GSM^3$ (157 GSM only)	K_0 = 113.23
				K_1 = 0.49
				K_2 = -0.00475
				K_3 = -1.8E-06

CHAPTER 8. PROJECT SUMMARY, CONCLUSION AND FUTURE SUGGESTION

8 Project Summary, Conclusion and Future suggestions

This study demonstrated that variations in Tencel woven fabric construction, dye classes, and methods of dyeing have considerable effects on colour intensity, dye fixation and uniformity of fibre colouration. The original aims of thesis, discussed in Chapter 1;

- To analyse the effects of weave structure and density on dyeing behaviour of Tencel fabrics.
- To improve the dye uptake of Tencel woven fabrics, when dyed by continuous dyeing processes such as pad-steam, pad-batch, pad-dry-thermosol and pad-dry-steam processes.
- To develop numerical methods of assessing the uniformity of fibre coloration and fabric porosity.
- To develop the fundamental numerical equations for predicting the colour depth and UFC value of Tencel fabrics comprises of different fabric density dyed by continuous dyeing methods.

8.1 Weave Structures

Tencel woven fabrics with the weave structures Plain, Twill 2/1, Twill 3/1 and Twill 5/1 fabric were dyed by the exhaust and continuous dyeing methods using Novacron (FN, LS and H for exhaust method and C for continuous methods) and Levafix (CA for continuous methods) dyes. In case of using Novacron LS dyes applied by the exhaust dyeing method plain fabric appeared deeper in colour depth than Twill 2/1 fabric. The Integ value of the twill weave fabrics increases in the order of Twill 2/1 > Twill 3/1 > Twill 5/1 fabric at both 0.5% and 2% dye concentration. Novacron H dyes applied by the exhaust method, and Levafix CA dyes applied by pad-batch and pad-dry-thermofix process showed similar trends.

Overall colour depth values using Novacron FN and Novacron LS dyes applied by the exhaust method was higher than the use of Novacron H dyes (exhaust method) on the Tencel woven fabric of different weave structures. The visual depth values obtained by exhaust dyeing methods was higher than by the continuous processes, because in exhaust dyeing methods dye has a longer time to react with fibre, while reaction time is very short in continuous dyeing methods.

Additionally, it has been observed from experiments that the highest visual depth of Tencel woven fabric was obtained using the pad-dry-thermosol method. Time and temperature both plays vital role to achieve high visual depth, exhaustion and fixation of dyes on Tencel woven fabrics of all structures.

In the exhaust method of dyeing, using Novacron FN and Novacron LS dyes gave dye exhaustion and fixation rating between 70% and 100%. In comparison Novacron H dyes gave low exhaustion and low fixation percentage (less than 80%).

In continuous dyeing methods the Levafix CA dyes showed the highest visual depth as well as high fixation in percentage (70 to less than 100%). The fixation percentage of Novacron C dyes in all continuous methods of dyeing varied from 50 to less than 100%. Overall, the plain Tencel woven fabric dyed by continuous methods showed the highest visual depth.

It was concluded from the microscopic studies that Tencel fabrics give uniform dye penetration of the fibre filaments in the yarns especially with the exhaust dyeing methods and the pad-dry-thermosol process of continuous dyeing. The white dots in images show that dyes are not uniformly distributed throughout the yarns. The quantitative analysis of UFC shows the variation in dye penetration depends on the fabric parameters as well as on the chemistry of the dyes such as dye structure and size. The Novacron H dyes have big molecular sizes, and show poor uniformity as compared to the Novacron LS and FN dyes. Additionally, method of dyeing has an effect, such as continuous dyeing processes which show higher standard deviation values as compared to the exhaust dyeing methods. In the continuous processes the standard deviation is in the order of Plain >< Twill 2/1 > Twill 3/1 > Twill 5/1 fabrics. The Twill 5/1 fabric shows low visual depth but has low standard deviation showing good uniformity of dyeing, which might be because of the 5 by 1 weave structure, allows dyes to penetrate easily into the filaments of the yarns of the fabric. The average UFC value indicates most repeated grey level intensity of an image using rating scale (1 to 5). It was observed that all woven fabrics of varying weave structure have almost same average UFC values varied with the dye types and dyeing methods. The negative dispersion of the intensity histogram further confirmed that fabrics were heavily dyed by the exhaust methods.

In twill weave structures due to their differences in fabric parameters (weave structure and thread density) it is more difficult to predict the dyeing behaviour.

8.2 Plain Weave Fabric

The plain weave is most common type of weave and is used for a variety of applications. Variation in weave parameters such as numbers of threads per cm and linear density give differences in fabric properties such as cover factor, porosity, fabric weight and physical and mechanical properties including dyeing behaviour.

8.2.1 Fabric Assessment

Software was developed using Matlab which assessed fabric porosity with respect to the number of bright pixels in a microscopic image. However, fabric properties such as ends and picks per cm, linear density, fabric cover factor and porosity were also calculated using BS standards and geometrical formulas. It was observed that the software measured the fabric porosity more accurately than the geometrical formulas, but both methods gave similar trends (porosity increases with fabric density). The fabric porosities of un-dyed loosely woven fabrics were slightly higher than the dyed woven fabrics, which show fabrics shrank or the yarns came closer to each other due to the wet treatment.

The fabric porosity has a profound effect on the flow of dye liquor in the fabric during dyeing. Higher porosity means there is a greater distance between the yarns (inter-yarn) of the weave structure hence it is easier for dye liquor to flow in between the yarns. However dye molecular size and geometrical structure have also effects on its flow and fixation in the fabric.

8.2.2 Colour Strength and Dye Uptake

The preliminary studies discussed in Section 7.2 showed that when the medium to tightly woven Tencel fabrics (132 – 163 GSM) were dyed, either by exhaust or continuous dyeing methods, ring dyeing effects were obtained. Various steps were taken, depending on the dyeing method to reduce ring dyeing. In case of exhaust dyeing method, dyeing at high temperature (110 °C) and for a longer duration shows excellent dyeing behaviour. For continuous dyeing methods fabrics were pre-treated using enzymes (cellulases), enzymes with caustic, caustic (various concentrations and temperatures) and cationic fixing agents. Among other pre-treatment processes caustic treatment using 2 mol dm^{-3} by pad-batch process improved dye uptake of Tencel fabrics dyed by using reactive dyes.

The caustic treatment opens the inter fibrillar layer of cellulosic chain. It was observed that Tencel fabrics, because of their high crystalline regions are difficult to dye by continuous dyeing methods because of the short dyeing times. For this reason, Tencel fabrics were dyed at different temperatures, ranging from standard conditions (20 °C) to 60 °C with no dwell time, to five min dwell time. As the temperature and time were increased uptake of dye also increased and gave excellent dye penetration. On the other hand, increased temperature (more than 40 °C) and time (5 min) caused dyeing problems such as a tailing effect. The 40 °C dyeing temperature with a 1 min dwell time was a compromise method which improved the dye uptake especially after caustic treatment. Temperatures higher than the standard condition with caustic pre-treatment speeded up the reaction between the dye and the fabric, so that the maximum amount of dye was transferred to the fabric in the short time available.

The plain weave fabrics with and without caustic treatment were dyed using reactive dyes at two different liquor temperatures with or without dwell time. The results of colour strength, dye uptake, and uniformity of fibre colouration of dyed fabrics at standard condition (room temperature without dwell time) after caustic and without caustic treatment were same. However, there was a difference in dyeing behaviour at 40 °C liquor temperature with a 1 min dwell time, after caustic pre-treatment. The fabrics had dye uptake of more than 50% higher, compared to the standard dyeing condition, and 30 - 40% higher compared to exhaust dyeing method. This dyeing method using reactive dyes

(Levafix CA and Novacron C dyes) is applicable for all types of fabrics varying fabric density.

The visual depth and dye uptake value decreases as the fabric density increases. When comparing different dyeing methods, visual depth and dye uptake trends increase in the order of pad-dry-thermosol > pad-dry-steam > pad-steam process.

8.2.3 Uniformity of Fibre Coloration

To determine the uniformity of fibre coloration (UFC), a numerical method was designed to measure objectively the colour depth of fibre filaments of the fabric by statistical analyses using Matlab software. Additionally, the UFC was assessed visually by counting the number of fibre filaments with respect to rating (1 to 5) as well. The software was designed not to only measure the number of fibre filaments with respect to its rating but also to present the results as a histogram. The dispersion and bandwidth value of histogram analyses the distribution of colour depth of fibre filaments.

The UFC value of plain weave fabrics increased in the order of pad-dry-thermosol > pad-dry-steam > pad-steam process. The loosely woven fabric because it had fewer ends and picks per cm, in all dyeing processes showed uniform dye penetration. The objective assessment results showed that at 40 °C liquor temperature with a 1 min dwell time after caustic treatment, the dyed fibre filaments had a rating of 4 to 5 (average grey intensity < 35 ≥ 0) as compared to room temperature dyeing, which gave a rating of only 3 (average grey intensity > 160 < 0).

The negative sign in the dispersion and the lower value of the bandwidth of the histogram as compared to the other dyeing methods further confirmed the 40 °C liquor temperature with a 1 min dwell time after caustic treatment dyed fabrics have a more uniform dye penetration and the fibres are darker. A fabric that has zero deviation has symmetrical histogram hence uniform dye penetration.

8.2.4 Fastness

The Levefix Red CA dyes show excellent washing fastness with no staining on multi fibre standard fabric. The rubbing fastness rating varied from 4 to 5 in pad-steam and pad-dry-steam process, and 4-3 to 5 in pad-dry-thermosol process.

8.2.5 Effect of Caustic Treatment

The caustic treatment as discussed above improved the dye uptake. The longitudinal images obtained on the scanning electron microscope of Tencel fibre after caustic treatment showed the presence of cracks and fibrillation of fibres. The change in fibre structure enhanced the uptake of dye during dyeing processes. On the other hand fibrillation gives frosty appearance but this can be minimized using functional reactive dyes. The effect of caustic was further analysed using cross-sectional views of Tencel fabric, which were same with or without caustic treatment. These analyses demonstrated that caustic treatment using 2 mol dm^{-3} had no effect on the Tencel fibre structure and enhance the dye uptake.

However, the Tencel fabrics had a minor loss of tensile strength after the caustic treatment. The fabric strength decreased as the fabric density increased. However, the behaviour of strength was different with the direction of measurement (warp or weft). Additionally, caustic treatment has minor effect on the handle of the fabric. The effect seemed to be more at very tightly woven fabrics and less with loosely woven fabrics. The fabrics had same handle after dyeing process.

8.2.6 Fibrillation Assessment

Olympus software was used to analyse the fibrillation of Tencel fabrics after dyeing. The fibrillation tendency of only the plain weave fabrics was examined. Fibrillation is expected to be minimized using bis-functional reactive dyes. The length and number of fibril was measured, mostly all of the plain weave fabrics had fibrils in the range of 15 µm in length.

8.2.7 Mathematical Modelling

Using the dyeing results (visual depth and uniformity of fibre colouration) of plain weave fabric, a mathematical model to predict the behaviour of fabrics of different GSM values was designed. The model is based on the relationship between the dyeing behaviour and fabric density. It is very useful for the commercial dyers in advance to predict the dyeing behaviour of Tencel plain weave fabrics with respect to its fabric density dyed by selected reactive dyes and it is important in shade matching.

8.3 Future Suggestions

- Vat dyeing: Tencel fabric, when dyed using vat dyes, shows ring dyeing effects, poor dye penetration both in the exhaust and continuous dyeing methods. However, in case of exhaust dyeing methods, it is easy to improve the dye penetration by increasing temperature and time. In the case of continuous dyeing methods, work should be done similar to that carried out in this thesis.

- Model: The equations derived in this research were based on the fabric density of Tencel plain weave fabrics. In future work can be carried out to develop a model that predicts dyeing variations such as Integ value, dye penetration and CIELAB values at different weave structure (balance and unbalance plain and twill weave) and densities (fabric weight).

- As dicussed in Chapter 2, the behaviour of standard Tencel fabric is different to the LF and A-100. Tencel A-100 has resistance to acid while standard Tencel has resistance to alkali. Therefore, there is a need to do work on the pre-treatment method of Tencel LF and A-100 for improving the dye uptake.

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10 Appendix

A Fabric Porosity

```
rgb_img = imread('110.jpg');
thresh = [0,150,255];
grey = rgb2gray(rgb_img);
meanGreyValue=mean(mean(grey));
[m,n]=size(grey);
noPixels=m*n
threshold=thresh(2)
noBrights=0;
i=1;
j=1;
            while (i<=m)
j=1;
             while (j<=n)
 if (grey(i,j)<=thresh(2));
            grey(i,j)=0;
 else
            grey(i,j)=255;
 noBrights=noBrights+1;
 end
            j=j+1;
end
            i=i+1;
end
            subplot(1,2,1),imshow(grey)
            subplot(1,2,2),imshow (rgb_img)
 light= noBrights;
 percentageBright= noBrights*100/noPixels
```

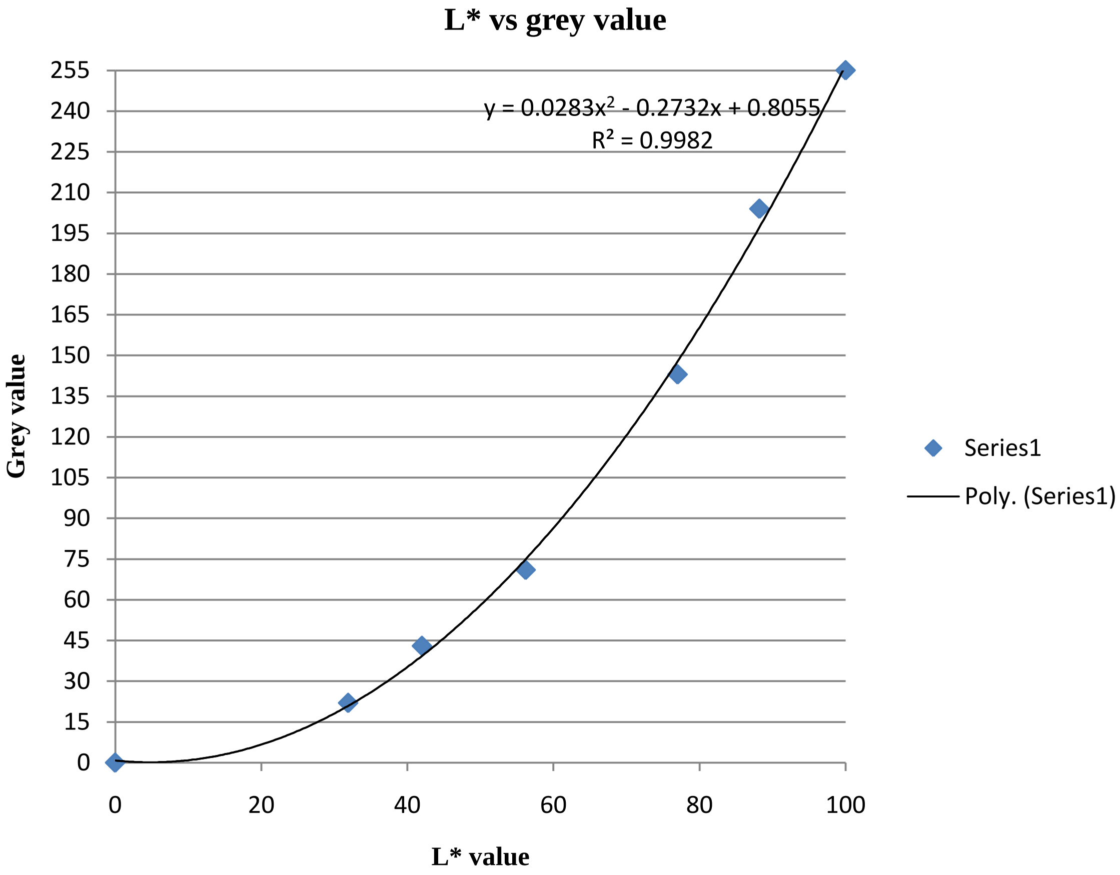
B Uniformity of Fibre Coloration

```
thresh = [0,7,35,86,160,256];
[s,threshNumber]= size(thresh);
greys = imread('yellow 3.5 grn.jpg');
a= rgb2gray(greys);
[pixelCount grayLevels] = imhist(a);
figure, imshow (a)
bar(pixelCount);
title('histogram');
xlim([0 grayLevels(end)]);% scale set manually.
yRange = ylim;
meanGL= mean2(a);
meanBinHeight = mean2(pixelCount);
line([meanGL meanGL], yRange);
% maximum pixels
[mValue pos] = max(pixelCount);
t = max(pixelCount);
v = pos
l = t/2;
q = t/4;
% Calculate min pos and max pos at a point t
ylim([q l])
l1 = input('please enter the midpoint right hand side value')
l2 = input('please enter the midpoint left hand side value')
q1 = input(' please enter the quarter right hand side value')
q2 = input('please enter the quarter left hand side value')
st1 = (l1-v);
st2 = (v - l2);
st3 = (q1 -v);
st4 = (v - q2);
if (st2< st1)
   r2 = st2/st1;
```

```
else
   r2 = -(st1/st2);
end
r = r2
if (st4< st3)
   r3 = st4/st3;
else
   r3 = -(st3/st4);
 end
 z = r3
[m,n]=size(a);
totalPix=0;
count=[0,0,0,0,0,0];
percentage = [0,0,0,0,0,0];
c=[5,4,3,2,1,1];
i=1;
j=1;
while (i<=m);
while (j<=n);
         k=1;
while (k<threshNumber);
         if (a(i,j)>=thresh(k));
         if (a(i,j)<thresh(k+1));
         count(k)=count(k)+1;
end
end
         k=k+1;
end;
         totalPix= totalPix+1;
         j=j+1;
end
         i=i+1;
         j=1;
```

```
end
percentage=count./totalPix*100.
sd=((sum(percentage.*c.^2))-(sum (percentage.*c))^2/100)/99;
sdd = sqrt(sd)
Average = (sum(percentage.*c))/100.
```

C Calibrated graph L value versus Grey value*



D Tensile strength

Table D.1.1 Tensile strength of Tencel woven fabric from warp yarns side (average)

	Tenacity (N/tex)								
GSM	**110**	**115**	**132**	**140**	**145**	**124**	**135**	**157**	**163**
Scoured Fabric	55	54.9	45.9	45.5	45.2	55.6	52.5	43.7	40.5
Pre-treated Fabric	53.9	48.6	45	46.6	44.4	49	48	43	42.9
Dyed Fabric	46.9	45.1	41.2	40	43.1	43.8	41.5	37.6	36.7
	Load at break, N								
Scoured Fabric	713.3	795.4	665.88	654.7	659.66	784.53	761.51	629.2	571.7
Pre-treated Fabric	685	704.3	649.33	670.4	647.54	451.42	647.12	619.7	605
Dyed Fabric	407	590.4	597.04	575.7	625.59	226.41	596.2	467.2	444.7
	Maxi Load, N								
Scoured Fabric	782.3	795.4	665.88	654.7	659.66	794.54	761.51	629.2	571.7
Pre-treated Fabric	771.2	704.3	652.43	670.5	647.54	700.8	695.92	619.7	605
Dyed Fabric	665.1	653.9	597.04	575.7	629.45	626.89	601.35	541.1	517.1
	Elongation,%								
Scoured Fabric	17.3	17	18.59	19.2	19.48	18.05	19.67	21.9	20.9
Pre-treated Fabric	30.8	32.1	31.24	29.9	29.12	34.23	34.41	32.2	30.4
Dyed Fabric	29.2	28.3	27.88	25.8	28.09	30.84	30.57	29.5	29.4

Table D.1.2 Tensile strength of Tencel woven fabric from weft yarns side (average)

	Tenacity (N/tex)								
GSM	**110**	**115**	**132**	**140**	**145**	**124**	**135**	**157**	**163**
Scoured Fabric	28.4	33.1	44.9	47.9	52.9	32	37	47.6	51.1
Pre-treated Fabric	33.5	36	43.8	48.3	54.4	32.2	39.4	46.1	52.2
Dyed Fabric	31.2	33.2	42.7	44.2	49.4	30.8	34.6	45	49.9
	Load at break, N								
Scoured Fabric	284.3	471.4	664.08	690.1	788.06	649.63	762.4	990.3	1056.8
Pre-treated Fabric	311.4	470.6	647.65	695.8	810.76	277.21	812.41	959.1	1080.4
Dyed Fabric	184.5	448.9	631.48	636.9	735.73	277.79	617.5	936.9	1033.8
	Maxi Load, N								
Scoured Fabric	417.3	482.9	664.08	690.1	788.06	652.33	762.4	990.3	1056.8
Pre-treated Fabric	492.3	525.5	647.65	695.8	810.76	657.33	812.41	959.1	1080.4
Dyed Fabric	459.3	484.5	631.48	636.9	735.73	627.63	713.69	936.9	1033.8
	Elongation,%								
Scoured Fabric	17.3	17.6	19.41	19.5	20.14	19.1	19.52	21.3	21.9
Pre-treated Fabric	25.5	19.4	23.53	24	26.08	20.09	21.16	25.7	27
Dyed Fabric	20.7	18.4	22.8	24.3	24.71	20.52	19.75	25.8	27.8

E Bending Length

Table E.2.1 Bending length and flexural rigidity of dry scoured fabrics (average)

Sample	**GSM**	**Bending length C cm**				**Flexural rigidity G mg cm^{-3}**			
		Warp		**Weft**		**Warp**		**Weft**	
		Face	**Back**	**Face**	**Back**	**Face**	**Back**	**Face**	**Back**
1	110	2.2	2.2	1.8	1.95	251.0	186.8	97.2	102.3
2	115	3.4	3.5	2.2	2.3	436.4	498.6	120.0	131.4
3	132	3.6	3.6	2.5	2.5	609.8	594.4	211.1	214.7
4	140	4.0	4.0	2.8	2.7	874.2	864.8	320.5	275.6
5	145	4.0	4.0	2.7	2.8	1019.1	993.7	322.0	345.3
6	124	4.1	4.1	2.8	2.9	989.1	1012.9	313.7	364.4
7	135	3.4	3.4	2.5	2.6	473.5	481.2	201.8	205.8
8	157	3.6	3.7	2.6	2.6	621.7	702.8	224.4	242.3
9	163	3.6	3.7	3.1	3.0	772.4	817.6	496.1	452.5

Table E 2.2 Bending length and flexural rigidity of 50% wetted scoured fabrics (average)

Sample	**GSM**	**Bending length C cm**				**Flexural rigidity G mg cm^{-3}**			
		Warp		**Weft**		**Warp**		**Weft**	
		Face	**Back**	**Face**	**Back**	**Face**	**Back**	**Face**	**Back**
1	110	2.2	2.2	1.8	1.95	118.0	119.9	68.6	81.6
2	115	2.2	2.3	2.2	2.3	122.6	88.3	79.6	100.4
3	132	2.7	2.7	2.5	2.9	255.3	245.8	214.8	310.7
4	140	2.9	2.8	2.8	3.1	325.5	313.3	308.1	417.1
5	145	3.0	3	3.4	3.4	417.0	424.8	593.6	611.9
6	124	2.8	3.1	3.2	3.2	304.0	413.0	454.8	294.1
7	135	2.3	2.3	2.2	2.4	145.2	147.7	135.9	171.4
8	157	2.4	2.4	2.5	2.7	191.6	190.6	215.2	251.8
9	163	3.1	3.1	3.6	3.8	463.5	487.3	781.9	865.4

Table E 2.3 Bending length and flexural rigidity of pre-treated fabrics (average)

Sample	**GSM**	**Bending length C cm**				**Flexural rigidity G mg cm^{-3}**			
		Warp		**Weft**		**Warp**		**Weft**	
		Face	**Back**	**Face**	**Back**	**Face**	**Back**	**Face**	**Back**
1	110	2.5	2.5	2.3	2.4	169.7	179.4	137.7	166.3
2	115	2.8	2.7	2.5	2.5	241.2	217.2	169.3	169.3
3	132	3.1	3.1	2.7	2.8	407.8	407.4	247.9	284.7
4	140	3.3	3.3	2.8	2.9	496.5	503.8	302.3	324.3
5	145	3.3	3.3	3.1	3.0	498.0	498.0	448.4	373.7
6	124	2.5	2.4	3.1	2.9	196.2	166.9	358.4	292.4
7	135	2.7	2.7	3.3	3.3	265.9	272.2	487.8	471.8
8	157	3.0	3.1	3.2	3.1	440.4	484.3	536.2	485.3
9	163	3.1	3.2	3.6	3.5	474.5	538.3	765.2	719.4

Table E 2.4 Bending length and flexural rigidity of dyed fabrics (average)

Sample	**GSM**	**Bending length C cm**				**Flexural rigidity G mg cm^{-3}**			
		Warp		**Weft**		**Warp**		**Weft**	
		Face	**Back**	**Face**	**Back**	**Face**	**Back**	**Face**	**Back**
1	110	2.1	2.3	2.2	2.3	107.1	137.1	120.6	140.6
2	115	2.5	2.4	2.4	2.4	176.2	114.0	113.8	117.4
3	132	2.8	2.8	2.6	2.7	292.0	275.1	242.0	270.5
4	140	2.8	2.8	2.6	2.7	305.1	302.7	251.1	265.9
5	145	2.7	2.7	2.9	2.8	276.8	298.0	338.3	294.1
6	124	2.4	2.4	2.5	2.6	172.4	179.5	198.0	222.2
7	135	2.6	2.6	2.6	2.6	246.9	247.3	233.8	234.5
8	157	2.9	2.8	3.0	3.0	369.9	345.3	405.8	410.0
9	163	3.2	3.22	3.0	3.0	526.9	510.2	423.0	431.7

F Bandwidth

ab or ac value / p		**Number of Pixels (p)**			
		80000	**60000**	**50000**	**40000**
a b or ac value	1	1.3E-05	1.7E-05	2.0E-05	4.2E-10
	2	2.5E-05	3.3E-05	4.0E-05	8.3E-10
	3	3.8E-05	5.0E-05	6.0E-05	1.3E-09
	4	5.0E-05	6.7E-05	8.0E-05	1.7E-09
	5	6.3E-05	8.3E-05	1.0E-04	2.1E-09
	6	7.5E-05	1.0E-04	1.2E-04	2.5E-09
	7	8.8E-05	1.2E-04	1.4E-04	2.9E-09
	8	1.0E-04	1.3E-04	1.6E-04	3.3E-09
	9	1.1E-04	1.5E-04	1.8E-04	3.8E-09
	10	1.3E-04	1.7E-04	2.0E-04	4.2E-09
	15	1.9E-04	2.5E-04	3.0E-04	6.3E-09
	20	2.5E-04	3.3E-04	4.0E-04	8.3E-09
	25	3.1E-04	4.2E-04	5.0E-04	1.0E-08
	30	3.8E-04	5.0E-04	6.0E-04	1.3E-08
	100	1.3E-03	1.7E-03	2.0E-03	4.17E-08