Reduced Salt Usage in Dyeing of 100% Cotton Fabric

A thesis presented in total fulfilment of the requirements
For the degree of
Master of Technology

By

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Bachelor App Sci (Textile Technology)
Declaration

This is to certify that this thesis comprises only the original work of the author, except where due acknowledgement has been made, and has not been previously submitted for assessment for any other degree.

Daniela Bernadette Gentile
Acknowledgements

I wish to thank and acknowledge Dr. Rajiv Padhye and Adjunct Professor Max White (my supervisors) and Mac Fergusson for their guidance and support throughout this work.

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Abstract

This study primarily focuses on the reduction of salts during the dyeing of cotton. Cotton fabrics were pretreated with Chitosan and Cibafix ECO respectively, and then dyed with reactive and direct dyes with various amount of salt in a dye bath, to determine the optimum pre-treatment conditions of a reduced salt concentration.

Cotton fabric was dyed with two different classes of reactive dyes and a direct dye with 100%, 75%, 50% and 0% of the recommended amount of salt. Various methods of pre-treatment application were trialed to determine the most effective and efficient method, as well as to determine the optimum conditions of the pre-treatments. Exhaustion levels of the dye bath as well as Total Dissolved Solids (TDS) levels were measured. Colour strength measurements were also studied along with colourfastness properties.

It was found that cotton fabric pre-treated with Cibafix ECO and dyed with 25% less salt was more effective than fabric pre-treated with Chitosan and dyed with 25% less salt. Any greater reduction in salt has detrimental effects on the levelness of dyeing. When using only 75% of the recommended amount of salt, the pre-treated fabrics showed higher extents of exhaustion compared with samples dyed without the pre-treatment. At optimum pre-treatment conditions a saving of 25% salt usage was observed for cotton dyed with direct and reactive dyes. In addition these samples also showed moderate to very high fastness properties.
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Chapter 1
Introduction and Literature Review
1.1 Introduction

Salt is an essential requirement for the dyeing of cotton with both reactive and direct dyes. However, the presence of large quantities of salt in dye house effluent streams creates problems for treatment plants and limits the opportunities for recycling treated effluent. City West Water, Melbourne, proposed a study be made into opportunities for reducing the amount of salt required in the reactive dyeing of cotton fabrics.

City West Water is a water-retailing business which is 100% owned by the Victorian Government [1]. As stated in their mission statement, “City West Water are proud to contribute to the environmental, economic and social well-being and growth of Victoria through the operation of a commercial organisation…” and “Guarantee affordable and safe water for today and tomorrow”.

In the greater metropolitan Melbourne area, City West Water is one of three retail water businesses along with South East Water and Yarra Valley Water. All three companies also provide sewerage, trade waste and recycled water services in Melbourne’s Central Business District (CBD) and the surrounding inner and western suburbs. Compared to the other metropolitan Melbourne water retailers, City West Water has the smallest customer base. They provide roughly 276,000 residential and 31,000 industrial and commercial customers with clean drinking water. However the majority of these are industrial and commercial customers. The industrial customer base includes automotive manufacturing, oil refining, brewing, chemical and textile manufacturing [2].

City West Water [3] operates a “Cleaner Production Strategy” program. This was developed in October 2004 in partnership with the Environmental Protection Agency Victoria (EPA) to reduce Melbourne’s potable water consumption and minimise the release of pollutants including Total Dissolved Solids (TDS) in trade waste. A common limiting factor for effluent re-use is the TDS load present in the sewer, resulting in higher than acceptable levels at the Western Treatment Plant, Werribee. In turn, this effects the long-term recycling options in the area. A major portion of the TDS load entering the Western Treatment Plant is a result of the commercial dyeing
processes used by a number of textile mills in City West Water’s customer base [N. Corby 2006, Private Communication via email, 30 July].

1.2 Aims and Objectives

The intended outcome of this study was to reduce the amount of salt, and possibly the amount of water, used in dyeing cotton fabric. These reductions in salt and water use should not impact on the final quality of the textile material. Any modifications to the cotton dyeing process should be cost effective and low risk in order for the industry to implement them.

This study aims to:

1. Investigate the effectiveness of selected pre-treatments in the reactive dyeing process.
2. Determine optimal requirement of salt when using a fabric that has been pre-treated.
3. Measure the effectiveness of rinsing when using a fabric that has been pre-treated.
5. Determine the basic economics surrounding the take up of pre-treatment for industry use.

All experiments were conducted in a laboratory using equipment designed to simulate commercial dyeing practice.
1.3 Effluent

1.3.1 Problems with Salt

A limiting factor for effluent recycling is the amount of Total Dissolved Solids (TDS) in trade waste. In the Western Treatment Plant, the volume of wastewater that is discharged from industry is 44% shown in Figure 1.1 [4].

![Pie Chart: Sources of Salinity in Flows to the Western Treatment Plant]

**Figure 1.1 Sources of Salinity in Flows to the Western Treatment Plant [4]**

Hard water, by definition, has high levels of TDS from calcium and magnesium salts. This can lead to problems such as scale build up in filters, pipes and valves as well as increasing maintenance costs and reduced performance of equipment [5].

According to the EPA [6], high salinity levels can also severely damage soil, leaving it unsuitable for cultivation. It can also kill aquatic animals, plants and land animals living near streams and leave water unsuitable for drinking.

1.3.2 Textile Dye Houses and Salt

Traditionally, textile dye houses have consumed large amounts of water and energy and generated large volumes of waste. One kilogram of a finished cotton textile
product can use up to 200 litres of water [M. Fergusson 2009, Private Communication via face to face interview, 24 May]. Thus a high demand for water, and serious effluent management problems can arise. Textile dye houses discharge hot, coloured effluent containing a wide variety of chemicals including salts into the sewer causing serious environmental issues [7].

The addition of salt is commonly required for some dyeing processes within the textile industry and is an important issue.

In terms of cost, salts such as sodium chloride and sodium sulphate are cheap. Therefore, their appeal for recovery as well as the small size of their ions makes them problematic when trying to remove them through standard effluent treatments. Biological treatments are of no use in the removal of salts and therefore removal by physical or chemical means is left as the only option [7].

1.3.3 Methods of Salt Removal

There are many physical and chemical means available for the removal of salt from textile dye house effluent. Costs can be quite high and are a critical factor when determining the most effective and economically attractive method of salt removal.

1.3.3.1 Membrane Technique/Reverse Osmosis

Skelly [8] has highlighted that membrane techniques and reverse osmosis for effluent treatment and salt removal have been of some interest for water recycling. Reverse osmosis involves a membrane with pores that prevent organic chemicals and soluble dyes of average molecular weight (between 100 – 2000) to pass through. However each dye house needs a separate examination to determine which pore size would be most suitable for the effluent produced. Once the effluent has moved through the membrane, all that remains is a concentrate, which contains the soluble dye and salt.

Some advantages to the membrane/reverse osmosis technique are that it can be used to remove both inorganic and organic compounds. The process is relatively simple and the technology has little need for the use of chemicals. Some disadvantages are
that the membranes are sensitive to abuse and require a reliable source of energy. There is also a risk of bacterial contamination within the membranes which can cause odour and poor taste to form in the newly cleaned water [9]. Further, membrane plants are expensive to install and have high operating costs.

1.3.3.2 Evaporation Method

The evaporation method involves three steps:

1. Initial evaporation when the effluent is preheated and concentrated close to the level of salt saturation;
2. The crystallization of salts is encouraged by exposing the concentrated effluent liquid to a process of evaporation and cooling;
3. Followed by centrifuging the crystallized salts to remove any excess liquid. If required the salts can be dried [10].

The process is illustrated in Figure 1.2.
1.3.3.3 Dilution

If effluent has previously been treated and still contains some organic matter, a dilution method can be employed. In order for the remaining effluent to have a lower demand for dissolved oxygen it is mixed with extra water to further dilute the wastewater and reduce the Biological Oxygen Demand (BOD). The remaining inorganic compounds become food for the micro-organisms, which convert the waste into inoffensive compounds. The treated effluent can then be discharged [11].

1.3.3.4 Reducing Salt at the Source

Another method of reducing the amount of salt in effluent is removing the salt at the dyeing stage. Salt plays a major role in promoting dye exhaustion and it is important to find alternatives that will allow the dyer to reduce the amount of salt, while maintaining the same quality of dyeing. One option is dyeing at a lower liquor ratio. Gokarneshan [12] states that lowering the liquor ratio lowers the volume of effluent, as less water is required. Dosing of the chemicals and auxiliaries required for dyeing are measured as grams per litre. Therefore the quantities of chemicals and auxiliaries being released in the effluent can be significantly reduced.

An additional method of reducing salt loads at the source is the use of dyes that require less salt. CIBACRON® LS dyes offer high fixation rates using only a quarter of the conventional amount of salt. This is possible because CIBACRON® LS dyes are a type of bifunctional dye [13]. Bifunctional dyes contain reactive groups within the one dye. They can be two different reactive groups, or two of the same reactive groups. Because these dyes have higher fixation they are less prone to hydrolysis, thus soaping is reduced. This is of benefit, as soaping often requires 4 times more water than the actual dyeing. Bifunctional dyes are also less sensitive to liquor ratio and temperature variations [14]. As a result, the time required for dyeing and material costs are reduced.

Pre-treating the fabric before dyeing with a cationic agent is another method of salt removal at the source. This involves modifying the surface characteristics of the
fabric to induce a positive charge at the fibre surface that will attract the dye to the fabric [15].

1.3.3.5 Evaluation of Salt Removal Methods

The above review suggests that the simplest and most cost effective method of salt removal is to reduce salt use in the dyeing process. In other words, for textile dye houses it is potentially easier to refrain from adding salt into the dye bath rather than trying to remove it from the effluent at the end of the process.

1.4 Salt and Textile Fibres

Salt acts as an electrolyte in the dye bath solution, promoting the exhaustion of the dye onto the fibre. Cellulosic fibres in water are negatively charged. Salt, as either sodium chloride or sodium sulphate, induces a positive charge at the fibre surface. This neutralises the electrostatic repulsion between the dyestuff and the fabric. The amount of salt required for dyeing depends on the fibre being dyed and the depth of shade, which in turn dictates which dye is to be used.

Textile fibres are often divided into four general categories, each category requiring differing amounts of salt [16]:

a. Cellulosic fibres which are made primarily from cellulose and can be found in vegetable material, such fibres include cotton, flax and viscose rayon;

b. Protein fibres which are derived from animal proteins and consist of fibres such as wool, mohair, cashmere, alpaca and silk;

c. Cellulose acetates which are derived from the raw material of cellulose and include fibres known as di-acetate and tri-acetate;

d. Synthetic polymer fibres such as polyester, nylon and the differing acrylics (Acrilan, Courtelle, Orlon).

As dyeing occurs in an aqueous medium, the majority of the dyestuffs are supplied in a water-soluble form. Dyes may be classified according to their application method
or their chemical constitution. It is common when referring to the application method to include the fibre type. Table 1.1 shows the classification of dyes based on the principal fibre classes [16].

<table>
<thead>
<tr>
<th>Cellulosic (Protein)</th>
<th>Wool Acetates</th>
<th>Cellulose Acetates</th>
<th>Nylon</th>
<th>Acrylic</th>
<th>Polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct</td>
<td>Acid (including metal-complex)</td>
<td>Disperse</td>
<td>Acid (including metal-complex)</td>
<td>Basic</td>
<td>Disperse</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Azoic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vat</td>
<td>Mordant</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactive</td>
<td>Reactive</td>
<td></td>
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Table 1.2 Cotton dyes – Average dye salt use (g/l) [47]

<table>
<thead>
<tr>
<th>Type of Dye</th>
<th>g/l</th>
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<td>Direct Dyes</td>
<td>20</td>
</tr>
<tr>
<td>Sulphur Dyes</td>
<td>20 – 40</td>
</tr>
<tr>
<td>Azoic Dyes</td>
<td>30</td>
</tr>
<tr>
<td>Vat Dyes</td>
<td>6 – 10</td>
</tr>
<tr>
<td>Reactive Dyes</td>
<td>50 – 100</td>
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</tbody>
</table>

Table 1.2 shows the average amount of salt required when batch dyeing cellulosic fibres. Although it appears a great deal of salt is required for sulphur dyes, this is rarely the case as they are usually used in continuous dyeing processes where minimal or no salt is required. Reactive dyes are the most commonly used dyes for cellulosic fibres and as shown in Table 1.2, require the highest concentration of salt. This study therefore, focuses on the dye class which is the major contributor to TDS in textile effluent; i.e. reactive dyes.

1.4.1 Effect of Colour in Effluent

As salt directly affects the amount of dye exhausted onto the fibre, the passing of colour to effluent is also a major environmental issue. Coloured effluent has become a particular concern when dyeing cellulosic fibres such as viscose rayon and cotton
with reactive dyes. As shown in Table 1.3 up to 50% of reactive dye used may be lost to effluent [17].

Table 1.3 Degree of fixation for different dye/fibre combinations [17]

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Fibre</th>
<th>Estimated loss to effluent %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Polyamide</td>
<td>5 – 20</td>
</tr>
<tr>
<td>Basic</td>
<td>Acrylic</td>
<td>0 – 5</td>
</tr>
<tr>
<td>Direct</td>
<td>Cellulose</td>
<td>5 – 30</td>
</tr>
<tr>
<td>Metal – Complex</td>
<td>Wool</td>
<td>2 – 10</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cellulose</td>
<td>10 – 50</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Cellulose</td>
<td>10 – 40</td>
</tr>
<tr>
<td>Vat</td>
<td>Cellulose</td>
<td>5 – 20</td>
</tr>
</tbody>
</table>

1.4.2 Viscose Rayon and Cotton

The two most commonly used cellulosic fibres are viscose rayon and cotton. Each of these fibres requires salt in the dyeing process; the amount of salt required depends on the class, the particular dye and the depth of shade. As shown in Table 1.3 more dye classes are available for cellulose than any of the other commonly used fibres.

1.4.2.1 Consumption of Viscose Rayon

Viscose rayon is regenerated cellulose, derived from wood pulp. The world demand for viscose rayon – particularly within the non-woven industry is around 4% of total world fibre demand [17].

1.4.2.2 Consumption of Cotton

In the United States alone the consumption of cotton is around 8.08 million bales (217kg per bale) [45] per annum with 57% of that going towards apparel, a third going towards home furnishings and the rest being used for industrial fabrics. Apparel can be items such as work wear, fashion wear, jeans and underwear. Whereas home furnishings are items such as bed sheets, towels and window shades. Industrial
use of cotton can be seen as medical supplies, bookbinding’s and zipper tapes [18]. Table 1.4 illustrates the worldwide consumption of cellulosic fibres.

### Table 1.4 Worldwide consumption of cellulosic fibres

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Quantity (1000 t)</th>
<th>Percent of total world fibre demand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Cellulosic Cotton</td>
<td>20,623</td>
<td>32.87</td>
</tr>
<tr>
<td>Natural Lignocellulosic Jute</td>
<td>3,222</td>
<td>5.14</td>
</tr>
<tr>
<td>Flax (Linen)</td>
<td>721</td>
<td>1.14</td>
</tr>
<tr>
<td>Ramie</td>
<td>201</td>
<td>0.32</td>
</tr>
<tr>
<td>Manufactured Cellulosic Viscose, Polyviscose, Modal, High Wet Modulus, Cupro &amp; Lyocell</td>
<td>2,715</td>
<td>4.32</td>
</tr>
<tr>
<td><strong>Total world fibre demand (all fibres)</strong></td>
<td>62,733</td>
<td>100</td>
</tr>
</tbody>
</table>

Source: Fibre Organon, 2003, 74 (6), 95

The total world consumption of cellulosic fibres is 44% making up nearly half of the world’s consumption of fibres – both natural and man made.

### 1.4.3 Salt Sources in Cotton Processing

Acids, alkalis and salts are used extensively in processing woven and knitted cotton fabrics. The three key processes that contribute significant quantities of TDS are mercerising, scouring and bleaching.

Mercerisation is a process that causes the cotton fibre to undergo significant chemical changes when it is treated under tension in a strong solution of sodium hydroxide. As a general rule, the concentration of sodium hydroxide is between 240 and 280 g/l. Mercerisation increases dye absorption for the cotton fibre. Figure 1.3 shows the effect of mercerisation on cotton fibres [21].
Dyeing requires the use of salt when applying colour to cotton. The reason is that the fibre and the dyestuff are both negatively charged. The need for an electrolyte in the dye bath is essential in order for the dyestuff to be attracted to the fabric. As the salt is added in the dye bath the charge of the fibre surface is changed from negative to positive. Substantial amounts of salt are required usually between 50 – 100 grams per litre depending on the depth of shade and the reactivity of the dye.

Of all the production stages for cotton, dyeing is the one that uses the most amount of salt and thus poses the biggest problem for the industry.

1.5 **Dyeing Processes for Cotton**

Dyes are sourced from the dye class (vat, azoic, sulphur, direct and reactive) according to the end use of the fabric. Vat, azoic and sulphur dyes are typically used in the continuous dyeing where large volumes of single shades are required, for example 20,000 metres for a light blue shirting fabric. Direct and reactive dyes are typically used for batch dyeing of fashion wear fabrics.
1.5.1 Direct Dyes

Direct dyes are primarily used for pale to medium depth shades but are sometimes used for deeper depths when fastness properties are not an issue.

1.5.1.1 Chemical Properties of Direct Dyes

Direct dyes have planar molecular structures and predominantly consist of sulphonated poly azo dyes (Figure 1.4). These compounds usually consist of bis-, tris- or tetra-azo compounds typically with the latter compounds being brown and black [14].

![Figure 1.4 Molecular Structure of Dye CI Direct Red 16 (27680)](image)

1.5.1.2 Direct Dye Classifications

Direct dyes have a wide variety of dyeing behaviours and as a result are classified into groups according to their dyeing behaviour. The most familiar classifications are those set out by the Society of Dyers and Colourists (SDC) which ‘separates the dyes based on their levelling ability, their response to the increase in dyeing temperature and to added salt during exhaust dyeing’ [14]. The three classes as set out by the SDC are designated as A, B and C.

Direct dyes in class A have good migration and self-levelling properties and do require a significant amount of salt due to their lower substantivity. Class B direct dyes have poor levelling properties that are salt sensitive. Class B dyes also give an increased exhaustion rate when small amounts of salt are added into the dye bath. Class C dyes have poor migration properties and are both salt and temperature sensitive. Class C dyes also have better wet fastness properties [14].
1.5.1.3 Dyeing with Direct Dyes

A neutral pH solution is required when dyeing direct dyes. To encourage distribution and levelling of the dye, the dye bath is steadily heated and salt additions are made gradually to exhaust the dye bath.

Generally, direct dyes have good solubility properties. However, in the presence of salt the solubility lowers. This can cause a problem when dyeing deep shades at low liquor ratios and temperatures. Any undissolved dye can attach to the surface of the fabric leaving dark spots, giving the appearance of an unlevel dyeing [14].

1.5.1.4 Problems in Batch Dyeing with Direct Dyes

Some issues that arise when dyeing with direct dyes is the dullness in the range of colours especially when fading after laundering [22]. It is also necessary for textile materials dyed with direct dyes to undergo some form of post-treatment to improve wash fastness properties. Such post-treatments may include chelation with salts of metals such as copper or chromium, treatments with formaldehyde and cationic dye-complexing resins [23].

Post-treatments such as those mentioned above can prove to be costly and difficult to perform and can also pose a problem for colour matching and shade correction as some post-treatments can often change the hue of the coloured textile material. Direct dye post-treatments have limited use. Reactive dyes produce dyeings with higher wash fastness properties [14].

1.5.2 Reactive Dyes

In 1956 Imperial Chemical Industries (ICI) introduced the Procion dyes (dichlorotriazine) that gave excellent wash fastness while utilising a relatively simple dyeing method. When compared to direct dyes, the reactive dyes had a much simpler chemical structure and gave brighter dyeings [23]. Figure 1.5 shows the typical structure of a dichlorotriazine dye (C.I. Reactive Red 1).
1.5.2.1 Chemical Properties of Reactive Dyes

The typical structures of reactive dyes include azo, anthraquinone, triphenodioxazine or copper chromophores, shown here in Figure 1.5 and Figure 1.6. Each of the structural features can influence the dyeing and fastness properties [14].

Figure 1.5 Nucleophilic Substitution (a, azo) and addition reactions (b, anthroquinone) of reactive dyes with cellulose

Figure 1.6 Triphendodioxazine (1) and copper phthalocyanine (2) reactive dyes
1.5.2.2 Bifunctional Reactive Dyes

Bifunctional reactive dyes consist of either two different, or two identical, reactive groupings and are referred as hetero bifunctional dyes and homo bifunctional dyes respectively.

Homo bifunctional dyes that have two identical reactive groups have a higher molecular weight than traditional reactive dyes, giving them an increase in substantivity that is excellent for exhaust dyeing with higher liquor ratios.

Hetero bifunctional dyes with two different reactive groups have different optimal fixation conditions and also give a more uniform degree of fixation. These types of bifunctional reactive dyes have a higher degree of fixation, resulting in lower colour in the effluent [14]. This is due to the lower tendency of the bifunctional dye to hydrolyse.

1.5.2.3 Dyeing with Reactive Dyes

When dyeing cotton with reactive dyes, the dyeing occurs in a neutral to slightly acid pH in the presence of salt to encourage exhaustion [14]. The principle reason for this is to prevent premature fixation due to pH variations in the salt and water during the exhaustion stage. If fixation is premature the dyeing will be unlevel [M. Fergusson 2009, Private Communication via face to face interview, 3 March].

When dyeing with a reactive dye there is a predisposition for the dye to hydrolyse. This occurs when the hydroxide ions of the water react with the reactive group of the dye under the alkaline conditions producing the hydrolysed dye, which cannot react with the fibre. As a result any hydrolysed dye in the dye bath must be removed from the cotton fibre through soaping, if not removed the wash fastness is reduced [14].

\[
D - SO_2CHCH_2OH + H_2O \rightarrow D - SO_2CH_2CH = OH + OH^-
\]

Figure 1.7 Hydroxyl ion attaching ether bond of dyed fibre resulting in hydrolysis [25]
1.5.2.4 Problems in Dyeing with Reactive Dyes

The low level of fixation can be a major problem when dyeing with reactive dyes when less than 70% of the dye reacts with the fibre. This results in unfixed dye being discharged into the dye house effluent. This problem, coupled with high salt concentrations used when dyeing with reactive dyes, causes a significant environmental problem [14].

1.6 Dyeing Processes

Dye can be applied to a textile material at the following stages:

- Fibre;
- Yarn;
- Fabric;
- Garment

At each stage a different dyeing method needs to be employed.

1.6.1 Fibre Dyeing Processes

Fibre dyeing is usually carried out in machines where the dye liquor is pumped through a compressed pack of loose fibre. When dyeing in fibre form, extremely good wet fastness properties are required as the fibre, usually spun into yarn, is going to be exposed to a number of varying processes before completion. Levelness in shade is less critical and shade matching is much easier when dyeing in fibre form than in fabric form, as the fibres are more likely to be blended with other varying batches during carding [26].

However, cotton fibre is rarely dyed in loose fibre form. This is due in part to the problem of compacting and swelling resulting in poor dye penetration throughout the fibre mass.
1.6.2 Yarn Dyeing Processes

Yarn dyeing is usually carried out in two forms: generally in hanks for embroidery and craft yarns, and in cone form for knitting yarns.

1.6.2.1 Yarn Dyeing Cones of Cotton

Cone dyeing of cotton often follows this procedure:

1. Raw yarn is wound on to a spring tube - this allows the yarn to be packed in suitable form to give maximum penetration of the dye into the yarn.
2. The packages are then slotted onto a dyeing carrier’s spindle and pressed to achieve a suitable height and density of packing. Careful attention to the package density is required to prevent channelling.
3. The liquor is alternately circulated from inside to outside and then from outside to inside. This change in liquor circulation ensures level dyeing.
4. Once dyeing is complete the packages are unpacked and then hydro extracted to remove excess water and dried.

The advantages of dyeing in yarn form are shades can be selected closer to the end product making the choice of selecting more fashionable shades easier to predict. Dyeing in yarn form also allows for more efficient spinning of undyed fibre [26].

1.6.3 Fabric Dyeing Processes

Before fabric can be dyed it requires pre-treatment to remove impurities and any unwanted natural colour that may interfere with the final colour of the product. The various pre-treatment processes include desizing, scouring, bleaching and in some cases mercerisation [27].

1.6.3.1 Fabric Preparation for Dyeing

Size is applied to cotton yarns to improve their strength and bending properties. Cotton warp yarns are invariably sized as weaving applies a high level of stress on the
yarns during weft insertion. The water-insoluble starch, that is applied as the size needs to be removed once the fabric manufacturing process is complete. The size is removed by treating the fabric in a hot enzyme bath [27]. The importance of removing starch from the fabric is to prevent unlevel dyeing.

The purpose of scouring is to remove any impurities such as dirt and lubricants from the fabric usually in an alkaline solution using sodium hydroxide. An alkali stable detergent is added to assist in the removal of the natural waxes present in cotton. Table 1.5 shows the various impurities present in cotton.

Table 1.5 Chemical composition of cotton [43]

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percent (dry basis*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
</tr>
<tr>
<td>Cellulose</td>
<td>94.0</td>
</tr>
<tr>
<td>Protein**</td>
<td>1.3</td>
</tr>
<tr>
<td>Pectic substances</td>
<td>0.9</td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
</tr>
<tr>
<td>Wax</td>
<td>0.6</td>
</tr>
<tr>
<td>Malic, citric and other</td>
<td>0.8</td>
</tr>
<tr>
<td>organic acids</td>
<td></td>
</tr>
<tr>
<td>Total sugars</td>
<td>0.3</td>
</tr>
<tr>
<td>Pigment</td>
<td>Trace</td>
</tr>
<tr>
<td>Other</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Bleaching a fabric before dyeing removes any unwanted natural colour or colour from a previous manufacturing process and increases brightness and whiteness. If a fabric is not bleached prior to dyeing, any colour present in the fabric may result in an incorrect shade or an unlevel dyeing. Bleaching is particularly important for top quality white goods or fabric that is to be dyed pale colours. As well as removing colour, the bleaching process further removes any impurities that may have escaped the previous processes. The most common bleaching agent used today is an alkaline solution of hydrogen peroxide (H₂O₂). The hydrogen peroxide destroys any colour in the fabric through oxidisation with minimal damage to the fibre [14].

The scouring and bleaching pre-treatments are also essential to ensure level and even dyeing. This is particularly important as unlevel dyeings result in second grade fabrics that must be sold at a discount. [14].
The colouring of a textile fabric usually occurs in one of two ways, continuous and batch.

1.6.3.2 Continuous Dyeing

The continuous dyeing process is more appropriate when extremely long runs of the same colour are required. Most commonly, the continuous process is used for dyeing woven cotton and cotton/polyester blended fabrics. The continuous dyeing process can be broken into four stages; dye application by padding, dye fixation, washing off and drying [14].

Cold pad batch dyeing is often used for knitted fabrics. Pad steam dyeing is mostly used for woven fabrics. In this process the dye solution, together with alkali and salt, is padded onto the fabric, which is then immediately steamed at 105°C in saturated steam for 10 minutes.

1.6.3.3 Exhaust Dyeing

Exhaust dyeing is where the dye is exhausted from a larger volume of water into the substrate or fabric. Dyeing time is longer and as dyeing progresses the concentration of dye per litre of liquor decreases as the dye exhausts into the fibre. Batch dyeing is more suited for shorter production runs, allowing for quicker colour changes if required. Further, the machinery takes up less space also permitting multiple machines to be set up for a range of colours.

Within the batch dyeing process there are three different basic methods available. These are:

- the fabric circulates through the liquor;
- the water circulates through the fabric;
- both the fabric and liquor circulated together.

Batch dyeing can vary with the liquor ratio (the quantity of water used per kilogram of fabric), the dyeing temperature and auxiliaries to be used, the type of dyestuff, the
rate and extent of exhaustion, the number of rinse baths required and any subsequent post dyeing treatments [28].

In jig dyeing (Figure 1.8) the fabric is held at full width and passes through the dye liquor. As the fabric is unwound from one roller, it passes through the dye bath and is rewound on the second roller. This process continues until the required depth and levelness in shade is achieved [29]. Salt concentrations can be very high in jig dyeing because of the very low liquor ratio (3-5:1). However the liquor volumes are small and can easily be segregated from the main effluent streams for separate treatment if the dye house is under pressure to reduce salt or colour discharges.

![Figure 1.8 Cross section of a jig dyeing machine [30]](image)

Jet dyeing is a form of dyeing that involves the liquor moving around the fabric and the fabric moving through the liquor typically in a pressure chamber. The dye liquor, which is heated to the required temperature dependant on the dyes being used, penetrates and dyes the fabric. After which, the fabric is then floated through a tube where the liquor also passes through at a faster rate so that the fabric does not touch the side of the tube. This type of dyeing is even ideal for delicate fabrics as there is no tension or pressure applied on the fabric [29]. Jet dyeing represents the most advanced and economical form of dyeing piece goods. Liquor ratios can be as low as 4:1 thereby reducing water usage. However because salts are added in proportion to the fabric weight, the TDS of discharged effluents become greater. It is estimated that over 80% of all fashion apparel world wide is dyed in a jet machine.
In winch dyeing the fabric, in rope form, is drawn through the dye liquor by means of a driven winch creel (Figure 1.10). The fabric is transported under low or zero tension. Long liquor ratios up to 40:1 are employed and therefore high concentrations of salt are required. Care must be taken to ensure that creasing does not occur, as this may cause running marks on the fabric.
1.6.4 Garment Dyeing Processes

An alternative to fabric dyeing, where the fabric is coloured before being cut and sewn into a garment, is garment dyeing [31]. This makes it possible for the dyer to have a stock of greige garments and await instructions as to the colour required. Therefore colouration can take place in a short amount of time. Also, the ability to produce many small batches of different colours is more economically attractive than dyeing cones of yarn various different shades [32].

The process works by loosely packing completed garments into a large nylon net bag. The bag is then placed in a machine known as a paddle dyer, which contains a paddle that agitates the liquor to ensure level dyeing. Garment dyeing is principally used for colouring made up cotton garments [29].

1.7 Options for Reducing Salt

There are two principal ways of reducing the amount of salt used when dyeing cotton. One is to use low salt dyes such as those developed by Ciba. Another option is to pre-treat the fabric with a reagent that performs some of the functions attributed to salt, so that the amount of salt added into the dye bath is reduced.

1.7.1 Low Salt Dyes

In 1995 Ciba developed a type of multifunctional dye known as the CIBACRON® LS dye-stuff range which requires only 25% of the usual recommended amount of salt. It is believed that these dyes contain two monofluorotriazine reactive groups [33].

CIBACRON® LS dyes are less sensitive to changes in the dye liquor ratio and are designed for a hot-exhaust application on cellulosic fibres and fibre blends making it easier to achieve consistent dyeings first time [34].
1.7.2 Pre-treatments

Research studies have identified a number of pre-treatments, which lower the amount of salt required for dyeing cotton. The first study discusses the pre-treatment of cotton with cationic agents [35]. The second, pre-treatment of cotton with fibre reactive chitosan derivatives [36] and the third examines the pre-treatment of cotton with poly(vinylamine chloride) [37].

1.7.2.1 Pre-treatment of Cotton with Cationic Agents

The cationic agents Matexil FC-PN, Matexil FC-ER (ICI Surfactants) and Solfix E (Ciba) have been assessed (Burkinshaw and Gotsopoulos [35]) for the pre-treatment of cotton when dyeing with anionic dyes such as direct dyes.

These three cationic agents are traditionally used as aftertreatments for direct dyes however; in this case they were used as pre-treatments as well as aftertreatments.

Cotton fabric was scoured, bleached and dyed with four different commercial direct dyes; Solophenyl Blue FGL (C.I. Direct Blue 85), Solophenyl Bordeaux 3BL (C.I. Direct Red 83), Solophenyl Scarlet BNL (C.I. Direct Red 89) and Solophenyl Yellow ARL (C.I Direct Yellow 106).

Figure 1.11 illustrates the method in which the pre-treatments were applied to the fabric. The pre-treatments were applied at varying levels of concentration on the weight of the fabric (o.w.f), (0.5%, 1.0%, 2.0% and 5.0%). The application time of the pre-treatment also varied from 10, 20 and 30 minutes, Solfix E was only applied for 30 mins. After treatment, the samples were rinsed in tap water and allowed to air dry.
Figure 1.11 Application methods for cationic fixing agents (numbers in brackets refers to aftertreatment conditions)

Figure 1.12 illustrates the dye application method, after which samples were again rinsed under tap water and allowed to air dry. The samples were dyed with 2 levels of salt concentration, one group was dyed with no salt and the other with 20g/l. The pretreatment chemicals were then reapplied as an aftertreatment in the same manner demonstrated in Figure 1.11, however Matexil FC-PN and Matexil FC-ER were applied at 4% o.w.f and Solfix E was applied at 6% o.w.f.
The colour strength values of the dyeings were analysed as well as the wash and light fastness properties. The values were then compared with those of standard after treated dyeings. The outcomes that arose were that the pre-treated samples had increased colour strength. When dyed in the absence of an electrolyte the pre-treated samples always had higher K/S values than those samples that were not pre-treated.

Of the three pre-treatment chemicals, it was found that Matexil FC-PN and Solfix E behaved similarly. The higher the concentration of the chemical applied onto the fabric, the higher the colour strength of the dyed sample. Overall however, Solfix E was found to be more effective.

The samples that were pre-treated and dyed in the presence of an electrolyte were found to have lower colour strength values, compared to the standard samples dyed under the same conditions. It was also found that the wash fastness properties were unaffected by the pre-treatments. However, the light fastness properties were found to have decreased slightly compared to the light fastness properties of the standard samples.

1.7.2.2 Pre-treatment of Cotton with Fibre Reactive Chitosan Derivatives

A trial on the pre-treatment of cotton was conducted by Lim and Hudson [36]. The aim of their experiment was to trial a fibre-reactive chitosan derivative known as chitosan chloride, with the fibre reactive group being O-acrylamidomethyl-N-[(2-hydroxy-3-trimethyl-ammonium)propyl] – NMA-HTCC. To evaluate the dyeability and fastness properties of the cotton fabric, also the claimed antimicrobial properties were analysed. The NMA-HTCC was applied to the cotton fabric under alkaline conditions and was able to form a covalent bond with the cotton fibre, demonstrated here in Figure 1.13.
In this work 100% cotton fabric that was previously bleached, desized and mercerised was used. Two direct and two reactive dyes were tested, namely, C.I. Direct Blue 78 and C.I. Direct Red 80 and C.I. Reactive Blue 21 and C.I. Reactive Orange 107. The pre-treatment agent NMA-HTCC was dissolved to give three solutions at varying concentrations (0.25%, 0.5% and 1.0%). Each solution had 1.5% sodium hydroxide added as a catalyst. The method of application was by padding with 100% wet pick-up, the samples where then sealed in plastic bags to avoid penetration by air. The samples were left sealed for 24 hours followed by a rinse under cold tap water and then washed in a domestic washing machine for 6 minutes in warm water and air dried.

Both the standard and pre-treated samples were dyed omitting the electrolyte in the pre-treated sample dye bath, Figure 1.14 illustrates the dyeing method.
Figure 1.14 Application method of direct dyes

After dyeing with the direct dyes the samples were thoroughly rinsed in hot water. Those samples that were untreated were rinsed twice more in a 5g/l sodium chloride solution and rinsed under cold tap water until the water ran clear, finally all samples were air dried.

Those standard and pre-treated samples that were dyed with the reactive dyes were dyed using the method illustrated in Figure 1.15. Again those samples that were pre-treated prior to dyeing were dyed without the presence of an electrolyte.

At the completion of dyeing, the samples were rinsed in hot water and soaped with Triton X-100 (a non-ionic surfactant based on nonylphenol ethoxylate at 1g/l at 90°C for 20 minutes. The fabrics were then rinsed thoroughly and air-dried.
The dyed samples were evaluated for their colour strength and fastness properties to washing and light. All fastness tests were carried out according to the American Association of Textile Chemists and Colourist (AATCC) methods.

After evaluating the results, it was found that the samples that were pre-treated with 1% NMA-HTCC and dyed with no salt, had higher colour strength values than those samples that were dyed as per the recommended method in the pattern card with a larger amount of salt. One of the dyes, C.I. Direct Blue 78 when used to dye a sample at 3% o.w.f on fabric pre-treated with 1% NMA-HTCC gave complete dye bath exhaustion and showed a higher colour strength than that of the untreated cotton dyed at 4% o.w.f.

It was found that the wash fastness properties of the pre-treated cotton fabrics were far superior to those of the untreated samples for both the direct and reactive dyes. However, when the light fastness samples were examined it was found that the pre-treated samples exhibited poorer light fastness properties than those of the untreated samples. It was decided that further investigation would be required in order to overcome this problem.

1.7.2.3 Pre-treatment of Cotton with Poly(vinylamine chloride)

Zhang, Tang and Yang [37] studied poly(vinylamine chloride) (PVAmHCL) as a pre-treatment to be applied to cotton in order to achieve salt free dyeing when using reactive dyes. PVAmHCL (Figure 1.16) has been explored as a physical modifying agent and due to its wide variety of properties PVAmHCL has also found use in catalysis, liquid chromatography, treatment of wastewater and in polymeric dyes. The aim of this work was to determine the effectiveness of PVAmHCL as a pre-treatment for cotton in reactive dyeing to improve its dyeability and evenness in dye uptake and finally whether or not the pre-treatment had any effect on the fastness properties of the dyed fabric.

![Figure 1.16 Molecular structure of PVAmHCL](image-url)
100% cotton fabric, which had previously been bleached, sized and mercerised was
dyed with six dyes namely, C.I Reactive Red 2, 3 and 195, C.I. Reactive Blue 4 and
19 and C.I. Reactive Orange 16.

The PVAmHCL was applied via the pad-bake method, applying 5g/l of the
PVAmHCL with 80% wet pick up. The fabric was dipped and nipped twice and then
dried at room temperature before being baked for 10 minutes at 100°C.

As well as dyeing the pre-treated fabrics; standard fabrics were also dyed. Once
dyeing was complete the samples were rinsed in cold, hot and then cold water before
being boiled in a solution containing 2g/l of an anionic detergent followed by a final
rinsing. The samples were then allowed to air dry.

The degree of dye exhaustion was evaluated. Cross-sections of the fabrics were
examined microscopically, and the colourfastness to washing and rubbing determined.

The conclusions that arose from the experimental work were; fabrics pre-treated with
5g/l of PVAmHCL at pH 7, when compared to fabrics dyed in the conventional
manner, displayed improved reactivity and fixing for the majority of the reactive
dyes dyed without salt. Through a cross-section examination it was discovered that
the dye penetrated the entire fibre, from outer to core. The wash fastness and rub
fastness properties were reduced however; dye in the effluent was also reduced which
demonstrated the commercial potential of PVAmHCL as a pre-treatment for cotton.

1.8 Summary

Generally, it is now widely known that the amount of salt used in the direct dyeing
and reactive dyeing processes is having a serious impact on the environment. One
conclusion that a number of researchers have drawn to is to change the surface of the
cotton fabric/fibre in order for it to become more attractive to a direct or reactive dye
therefore reducing the need for such a large amount of salt.

This study aims to investigate two new pre-treatment agents on their ability to reduce
salt usage when dyeing 100% cotton fabric with reactive and direct dyes. The study
also explores the most efficient method of application of the pre-treatments. The outcomes have applicability to jet dyeing woven and knitted cotton fabric.
Chapter 2
Materials and Methodology
2.1 Introduction

The aim of this research was to reduce the amount of salt used in dyeing of 100% cotton fabric. Modification of steps within the dyeing process may reduce the requirement for salt and water throughout the process, without impacting upon the final quality of the product. Such modifications would have to be cost effective and of low risk for industry to implement.

2.2 Materials

2.2.1 Fabric

100% cotton fabric – bleached, scoured and ready to dye with the following specifications was used in the present investigation:

Fabric weight: 188.7g/m²
Fabric construction: plain weave, 25 ends/cm and 20 picks/cm

2.2.2 Chemicals

2.2.2.1 Pre-treatment Chemicals

2.2.2.1 (A) Chitosan

Chitosan, a derivative of chitin, is a polysaccharide sourced from crab and lobster shells (Figure 2.1).

![Chemical structure of Chitosan](image)

Figure 2.1 Chemical structure of Chitosan [46]
Chitosan, when applied to cotton prior to dyeing, is known to increase the dyeability of direct and reactive dyes. It is also known to minimise the colour difference between mature and immature cotton on dyeing [40]. Chitosan used was supplied by Sigma Aldrich [41] and a Material Safety Data Sheet for Chitosan can be found in Appendix I.

2.2.2.1 (B) Cibafix ECO

Cibafix ECO is a proprietary polyethylene polyamine manufactured and supplied by Ciba Specialty Chemicals, which is also free from formaldehyde and zinc. It is used in industry to improve the wet fastness improver of dyeings. This product also prevents dye migration after dyeing and protects the dye/fibre linkage of reactive dyes against acid hydrolysis and thermo-cracking [42]. A MSDS for Cibafix ECO (now known as Albafix ECO) can be found in Appendix II.

2.2.2.2 Dyestuffs

Three dyes were used throughout this investigation. Two were different reactive dyes; Sumifix Supra Navy 3GF 150% supplied by Sumitomo Chemicals a hetero bifunctional reactive and Procion Brilliant Scarlett H-EXL a homo bifunctional reactive supplied by BASF. The third dye used was a direct dye – Solophenyl Rubine RNL a SDC class B direct supplied by Ciba Specialty Chemicals. The colour of the three dyes is shown in Figure 2.2.

![Figure 2.2](image)

(1) Sumifix Supra Navy 3GF 150%, (2) Procion Brilliant Scarlett H-EXL, (3) Solophenyl Rubine RNL

The principal dye used throughout the trial was the Sumifix Supra Navy 3GF 150% because this is a bifunctional dye which contains higher colour strength and higher exhaustion properties.
2.2.3 Other Chemicals and Auxiliaries

A list of the various chemicals and auxiliaries used is given below along with the supplier:

- Sodium Hexametaphosphate Powder: Ajax Chemicals
- Glauber’s Salt Anhydrous GR: Chemplas
- Sodium Carbonate (Soda Ash) GR: Science Supply Australia
- Acetic Acid GR: Science Supply Australia
- Dispersant AD: York Chem Australia Pty Ltd
- Dispersant 2000: York Chem Australia Pty Ltd

2.3 Pre-treatment of Fabrics

A stock solution of Chitosan was prepared by dissolving Chitosan powder in a 1.25% solution of acetic acid. Cibafix ECO was used in liquid form as received.

2.3.1 Application of Chitosan and Cibafix ECO – Method 1

Auxiliaries:
- 10% solution of sodium carbonate
- 1.67% solution of Chitosan (in 1.25% acetic acid) or, Cibafix ECO
- 10% solution of acetic acid

During pre-treatment of cotton fabric the Chitosan and Cibafix ECO were both applied to the cotton by exhaustion method using the Ahiba Turbocolour machine at a liquor ratio at 10:1. Approximately 55g of cotton fabric was treated with 0.5, 0.8 and 1.0% of Chitosan, and 1.0, 2.0, 5.0 and 7.0% of Cibafix ECO respectively. The fabric was wound onto a perforated cylinder, which allowed complete and even coverage by the pre-treatment chemical onto the fabric. The cylinder was then placed in the machine and the machine was filled with the initial amount of water. The pH was adjusted to pH 7.5 – 8 and left to circulate for 5 minutes at room temperature. Either
Chitosan or Cibafix ECO was added to the baths as required and the temperature was raised to 60°C for Chitosan and 40°C for Cibafix ECO, over 20 minutes. The fabrics were then treated at this temperature for further 20 minutes. The pH was then reduced to pH 5 – 5.5 with acetic acid and circulation was continued for 5 minutes, followed by thorough rinsing in cold water. All samples were placed in a cabinet dryer to be air-dried before dyeing.

2.3.2 Pre-treat, Rinse, No Dry – Method 2

Auxiliaries:
10% solution of sodium carbonate
1.67% solution of Chitosan or, Cibafix ECO
10% solution of acetic acid

A second group of fabric samples was pre-treated in a similar manner to that mentioned in 2.3.1. However in this instance, once the rinse bath was dropped a fresh bath of water was immediately refilled ready for the dyeing process to begin.

2.3.3 Pre-treat, No Rinse, No Dry – Method 3

Auxiliaries:
10% solution of sodium carbonate
1.67% solution of Chitosan or, Cibafix ECO
10% solution of acetic acid

A third group of fabrics were pre-treated also in a similar way to that discussed in 2.3.1 however, in this series, the final rinse was omitted and the bath immediately refilled ready for the dyeing process to begin.
2.4 Dyeing of Fabrics

2.4.1 Dyeing with Sumifix Supra Navy 3GF 150%

The pre-treated fabric samples were dyed according to the procedure shown in Figure 2.3. Fabric samples pre-treated with Chitosan and Cibafix ECO were dyed with a varying amount of salt from each group as given in Table 2.1. A reference sample was also dyed with no pre-treatment being applied and as per the pattern card with 100% of the required amount of salt. This reference sample was then compared with the dyed samples for colour strength and fastness properties.

![Figure 2.3 Dye method from Sumitomo pattern card](image)

Auxiliaries used in dyeing (as per pattern card):
- 1g/l Sodium Hexametaphosphate
- 50g/l Glauber’s Salt Anhydrous
- 20g/l Sodium Carbonate
- 20g/l Acetic Acid
- 2g/l Dispersant AD

Each group contained 7 fabric samples; three were pre-treated with Chitosan at the concentrations of 0.5%, 0.8% and 1.0% and four were pre-treated with Cibafix ECO at the concentrations of 1.0%, 2.0%, 5.0% and 7.0%.
Table 2.1 Fabric groups and levels of salt used for dyeing

<table>
<thead>
<tr>
<th>Group</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
<th>Group 4</th>
<th>Group 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%, 0.8% &amp; 1.0% Chitosan treated 1.0%, 2.0%, 5.0% &amp; 7.0% Cibafix ECO treated</td>
<td>100% salt 50g/l</td>
<td>75% salt 37.5g/l</td>
<td>50% salt 25g/l</td>
<td>25% salt 12.5g/l</td>
<td>0% salt 0g/l</td>
</tr>
</tbody>
</table>

Though the dye manufacturer’s pattern card recommends a liquor ratio of 20:1, because of the limitations due to the capacity of the machine, the dyeings were carried out at a liquor ratio of 10:1. Fabrics were dyed one at a time on an Ahiba Turbocolour machine. The fabric samples were individually wound on to perforated cylinders, similar to those used for the pre-treatment application and inserted into the machine. Dyeing then proceeded according to the pattern card (Figure 2.3) except with the varying amount of salt depending on which group was being dyed. Once dyeing was complete, the dye bath was drained and a fresh bath of water was introduced. The sample was then neutralised with acetic acid and left to circulate. The bath was again drained and a fresh bath introduced. A hot rinse was then performed with the temperature raised to 80–90°C (85°C) over 10 minutes and left to circulate for a further 10 minutes. The holder was again emptied and refilled with 2g/l of dispersant AD and the temperature raised to 95–98°C (97°C) over 10 minutes and continued to circulate for a further 10. Finally the liquor was drained, refilled with water and a cold rinse was applied for 5 minutes. All samples were then left to air dry in a cabinet dryer.

2.5 One-bath Method

During the study, the question was raised whether or not the pre-treatment chemical could be added into the dye bath to create a one bath pre-treatment/dyeing process. If so, would this allow the elimination of the pre-treatment as a separate step and result in less water usage and a shorter process cycle? These trials were conducted with 2.0% Cibafix ECO and dyed with 75% of the recommended amount of salt.
2.5.1 Pre-treatment Chemical Added in Dye Bath

Auxiliaries used in dyeing (as per pattern card):
1g/l Sodium Hexametaphosphate  
50g/l Glauber’s Salt Anhydrous  
20g/l Sodium Carbonate  
2.0% Cibafix ECO  
20g/l Acetic Acid  
2g/l Dispersant AD

Approximately 55g of cotton fabric was wound on a perforated cylinder and inserted into the Ahiba Turbocolour machine. The machine was filled with water at a temperature of 40°C. The required amount of Cibafix ECO was introduced into the bath and was left to circulate for 30 minutes. Dyeing then continued as normal according to the Sumitomo pattern card illustrated in Figure 2.3. The samples were rinsed as previously mentioned, with one hot rinse at 85°C, a soaping off at 97°C, and a cold rinse. The samples were then air dried in a cabinet dryer.

2.5.2 Pre-treatment as Post-treatment

Auxiliaries used in dyeing (as per pattern card):
1g/l Sodium Hexametaphosphate  
50g/l Glauber’s Salt Anhydrous  
20g/l Sodium Carbonate  
2.0% Cibafix ECO  
20g/l Acetic Acid  
2g/l Dispersant AD

Approximately 55g of cotton fabric was wound on a perforated cylinder and inserted into the Ahiba Turbocolour machine. Dyeing was carried out according to the pattern card (Figure 2.3). After 45 minutes of dyeing, the required amount of Cibafix ECO was added, and dyeing continued as normal. The liquor was drained and refilled and the sample was neutralised with acetic acid. The sample was rinsed at a temperature of 80 – 90°C (85°C) for 10 minutes. This was followed by a soaping off in a fresh
bath of water at a temperature of 95 – 98°C (97°C), for 10 minutes. Finally, a cold rinse was applied to remove any residual dye remaining on the surface of the fabric. The sample was then air dried in a cabinet dryer.

2.6 Dyeing with Procion Brilliant Scarlett H-EXL

Two fabric samples weighing approximately 55g were dyed with Procion Brilliant Scarlett H-EXL. One fabric was pre-treated with 2.0% Cibafix ECO and dyed with 75\% of the required amount of salt as recommended by the manufacturer; the other was a reference sample with no pre-treatment applied and dyed with 100\% of the recommended amount of salt.

Auxiliaries used in dyeing (as per pattern card):
Dye: 2\% owf
1g/l Sodium Hexametaphosphate
60g/l Glauber’s Salt Anhydrous
20g/l Soda Ash
2g/l Dispersant 2000

The fabric samples were wound on a perforated cylinder and inserted to the Ahiba Turbocolour dyeing machine. The pattern card recommended starting temperature of 30 – 35°C was employed. Glauber’s salt and sodium hexametaphosphate was added to the bath and circulated for 5 minutes. The required amount of dye was added into the liquor and the temperature was raised to 80°C over 20 minutes. Once at 80°C, half the required amount of soda ash was added and left to circulate for 10 minutes, after which the second half was added. Dyeing continued for 60 minutes, after which the liquor was drained and refilled to allow a rinse to circulate at 85°C for 10 minutes. The liquor was then drained and refilled and a soaping off was performed at 97°C with 2g/l of dispersant 2000. The samples were then air dried in a cabinet dryer.
2.7 Dyeing with Solophenyl Rubine RNL

Two fabric samples weighing approximately 55g were dyed with Solophenyl Rubine RNL. One fabric was pre-treated with 2.0% Cibafix ECO and dyed with 75% of the required amount of salt recommended by the manufacturer; the other was a reference sample with no pre-treatment applied and dyed with 100% of the recommended amount of salt.

Auxiliaries used in dyeing (as per pattern card):
Dye: 2% owf
1g/l Sodium Hexametaphosphate
20g/l Glauber’s Salt Anhydrous
2g/l Dispersant 2000

The samples were wound on a perforated cylinder and inserted into the Ahiba Turbocolour machine. The pattern card recommended a starting temperature of 50°C. The liquor was set to circulate for 5 minutes to wet out the fabric (Figure 2.4). The glauber’s salt and sodium hexametaphosphate were then added to the bath and circulated for 5 minutes. The required amount of dye was added to the liquor and the temperature of the dye bath was raised to 100°C over 30 minutes. The dyeing process continued for 60 minutes. The dye bath was then drained and refilled, and a warm (40°C) rinse was carried out followed by soaping off with 2g/l of dispersant 2000. The samples were then air dried in a cabinet dryer.

Figure 2.4 Dye method by Ciba pattern card
2.8 Measurement of Exhaustion Levels

During each of the dyeings, samples of liquor were taken at various stages to measure the level of exhaustion throughout the dyeing process. These stages were:

- Before the addition of alkali;
- Every 10 minutes after dye temperature was reached.

Dye liquor samples were then measured on a Hitachi/Model 101 Absorption Spectrophotometer (Figure 2.5).

![Figure 2.5 Hitachi/Model 101 Absorption Spectrophotometer](image)

A calibration curve was generated to determine how much dye (g/l) remained in the liquor at the various intervals during the dyeing process (Figure 2.6). This was determined by having a known amount of dye in liquor and gradually diluting it to obtain known transmission values.

![Figure 2.6 Calibration Curve](image)
The calibration curve illustrates that as the transmission value increases, the amount of dye remaining in the liquor decreases. Using this graph in conjunction with the other graphs produced it is possible to determine the amount of dye that has exhausted onto the fabric during the dyeing process.

2.9 TDS Evaluation by Evaporation

A sample of the dye bath liquor was taken from each dyeing upon completion, and TDS was measured through a process of evaporation. The procedure was as follows; porcelain dishes were prepared by placing them in an oven to dry at 105°C±3°C for a 1 hour minimum. With tongs, the dishes were then removed from the oven and placed into a desiccator, cooled for 2 hours. Each dish was weighed. A known measurement of dye bath liquid (where possible, 25mls was taken otherwise the maximum amount possible) was poured into the dish while still on the scales and the weight recorded. Then the dish, filled with the dye bath liquor was placed in the oven with a set temperature of 105°C to evaporate overnight. Once evaporated the dishes were removed from the oven with tongs and cooled in the desiccator for 2 hours. The dishes were re-weighed and the weights recorded. Table 2.2 demonstrates the calculation of TDS via the evaporation method.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of porcelain dish (g)</td>
<td>Mass of porcelain dish plus solids (g)</td>
<td>Mass of solids (mg)</td>
<td>Total volume (L)</td>
<td>TDS (mg/l)</td>
</tr>
<tr>
<td>72.37</td>
<td>72.40</td>
<td>30</td>
<td>0.025</td>
<td>1200</td>
</tr>
</tbody>
</table>

Procedure for calculations.
A – mass of empty dish
B – mass of dish with dried solids
C – mass of solids (g) = B – A
D – total volume (L) = ml water / 1000
E – TDS = C/D
2.10 Colour Strength Evaluation

On completion of dyeing and drying the colour strength (K/S) was measured using a Datacolor Spectraflash (SF) 600 spectrophotometer (Figure 2.7) and Datacolor TOOLS® software. Three measurements were taken from each sample and then averaged.

![Figure 2.7 Datacolor Spectraflash (SF) 600 spectrophotometer](image)

2.10.1 K/S Values

The Kubleka-Munk series of equations is the mathematical basis of all colour measuring software (Tech Exchange, 2008). These equations indicate that “for opaque samples such as textile materials, the ratio of total light absorbed and scattered by a mixture of dyes is equal to the sum of the ratios of light absorbed and scattered by the dyes measured separately”. If absorption is defined as ‘K’ and scattering defined as ‘S’, Kublka-Munk states that:

\[
\text{K/S mixture} = (\text{K/S}) \text{ dye 1} + (\text{K/S}) \text{ dye 2} + (\text{K/S}) \text{ dye 3} + \ldots
\]

K/S is calculated from the reflectance value of a sample (R) by the Kublka-Munk equation, which states:

\[
\frac{\text{K/S}}{\text{2R}} = (1 - \text{R})
\]

One example, if a fabric has a reflectance of 20% at a 500nm wavelength, the K/S value can be calculated as:
\[
K/S = \left(1 - 0.2\right) = 1.6 \\
2(0.2)
\]

K/S equations can be used to calculate the build up of a particular dye. There is a direct relationship between K/S and dye concentration. When dark shades such as navy and black are used there can be considerable differences in reflectance at high concentrations. This can result in divergences from the linearity from the Kubelka-Munk theory mainly due to surface reflection characteristics resulting in lower reflectances [22]. As the main dye used in this study was a navy blue this statement may need to be considered when taking measurements for evaluation further on.

2.11 Colourfastness Testing

Colourfastness testing was performed on all dyed samples in order to evaluate the fastness properties of the fabric when exposed to various conditions. All colourfastness testing was carried out in the laboratories of RMIT Textile Testing Services.

2.11.1 Colourfastness to Washing

Washing fastness was assessed in prolonged (60 minutes), moderate temperature (60°C) conditions of machine laundering in the presence of soap and sodium carbonate and was carried out in a James Heal & Co. gyrowash featured in Figure 2.8 and 2.9. Tests were carried out according to AS 2001.4.15 – 2006, Colourfastness tests – Determination of colourfastness to washing – Test E.

![Figure 2.8 James Heal & Co. Gyrowash](image1)

![Figure 2.9 Steel canisters inside the Gyrowash](image2)
2.11.2 Colourfastness to Perspiration

Colourfastness to perspiration tests were carried out to determine the fastness properties of the samples when exposed to both alkaline and acidic perspiration. The test was carried out according to AS 2001.4.E04 – 2005, Colourfastness tests – Determination of colourfastness to perspiration.

2.11.3 Colourfastness to Rubbing

Rubbing tests were carried out on a crockmeter to assess the level of dye transfer when rubbed. Tests were carried out according to AS 2001.4.3 – 1995, Colourfastness tests – Determination of colourfastness to rubbing.

2.11.4 Colourfastness to Light

Samples were exposed to an MBTF lamp for a total of 120 hours to measure their resistance to fading when exposed to light. This is a modified test, which was carried out according to AS 2001.4.21 – 2006, Colourfastness tests – Determination of colourfastness to light using an artificial light source (mercury vapour, tungsten filament, internally phosphor-coated lamp) with the modification being 120 hour exposure.
Chapter 3
Results and Discussion
3.1 Introduction

The experimental results are presented in a series of tables and graphs. This allows evaluation of how the various pre-treatments and their different methods of application affect the amount of colour and salt released to effluent. The amount of colour remaining in the dye liquor on completion of dyeing was measured. TDS levels were also measured on completion of dyeing. Colour strength was assessed instrumentally and colourfastness properties were considered.

The manufacturer’s salt recommendation was 50g/l; as such 100% salt indicates that the total amount of salt recommended was used. Where 75% salt is stated this means that only 37.5g/l of salt was used instead of the recommended 50g/l. 50% salt is equal to 25g/l, 25% salt is equal to 12.5g/l and 0% salt means that no salt was used. For simplicity and better understanding results, with different classes of dyes such as Sumifix Supra Navy 3GF 150%, Procion Brilliant Scarlett H-EXL and Solophenyl Rubine RNL are discussed separately in 3.2.1 and 3.6 and 3.9 respectively.

3.2 Samples dyed with Sumifix Supra Navy 3GF 150%

3.2.1 Rate and Extent of Dye Exhaustion

3.2.1.1 Pre-treated Samples Dyed – 100% Salt

These samples were dyed using Sumifix Supra Navy 3GF 150% using 100% salt. The method of pre-treatment application through to dyeing was pre-treat, rinse, dry and then dye.
The presence of Chitosan accelerates the rate of dyeing and increases the exhaustion level of the bath. For the first 40 minutes of dyeing the rate of dyeing increases as the concentration of Chitosan on the fibre increases (Figure 3.1). After 40 minutes of dyeing the rate differences between the different levels of Chitosan decreased. This may be due to a transfer of Chitosan from the fabrics. While this may occur the results clearly show that Chitosan increases both the rate of dyeing and the exhaustion. The quality of the dyed samples was acceptable as there was no unlevel appearance on the fabric surface.

The presence of Cibafix ECO also increases the exhaustion (Figure 3.2). However in this case a concentration of 5% and 7% is required to produce a meaningful improvement. The quality of the dyed sample was also acceptable as it had a level appearance.

This shows that the presence of Chitosan and Cibafix ECO caused improved transfer of dye from the bath to the fibre. Using the calibration curve shown in Figure 2.6, along with Figures 3.1 and 3.2, the amount of dye remaining in the dye bath at the end of the dyeing process was determined.
The relevance of the exhaustion results indicates how much dye was exhausted from the bath onto the fibre. With the exception of 1.0% Cibafix ECO sample all pretreated samples exhausted 2 – 3% more than the reference sample. This results in more dye being passed onto the fibre and not into the effluent.

Table 3.1 Residual dye in bath on completion of dyeing – 100% salt

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>Dye in liquor g/l (initial amount 3g/l)</th>
<th>Exhaustion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0% Chitosan</td>
<td>0.36</td>
<td>88.0</td>
</tr>
<tr>
<td>5.0% Cibafix ECO</td>
<td>0.37</td>
<td>87.7</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
<td>0.38</td>
<td>87.7</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>0.40</td>
<td>86.7</td>
</tr>
<tr>
<td>0.8% Chitosan</td>
<td>0.42</td>
<td>86.0</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>0.45</td>
<td>85.0</td>
</tr>
<tr>
<td>Reference</td>
<td>0.47</td>
<td>84.3</td>
</tr>
<tr>
<td>1.0% Cibafix ECO</td>
<td>0.49</td>
<td>83.7</td>
</tr>
</tbody>
</table>
3.2.1.2 Pre-treated Samples Dyed – 75% Salt

This experiment again uses samples dyed with Sumifix Supra Navy 3GF 150% but with only 75% salt. The method of pre-treatment application through to dyeing was pre-treat, rinse, dry then dye.

Figure 3.3 Extent of exhaustion of Chitosan samples dyed with 75% salt

Figure 3.4 Extent of exhaustion of Cibafix ECO samples dyed with 75% salt

Figure 3.4 shows that when the salt concentration is decreased by 25% the absorption of dye onto the fibre decreases. The best exhaustion was achieved with 7.0% Cibafix
ECO closely followed by 2.0% Cibafix ECO sample, which finished just below the reference sample dyed with 100% salt. However, both Cibafix ECO samples achieved greater exhaustion than the reference sample dyed with 75% salt. The extent of exhaustion of the Chitosan samples (Figure 3.3) was poorer than both the reference samples.

Figure 3.3 shows that the dye uptake of the 7.0% Cibafix ECO sample was quite rapid in the first twenty minutes after the dyeing temperature was reached. It then continued to increase at a steady rate until the end of the dyeing, i.e. after the initial phase of the dyeing the exhaustion rate slows down to become constant.

The initial dye uptake of the 2.0% Cibafix ECO sample was gradual until the interval between the tenth and twentieth minutes. Here, there was a rapid increase in dye uptake. From the twentieth minute onwards, the sample continued to absorb dye at a steady rate.

For the 1.0% Chitosan sample, Figure 3.3 indicates that the exhaustion occurred in a similar pattern to the 2.0% Cibafix ECO sample in Figure 3.4. Table 3.2 demonstrates the exhaustion rate in g/l.

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>Dye in liquor g/l</th>
<th>Exhaustion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0% Cibafix ECO</td>
<td>0.31</td>
<td>89.7</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>0.38</td>
<td>87.3</td>
</tr>
<tr>
<td>75% Reference</td>
<td>0.44</td>
<td>85.3</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>0.46</td>
<td>84.7</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
<td>0.47</td>
<td>84.3</td>
</tr>
<tr>
<td>100% Reference</td>
<td>0.47</td>
<td>84.3</td>
</tr>
</tbody>
</table>

### 3.2.1.3 Pre-treated Samples Dyed – 50% Salt

These samples were dyed with Sumifix Supra Navy 3Gf 150% using 50% salt. The method of pre-treatment application through to dyeing was pre-treat, rinse, dry then dye.
Figure 3.5 and Figure 3.6 clearly show that when the amount of salt is significantly reduced, the pre-treatments become negative in their effect on dye exhaustion.

The exhaustion levels of both reference samples have superior exhaustion capabilities than the pre-treated samples. 1.0% Cibafix ECO performed worse when dyed with 100% salt. This pre-treatment is most effective and results a degree of exhaustion closest to the reference sample.

Figure 3.5 Extent of exhaustion of Chitosan samples dyed with 50% salt

Figure 3.6 Extent of exhaustion of Chitosan samples dyed with 50% salt
Using the calibration curve, the amount of dye left in the liquor was determined and is shown in Table 3.3.

As the level of salt used decreases, the performance of the Cibafix ECO appears stronger than the Chitosan. Whereas, in comparison, Table 3.1 shows the performance of exhaustion levels alternating between Chitosan and Cibafix ECO.

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>Dye in liquor g/l</th>
<th>Exhaustion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Reference</td>
<td>0.47</td>
<td>84.3</td>
</tr>
<tr>
<td>1.0% Cibafix ECO</td>
<td>0.48</td>
<td>84.0</td>
</tr>
<tr>
<td>75% Reference</td>
<td>0.49</td>
<td>83.7</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>0.50</td>
<td>83.3</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>0.58</td>
<td>80.7</td>
</tr>
<tr>
<td>0.8% Chitosan</td>
<td>0.79</td>
<td>73.7</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
<td>0.91</td>
<td>69.7</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>0.91</td>
<td>69.7</td>
</tr>
</tbody>
</table>

### 3.2.1.4 Pre-treated Samples Dyed – 25% Salt

These samples were dyed with Sumifix Supra Navy 3Gf 150% using 25% salt. The method of pre-treatment application through to dyeing was pre-treat, rinse, dry then dye.
In Figure 3.7 and Figure 3.8 the pre-treated samples dyed with 25% of the required amount of salt along with those dyed with 50% salt, are not commercially viable. Due to the poor exhaustion levels of the dye, the sample treated with 0.5% Chitosan did not appear to absorb any dye until 30 minutes after dyeing temperature had been reached. Figures 3.7 and 3.8 indicate that, salt is still an important part of the dyeing process. This Figure also confirms that, as the salt concentration decreases, the presence of Chitosan becomes increasingly negative on dye exhaustion. Figures 3.7 and 3.8 also confirm that dyeing becomes virtually ineffective at salt concentrations less than 50% of the manufacturer’s recommended levels of salt.
Table 3.4 Residual dye in bath on completion of dyeing – 25% salt

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>Dye in liquor g/l</th>
<th>Exhaustion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Reference</td>
<td>0.47</td>
<td>84.3</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>0.48</td>
<td>84.0</td>
</tr>
<tr>
<td>5.0% Cibafix ECO</td>
<td>0.65</td>
<td>78.3</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>0.68</td>
<td>77.3</td>
</tr>
<tr>
<td>1.0% Cibafix ECO</td>
<td>0.80</td>
<td>73.3</td>
</tr>
<tr>
<td>25% Reference</td>
<td>0.90</td>
<td>70.0</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>0.98</td>
<td>67.3</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
<td>1.15</td>
<td>61.7</td>
</tr>
<tr>
<td>0.8% Chitosan</td>
<td>1.15</td>
<td>61.7</td>
</tr>
</tbody>
</table>

Table 3.4 also indicates that Cibafix ECO pre-treatment is more effective as a ‘salt replacement’ than Chitosan. This indicates that Cibafix ECO seems to be more viable as a pre-treatment for commercial purposes.

3.2.1.5 Pre-treated Samples Dyed – With No Salt

These samples were dyed with Sumifix Supra Navy 3Gf 150% without any salt. The method of pre-treatment application through to dyeing was pre-treat, rinse, dry and then dye.

Figure 3.9 Extent of exhaustion of Chitosan samples dyed with no salt
Figure 3.9 and Figure 3.10 display extremely poor exhaustion levels for the pre-treated samples. According to Figure 3.9, the 0.5% Chitosan sample appears to not have absorbed any dye. This shows that some salt must be included in the dye bath to promote exhaustion.

**Figure 3.10 Extent of exhaustion of Cibafix ECO samples dyed with 0% salt**

**Table 3.5 Residual dye in bath on completion of dyeing – 0% salt**

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>Dye in liquor g/l</th>
<th>Exhaustion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Reference</td>
<td>0.47</td>
<td>84.3</td>
</tr>
<tr>
<td>1.0% Cibafix ECO</td>
<td>0.83</td>
<td>72.3</td>
</tr>
<tr>
<td>5.0% Cibafix ECO</td>
<td>1.15</td>
<td>61.7</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>1.15</td>
<td>61.7</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>1.21</td>
<td>59.7</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
<td>1.27</td>
<td>57.7</td>
</tr>
<tr>
<td>0.8% Chitosan</td>
<td>1.27</td>
<td>57.7</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>1.27</td>
<td>57.7</td>
</tr>
</tbody>
</table>

Referring to Table 3.5, the amount of dye left in the dye bath liquor for all samples – excluding the 1.0% Cibafix ECO sample, was greater than 1g/l. This amount is more than double that of the reference sample when dyed with 100% salt. It can be concluded that dyeing the pre-treated samples with 0% salt and 25% was not a viable option for commercial use. Once again all the Cibafix ECO samples finished above
the Chitosan samples. Also, all of the Chitosan samples achieved the same result of 1.269g/l when evaluated on the absorption spectrophotometer resulting in 57.7% of dye being exhausted from the bath.

![Figure 3.11 Extent of Exhaustion vs Levels of salt when using Chitosan](image1)

![Figure 3.12 Extent of Exhaustion vs Levels of salt when using Cibafix ECO](image2)

Figures 3.11 and 3.12 show that even with the use of pre-treatment chemicals such as Chitosan and Cibafix ECO salt is still a necessary part of the dyeing process. However, Chitosan and Cibafix ECO could be used partly as a ‘salt substitute’. Figure 3.11 shows that Chitosan is really only effective when 100% of the
manufacturer’s recommended salt levels are used, whereas Figure 3.12 promotes exhaustion relative to salt alone at all concentrations.

Having trialled varying amounts of salt in the dyeing process, it was concluded that the optimum amount required when used in conjunction with the pre-treatment was 75%. This amount of salt was used in further trials.

3.2.2 Pre-treat, Rinse, Dye – 75% Salt

In the following series of experiments the drying step was omitted to provide a simpler ‘one-step’ process. All other procedures remained the same.

![Figure 3.13 Extent of Exhaustion of samples dyed with 75% salt with a rinse in between](image)

All pre-treated samples began the dyeing process with higher exhaustion levels than the reference sample (Figure 3.13). However, between the 10th and 20th minute, both Chitosan samples begin to fall below the reference sample. The best performing sample was the 7.0% Cibafix ECO treated sample finishing with 87% exhaustion. The 0.5% and 1.0% Chitosan samples finished with an exhaustion level of 84% and 85% respectively. The 2.0% Cibafix ECO sample finishes with the same extent of exhaustion as the reference sample – 84.3%.
When compared to Figure 3.3 and Figure 3.4, the samples in Figure 3.13 all finish with lower exhaustion levels except for the sample pre-treated with 2.0% Cibafix ECO which had an increase in exhaustion to 84.3% to match the reference sample.

### 3.2.3 Pre-treat, No Rinse, Dye – 75% Salt

This procedure is the same for the above experiment except that the rinse step is omitted; again to simplify the process.

Again, all the samples in Figure 3.14 begin the process with an initial higher dye uptake than the reference sample. Both Cibafix ECO samples resulted in a higher level of dye exhaustion than the reference sample. The two Chitosan samples again finished below the reference. The 0.5% Chitosan finished with an extent of exhaustion of 84.5% and the 1.0% Chitosan treated finished with an exhaustion level of 85%. The 7.0% Cibafix ECO finished with the highest exhaustion level of 90.2%. Finally, the 2.0% Cibafix ECO sample also finished higher than the reference sample with 87.7% of dye being exhausted from the dye bath.

![Figure 3.14 Extent of exhaustion of samples dyed with 75% salt with no rinse in between](image)

The exhaustion level of the samples dyed in Figure 3.14 is greater than those samples dyed in Figure 3.3 and Figure 3.4. This is most likely due to the loss of Chitosan and
Cibafix ECO when the rinsing step is included as it was for the samples shown in Figures 3.3 and 3.4.

The following experiments show the effectiveness of Cibafix ECO when the fabric is firstly pre-treated as normal, and then in the same bath dyeing continued as normal. The aim of this experiment was to determine if this pre-treatment process was still effective while saving time by eliminating rinse cycles and also to see if any additional water could be saved.

The second experiment where Cibafix ECO was used as a post-treatment, was to determine the effectiveness of the chemical when added towards the end of the dyeing process – as Cibafix ECO is traditionally used as an after treatment.

3.2.4 Pre-treatment Chemical Added in Dye Bath

This procedure is the same as 3.2.2 and 3.2.3 except that the dropping of the pre-treatment bath was omitted in order to continue dyeing in the same liquid.

![Graph showing extent of exhaustion]  
**Figure 3.15 Extent of exhaustion – 75% salt with pre-treatment applied in the same bath as dyeing**

As shown in Figure 3.15 the 0.5% and 1.0% Chitosan samples and 2.0% Cibafix ECO sample complete the dyeing process with a lower extent of exhaustion than the reference sample dyed with 100% salt. However, the 1.0% Chitosan and 2.0% Cibafix ECO treatment exhausted more than the reference sample dyed with the same
level of salt i.e. 75%. The 0.5% Chitosan sample completed the dyeing with an exhaustion level of 76.7%. The 1.0% Chitosan sample ended the process with 85.3% exhaustion.

However, the behaviour of the 2.0% Cibafix ECO sample demonstrates an unusual dyeing pattern. The sample starts with an initial dye uptake of 0.406g/l. Over the next 20 minutes the dye appears to come off the fabric and re-enter the dye bath. The sample then finishes the dyeing process with 0.413g/l of dye remaining in the dye bath. This is due to the dye penetrating and levelling within the fibre.

The 7.0% Cibafix ECO demonstrated excellent exhaustion properties, finishing with 0.069g/l of dye in the liquor. However, during the sampling of the dye bath it was observed that when left to settle in the test tubes the dye began to separate from the liquor (Figure 3.16).

![Figure 3.16 Dye bath liquor of 7.0% Cibafix ECO during one bath process](image)

The samples were left to sit in the test tubes for 30 minutes. After which, the clear liquid could be poured out leaving the precipitated dye remaining in the test tube.

This clearly shows that the dye was precipitating and separating out from the dye bath and not transferring into the fabric. Although a result such as this would totally uncommercial from a dyer’s point of view. However, from an environmental point of view, this type of result could be seen as another way to remove colour from dye house effluent.
3.2.5 Cibafix ECO as a Post-treatment

![Graph showing extent of exhaustion of 2.0% Cibafix ECO dyed with pre-treatment as post-treatment.](image)

Figure 3.17 Extent of exhaustion - 75% salt with pre-treatment added at the 45th minute as a post-treatment

This post treatment experiment was performed only with 2.0% Cibafix ECO. Approximately 55g of untreated cotton fabric was dyed as per the pattern card according to the manufacturer’s recommendations. Here the Cibafix ECO was added at the 45th minute of dyeing time in order to determine whether the chemical had any effect on the uptake of dye when used a post-treatment.

The pre-treated sample does not appear to be absorbing dye from the dye bath, until the 50th minute of dyeing when a rapid increase in dye uptake finishing the process with less dye remaining in the bath. When analysing this graph against the calibration curve (Figure 2.6) the amount of dye in the dye bath was 0.388g/l. The reference sample liquor contained 0.469g/l.

3.3 Total Dissolved Solids – Sumifix Supra Navy 3GF 150%

TDS was measured from the dye bath liquor at the end of dyeing. The samples were tested as received. Measurement of TDS was carried out according to the method described in section 2.8 – by evaporation.
3.3.1 Pre-treated Samples Dyed with 100% of the Required Salt

All the three Chitosan samples had higher TDS readings than the reference sample. This suggests that during dyeing some of the Chitosan has been removed from the fabric and re-entered the dye bath liquid. However, if this is the case, the effect on TDS should increase with Chitosan concentration. The results clearly show that the TDS decreased with increasing concentration of Chitosan.

The four Cibafix ECO dyeings resulted in TDS readings either equal to or lower than the reference sample (Figure 3.18). This shows that even when the fabrics are dyed with the same amount of salt and dye the amount of TDS is reduced.

The right hand column shows the TDS result for a blank dyeing with 2.0% Cibafix ECO. The TDS of this blank dyeing is slightly lower than the 2.0% Cibafix ECO dyeing using 100% salt. Note however, that the higher levels of Cibafix ECO on the fabric result in lower TDS. The effect is substantial, and increases with the concentration of Cibafix ECO on the fabric. One explanation could be that the Cibafix ECO is acting to cause the salt to be absorbed by the fabric.
3.3.2 Pre-treated Samples Dyed with 75% of the Required Salt

Figure 3.19 shows the TDS levels of the pre-treated samples were greater than the relevant control (75% salt). Yet, all pre-treated samples have a higher TDS level than the 75% salt reference sample, possibly due to the pre-treatment which is the only difference between the them. This shows a direct link between the amount of salt used and the amount of TDS at the end of the dyeing process.

However, this group does not reveal the same trend as the samples dyed with 100% salt. The fabrics with the lower percentage of pre-treatment applied have lower TDS levels than the fabrics with the higher percentage of pre-treatment. Previously the higher the concentration of pre-treatment chemical, the lower the TDS. This suggests some complex interaction between salt and the pre-applied chemicals which, is outside the scope of this study.
3.3.3 Pre-treated Samples Dyed with 50% of the Required Salt

As shown in Figure 3.20 TDS levels of the pre-treated samples are at least half of the 100% reference sample and are all equal to or less than the 50% salt reference sample. Data from both reference samples confirms a linear correlation between the amount of salt used, and the level of TDS remaining in the dye bath.

3.3.4 Pre-treated Samples Dyed with 25% of the Required Salt

Figure 3.21 TDS levels of dye bath liquid dyed with 25% salt
In particular Figure 3.21 shows the 2.0% and 5.0% Cibafix ECO samples obtain TDS levels lower than 2000mg/l, which is a 95% reduction from the reference sample.

3.3.5 Pre-treat, Rinse, No Dry & Pre-treat, No Rinse, No Dry with 75% of the Required Salt

![Figure 3.22 TDS levels of dye bath liquid dyed with 75% salt with a rinse in between pre-treatment and dyeing](image)

The results of the two experiments shown in Figures 3.22 and 3.23 are almost identical. Both graphs indicate that the 0.5% Chitosan treated and the 2.0% Cibafix ECO treated have the lowest TDS levels. Overall the 2.0% Cibafix ECO treated sample has the lowest TDS reading of both trials.
As can be seen in Table 3.6, there is very little difference between the TDS levels for the no rinse trial and the rinse trial that Figures 3.22 and 3.23 are almost identical.

Table 3.6. Comparison of TDS levels between trials where a rinse and no rinse was employed

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>No Rinse</th>
<th>With Rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Chitosan</td>
<td>32,381mg/l</td>
<td>32,857mg/l</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>36,410mg/l</td>
<td>37,368mg/l</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>31,905mg/l</td>
<td>31,579mg/l</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>36,410mg/l</td>
<td>37,083mg/l</td>
</tr>
</tbody>
</table>

Between the two experiments, no rinse in between pre-treatment and dyeing had lower TDS readings than the group that had a rinse in between.
### 3.3.6 Pre-treatment Chemical Added in Dye Bath

<table>
<thead>
<tr>
<th>Type and levels of Pre-treatment</th>
<th>TDS levels of dye bath liquid of samples dyed with pre-treatment chemical in dye bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Chitosan Treated</td>
<td><img src="chart1.png" alt="TDS levels chart for 0.5% Chitosan treated" /></td>
</tr>
<tr>
<td>1.0% Chitosan Treated</td>
<td><img src="chart2.png" alt="TDS levels chart for 1.0% Chitosan treated" /></td>
</tr>
<tr>
<td>2.0% Cibafix Eco Treated</td>
<td><img src="chart3.png" alt="TDS levels chart for 2.0% Cibafix Eco treated" /></td>
</tr>
<tr>
<td>7.0% Cibafix Eco Treated</td>
<td><img src="chart4.png" alt="TDS levels chart for 7.0% Cibafix Eco treated" /></td>
</tr>
<tr>
<td>100% Reference</td>
<td><img src="chart5.png" alt="TDS levels chart for 100% Reference" /></td>
</tr>
<tr>
<td>75% Reference</td>
<td><img src="chart6.png" alt="TDS levels chart for 75% Reference" /></td>
</tr>
</tbody>
</table>

Figure 3.24 TDS levels of dye bath liquid dyed with 75% salt with pre-treatment chemical added in dye bath

The 0.5% Chitosan treated and the 2.0% and 7.0% Cibafix ECO treated performed similarly shown in Figure 3.24. The 1.0% Chitosan treated performed the best in the one bath process with a TDS saving of 28.7%. Figure 3.24, when compared with Figure 3.19 appear to be very similar showing that Chitosan and Cibafix ECO display similar characteristics whether being applied directly to the fabric or added in the dye bath.

The samples in this experiment appear to have performed, on average 2.0% better than the trial where the pre-treatment was applied separately using the same amount of salt. The result was a more level dyeing.

### 3.4 Colour Strength Evaluation – Sumifix Supra Navy 3GF 150%

The change in shade of those samples dyed with no pre-treatment and as per the manufacturer’s recommendations, were analysed against the samples that were pre-treated and dyed with varying reductions in salt. As differences in shade are important to the colour matching process, and the ability of a dyer to reproduce the same shade time and time again. The K/S values were measured to determine how
the Chitosan and Cibafix ECO pre-treatments affected the depth of shade when dyed with the same amount of dye.

3.4.1 Pre-treated Samples Dyed with 100% Required Salt

![Figure 3.25 K/S values of pre-treated samples dyed with 100% salt](image)

All pre-treated samples illustrated in Figure 3.25 show a higher colour strength values than the reference sample. This indicates that more dye has been absorbed into the fabric than exhausted into the reference sample.

It was observed the samples pre-treated with the lower amounts of the chemical had higher K/S readings than those samples pre-treated with a greater amount of the chemical. A higher K/S value means that more colour is absorbed into the fabric and also better use of the dye, an ideal K/S reading would be one as close to the reference sample as possible.

3.4.2 Pre-treated Samples Dyed with 75% of the Required Salt

The data shown in Figure 3.26 shows the colour strength properties of the pre-treated samples dyed with 75% of the required amount of salt. The K/S values are still stronger than the reference sample.

The sample with the strongest K/S value was the sample pre-treated with 2.0% Cibafix ECO, with a K/S value of 13.009. However, the sample that obtained the K/S
value closest to the reference sample was the 7.0% Cibafix ECO treated sample with a K/S value of 11.884, a colour that is 7.2% stronger than the reference.

Figure 3.26 K/S values of pre-treated samples dyed with 75% salt

One way to counteract the difference in the colour depth would be to reduce the amount of dye that is added to the dye bath. Reducing the amount of dye included in the dyeing process could potentially cover the costs of the pre-treatment chemical if adopted for industry use.
3.4.3 Pre-treated Samples Dyed with 50% of the Required Salt

Figure 3.27 K/S values of pre-treated samples dyed with 50% salt

Figure 3.27 reveals all samples, with the exclusion of two, fall below the reference sample. The 7.0% Cibafix ECO treated sample has the closest K/S value to the reference and 5.0% Cibafix ECO finished with the strongest depth of shade.

What has been confirmed in Figure 3.27 is the correlation between salt and the amount of colour exhausted into the fabric. In turn this has a direct effect on the colour strength of the fabric. Nevertheless, two of the samples pre-treated with Cibafix ECO – the 5.0% and the 7.0% have still maintained higher K/S values than the reference sample.
3.4.4 Pre-treated Samples Dyed with 25% & 0% of the Required Salt

The reduction in the amount of salt used in the dyeing process effects the amount of colour exhausted onto the fabric (Figure 3.28 and Figure 3.29). It is also demonstrated that similarly to those samples dyed with 50% salt, the Cibafix ECO samples are showing higher K/S values than the Chitosan samples. In this graph, the gap between the two chemicals has increased, with none of the samples having K/S
values as strong as the reference sample. A list of the exact K/S values is displayed in Table 3.7.

Table 3.7 K/S values of pre-treated samples dyed with 25% salt and 0% salt

<table>
<thead>
<tr>
<th>Type and Level of Pre-treatment</th>
<th>K/S Values of 25% of required amount of salt</th>
<th>K/S Values of 0% of required amount of salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Chitosan</td>
<td>8.05</td>
<td>3.49</td>
</tr>
<tr>
<td>0.8% Chitosan</td>
<td>8.70</td>
<td>3.31</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>8.53</td>
<td>3.35</td>
</tr>
<tr>
<td>1.0% Cibafix ECO</td>
<td>9.77</td>
<td>3.60</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>10.25</td>
<td>4.63</td>
</tr>
<tr>
<td>5.0% Cibafix ECO</td>
<td>10.38</td>
<td>4.64</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>9.50</td>
<td>4.88</td>
</tr>
<tr>
<td>75% Reference</td>
<td></td>
<td>10.95</td>
</tr>
<tr>
<td>100% Reference</td>
<td></td>
<td>11.08</td>
</tr>
</tbody>
</table>

Table 3.7 demonstrates a 57.2% difference in shade between the two groups and since all trialled samples fall below the reference sample, none would be practical for industry use.

3.4.5 Pre-treat, Rinse, Dry, Dye & Pre-treat, No Rinse, No Dry Dyed – 75% Salt

![Figure 3.30 K/S values of pre-treated samples dyed with a rinse in between](image)
The poorest performing sample was the 0.5% Chitosan treated sample from the trial where a rinse was included between pre-treatment and dyeing. It gave a K/S value of 6.43.

The strongest K/S value belongs to the 2.0% Cibafix ECO sample with a value of 12.91 for the trial where no rinse was applied. This same sample also has the strongest colour shade in the trial where a rinse was applied with a K/S value of 10.64. A value, which is 17.5% weaker than the same level of pre-treatment, dyed with no rinse in between.

Again, the 2.0% Cibafix ECO sample, which had the attributes most like the reference sample. This sample has a K/S value that is 16.5% higher when trialled with no rinse in between samples and has performed 4.0% weaker than the reference sample when a rinse was applied after the pre-treatment before the dyeing process.

Even though the difference between one sample is a lot smaller when compared to the reference sample than the other, it is believed the 2.0% Cibafix ECO sample would be more feasible in industry use. This is because the amount of dye will need to be reduced to achieve the same colour shade as the reference sample, therefore saving the dyer money. As mentioned previously, this cost saving in dye could potentially cover the cost of the pre-treatment chemical.
3.5 Evaluation of Colourfastness Properties – Sumifix Supra Navy 3GF 150%

Each sample tested for colourfastness to washing and perspiration were prepared using Society of Dyers and Colourists (SDC) standard Multifibre Fabric. Also standard grey scales for assessing change in colour (ISO 105 A02) and staining (ISO 105 A03) were used to obtain ratings. Table 3.8 outlines the results of the reference sample.

Table 3.8 Colourfastness results for reference sample dyes as per pattern card

<table>
<thead>
<tr>
<th>Colourfastness to washing</th>
<th>Staining</th>
<th></th>
<th></th>
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<td>Polyester</td>
<td>Nylon 6.6</td>
<td>Cotton</td>
<td>Acetate</td>
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Colourfastness to perspiration - alkali

<table>
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Colourfastness to perspiration - acid

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Colourfastness to rubbing

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<th>Stain</th>
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<td>4-5</td>
<td>Width</td>
<td>3-4</td>
<td>4-5</td>
</tr>
</tbody>
</table>

Colourfastness to light

4

The grey scales for colour change and staining is a scale of 1 to 5; 5 being the best with no colour change or staining occurring and 1 being the worst where there is a large colour change from the original sample or staining from the tested sample to the standard fabric. The grey scales are used to rate any change in colour or any staining that occurs on samples that have been tested for their colourfastness properties to
washing, perspiration, water and rubbing. A blue scale is used to rate samples that have been tested for colourfastness to light. The blue scale is exposed with the tested samples, the rating scale from 1 to 8; 8 being the best with no change and 1 being the worst with significant change.

The colourfastness results for the reference sample indicate that it has relatively good colourfastness properties. Table 3.8 shows that for the colourfastness to washing and both the acid and alkali perspiration tests, the reference sample received a grey scale rating of 4-5. For the colourfastness to rubbing test the reference sample received a rating of 3-4 and for the colourfastness to light a blue scale rating of 4 was achieved.

The data illustrated in Table 3.9 shows overall, the best performing sample is the 0.5% Chitosan treated. This sample performed the best in all the colourfastness tests receiving ratings of 4-5 for the colourfastness to washing, both perspiration tests, a 4-5 for the dry rubbing test and a 3 for the wet rubbing test and finally a rating of 4 for the colourfastness to light test.

Table 3.10 presents the results of the colourfastness testing for the groups dyed with 75% of the required amount of salt. The best performing sample was the 2.0% Cibafix ECO treated sample. This sample had the best colourfastness properties in four of the five tests performed; receiving a 4-5 for the colourfastness to washing, alkali perspiration and acid perspiration and a 4 for colourfastness to light. The best performing sample in the colourfastness to rubbing test was the 1.0% Chitosan sample, which received a 2-3 for the wet rubbing, only half a grade higher than the rating of 2 which the 2.0% Cibafix ECO sample acquired.

The Figures in Table 3.11 show that the best sample for this group was 7.0% Cibafix ECO receiving the highest rating in four of the five tests. This sample received a 4 for the colourfastness to washing test a 4-5 for both the colourfastness to perspiration tests and a 3-4 for the colourfastness to light. Again, a Chitosan sample received the best result, a 3, for the colourfastness to rubbing which was the 0.5% treated sample.
Table 3.9 Colourfastness results for pre-treated samples dyed according to the pattern card with 100% of the required amount of salt.

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Table 3.10 Colourfastness results for pre-treated samples dyed according to the pattern card with 75% of the required amount of salt.

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Table 3.11 Colourfastness results for pre-treated samples dyed according to the pattern card with 50% of the required amount of salt.

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<td>Polyester</td>
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In Table 3.12, both the 2.0% Cibafix ECO and the 7.0% Cibafix ECO treated samples received the best ratings. Both received a 4 and a 4-5 for the washing test and perspiration tests respectively and a 3-4 for the light test. Again, the 0.5% Chitosan sample received the highest rating of 3 for the wet rubbing test whereas the 2.0% Cibafix ECO sample received a rating of 2-3. The 7.0% sample received a 2 for the wet rubbing in the length direction and a 2-3 in width direction.

Again there were two samples revealed in Table 3.13 – the group dyed with 0% of the required amount of salt that performed the best overall. These two samples are the 1.0% Chitosan sample and the 2.0% Cibafix ECO sample. The samples performed the best in three out of the five tests however; the best results obtained for these samples were from different groups. For the colourfastness to washing test the 2.0% Cibafix ECO sample received a rating of 4-5 and the same for both perspiration tests. The 1.0% Chitosan sample received a 4-5 the colourfastness to acid perspiration test and a 3-4 for the wet rubbing tests in both the length and width directions and a rating of 2 for the colourfastness to light test.

The results for the group where the pre-treatment chemical was applied separately and then dyed with no rinse in between is given in Table 3.14. The sample that performed the best in this group of colourfastness tests was the again the 2.0% Cibafix ECO sample. It achieved a rating of 4 for the washing test and a 4-5 for both perspiration tests. The 1.0% Chitosan sample performed the best in the colourfastness to rubbing test with a rating of 3. The 2.0% Cibafix ECO sample received a rating of 3-4.

Finally, Table 3.15 was also pre-treated separately but a rinse was used in between pre-treatment and dyeing. In this group the best performing sample was the 7.0% Cibafix ECO treated sample, receiving the highest rating in four out of the five tests. The sample received a 4-5 for the colourfastness to washing test and both the perspiration tests and a blue scale rating of 4 for the colourfastness to light test. Once again it was a Chitosan treated sample – 0.5% treated, that performed the best for the colourfastness to rubbing test receiving a grey scale rating of 3 in the length and 3-4 in the width.
Table 3.12 Colourfastness results for pre-treated samples dyed according to the pattern card with 25% of the required amount of salt.

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<tbody>
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</tr>
<tr>
<td></td>
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<tr>
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<tr>
<td>7.0% CibafixECO</td>
<td>4-5</td>
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<td>Wool</td>
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<td>2.0% CibafixECO</td>
<td>4-5</td>
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<table>
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<th>Colourfastness to perspiration - acid</th>
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<td>Wool</td>
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<tr>
<td>1.0% Chitosan</td>
<td>4-5</td>
<td>4-5</td>
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<tr>
<td>2.0% CibafixECO</td>
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<td>4-5</td>
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<table>
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<td>Length</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>Length</td>
</tr>
<tr>
<td>2.0% CibafixECO</td>
<td>Length</td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
<td>Length</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colourfastness to light</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Chitosan</td>
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<tr>
<td>1.0% Chitosan</td>
<td>3-4</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>3-4</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>3-4</td>
</tr>
</tbody>
</table>
Table 3.13 Colourfastness results for pre-treated samples dyed according to the pattern card with 0% of the required amount of salt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colour Change</th>
<th>Wool</th>
<th>Acrylic</th>
<th>Polyester</th>
<th>Nylon 6.6</th>
<th>Cotton</th>
<th>Acetate</th>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td></td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
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</tr>
<tr>
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<td>4-5</td>
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<td>4-5</td>
<td>4-5</td>
<td></td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
<td>4-5</td>
<td>4-5</td>
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<table>
<thead>
<tr>
<th>Colourfastness to perspiration - alkali</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
</tr>
<tr>
<td>2.0% CibafixECO</td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Colourfastness to perspiration - acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
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<tr>
<td>--------</td>
</tr>
<tr>
<td>0.5% Chitosan</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
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<tr>
<td>2.0% CibafixECO</td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
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</table>

<table>
<thead>
<tr>
<th>Colourfastness to rubbing</th>
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</thead>
<tbody>
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<td>--------</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<tr>
<td>1.0% Chitosan</td>
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<tr>
<td></td>
</tr>
<tr>
<td>2.0% CibafixECO</td>
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<tr>
<td></td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
</tr>
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<table>
<thead>
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<th>Sample</th>
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<tr>
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<tr>
<td>1.0% Chitosan</td>
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<tr>
<td>2.0% Cibafix ECO</td>
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<tr>
<td>7.0% Cibafix ECO</td>
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</table>
Table 3.14 Colourfastness results for samples pre-treated with no rinse in between and dyed according to the pattern card with 75% of the required amount of salt.

### Colourfastness to washing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Colour Change</th>
<th>Staining</th>
<th>Wool</th>
<th>Acrylic</th>
<th>Polyester</th>
<th>Nylon 6.6</th>
<th>Cotton</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td></td>
<td>3-4</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
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<td>4-5</td>
</tr>
<tr>
<td>2.0% Cibafix ECO</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
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<td>4-5</td>
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<tr>
<td>7.0% Cibafix ECO</td>
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### Colourfastness to perspiration - alkali

<table>
<thead>
<tr>
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<th>Staining</th>
<th>Wool</th>
<th>Acrylic</th>
<th>Polyester</th>
<th>Nylon 6.6</th>
<th>Cotton</th>
<th>Acetate</th>
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<td>4-5</td>
<td>4-5</td>
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</tr>
<tr>
<td>1.0% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
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</tr>
<tr>
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<td>4-5</td>
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### Colourfastness to perspiration - acid

<table>
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<th>Staining</th>
<th>Wool</th>
<th>Acrylic</th>
<th>Polyester</th>
<th>Nylon 6.6</th>
<th>Cotton</th>
<th>Acetate</th>
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<tr>
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<td>4-5</td>
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<td>4-5</td>
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<tr>
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<td>4-5</td>
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<td>4-5</td>
</tr>
<tr>
<td>7.0% Cibafix ECO</td>
<td>4-5</td>
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<td>4-5</td>
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### Colourfastness to rubbing

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<th>WET</th>
<th>Stain</th>
<th>Mark off</th>
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<tbody>
<tr>
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<td>Length</td>
<td>4-5</td>
<td>4-5</td>
<td></td>
<td>Length</td>
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</tr>
<tr>
<td></td>
<td>Width</td>
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<td></td>
<td></td>
<td>Width</td>
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</tr>
<tr>
<td>1.0% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
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<td>Length</td>
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</tr>
<tr>
<td></td>
<td>Width</td>
<td></td>
<td></td>
<td></td>
<td>Width</td>
<td>3</td>
</tr>
<tr>
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<td></td>
<td>Length</td>
<td>2</td>
</tr>
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<td>Width</td>
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</tr>
<tr>
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<td>Length</td>
<td>4-5</td>
<td>4-5</td>
<td></td>
<td>Length</td>
<td>2-3</td>
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</table>

### Colourfastness to light

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</thead>
<tbody>
<tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>7.0% Cibafix ECO</td>
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</table>
Table 3.15 Colourfastness results for samples pre-treated with a rinse in between and dyed according to the pattern card with 75% of the required amount of salt.

<table>
<thead>
<tr>
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<th>Colour Change</th>
<th>Staining</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wool</td>
<td>Acrylic</td>
<td>Polyester</td>
<td>Nylon 6.6</td>
<td>Cotton</td>
</tr>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>3</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4</td>
</tr>
<tr>
<td>7.0% CibafixECO</td>
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Colourfastness to perspiration - alkali

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<th>Staining</th>
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<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Wool</td>
<td>Acrylic</td>
<td>Polyester</td>
<td>Nylon 6.6</td>
<td>Cotton</td>
</tr>
<tr>
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<td>4-5</td>
<td>4-5</td>
<td>2</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
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<td>4-5</td>
<td>4-5</td>
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<td>4-5</td>
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Colourfastness to perspiration - acid

<table>
<thead>
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<th>Staining</th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>Wool</td>
<td>Acrylic</td>
<td>Polyester</td>
<td>Nylon 6.6</td>
<td>Cotton</td>
</tr>
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<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
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Colourfastness to rubbing

<table>
<thead>
<tr>
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<th>DRY</th>
<th>Stain</th>
<th>Mark off</th>
<th>WET</th>
<th>Stain</th>
<th>Mark off</th>
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</thead>
<tbody>
<tr>
<td>0.5% Chitosan</td>
<td>Length</td>
<td></td>
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<td>Length</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td></td>
<td></td>
<td>Width</td>
<td></td>
<td>3-4</td>
</tr>
<tr>
<td>1.0% Chitosan</td>
<td>Length</td>
<td></td>
<td></td>
<td>Length</td>
<td></td>
<td>2-3</td>
</tr>
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<tr>
<td>2.0% CibafixECO</td>
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<td>Length</td>
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<td>7.0% CibafixECO</td>
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Sample | Colourfastness to light

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0.5% Chitosan</td>
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<tr>
<td>1.0% Chitosan</td>
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<tr>
<td>2.0% CibafixECO</td>
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</tr>
<tr>
<td>7.0% CibafixECO</td>
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</tbody>
</table>
3.6 Samples dyed with Procion Brilliant Scarlett H-EXL

3.6.1 Rate and Extent of Dye Exhaustion

The same pre-treatment process was used for the dyeing of Procion Brilliant Scarlett H-EXL as discussed in section 3.2.3. Following the pre-treatment process dyeing continued as normal according to the manufacturer’s recommendation. The dyeing temperature for this type of dye was 80˚C.

![Transmission](image)

**Figure 3.32 Extent of exhaustion of samples dyed with Procion Brilliant Scarlet H-EXL pre-treated with 2.0% Cibafix ECO dyed with 75% salt**

As shown in Figure 3.32 the reference sample dye with 100% salt, initial strike did not occur until the 20th minute of dyeing. Once exhaustion for the reference sample, it continued at a constant rate until the end of dyeing. The dye strike for the reference sample dyed with 75% was further delayed (30 minutes) moved through the dyeing process at a steady rate until the 50th minute when the sample experienced a marked increase in dye uptake.

The pre-treated sample had a higher initial strike rate where the dye exhausted on the fibre more quickly. High exhaustion rates can result in an unlevel dyeing. However, this did not occur. The levelness of the pre-treated sample was good with no flecks of dye or dark/light spots on the fabric.
3.7 Total Dissolved Solids – Procion Brilliant Scarlett H-EXL

TDS was measured from the dye bath liquor at the end of dyeing. The samples were used as received. Measurement of TDS was carried out according to the method described in section 2.8 via an electronic TDS meter.

The TDS levels of the samples dyed with Procion Brilliant Scarlett H-EXL are shown in Figure 3.33. With a 25% reduction in salt use the amount of TDS remaining in the dye bath has decreased by approximately 45%. The reference sample finished the dyeing process with a TDS level of 69,500mg/l and the sample pre-treated with Cibafix ECO finished with a TDS value of 37,800mg/l. Initially the assumption was that a 25% reduction in salt use would amount to a 25% reduction in TDS. However in this experiment as well as throughout the previous trials Cibafix ECO has shown to be an effective agent in lowering the level of TDS released to dye house effluent, though not yet on a universal scale.
3.8 Colour Strength Evaluation – Procion Brilliant Scarlet H-EXL

![Bar chart showing K/S values for pre-treated Procion Brilliant Scarlet H-EXL samples dyed with 75% salt.](image)

The K/S values shown in Figure 3.34 demonstrate that the pre-treated sample had a greater depth of shade compared to the reference sample. There is a 4.7% difference in shade between the two samples. Although a difference in shade is not ideal for the dyer, a reduction in the amount of dye used in order to match the original shade could potentially save the dyer money in the long run.

3.9 Samples dyed with Solophenyl Rubine RNL

3.9.1 Rate and Extent of Dye Exhaustion

The same pre-treatment process was used for the dyeing of Solophenyl Rubine RNL as discussed in section 3.2.3. Following, the pre-treatment process dyeing continued as normal according to the manufacturer’s recommendations. The dyeing temperature for this type of dye was 100°C.
Figure 3.35 shows the dyeing behaviour of the sample pre-treated with 2.0% Cibafix ECO and dyeing with 75% of the required amount of salt and the reference sample dyed with 100% of the required amount of salt were very similar. The pre-treated sample had a higher extent of exhaustion with more dye being exhausted onto the fibre than the reference sample. This shows promise in that Cibafix ECO can reduce the amount of salt used when dyeing with not only reactive dyes but also direct dyes. The improvement in dye utilisation (90% transmission in the presence of Cibafix ECO versus 67% transmission for the standard dyeing) was marked and may have a cost benefit for dye houses.

3.10 Total Dissolved Solids – Solophenyl Rubine RNL

TDS was measured from the dye bath liquor at the end of dyeing. The samples were used as received. Measurement of TDS was carried out according to the method described in section 2.8 via an electronic TDS meter.

In Figure 3.36 the TDS levels of the samples dyed with the direct dye Solophenyl Rubine RNL are shown. The reference sample ended the dyeing process with a TDS level of 20,960mg/l. The sample that was pre-treated with 2.0% Cibafix ECO and dyed with 75% of the required amount of salt ended the dyeing process with 11,970mg/l of TDS remaining in the dye bath liquor.
Figure 3.36 TDS levels of samples dyed with Solophenyl Rubine RNL pre-treated with 2.0% Cibafix ECO dyed with 75% salt

The TDS level of the direct dye is reduced by 43%, a similar value to what was achieved in the experiment using the Procion reactive dye.

3.11 Colour Strength Evaluation – Solophenyl Rubine RNL

Figure 3.37 K/S values of pre-treated Solophenyl Rubine RNL samples dyed with 75% salt

Figure 3.37 shows the K/S values of the samples dyed with Solophenyl Rubine RNL. The K/S value of the pre-treated sample compared to the reference sample is 103%
stronger resulting in a much darker shade. Again this could be corrected by reducing the amount of dye used to match the shade of the reference sample.

3.12 Summary

The extent of exhaustion, TDS levels, K/S values and fastness properties of all samples were evaluated.

The results of this study suggest:

- the amount of salt used in dyeing can be reduced;
- both pre-treatments aid in reduction of salt use when dyeing 100% cotton fabrics with reactive dyes;
- less water can be used by eliminating a rinse cycle after pre-treatment;
- the elimination of a drying process can save time and energy when processing a sample;
- Cibafix ECO is effective when dyeing with different types of reactive dyes as well as direct dyes.

Overall, Cibafix ECO was found to be a more effective pre-treatment when dyeing cotton fabrics with reactive dyes at 75% salt.
Chapter 4
Conclusions and Recommendations
4.1 Introduction

This study has demonstrated that salt remains an important factor in the reactive dyeing process. Further, it confirms the removal of salt equates to poorer exhaustion of the dye onto the fibre, and hence, reduced yields.

4.2 Chitosan vs. Cibafix ECO

It was concluded the performance of Cibafix ECO was more viable and economical for industry use over Chitosan. The most effective amount of pre-treatment chemical applied was Cibafix ECO at a 2.0% concentration. Cibafix ECO is also a more cost effective and easier to use product than Chitosan. A lesser amount of Cibafix ECO is required. Cibafix ECO is also considerably cheaper in comparison to Chitosan and may be more attractive to industry.

4.3 Reduction in Salt

The study has shown that a 25% reduction in salt can be achieved. Greater reductions, even at higher concentrations of Cibafix ECO were not successful due to lower dye yields. Further, dyeings carried out with a reduction in salt of more than 25% were uneven and unlevel.

4.4 Optimal Pre-treatment – Dyeing Method

The following pre-treatment application/dyeing processes were investigated:

- Two stage; pre-treatment, drying and then dyeing process;
- Pre-treatment chemical added into dye bath to create a one bath process;
- Pre-treatment chemical added as a post-treatment;
- Two stage; pre-treatment application with no drying before dyeing and;
- Pre-treatment but, with no rinse and no drying before dyeing.

It was concluded that last application/dyeing method was the most effective and time saving process for applying the pre-treatment chemical and dyeing the fabric. With the elimination of the rinse cycle in between the pre-treatment application process and
the dyeing process, a saving in water usage of 14% was achieved. Also, the removal of the drying stage in between pre-treatment and dyeing cuts down on energy requirements and time.

4.5 Recommendations

This study has demonstrated the effectiveness of Cibafix ECO in reducing the amount of salt needed for reactive dyeing of cotton. This product is established in the industry as a post-treatment to improve wet fastness and prevent dye migration after dyeing.

The viability of the 25% reduction in salt used achieved under laboratory conditions should be confirmed through industry trials at the recommended liquor ratio of 20:1. Being limited to laboratory equipment meant that a reduced liquor ratio (10:1) was used. The suitability of the method developed for reducing salt use by 25% should be extended to cover a wider range of reactive and direct dyes.

The results of this research also suggest that Cibafix ECO may be a suitable cost effective flocculant for removal of colour from dye house effluent.
References


http://www.merinoinnovation.com/wps/wcm/resources/file/eb1c7e0d700fa9e/wetpro_colouration.pdf


http://www.dyespigments.com/batch-dyeing-process.html


http://www.dyespigments.com/machinery.html

http://dyehouseltd.com/why.html


http://www.indiantextilejournal.com/articles/FAdetails.asp?id=793


[41] [www.sigma-aldrich.com](http://www.sigma-aldrich.com)


[47] Various dye pattern cards.
Appendix I
1. PRODUCT AND COMPANY IDENTIFICATION

Product name: Chitosan
Product Number: 419419
Brand: Aldrich
Company: Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA
Telephone: +1 800-325-5832
Fax: +1 800-325-5052
Emergency Phone #: (314) 776-6555

2. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms: Poly(D-glucosamine)
Deacetylated chitin
Chitosan from crab shells

Formula: C12H24N2O9

<table>
<thead>
<tr>
<th>CAS-No.</th>
<th>EC-No.</th>
<th>Index-No.</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan</td>
<td>9012-76-4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3. HAZARDS IDENTIFICATION

Emergency Overview
OSHA Hazards
No known OSHA hazards

HMIS Classification
Health Hazard: 0
Flammability: 0
Physical hazards: 0

NFPA Rating
Health Hazard: 0
Fire: 0
Reactivity Hazard: 0

Potential Health Effects
Inhalation: May be harmful if inhaled. May cause respiratory tract irritation.
Skin: May be harmful if absorbed through skin. May cause skin irritation.
Eyes: May cause eye irritation.
Ingestion: May be harmful if swallowed.
4. FIRST AID MEASURES

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration

In case of skin contact
Wash off with soap and plenty of water.

In case of eye contact
Flush eyes with water as a precaution.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Avoid dust formation.

Environmental precautions
No special environmental precautions required.

Methods for cleaning up
Sweep up and shovel. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling
Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire protection.

Storage
Keep container tightly closed in a dry and well-ventilated place.
Keep in a dry place.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Contains no substances with occupational exposure limit values.

Personal protective equipment

Respiratory protection
Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
For prolonged or repeated contact use protective gloves.

Eye protection
Safety glasses

Hygiene measures
General industrial hygiene practice.
9. PHYSICAL AND CHEMICAL PROPERTIES

**Appearance**
- Form: powder
- Colour: yellow

**Safety data**
- pH: no data available
- Melting point: no data available
- Boiling point: no data available
- Flash point: no data available
- Ignition temperature: no data available
- Lower explosion limit: no data available
- Upper explosion limit: no data available
- Water solubility: no data available

10. STABILITY AND REACTIVITY

**Storage stability**
Stable under recommended storage conditions.

**Materials to avoid**
Strong oxidizing agents

**Hazardous decomposition products**
Hazardous decomposition products formed under fire conditions. - Nature of decomposition products not known.

11. TOXICOLOGICAL INFORMATION

**Acute toxicity**
LD50 Oral - rat -> 10,000 mg/kg

**Irritation and corrosion**
no data available

**Sensitisation**
no data available

**Chronic exposure**

**IARC:**
No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

**ACGIH:**
No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

**NTP:**
No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

**OSHA:**
No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

**Potential Health Effects**

**Inhalation**
May be harmful if inhaled. May cause respiratory tract irritation.

**Skin**
May be harmful if absorbed through skin. May cause skin irritation.

**Eyes**
May cause eye irritation.
Ingestion  May be harmful if swallowed.

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)
no data available

Ecotoxicity effects
  Toxicity to fish  LC50 - Oncorhynchus mykiss (rainbow trout) - 0.038 mg/l - 48 h

Further information on ecology
no data available

13. DISPOSAL CONSIDERATIONS

Product
Observe all federal, state, and local environmental regulations.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)
Not dangerous goods

IMDG
Not dangerous goods

IATA
Not dangerous goods

15. REGULATORY INFORMATION

OSHA Hazards
No known OSHA hazards

TSCA Status
On TSCA Inventory

DSL Status
All components of this product are on the Canadian DSL list.

SARA 302 Components
SARA 302: No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components
SARA 313: This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards
No SARA Hazards

Massachusetts Right To Know Components
No Components Listed

Pennsylvania Right To Know Components

New Jersey Right To Know Components

<table>
<thead>
<tr>
<th>CAS-No.</th>
<th>Revision Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>9012-76-4</td>
<td></td>
</tr>
</tbody>
</table>
California Prop. 65 Components
This product does not contain any chemicals known to State of California to cause cancer, birth, or any other reproductive defects.

16. OTHER INFORMATION

Further information
Copyright 2008 Sigma-Aldrich Co. License granted to make unlimited paper copies for internal use only. The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.
Material Safety Data Sheet

OSHA / ANSI Z400.1-2004 Compliant

MSDS date: 21-Sep-2006

1. PRODUCT AND COMPANY IDENTIFICATION

Product Name: ALBAFIX ECO
Product Number: 1377091
Chemical Family: Polymer Mixture
Intended Use: Dye Fixing Agent
Manufacturer/Supplier: Huntsman International, LLC
10003 Woodloch Forest Drive
The Woodlands, Texas 77380
Huntsman Company: (800) 328-8501 or (409) 727-0831
CHEMTREC: (800) 424-9300 (within US, Canada and Virgin Islands)
CHEMTREC: (703) 527-3887 (outside the US, Canada and Virgin Islands. Collect calls are accepted.)
Medical Emergencies: (409) 722-9673

2. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Signal Word: NOTICE!
Physical Form: Liquid
Color: Amber
Odor: Slight
Health: This product has no known adverse effect on human health.
Physical Hazards: None Expected.

OSHA Hazardous Substance: This material is classified as not hazardous under OSHA regulations.
Potential Health Effects: No known hazards.
Primary Route(s) of Entry: Skin, Inhalation.

3. COMPOSITION/INFORMATION ON INGREDIENTS
This material does not contain any hazardous components above OSHA thresholds

4. FIRST AID MEASURES

Eyes: In the case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Skin: Wash off immediately with soap and plenty of water. Get medical attention if irritation occurs.

Inhalation: Remove to fresh air, if not breathing give artificial respiration. If breathing is difficult, give oxygen and get immediate medical attention.

Ingestion: Do not induce vomiting. If vomiting occurs naturally, have casualty lean forward to reduce the risk of aspiration. Seek medical attention immediately.

5. FIRE FIGHTING MEASURES

Fire Fighting Measures: Standard procedure for chemical fires.

Suitable Extinguishing Media: Carbon dioxide, dry chemical or foam.

Fire Fighting Equipment: Wear self-contained breathing apparatus and protective suit.

Hazardous Combustion Products: Burning may produce toxic combustion products.

6. ACCIDENTAL RELEASE MEASURES

Cleanup Instructions: Absorb spill with inert material (e.g. dry sand or earth), then place in a chemical waste container. Wear suitable protective equipment. Should not be released into the environment.

7. HANDLING AND STORAGE

Handling: As with all industrial chemicals, use good industrial practices when handling. Avoid eye, skin, and clothing contact. Do not inhale. Do not taste or swallow. Use only with adequate ventilation.

Storage: Keep containers tightly closed in a cool, well-ventilated place.

For Industrial Use Only

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Exposure Guidelines:

There are no OSHA or ACGIH exposure guidelines available for component(s) in this product.

Personal Protective Equipment

Eye/Face Protection: Wear splash proof chemical goggles.
Skin Protection: Wear chemical resistant gloves and protective clothing.
Respiratory Protection: Use NIOSH approved respirator as needed to mitigate exposure.
Engineering Controls: Work in well ventilated areas. Do not breathe vapors or mist.

9. PHYSICAL AND CHEMICAL PROPERTIES

Physical Form: Liquid
Color: Amber
Odor: Slight.
Boiling Point: ~ 100°C (212°F)
Freezing/Melting Point: Not determined
Solubility in water: Miscible
Vapor Density: Not determined
Vapor Pressure: Not determined
Density: Not determined
Specific Gravity: 1.08 (Water = 1)
pH: 7 - 8
Percent Volatile: 60 - 65% (Water)
VOC: 10.56% (Estimated, based on component wt. %)
Decomposition Temperature: Not determined
Flammability Limits in Air:
Flash point: None (Aqueous Solution)
Test Method (for Flash Point): Not determined

10. STABILITY AND REACTIVITY

Stability: Stable.
Conditions to Avoid: None known
Incompatibility: None known.
Possibility of Hazardous Reactions: None expected.

11. TOXICOLOGICAL INFORMATION

Acute Oral Toxicity: (Rats) LD50 > 2000 mg/kg *
Acute Dermal Toxicity: Not determined
Acute Inhalation Toxicity: Not determined.
Eye Irritation: (Rabbits) Not an irritant. *
Skin Irritation: (Rabbits) Not an irritant. *
Skin Sensitization: Not evaluated
Carcinogenicity (IARC; NTP; OSHA; ACGIH): None of the components in this product at concentrations greater than 0.1% are listed by IARC; NTP, OSHA or ACGIH as a carcinogen.
Carcinogenicity Studies: Not evaluated.
Mutagenicity: Not evaluated.
Reproductive Toxicity: Not evaluated.
Teratogenicity: Not evaluated.
Neurotoxicity: Not determined
Subacute Toxicity: Not determined
Subchronic Toxicity: Not determined
Chronic toxicity: Not determined
Absorption / Distribution / Excretion / Metabolism: Not determined

Additional Information: *Note: The toxicology data is based on a product of comparable composition.

12. ECOLOGICAL INFORMATION

Toxicity to Fish: (Zebra fish) LC50 = 2 mg/L (48 hour) *
Toxicity to Invertebrates: Not determined
Toxicity to Algae: Not determined
Toxicity to Sewage Bacteria: Not determined
Activated Sludge Respiration Inhibition Test: Not evaluated
Biochemical Oxygen Demand (BOD): 10 mg/g *
Chemical Oxygen Demand (COD): 255 mg/g *
Total Oxygen Demand (TOD): Not determined
Biodegradability: Not evaluated
Bioaccumulation: Not determined

Additional Environmental Data: * Note: The environmental data is based on a product of comparable composition.

13. DISPOSAL CONSIDERATIONS

Waste Disposal: Dispose in accordance with local, state, provincial and federal regulations.
14. TRANSPORT INFORMATION

U.S. Department of Transportation (DOT):
Not regulated for this mode of transport.

International Maritime Dangerous Goods (IMDG):
Not regulated for this mode of transport.

International Air Transportation Authority (IATA):
Not regulated for this mode of transport.

15. REGULATORY INFORMATION

Federal Regulations

OSHA Hazardous Substance: This material is classified as not hazardous under OSHA regulations

Clean Air Act - Hazardous Air Pollutants (HAP): This product does not contain any Hazardous Air Pollutants (HAP), as defined by the U.S. Clean Air Act Section 112 (40 CFR 61).

Clean Air Act - Volatile Organic Compounds (VOC): This product contains the following SOCMI Intermediate or Final Volatile Organic Compounds (VOC), as defined by the U.S. Clean Air Act Section 111 (40 CFR 50.100). Refer to VOC data in section 9.

<table>
<thead>
<tr>
<th>Components</th>
<th>CAA Section 111 Volatile Organic Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Propanediol (Propylene glycol)</td>
<td>Listed.</td>
</tr>
<tr>
<td>57-55-6</td>
<td></td>
</tr>
</tbody>
</table>

Clean Air Act - Ozone Depleting Substances (ODS): This product neither contains, nor was manufactured with, a Class I or Class II ozone depleting substance (ODS), as defined by the U.S. Clean Air Act Section 602 (40 CFR 82, Subpt. A, App. A+B).


SARA Section 302 Extremely Hazardous Substances (EHS): This product does not contain any components regulated under Section 302 (40 CFR 355) as Extremely Hazardous Substances.

SARA Section 304 CERCLA Hazardous Substances: This product contains the following component(s) regulated under Section 304 (40 CFR 302) as hazardous chemicals for emergency release notification ("CERCLA" List).

<table>
<thead>
<tr>
<th>Components</th>
<th>Section 304 CERCLA Hazardous Substances</th>
<th>CERCLA Reportable Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid, ammonium salt (Ammonium Acetate)</td>
<td>Listed.</td>
<td>5000 LBS</td>
</tr>
<tr>
<td>631-61-8 (2.94 %)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SARA Section 311/312 Hazard Communication Standard (HCS): This product is not regulated under Section 311/312 HCS (40 CFR 370).

SARA Section 313 Toxic Chemical List (TCL): This product does not contain any component(s) listed on the Section 313 Toxic Chemical List.

TSCA Section 8(b) Inventory Status: All component(s) comprising this product are either exempt or listed on the TSCA inventory.

TSCA Section 5(e) Consent Orders: This product is not subject to a Section 5(e) Consent Order.

TSCA Significant New Use Rule (SNUR): This product is not subject to a Significant New Use Rule (SNUR).

TSCA Section 5(f): This product is not subject to a Section 5(f)/6(a) rule.

TSCA Section 12(b) Export Notification: This product does not contain any component(s) that are subject to a Section 12(b) Export Notification

State Regulations

California Proposition 65: This product does not contain any components currently on the California list of Known Carcinogens and Reproductive Toxins.

Pennsylvania Right-To-Know: This product contains the following component(s) which are subject to Pennsylvania Right-to-Know disclosure requirement.

<table>
<thead>
<tr>
<th>Components</th>
<th>CAS Number</th>
<th>Pennsylvania Right-to-Know</th>
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<tbody>
<tr>
<td>1,2-Propanediol (Propylene glycol)</td>
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<td>Listed.</td>
</tr>
<tr>
<td>Acetic acid, ammonium salt (Ammonium Acetate)</td>
<td>631-61-8</td>
<td>Listed. Environmental hazard.</td>
</tr>
</tbody>
</table>

International Regulations

Chemical Weapons Convention (CWC): This product does not contain any component(s) listed under the Chemical Weapons Convention Schedule of Chemicals.

Domestic Substance List (DSL) Status: All components either exempt or listed on the DSL.

16. OTHER INFORMATION

Reason for revision: Name Change.

Disclaimer: The information contained herein is based upon data believed to be correct. However, no guarantee or warranty of any kind, expressed or implied, is made with respect to such data or information. The user is responsible for determining whether the product is suitable for its intended conditions of use.