

Pad-steam Dyeing of Cotton with Reactive Dyes Using Biodegradable Alkaline Organic Salts

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

Awais Khatri

B.E. Textile Engineering, Mehran University Pakistan, 2003

Diploma in Colouration, Society of Dyers and Colourists UK, 2007

C.Text. A.T.I., The Textile Institute UK, 2009

Textile Technology Discipline

School of Fashion and Textiles

Design and Social Context

RMIT University

November 2010

Declaration

This is to certify that except where due acknowledgement has been made, the work presented in this thesis is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out in the School of Fashion and Textiles, RMIT University, since February 2007; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Awais Khatri

09 November 2010

Acknowledgements

All praises are being to 'Almighty Allah' who gave me strength to accomplish this work. I would like to express my appreciations to all who have contributed to completion of the thesis. May Allah reward them for their contributions.

I am indebted to Dr Rajiv Padhye and Adjunct Professor Dr Max White for supervising the studies reported here through their invaluable advice, guidance, support, and encouragement. I am thankful to Mr Mac Fergusson for his consultancy and help in sourcing the materials and laboratory apparatus throughout the research. My appreciation is also extended to;

- Bruck Textiles Pty Ltd (Australia) for providing ready-to-dye cotton woven fabric,
- Popular Fabrics Pvt Ltd (Pakistan) for the industrial trial,
- Dr Nasar Momin for providing a technical input into dye diffusion studies,
- Ms Geraldine Van Lint for sourcing laboratory needs,
- Ms Zahra Homan and Mr Philip Francis (School of Applied Sciences, RMIT University) for providing access to the Varian Cary 50 UV-Vis Spectrophotometer and Leica DM 2500M Microscope respectively, and
- Staff of the Textile Testing Services, RMIT University, for providing services in their laboratories whenever needed.

This study was fully supported by a postgraduate scholarship from the Mehran University of Engineering and Technology, Jamshoro (Pakistan).

To all my colleagues and friends, thank you very much for helping me at one time or another.

Dedication

...to my beloved parents, wife and brother

Contents

<i>Declaration</i>	<i>ii</i>
<i>Acknowledgements</i>	<i>iii</i>
<i>Dedication</i>	<i>iv</i>
<i>Contents</i>	<i>v</i>
<i>Tables</i>	<i>x</i>
<i>Figures</i>	<i>xii</i>
<i>Abbreviations and symbols</i>	<i>xiv</i>
<i>Publications</i>	<i>xvii</i>
Summary	1
Introduction and Literature Review	3
Chapter 1: Dyeing of cotton with reactive dyes	4
1.1 Cotton textiles	4
1.2 Cotton fibre	4
1.2.1 Cotton polymer and fibre polymer system	6
1.2.2 Properties of cotton fibre	6
1.2.2.1 Hygroscopic properties	6
1.2.2.2 Chemical properties	7
1.2.2.3 Thermal properties	8
1.2.2.4 Mechanical properties	8
1.3 Dyeing of cotton	8
1.3.1 Preparing cotton for dyeing	8
1.3.2 Dye classes for cotton	9
1.3.3 Dyeing of cotton with anionic dyes	9
1.4 Reactive dyes for cotton	10
1.4.1 Historical development	10
1.4.2 Constitutional characteristics of reactive dyes	12
1.4.3 Reactive groups	13
1.4.4 Mechanisms of dye attachment to cellulose	15
1.4.4.1 Nucleophilic substitution mechanism	15
1.4.4.2 Nucleophilic addition mechanism	15
1.4.5 Dye reactivity	16
1.4.6 Multifunctional reactive dyes	16
1.4.6.1 Bifunctional reactive systems	16

1.4.6.2 Polyfunctional reactive systems	17
1.4.7 Dye substantivity	18
1.4.8 Dye exhaustion	18
1.4.9 Dye diffusion	18
1.4.10 Dye migration	19
1.4.11 Role of electrolyte cations and anions	19
1.4.12 Dye fixation	20
1.5 Reactive dye application procedures for cotton	21
1.5.1 Exhaust dyeing	21
1.5.1.1 Washing-off	22
1.5.2 Pad dyeings	22
1.5.2.1 Pad-batch process	23
1.5.2.2 Pad-dry-bake process	24
1.5.2.3 Steam fixation processes	24
1.6 Pad-steam dyeing	25
1.7 Reactive dyeing effluent	26
1.7.1 Biodegradability	26
1.7.2 Total Dissolved solids	27
Chapter 2: Environmental issues and developments in reactive dyeing of cotton	28
2.1 Introduction	28
2.2 Development of reactive dyes	29
2.2.1 Bifunctional reactive dyes	29
2.2.2 Polyfunctional reactive dyes	30
2.2.3 Dye mixtures	30
2.2.4 Reactive dye fixable at neutral pH	31
2.2.5 Acid fixing reactive dyes	31
2.2.6 Low-salt reactive dyes	31
2.2.7 Cationic reactive dyes	32
2.3 Developments in dyeing machinery and processes	32
2.3.1 Low liquor-to-fibre ratio dyeing	32
2.3.2 Low padding trough volumes	32
2.3.3 Hot washing-off	33
2.3.4 Aftertreatments to fix hydrolysed dye on the fibre	33
2.3.5 Urea- and electrolyte-free dyeing process	33
2.3.6 Polymerisation techniques for dye fixation	34

2.4 Chemical modification of cotton fibre prior to dyeing	34
2.5 Use of organic compounds in place of inorganic chemicals	35
2.6 Proposed research objective	35
Research Proposal	37
Chapter 3: Research proposal and hypotheses	38
3.1 Aims and objectives	38
3.2 Research questions	38
3.3 Rationale	39
3.4 Hypotheses	40
Experimental	42
Chapter 4: Materials, methods and measurements	43
4.1 Introduction	43
4.2 Materials	43
4.2.1 Cotton fabric	43
4.2.2 Dyestuffs and chemicals	43
4.2.3 Deionised water	44
4.3 Methods	44
4.3.1 Dyeing methods	44
4.3.1.1 Pad-steam dyeing	44
4.3.1.2 Pad-dry-bake dyeing	44
4.3.1.3 Pad-batch dyeing	45
4.3.1.4 Exhaust dyeing	45
4.3.1.5 Washing-off	46
4.3.2 DMF treatment	46
4.3.3 Industrial trial	46
4.4 Measurements and testing	47
4.4.1 Colour yield	47
4.4.2 Dye diffusion	47
4.4.3 Dye fixation	48
4.4.4 Dye exhaustion	48
4.4.5 Cross-sections of dyed cotton fibre	49
4.4.6 Ionic strength of dyebath	49
4.4.7 Colourfastness	50
4.4.8 Total dissolved solids (TDS)	50
4.4.9 FTIR analysis	51

4.5 Reproducibility of results and replicate experiments	51
Results and Discussion	52
Chapter 5: Determining the diffusion of reactive dyes into cotton fibre in pad dyeings using K/S values	53
5.1 Introduction	53
5.2 Hypothesis	55
5.3 Procedure for the proposed method of measuring diffusion	56
5.3.1 Determining $K/S_{reference}$	56
5.3.2 Determining $K/S_{diffusion\ index}$	56
5.4 Validation of the new method	57
5.4.1 Effect of electrolyte concentration on dye diffusion (pad-steam dyeing)	57
5.4.1.1 Microscopic analysis	57
5.4.1.2 New method for the extent of dye diffusion (%D)	57
5.4.2 Dye diffusion vs dye fixation and colour yield (pad-steam dyeing)	58
5.4.3 Rate of dye diffusion during steaming, baking and batching	60
5.4.4 Effect of dye concentration on diffusion	63
5.5 Industrial applications	64
5.6 Conclusion	64
Chapter 6: Role of dyebath ionic strength in pad-steam dyeing of cotton with reactive dyes	65
6.1 Introduction	65
6.2 Hypothesis	66
6.2 Selection of electrolytes for the study	66
6.4 Effect of different inorganic electrolytes on dye diffusion (constant electrolyte concentrations vs constant ionic strength)	67
6.5 Total dyebath ionic strength	69
6.6 Testing the hypothesis for dye exhaustion (exhaust dyeing)	69
6.7 Testing the hypothesis for using an organic electrolyte in pad-steam dyeing	71
6.6 Conclusion	72
Chapter 7: Use of alkaline polycarboxylic sodium salts in pad-steam dyeing of cotton with reactive dyes	73
7.1 Introduction	73
7.2 Optimum inorganic electrolyte concentration	75
7.3 Effect of inorganic alkali concentration	75
7.4 Determining optimum alkaline polycarboxylic sodium salt concentrations	76

7.4.1 Via laboratory dyeings (industrial practice)	76
7.4.2 Via calculating dyebath ionic strength	78
7.5 Use of tetrasodium GLDA	79
7.6 Effect of steaming time using optimum concentration of alkaline polycarboxylic salts	80
7.7 Comparison between traditional dyeing and dyeings using organic salts	81
7.7.1 Dye fixation and colour yield	81
7.7.2 Colourfastness properties	83
7.7.3 Effluent analysis	84
7.7.4 Economic considerations	85
7.7.5 FTIR analysis	85
7.8 Selection of electrolyte and alkali for dyeing cotton with reactive dyes	87
7.9 Industrial dyeing	88
7.10 Conclusion	88
Conclusions	89
Chapter 8: Overall conclusions and recommendations	90
8.1 Conclusions	90
8.2 Recommendations for future research	91
References	92
<i>Appendix I: Dyeing results for calculating dye diffusion, fixation and exhaustion</i>	101
<i>Appendix II: Material safety data sheets</i>	110

Tables

Table 1.1:	Typical composition of raw cotton	9
Table 1.2:	Summary of industrial history of reactive dyes for cellulosic fibres	12
Table 1.3:	Common reactive groups in order of increasing reactivity	14
Table 1.4:	Typical fixation percentages of cotton dyes	21
Table 4.1:	Washing-off conditions on Benninger dyeing range	47
Table 6.1:	Electrolyte concentration vs ionic strength	68
Table 7.1:	Optimum alkaline polycarboxylic sodium salt calculated on the basis of dyebath ionic strength	79
Table 7.2:	Colourfastness of cotton fabrics dyed at 120 sec steaming	83
Table 7.3:	TDS of dyeing effluents	84
Table 7.4:	Electrolytes and alkalis used for dyeing cotton with reactive dyes	87
Table A 1.1:	$K/S_{reference}$	101
Table A 1.2:	Effect of sodium chloride concentration (pad-steam dyeing)	101
Table A 1.3:	Effect of inorganic alkali concentration (pad-steam dyeing)	102
Table A 1.4:	Effect of sodium edate concentration (pad-steam dyeing)	102
Table A 1.5:	Effect of trisodium NTA concentration (pad-steam dyeing)	103
Table A 1.6:	Effect of tetrasodium GLDA concentration (pad-steam dyeing)	103
Table A 1.7:	Effect of steaming time (using optimum sodium edate)	104
Table A 1.8:	Effect of steaming time (using optimum trisodium NTA)	104
Table A 1.9:	Effect of steaming time (using optimum tetrasodium GLDA)	104
Table A 1.10:	Effect of steaming time (using optimum inorganic electrolyte and alkali)	105
Table A 1.11:	Effect of baking time (using optimum urea, alkali and antimigrant)	105
Table A 1.12:	Effect of batching time (using optimum sodium hydroxide and sodium carbonate/sodium silicate)	106

Table A I.13: Effect of dye concentration (pad-steam dyeing)	106
Table A I.14: Effect of dye concentration (pad-batch dyeing)	107
Table A I.15: Effect of different electrolytes at constant concentration (pad-steam dyeing)	107
Table A I.16: Effect of different electrolytes at constant ionic strength (pad-steam dyeing)	108
Table A I.17: Effect of different electrolytes at constant concentration (exhaust dyeing)	108
Table A I.18: Effect of different electrolytes at constant ionic strength (exhaust dyeing)	109
Table A I.19: Results of a cotton fabric dyed with 20 g/l CI Reactive Red 147 on production scale	109

Figures

Figure 1.1:	A morphological diagram of the cotton fibre	4
Figure 1.2:	Scanning electron micrographs of raw cotton fibres	5
Figure 1.3:	The chemical structure of cotton cellulose	6
Figure 1.4:	The dissociation of cellulose	7
Figure 1.5:	Covalent bond formation of cellulosate anion with a reactive dye	13
Figure 1.6:	Nucleophilic substitution mechanism	15
Figure 1.7:	Nucleophilic addition mechanism	15
Figure 1.8:	Molecular structure of CI Reactive Black 5 containing bis(sulphatoethylsulphone) reactive group	17
Figure 2.1:	Aminonicotinotriazine reactive group	31
Figure 5.1:	Fibre cross-sections of cotton fabrics dyed with 20 g/l CI Reactive Red 147 (before washing-off) at 60 sec steaming	57
Figure 5.2:	Effect of electrolyte concentration on dye diffusion	58
Figure 5.3:	Effect of electrolyte concentration on dye fixation and colour yield	59
Figure 5.4:	Dye diffusion vs dye fixation and colour yield	59
Figure 5.5:	Rate and extent of dye diffusion during steaming	60
Figure 5.6:	Rate and extent of dye diffusion during baking	61
Figure 5.7:	Rate and extent of dye diffusion during batching	62
Figure 5.8:	Optimum dye diffusion obtained with steaming, baking and batching	62
Figure 5.9:	Effect of dye concentration on dye diffusion at constant electrolyte (50 g/l), alkali (15 g/l) and steaming time (60 sec)	63
Figure 6.1:	Effect of different electrolytes on dye diffusion at constant concentration and constant ionic strength	68
Figure 6.2:	Effect of inorganic alkali on dye diffusion at 60 sec steaming	69

Figure 6.3:	Effect of different electrolytes on dye exhaustion at constant concentration and constant ionic strength	70
Figure 6.4:	Effect of inorganic alkali on dye exhaustion	71
Figure 6.5:	Effect of organic electrolyte on dye diffusion at constant concentration and constant ionic strength	71
Figure 7.1:	Molecular structure of alkaline polycarboxylic sodium salts	74
Figure 7.2:	Effect of inorganic electrolyte concentration on dye diffusion at 60 sec steaming	75
Figure 7.3:	Effect of inorganic alkali concentration on dye fixation and colour yield	76
Figure 7.4:	Effect of alkaline polycarboxylic sodium salt concentration on dye diffusion and dye fixation	77
Figure 7.5:	Effect of alkaline polycarboxylic sodium salt concentration on dye colour yield	78
Figure 7.6:	Effect of tetrasodium GLDA concentration on dye fixation and colour yield	80
Figure 7.7(a):	Effect of steaming time on dye fixation using alkaline polycarboxylic sodium salt	81
Figure 7.7(b):	Effect of steaming time on colour yield using alkaline polycarboxylic sodium salt	81
Figure 7.8:	Dye fixation and colour yield of 20 g/l shade using optimum inorganic chemicals and alkaline polycarboxylic sodium salts	82
Figure 7.9:	Spectra of dyed cotton subtracted by the spectra of undyed cotton and the dye	86
Figure 7.10:	Dye fixation and colour yield of 20 g/l CI Reactive Red 147 using optimum inorganic chemicals and sodium edate on production scale	88

Abbreviations and symbols

A_0	Maximum absorbance of dyebath before fabric immersion in exhaust dyeing
A_1	Maximum absorbance of dyebath before adding alkali in exhaust dyeing
A_2	maximum absorbance of dyebath at the end of exhaust dyeing
AATCC	American Association of Textile Chemists and Colourists
Al^{3+}	Aluminium ion
AS	Australian Standard
AUD/Kg	Australian dollars per kilogram
BASF	Badische Anilin und Soda Fabrik
Ca^{2+}	Calcium ion
CO_3^{2-}	Carbonate ion
$(...COO)^-$	Carboxyl radical
Cs^+	Caesium ion
cm/sec	centimetre per second
cm^{-1}	per centimetre
CI	Colour Index
K/S	Colour strength value
K/S_{DMF}	Final colour yield of the dyed fabric after DMF treatment
Cl^-	Chlorine ion
CIE	Commission Internationale de l'Eclairage
$^{\circ}C$	Degree centigrade
$^{\circ}B\acute{e}$	Degree Baumé
DMF	N,N-dimethyl formamide
EDTA	ethylene diamine tetra-acetic acid
e.g.	example
FTIR	Fourier Transform Infrared Spectroscopy

GLDA	N,N-bis(carboxylatomethyl)-L-glutamate
g/l	grams per litre
g/mol	grams per mole
g/m ²	grams per square metre
H ₂ O	Molecular formula of water
HSO ₄ ⁻	Bisulphate ion
-OH	Hydroxyl group
hrs	hours
ICI	Imperial Chemical Industries
μ	Ionic strength
K	Absorption coefficient
K ⁺	Potassium ion
K/S	Absorption and scattering ratio (a measure of the colour strength)
L ⁺	Lithium ion
LSCM	Laser Scanning Confocal Microscopy
l/m	litres per minute
λ _{max}	Maximum absorption wavelength
m	metres
MI	Migration Index
Mg ²⁺	magnesium ion
mg/l	milligrams per litre
ml/l	millilitre per litre
mm	millimetres
min	minutes
NA	Not applicable
Na ⁺	Sodium ion
Na ₂ CO ₃	Molecular formula of sodium carbonate

$\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$	Molecular formula of tetrasodium EDTA
$\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$	Molecular formula of tetrasodium EDTA dihydrate
NaCl	Molecular formula of sodium chloride
NH_4^+	Ammonium ion
NTA	Nitrilo triacetate
o.m.f.	on mass of fibre
OH^-	Hydroxide ion
%	Per cent
%D	Per cent dye diffusion
%E	Per cent dye exhaustion
%F	Per cent dye fixation
%PE	Per cent primary dye exhaustion
%T	Per cent transmittance
%TE	Per cent total dye exhaustion
pH	The power of Hydrogen
R	Reflectance value
S	Scattering coefficient
sec	seconds
$-\text{SO}_3\text{Na}$	sodium sulphonate group
Σ	Summation
i.e.	that is to say
TDS	Total Dissolved Solids
%TE	Total per cent dye exhaustion
UATR	Universal Attenuated Total Reflection
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
vs	versus
w/w	weight per weight

Publications

Refereed Conferences

- [1] **A. Khatri**, R. Padhye and M. White, "Developments in reactive dyeing of cotton to improve sustainability", in *ERE 2010 "Transitions to a Sustainable Future"*, CQ University, Rockhampton QLD Australia.
- [2] **A. Khatri**, R. Padhye, M. White and K. Cowlshaw, "Biodegradable organic salts for reactive dyeing of cotton", in *IFFTI Conference 2010, Fashion: Sustainability and Creativity*, Fu Jen Catholic University, Taipei Taiwan.
- [3] **A. Khatri**, R. Padhye and M. White, "Environmentally improved approach for pad-steam dyeing of cotton with reactive dyes using sodium edate", in *ICEE 2009 "Role of Energy Resources in Sustainability of Environment"*, Quaid-e-Awam University of Engineering, Science and Technology, Nawabshah Pakistan.

Refereed Journals

- [1] **A. Khatri**, R. Padhye and M. White, "Use of tetrasodium ethylene diamine tetraacetate in pad-steam dyeing of cotton with reactive dyes", *Quaid-e-Awam University Research Journal of Engineering, Science and Technology*, vol. 9, pp. 1-6, 2010.
- [2] **A. Khatri**, R. Padhye and Max White, "The use trisodium nitrilo triacetate in pad-steam dyeing of cotton with reactive dyes", *Colouration Technology*, submitted, September 2010.

Summary

This thesis presents the results of studies into the effectiveness of biodegradable alkaline organic salts as alternatives to traditional nonbiodegradable inorganic salts (electrolytes) and alkalis used in pad-steam dyeing of cotton with reactive dyes. The primary objective of the study was to develop improved environmentally sustainable dyeing systems. A difluorochloropyrimidine and a *bis*(sulphatoethylsulphone) dye were used in this study.

After early encouraging results using alkaline polycarboxylic sodium salts, it became clear that current literature and dyeing theories on the role of the electrolyte cations and anions needed further explanation for pad dyeing methods. Accordingly, studies were carried out on a range of electrolytes of different cations and anions. These studies have resulted in a new theory for dyeing of cotton with anionic dyes using electrolytes. Traditionally, industry and dye research laboratories have determined the optimum concentration for an electrolyte, in grams per litre, via laboratory tests. This research has shown that for a given cation the required concentration of an alternative electrolyte can be determined by its ionic strength, i.e. $\mu = \frac{1}{2} \sum [\text{molar concentration of the salt} \times (\text{ionic charge})^2]$. In other words, having determined the optimum concentration for, say, sodium chloride, the optimum concentration of any other sodium salt is the concentration required to give the same ionic strength. These findings also lead to an improved understanding of the use of electrolytes. The driving force for dye diffusion and also dye exhaustion (exhaust dyeings) is the dyebath ionic strength; i.e. it is independent of the type of electrolyte and alkali.

In pad dyeing of cotton, dye fixation and ultimate colour yield significantly depend on the dye diffusion and the subsequent uniformity of distribution of dye molecules throughout the fibre. A hypothesis for a new and simple method of determining the extent of dye diffusion in pad dyeing of cotton with reactive dyes was proven. The new method is based on reflectance measurements for quantifying the dye diffusion.

The new theory on the role of electrolyte cations and anions and the new method for determining the extent of dye diffusion were then used in the study on a range of biodegradable alkaline organic salts as alternatives to traditional nonbiodegradable inorganic electrolytes and alkalis for pad-steam of dyeing of

cotton with reactive dyes. The research presents results where any of the two biodegradable alkaline polycarboxylic sodium salts, tetrasodium ethylene diamine tetra-acetate and trisodium nitrilo triacetate can be used as alternatives to traditionally used inorganic electrolyte and alkali in the pad liquor. A third alkaline polycarboxylic sodium salt, tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate, was identified late in the research study. It was also shown to have potential as an alternative organic salt. The optimum concentrations of the organic salts were determined for dye diffusion, dye fixation and colour yield. The dye fixation, colour yield and ultimate colourfastness achieved by using alkaline polycarboxylic salts were closely comparable to those obtained by using inorganic electrolyte and alkali. More interestingly, the dyeing effluent showed considerable reductions in total dissolved solids content with the organic salts. In order to examine the applicability of the alkaline polycarboxylic salt, an industrial trial was carried out using sodium edate which gave similar encouraging results.

Introduction and Literature Review

Chapter 1

Dyeing of cotton with reactive dyes

1.1 Cotton textiles

Cotton fabrics are known to have been in use at least for 7000 years [1]. Although, numerous synthetic fibres such as polyesters, acrylics, polyamides and polypropylenes have entered the market over the past 50 years, cotton has still maintained its strong consumer demand worldwide. Today, cotton textiles represent more than half of the global textile market [2], and the demand is expected to continue [3, 4]. This dominance of cotton fibre is mainly due to its natural comfort, performance and appearance.

1.2 Cotton fibre

Cotton is the purest form of the natural cellulose polymers. The fibre is a single plant cell found as the seed hair of a genus of the plants called 'gossypium' [5]. Like all plant cells, a mature cotton fibre has a distinct cuticle, well developed primary and secondary walls and a lumen (Figure 1.1) [6].

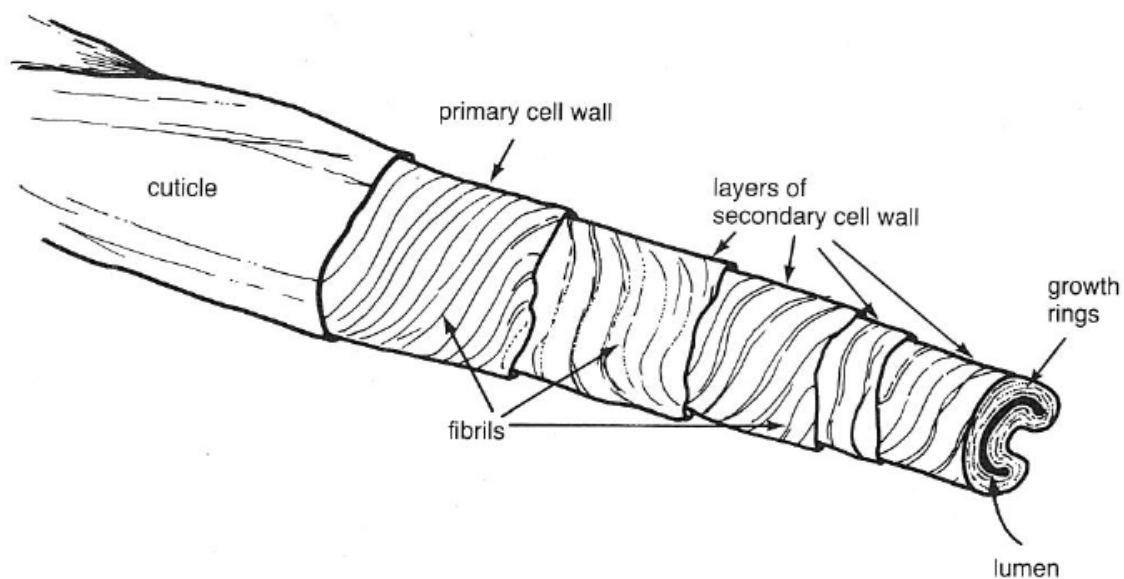


Figure 1.1: A morphological diagram of the cotton fibre (source: [6])

The cuticle is the very outside or 'skin' of the fibre. It is composed of pectins, protein and waxes. Therefore, it makes the fibre hydrophobic unless a wetting agent is used. The primary cell wall is immediately underneath the cuticle. The secondary wall, beneath the primary wall, forms the bulk of the fibre. Inadequate development of the secondary wall during the growth of cotton fibres on the plant creates 'immature' fibres. If there is no development of the secondary wall, then the fibre is referred to as a 'dead' cotton fibre. The immature and dead fibres tend to become entangled into small fibrous bundles, called neps, during the mechanical processes for producing yarns [7, 8]. The immature fibres cannot be dyed to shades as dark as mature fibres and the dead fibres remain undyed. Therefore, neps can be instantly seen on the surface of the dyed fabrics appearing as white and light spots. The colour contrast between the dyed neps and mature fibres can be reduced by swelling of immature fibres during mercerising (Section 1.2.2.2). The primary and secondary walls are composed of cellulose 'fibrils'. The fibrils occur in the spiral form at certain angles to the fibre axis. The lumen is a longitudinally hollow canal in the centre of the fibre.

Micrographs of the raw cotton fibres are shown in Figure 1.2. Mature cotton fibres are flattened tubes and are highly convoluted. The surface of such fibre enables interfibre friction (cohesiveness) which is helpful in producing fine spun yarns of adequate strength. The appearance of the cross-section of cotton fibre is bean- or kidney-shaped. The convolutions and bean-shaped cross-section of the cotton fibre enable cotton apparel to be more comfortable. This is because the particular structure of cotton fibre is more compatible with human skin and makes apparel more moisture absorbent [6].

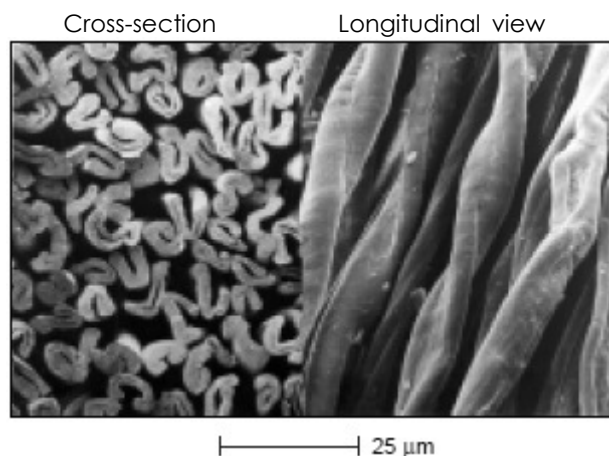


Figure 1.2: Scanning electron micrographs of raw cotton fibres (source: [5])

1.2.1 Cotton polymer and fibre polymer system

Cotton fibres are composed of cellulose polymers, mostly α -cellulose [8]. The basic molecular structure of cotton cellulose is shown in Figure 1.3. Its repeating unit is cellobiose. The degree of polymerisation of cotton cellulose is about 5000 based on cellobiose units [6].

Cotton polymer system is highly crystalline and oriented. Important groups on cotton polymer (cellulose) are hydroxyl and methylol groups. The presence of abundant hydroxyl groups and the polymer chain conformation cause intermolecular and intramolecular hydrogen bonding that enhances the rigidity of the fibre structure. The existence of van der Waal's forces is of little significance.

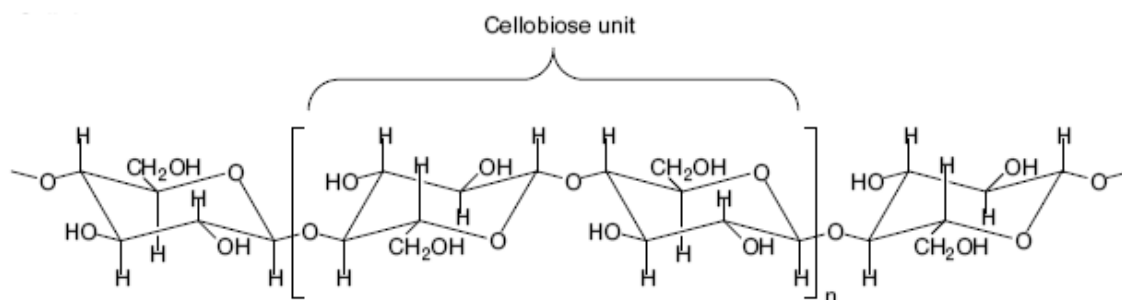


Figure 1.3: The chemical structure of cotton cellulose (source: [7])

1.2.2 Properties of cotton fibre

1.2.2.1 Hygroscopic properties

The cotton fibre is hydrophilic and water absorbent [7]. This is because the polar hydroxyl groups of cellulose polymer attract the polar water molecules. Its porous structure allows ready penetration of water molecules between the fibrils and into the amorphous regions of the fibre where they can easily form hydrogen bonds with free cellulose hydroxyl groups. Even the typical cotton dyes, being quite large molecules, easily penetrate into the accessible interfibrillar and amorphous regions.

The standard moisture regain of cotton fibre is about 8% and rises to around 25–30% at 100% relative humidity, at ambient temperature [7]. Cotton fibre swells with water absorption because of the swelling of the secondary wall. It is one of the few fibres which gains strength when wet [6]. This may be due to a temporary improvement in polymer alignment in the amorphous regions.

1.2.2.2 Chemical properties

The chemical reactions with cotton cellulose occur mainly due to the activity of hydroxyl groups and depend on the supermolecular structure. Any reaction is initiated in the more accessible amorphous regions and at the surfaces of crystalline regions [8]. The reactions can be broadly classified into two categories: esterification and etherification. Esterification is usually carried out under acidic conditions. These reactions include nitration, acetylation, phosphorylation, and sulphation. Acidic conditions hydrolyse the cotton cellulose at the glucoside oxygen atom which links the two glucose units to form the cellobiose unit (Figure 1.3) [6]. Stronger acids hydrolyse the cellulose more rapidly. A cotton fibre dissolves completely in a 70% aqueous sulphuric acid [9]. Etherification, on the other hand, is favoured in an alkaline medium. This reaction is important for dyeing cotton with reactive dyes. In the presence of even dilute base, cellulose behaves as a weak acid and ionises to form a cellulosate anion according to the chemical equation given in Figure 1.4 [10]. This anion is capable of reacting with suitable dyes by nucleophilic substitution or addition to form covalent bonds [11]. Vickerstaff provided the evidence for reactive dyes forming covalent bond with the cellulosate anion (Cellulose-O⁻) [12].

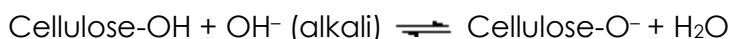


Figure 1.4: The dissociation of cellulose

Mercerising is a treatment of cotton with strongly alkaline solutions where fibre lustre, tensile strength and dye uptake are improved [6, 13]. Such improvements are principally due to the swelling of cotton fibre and the alignment of poorly oriented fibre polymers during this treatment. The swelling is fundamentally due to the imbibition of water as a consequence of the sorption of alkali by the cellulose [5].

Cellulose is readily attacked by oxidising agents, such as hypochlorites, chlorous, chloric, and perchloric acids, peroxides, dichromates, permanganates, periodic acid, periodate salts, and nitrogen tetroxide [8]. Oxidation of cellulose can lead to two products: reducing and acidic oxycellulose. In reducing oxycellulose, the hydroxyl groups are converted to carbonyl groups or aldehydes, whereas in acidic oxycellulose, the hydroxyl groups are oxidised to carboxyl groups or acids.

1.2.2.3 Thermal properties

Cotton fibres are heat conductive [6]. Excessive application of heat energy causes the cotton fibre to char and burn. Heating the fibre generally causes dehydration and decomposition of cellulose [8]. At temperatures above 150 °C, the extent of browning and hardening of the fibres increases [7]. If processing requires higher temperatures, shorter treatment times are set to avoid thermal damage.

1.2.2.4 Mechanical properties

Cotton fibres possess good mechanical properties such as tensile strength and cohesiveness. This is because they have high molecular weight, crystallinity, the countless, regular, hydrogen bonds formed between adjacent polymers within the fibre, and fibre surface structure [6, 7].

1.3 Dyeing of cotton

1.3.1 Preparing cotton for dyeing

Table 1.1 shows a typical composition of the raw cotton fibre. The raw cotton is not sufficiently water absorbent because of its natural contaminants specially oils and waxes. To make cotton ready for dyeing, the natural contaminants must be removed. This is achieved by treating cotton at the boil with the alkaline solutions where waxes are emulsified, oils (fats) and proteins are hydrolysed, and mineral salts are solubilised [7]. This alkaline treatment also removes some low molecular mass noncellulosic carbohydrates and results in around 7% loss in mass of the fibre. Such cleaning process is known as 'scouring'.

Preparation of cotton woven fabrics normally consists of singeing, desizing, scouring and bleaching [13]. In most other cases, scouring and bleaching are the only preparation processes. For certain end uses, mercerising is carried out. Singeing is the process of removing protruding fibres on the surface of the fabric. This process is omitted for certain end-use products such as flannel and velvet fabrics. Desizing is the process of removing the size on the most woven fabrics. Size is applied to reduce the frictional properties of warp yarns that improves weaving productivity by decreasing yarn breakages and increasing weft insertion speeds. Bleaching is

carried out to destroy the yellowish-brown colour naturally present in cotton fibres that results in the fibres having a pure white appearance to the fibres.

Table 1.1: Typical composition of raw cotton (source: [7])

Component	Main location	Amount (%)
Cellulose	Secondary wall	86.8
Oils, waxes	Cuticle	0.7
Pectins	Primary wall	1.0
Carbohydrates	Primary wall	0.5
Proteins	Lumen	1.2
Salts	Lumen	1.0
Water		6.8
Other		2.0

1.3.2 Dyeclasses for cotton

Today, the available synthetic dyeclasses for dyeing cellulosic fibres are direct dye, reactive dye, vat dye, sulphur dye and azoic dye. All of these dye classes have some advantages but also some limitations [14]. They may be categorised in two ways: ionic character, and the main way with which the dye molecules attach to the fibre (Section 1.4.12).

The vat, sulphur and azoic dyes can generally be categorised as nonionic dyes as they are generally water-insoluble in their original form. The whole molecules of these dyes are mechanically retained within the fibre polymer system. Direct and reactive dyes are water soluble anionic dyes as their anions are the colour constituents.

1.3.3 Dyeing of cotton with anionic dyes

Dyeing of textiles is fundamentally a process of transferring dye species onto the fibre through an aqueous medium (dye exhaustion) followed by dye penetration into the fibres (dye diffusion). When cotton fibres are immersed in an aqueous dyebath, the

fibre surface acquires an initial negative charge that is referred to as zeta potential [15]. This is due to a rearrangement of charge groups at the interface between the fibre and the aqueous environment. Anionic dyes are usually sulphonated to provide aqueous solubility and possess a negative charge in the aqueous dyebath. Therefore, there is an electrostatic repellency for the dyes to diffuse through the fibre-water interface. The only widely used method of overcoming this barrier is the addition of large quantities of inorganic electrolyte, such as sodium chloride or sodium sulphate.

When an electrolyte is added to the dyebath, it dissociates completely into its cations and anions, for example sodium ions (Na^+) and chlorine ions (Cl^-) in the case of sodium chloride. The negatively-charged surface of the fibre is suppressed by cations enabling the dye anion to enter the fibre more readily. The presence of electrolyte anions also assists the dye anion to leave the dyebath and enter the fibre polymer system due to the repulsion effect [6].

Direct dyes have inherent substantivity for cellulosic fibres. This is attributed to their large co-planar molecular structure (Section 1.4.7). The dyes are normally applied from an aqueous dyebath containing an electrolyte. The fibre is immersed into the dyebath containing the dissolved dyes. The bath is then gradually heated, usually to the boil, and the electrolyte is added for promoting dye exhaustion and diffusion. The most attractive feature is the simplicity of the dyeing process. However, a separate cationic aftertreatment is necessary for most direct dyeings to enhance washing fastness of the dyed fibre [16, 17].

The washing fastness standard, even when given a conventional aftertreatment, does not meet the demands for most cellulosic apparel and furnishing materials. Consequently, direct dyes have been replaced by reactive dyes to a great extent due to better washing fastness of reactive dyed cotton. The reactive dyes also provide exceptionally bright colours in many hues. The very good washing fastness of reactive dyes is because they form covalent bonds with the fibre.

1.4 Reactive dyes for cotton

1.4.1 Historical development

A variety of attempts have been made in the struggle to obtain the covalent bond formation between a dye and a fibre. There are two general approaches in this respect: producing a dye within the fibre, and producing a dye that is reactive

towards the fibre. In 1895, Cross and Bevan achieved a covalent dye-cellulose bond with respect to the first approach [18]. They showed that cellulose (Cellulose-OH) treated with strong alkali was changed into 'soda cellulose' (Cellulose-ONa). The soda cellulose could be treated with benzoyl chloride to form benzoyl cellulose. The resultant benzoyl cellulose was nitrated where the nitro group was reduced and the amino group was diazotised. Coupling the diazo group with N,N-dimethylaniline gave 'dyed' fibres [19].

The idea of covalent bond formation between the reactive group of a dye molecule and a fibre polymer was initiated in the early 1900s [20]. Various reactive entities were found which could react with the hydroxyl groups of cellulose and eventually be converted into coloured cellulose. In 1954, Rattee and Stephen developed the reactive dyes for cotton fibre containing highly reactive dichloro-s-triazine groups with a dyeing procedure [21]. They established that dyeing cotton with these dyes under mild alkaline conditions resulted in a reactive chlorine atom on the triazine ring of the dye being substituted by an oxygen atom from a cellulose hydroxyl group (Figure 1.6). The role of the alkali was to cause dissociation of some of the hydroxyl groups in the cellulose (Figure 1.4) to obtain cellulosate anion that reacts with the dye. This discovery led to the introduction of the first commercial reactive dye class for cellulose that was marketed by ICI in 1956 under the trade name of Procion M [11, 21, 22]. These dyes were introduced for the production of fast bright colours on cellulosic fibres using continuous dyeing methods [23]. Procion Brilliant Red M-2B (CI Reactive Red 1) is one of the early dyes of this range [18].

The major factor contributing to the long delay in producing the first reactive dye for cellulose was the belief that cellulose was a relatively inert fibre. Further was the fear that the conditions required to effect a chemical reaction would cause serious fibre degradation [18, 22]. Therefore, in early studies, dyestuff chemists were led astray in thinking that they needed to convert cellulose to the more reactive soda cellulose which could make fibre reactivity possible [22, 24]. No one expected that any reactive group would prefer to react with a hydroxyl group of cellulose when cotton is immersed in an aqueous dyebath containing numerous competitive hydroxide ions of water [20]. However, a large number of reactive dyes with a variety of reactive groups have been developed. Today, the fibre-reactive dyes are the largest single dye class used for dyeing cotton. A summary of the industrial history of commercial reactive dyes for cellulosic fibres is shown in Table 1.2 [18].

Table 1.2: Summary of industrial history of reactive dyes for cellulosic fibres

Year	Commercial name	Company *
1956	Procion M	ICI
1957	Procion H	ICI
1957	Cibacron	Ciba
1958	Remazol	Hoechst
1959	Levafix	Bayer
1959	Reacton	Geigy
1959	Drimarene	Sandoz
1961	Levafix E	Bayer
1963	Elisiane	Francolour
1964	Primazin P	BASF
1964	Solidazol	Cassella
1964	Procilan	ICI
1966	Levafix EA, Levafix P	Bayer
1966	Lanasol	Ciba
1968	Reactofil	Geigy
1970	Verofix	Bayer
1970	Drimalan	Sandoz
1970	Procion HE, Procion Supra	ICI
1977	Procion T	ICI
1978	Cibacron F	Ciba
1979	Sumifix Supra	Sumitomo
1984	Kayacelon	Nippon Kayaku
1987	Procilene	ICI
1988	Cibacron C	Ciba

1.4.2 Constitutional characteristics of reactive dyes

The four characteristic features of a typical reactive dye molecule are the chromophoric group, the water solubilising group(s) usually sulphonate ($-\text{SO}_3\text{Na}$), the reactive group, and the bridging group that attaches the reactive group either directly to the chromophore or to some other part of the dye molecule (Figure 1.5). Each of these structural groups has an effect on the physical properties of the dye molecule. The properties include colour, molecular size, solubility, substantivity, ability

* Today, the names of many companies have been changed because of the transfer, expansion, merger or division of the businesses. The names, mentioned here, are when the dyes were introduced.

to diffuse into fibres, migration within the fibre(s), colourfastness, and so on.

Typical reactive dye chromophores include the azo, triphenodioxazine, phthalocyanine, formazan and anthraquinone [20, 25]. Most commercial ranges of reactive dyes have a comprehensive colour gamut, many of which are particularly bright.

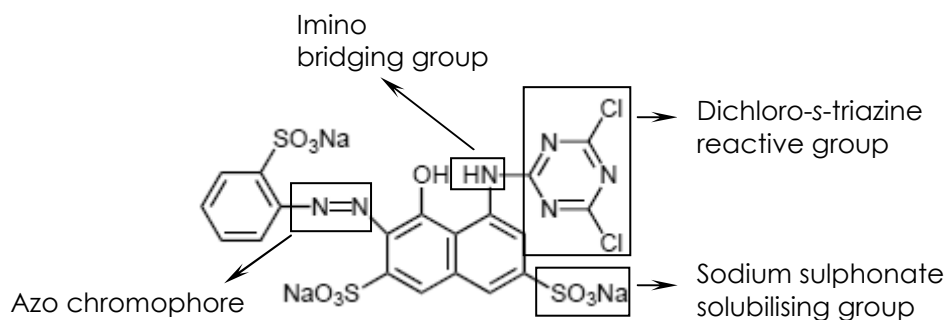
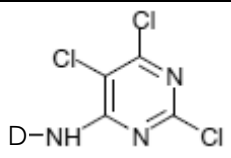
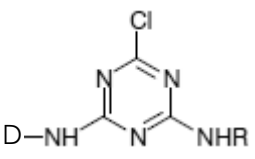
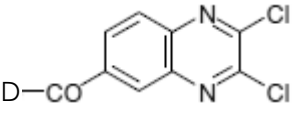
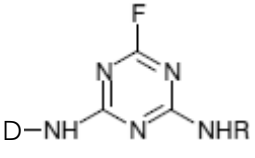
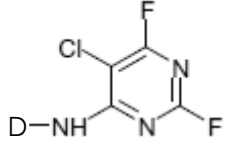
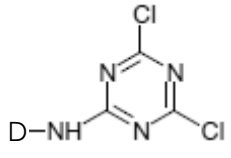


Figure 1.5: Molecular structure of CI Reactive Red 1 (source: [26])

1.4.3 Reactive groups

Reactive dyes possess their ability to form covalent bonds with the fibre due to the presence of the reactive groups in their structure. A wide range of possible reactive groups has been studied and evaluated by researchers and dyestuff manufacturers [20]. However, the production of the dyes of commercial interest is limited by a number of factors such as adequate reactivity towards cotton but lower reactivity towards water (Figures 1.6 and 1.7), adequate dye-fibre bond stability, ease of manufacture, dye stability during storage and cost of the final reactive dye. Table 1.3 shows some typical reactive groups. The CI Reactive Red 147 containing difluorochloropyrimidine reactive group was used in this study. The reactive groups can be divided into two distinct categories depending on the mechanism of formation of the dye-fibre bond, and the stability of this bond to subsequent treatments. They are the carbon-nitrogen (heterocyclic) ring structures such as triazinyl and pyrimidinyl, and the masked vinyl sulphones usually in the form of sulphatoethylsulphone precursor group.

Table 1.3: Common reactive groups in order of increasing reactivity

Reactive group †	Typical commercial name(s)	Reactivity
 Trichloropyrimidine	Drimarene X (Clariant)	Low
 Amino-chloro-s-triazine	Procion H (DyStar) Basilen (BASF) Cibacron (Ciba)	Low
$D-SO_2CH_2CH_2OSO_3Na$ Sulphatoethylsulphone	Remazol (DyStar)	Moderate
 Dichloroquinoxaline	Levafix E (DyStar)	Moderate
 Amino-fluoro-s-triazine	Cibacron F (Ciba)	Moderate
 Difluorochloropyrimidine	Drimarene K (Clariant) Levafix E-A (DyStar)	Moderate to high
 Dichloro-s-triazine	Procion MX (DyStar)	High

† D = Dye chromophore

1.4.4 Mechanisms of dye attachment to cellulose

1.4.4.1 Nucleophilic substitution mechanism

Reactive groups based on carbon-nitrogen ring structures undergo nucleophilic substitution (Figure 1.6) [26]. They react with cellulose by the substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group. The adjacent nitrogen atom in a heterocyclic ring activates the system for nucleophilic attack. The attacking nucleophile can be either a cellulose anion or a hydroxide ion of water. The reaction with cellulose anion leads to 'fixation' of the dye on the fibre and that with hydroxide ion results in 'hydrolysis' of the reactive dye.

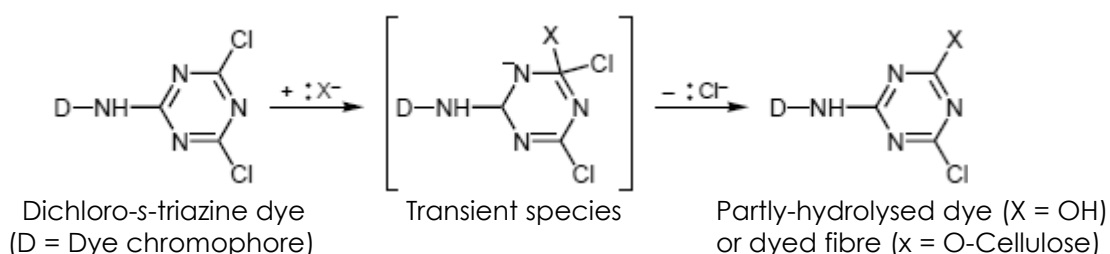


Figure 1.6: Nucleophilic substitution mechanism (source: [26])

1.4.4.2 Nucleophilic addition mechanism

Reactive groups based on masked vinyl sulphone structures undergo nucleophilic addition (Figure 1.7). They react with cellulose by addition to a carbon-carbon double bond, usually activated by an adjacent electron-attracting sulphone group. This type of group is usually generated in the dyebath by elimination of sulphate ion from a sulphatoethylsulphone precursor group in the presence of alkali. Again, the nucleophilic addition of hydroxide ion of water leads to dye hydrolysis.

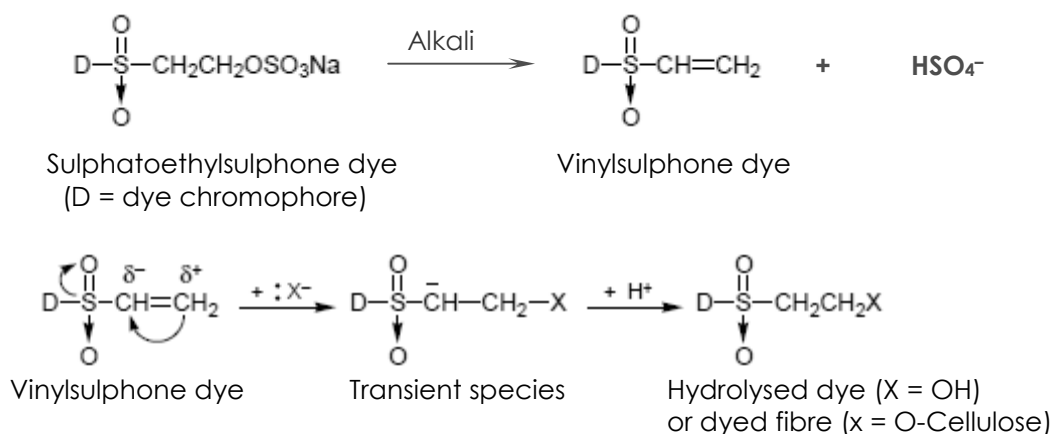


Figure 1.7: Nucleophilic addition mechanism (source: [26])

1.4.5 Dye reactivity

Dye reactivity refers to the rate at which a reactive group tends to undergo a nucleophilic substitution or addition reaction with the fibre polymer. The reactive groups of various types possess a wide range of reactivities. The dyes of high reactivity, such as dichloro-s-triazine reactive dyes, are applied to cotton at lower temperatures and only require a weak alkali such as sodium bicarbonate or sodium carbonate for fixation. The less reactive types, such as aminochloro-s-triazine dyes, need higher temperatures and stronger alkalis such as sodium carbonate and/or sodium hydroxide. Table 1.3 gives the typical reactive groups commercially popular with reference to their relative reactivity.

1.4.6 Multifunctional reactive dyes

1.4.6.1 Bifunctional reactive systems

The early reactive dyes had only one reactive group in the dye molecule. Such dyes are referred to as monofunctional reactive dyes. Many of the reactive dyes available today are bifunctional with molecules having two identical or different reactive groups. Dyes with two identical reactive groups are known as homo-bifunctional reactive dyes and those with different groups as hetero-bifunctional. Technically, the bifunctional dyes have increased probability of reaction with the fibre. Thus, they give higher fixation yields and thus leave less colour in the dyehouse effluent. The CI Reactive Black 5 (Figure 1.8, source: [26]) is a dye containing two sulphatoethylsulphone precursor groups. This dye has long been successful and known to produce a high degree of fixation. The CI Reactive Blue 250 has a similar reactive system and was used in this study. The idea of two reactive groups in a dye molecule then led to the introduction of the first commercial range of homo-bifunctional dyes, based on two aminochloro-s-triazine reactive groups in the same molecule. They were called Procion HE (Table 1.2). The Kayacelon React (Table 1.2) and most of the Cibacron LS (the low-salt) reactive dyes are homo-bifunctional. The brief description on Kayacelon React and Cibacron LS is given in the next chapter.

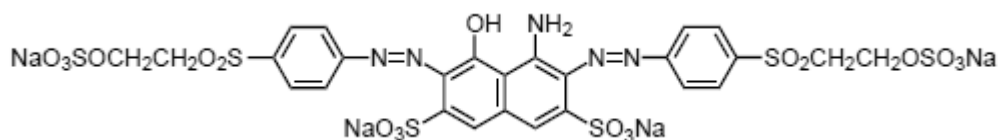


Figure 1.8: Molecular structure of CI Reactive Black 5 containing bis(sulphatoethylsulphone) reactive group

A hetero-bifunctional dye possesses two different reactive groups and thus has two different extents of reactivity towards the cotton and two possible optimal temperature and pH conditions for dye-fibre reaction. Therefore, such a dye can give a more uniform degree of fixation over a wider range of fixation temperature and pH conditions than a homo-bifunctional dye. Amongst the earliest hetero-bifunctional reactive dyes were those capable of reacting with cellulose via both mechanisms, nucleophilic substitution and nucleophilic addition. This is because they contained a halogenotriazine and a sulphatoethylsulphone precursor groups. The typical examples are the Sumifix Supra (monofluorotriazine and sulphatoethylsulphone) and Cibacron C (monochlorotriazine and sulphatoethylsulphone) mentioned in Table 1.2. Many such hetero combinations have been described, but not all have achieved commercial success [26, 27]. However, most reactive dye manufacturers today market at least one range of hetero-bifunctional dyes.

1.4.6.2 Polyfunctional reactive systems

Incorporating more than two reactive groups into the dye molecule should theoretically increase the fixation efficiency. However, these additional reactive groups can have an impact on important dyeing properties such as substantivity and migration because they change the molecular size and alter the extent and mode of reactivity. Therefore, the idea of additional reactive group(s) have been more of patenting interest [27, 28]. For example, DyStar disclosed a dye containing the monochlorotriazine, monofluorotriazine and vinylsulphone combinations [28]. A few of these dyes have successfully been marketed such as Cibacron Red C-2G and Remazol Red BS (CI Reactive Red 181) [27-29]. Tertafunctional and pentafunctional dyes have also been discovered by researchers and dye manufacturers [28]. However, none of these has advanced to the level of being commercialised.

1.4.7 Dye substantivity

The term 'substantivity' was originally derived from popular substantive dyes (Direct dyes) and refers to the ability of a dye to uptake from a liquid medium onto a textile fibre and to set [30]. The quantitative measurement of the force with which the dye is captured by the fibre is determined as 'affinity'. However, substantivity is often used as a qualitative description of the affinity of a dye for a particular fibre.

The substantivity of a dye generally depends on the extent of its solubility, and on its molecular size and structure. Substantivity is favoured by the formation of multiple dye-fibre bonds [31]. In reactive dyeing of cotton, these bonds are hydrogen bonds and covalent bonds. Thus, reactive groups also exert a significant effect on the substantivity.

1.4.8 Dye exhaustion

In exhaust dyeing, the fibre starts absorbing the dye as soon as it is immersed into the dye liquor. As a result, the concentration of dye in the dyebath decreases gradually [32]. This shift of dyes towards the fibre is generally referred to as exhaustion. The degree of dyebath exhaustion as a function of time describes the rate and extent of the dyeing process. For a single dye, the exhaustion is expressed as the mass of dye taken up by the fibre divided by the total mass of the dye originally used in the dyebath of constant volume [30] (Equation 1.1).

$$\% \text{Exhaustion} = [(C_o - C_s) / C_o] \times 100 \quad (1.1)$$

Where, C_o and C_s are the concentrations of dye in the dyebath initially and at sometime later during the process, respectively.

1.4.9 Dye diffusion

The penetration of a dye into the fibre polymer system from the dye-fibre interface is known as dye diffusion. Fick's second law states that the rate at which the dye diffuses across a unit area in the fibre is proportional to the concentration gradient across that area, the proportionality constant being the diffusion coefficient [33]. The coefficient of diffusion is a parameter used in most fundamental studies on dye diffusion. The extent of dye diffusion as a percentage of the total dye on the fibre has not been generally reported. Extensive studies on reactive dye diffusion into

cotton in pad dyeings are presented in Chapter 5, where a new method of determining diffusion percentage has been proven.

1.4.10 Dye migration

The mobility of dye molecules within the fibre is referred to as dye migration. The extent of this mobility depends mainly on dye substantivity and dye-fibre bonding. In the case of dyeing cotton with reactive dyes, covalently-fixed dyes can not migrate during the dyeing process. Accordingly, the dye can not diffuse into the fibre when it is fixed on the surface of the fibre [34].

1.4.11 Role of electrolyte cations and anions

In dyeing of cotton with anionic (direct or reactive) dyes, the principle role of the cation of an electrolyte has been widely reported to reduce or even extinguish the negative charge built-up (the zeta potential) on the fibre in an aqueous media [6, 17, 20, 35-37]. The negative charge on the fibre is not required because it repels anionic dye molecules in the dyebath. Iyer et al [38] have studied the effect of three different Group 1A metal chlorides (i.e. lithium chloride, sodium chloride and potassium chloride) in the dyeing process. They found that increased dye exhaustion was obtained with increasing size of the alkali metal cation: potassium (K^+) > sodium (Na^+) > Lithium (Li^+). Potassium chloride gave the highest dye exhaustion and the lithium chloride provided the lowest. This supported the previous work by Nango et al [39], where they proposed the similar order, i.e. caesium (Cs^+) > K^+ > Na^+ . This was thought to be due to the increasing disrupting effect of electrolyte cations on the water molecules around the dye molecules with the increasing size of the cation. One may visualise the role of the cation as perturbing the intermolecular hydrogen bonds of the water.

Noah et al [35] extended the similar work and included Group 2A metals (calcium (Ca^{2+}) and magnesium (Mg^{2+})), aluminium (Al^{3+}), and other cations. They found that electrolytes of Group 2A alkaline earth metals outperformed for dye exhaustion comparing to Group 1A alkali metals. However, many other studies have shown that using calcium or magnesium salts is not favourable in the dyeing processes [40-43]. This is because these salts tend to promote dye aggregation and to increase water hardness. The aluminium salts did not support the dye exhaustion

adequately. This is probably due to the fact that their large trivalent cation tends to form insoluble aluminium-dye complexes.

Nango et al [39] also looked at the effect of different anions of the electrolyte but found that there were no significant changes in the dye uptake. However, Noah et al [35] later obtained different depths of shade with different electrolyte anions (chloride and sulphate) in dyeing with direct dyes. They achieved deeper shades with the chloride counter-ion.

Most studies on the role of electrolyte cations and anions have been carried out for exhaust dyeings, and most of these were carried out for dye exhaustion, uptake or adsorption. Some conclusive results on the role of electrolyte cations and anions on reactive dye diffusion into cotton fibre in pad-steam dyeing are presented in Chapter 6.

1.4.12 Dye fixation

There are three main ways in which dye molecules can become attached (fixed) to the cotton fibre: mechanical retention, physical bonding and chemical reaction [10]. Vat, sulphur and azoic dyes are fixed principally with mechanical retention, i.e. the dye molecules are trapped in an insoluble pigmentary form within the fibre polymer system. Direct dyes are fixed with physical hydrogen bonding and van der Waal's forces. Reactive dyes are fixed mainly by reaction with the fibre polymer leading to the formation of covalent bonds.

Dye fixation is generally determined as an estimate of the average proportion of dye actually fixed on a textile fibre [30]. The typical fixation percentages of cotton dyes are given in Table 1.4 [44]. The lower fixation levels of reactive dyes are essentially due to unavoidable dye hydrolysis during dyeing. There have been various analytical ways for estimating the extent of dye fixation and dye hydrolysis. Today, the percentage of dye fixation is usually determined by using absorbance measurements of dyebath solution and/or colour strength measurements of the fabric during dyeing [45-47]. The latter method was used for studies presented in this thesis and is described in Chapter 4.

Table 1.4: Typical fixation percentages of cotton dyes

Dye class	Fixation (%)
Azoic	83–93
Direct	70–95
Reactive	50–80
Sulphur	60–70
Vat	80–95

1.5 Reactive dye application procedures for cotton

The dyeing procedures may be divided into two major classes of immersion exhaustion (exhaust dyeing) and pad impregnation (pad dyeing) processes.

1.5.1 Exhaust dyeing

Exhaust dyeing is a process of immersion of the fabric in the dyebath, transfer of the dye to, and its gradual diffusion into, the fibre, so that the dyebath concentration decreases. In the typical exhaust dyeing of cotton with reactive dyes, the first phase of dyeing is carried out under neutral pH conditions to allow dye exhaustion and diffusion [20]. This promotes uniform colouration. Sodium chloride or sodium sulphate is often present initially, or added gradually to the dyebath during this phase, to promote exhaustion. The temperature of the dyebath may also be gradually increased to aid penetration of dye into the fibres, and to assist uniform migration. Fixation of the dye is then achieved by adding a suitable alkali to the dyebath, either completely or gradually, to activate the cellulose anions. The reaction phase of the dyeing occurs over 30–60 min with typical dyeing temperatures within the range from 30 to 90°C, depending upon the type of reactive group and its reactivity. The fixation process results in additional dye transfer to the fibre which is often referred to as secondary exhaustion [48, 49]. The secondary dye exhaustion and dye-fibre reaction then progress until no further dye is taken by the fibre. The important parameters in exhaustive reactive dyeing are the liquor-to-fibre ratio, temperature, pH and time.

1.5.1.1 Washing-off

After completion of the dye exhaustion and dye-fibre reaction phases, the fabric contains covalently-bonded dye, absorbed but unreacted dye, and the hydrolysed dye. The unreacted and hydrolysed dyes are generally referred to as unfixed dyes. The fabric also contains the residual electrolyte and alkali which should be removed. The unfixed dye is weakly trapped within the fibre through hydrogen bonds and van der Waal's forces which can desorb easily during washings by the consumer of the dyed cotton textiles. In other words, the presence of unfixed dye in a reactive dyed fabric gives poor washing fastness. Thorough washing-off after dyeing of reactive dyed cotton is therefore essential to remove all of the unfixed dye, residual electrolyte and alkali. This washing-off is a series of thorough rinsings including boiling with a detergent. This needs large amounts of good quality water [44]. In traditional reactive dyeings, around three quarters of the total water consumed is required for washing-off phase [50].

1.5.2 Pad dyeings

The lowest possible liquor-to-fibre ratio in exhaust dyeing is 3:1 with ultra-low-liquor-ratio dyeing machines. However, pad dyeings extend this further, to the range of 1:1 to 0.5:1. Thus, the dye absorption and fixation is significantly enhanced further with the pad dyeing processes. Another advantage of fully-continuous pad dyeing is the mass production of fairly large fabric lots. Continuous pad impregnation is a process where a fabric is passed in open-width form through a small bath (trough) containing dye solution and through the pressure squeezing rollers to remove the excess liquid evenly. The amount of dye solution taken as the percentage of mass of the fabric is the per cent pickup. The impregnation and uniform squeezing together are called padding and the device is known as a padder. For continuous pad dyeing, fixation must be rapid (30–120 sec) and usually involves heating (by baking or steaming) the impregnated fabric. The exception to this is the cold pad-batch process, where the fabric is padded with dye and alkali and then batched at ambient temperature for 6–24 hrs. The cold pad-batch dyeing is also referred to as a semicontinuous dyeing because of such a prolonged fixation time. As discussed in Section 1.5.1.1, the fabric is finally subjected to a thorough washing-off after the dye fixation step. This is usually

done on the continuous washing range. The washing-off procedures, used in this research are given in Chapter 4.

Padding is the most important process of continuous and semicontinuous dyeings [51]. Dye build-up, levelness and evenness on the fabric largely depend on this step. Factors of concern being the wetting of the fabric, the dwell time in the padder, the type of fibre and the construction of the fabric, per cent pickup, preferential adsorption of dyebath components because of substantivity of dyes, reaction of reactive dyes in the dyebath, dye aggregation, and the transfer of impurities in the fabric from a pretreatment step into the padder.

1.5.2.1 Pad-batch process

Pad-batch dyeing process is the most economical of all pad dyeing processes for the reactive dyeing of cotton [52]. In fact, for small lots of around 1000–10,000 metres, this process is more economical than exhaust dyeing, mainly due to minimal energy requirements. This process involves padding the fabric with a dye solution containing a suitable alkali system and then winding up the padded fabric onto a suitable roller [20, 26]. For dye fixation, the fabric wound on the roller is batched for 6–24 hrs at ambient temperature. This process is therefore often called 'cold' pad-batch dyeing. For dye fixation at ambient temperature, the dyes must have adequate reactivity. The dyes of low reactivity are not preferred. During batching, the roller should preferably be rotating at low speed to avoid drainage of the internal liquid within the batch. In order to avoid evaporation from the exposed surfaces and edges of the roll, the fabric is wrapped with the winder end-cloth around the entire roll and covered with a plastic film. After batching, the fabric must be thoroughly washed to remove unfixed dye and residual chemicals. This is done either on a continuous washing range or on a batch dyeing machine. If the fabric is wound on a perforated beam, the washing-off can be carried out using a beam dyeing machine. The fabric is claimed to have a better handle and surface appearance because it is not continuously circulating around as in the exhaust dyeing machines. Prolonged fixation at ambient temperature often results in better dye diffusion. Some results on diffusion studies for pad-batch dyeing are given in Chapter 5.

1.5.2.2 Pad-dry-bake process

The simplest of this sequence is the pad-dry process where dyes of fairly high reactivity are applied on cotton using a mild alkali, usually sodium bicarbonate [26]. Pad-dry-bake dyeing of cotton with reactive dyes, as its name implies, involves padding, intermediate drying and dye fixation by baking at high temperatures up to 160°C for 60–120 sec. At such high dry temperatures, the dyes of low reactivity are preferred for this sequence. The process is finally followed by the washing-off. Padding solution is composed of the dye, an alkali (usually sodium carbonate), urea and an antimigrant (usually a diluted alginate based thickener). A high concentration of urea, in the range from 50–200 g/l is used, due to its highly hydrotropic nature, to help the cotton fibres retain water during drying and subsequent baking [52]. This possibly provides a fluid medium for dye diffusion in the fibres in the hot dry environment that improves dye fixation and colour yield [26, 53-55]. Sometimes, urea is also used in any pad dyeing process for improving the solubility of sparingly-soluble dyes. All this urea is removed during the washing-off after fixation, and poses a pollution problem [20]. This is because urea is a source of nitrogen nutrients for algal growth.

Intermediate drying is a critical process in any continuous dyeing sequence, where excessive rates of high evaporation and dye migration are the key problems. An antimigrant is used in the padding liquor to avoid dye migration which causes shade changes on both sides of the fabric (which is often called the 'two sided effect'). Predrying using hot cylinders or infrared heating are also utilised to avoid this problem [56].

1.5.2.3 Steam fixation processes

The initial successful steam process for reactive dyeing of cotton followed the following sequence: pad (with neutral dye solution) – dry – pad (with caustic soda in brine) – steam – wash. This sequence is often referred to as pad-dry-chemical pad-steam process. This process sequence is quite similar to the continuous vat dyeing of cotton fabrics. The fabric is first padded in a neutral reactive dye solution and dried in a hot flue. After intermediate drying, the fabric is padded with a dilute solution of sodium hydroxide in saturated brine followed by steaming to complete the dye-fibre reaction. Heavy concentrations of the electrolyte are used to avoid colour bleeding

during the second alkali padding. Few colour-bleed problems are still encountered. Vacuum extraction of the padded fabric has been shown to be a viable alternative to intermediate drying, to restrict the dye bleeding into the chemical pad solution. This is because the wet vacuumed fabric can retain sufficient alkaline brine liquor to give satisfactory fixation at the steaming stage [57].

The pad-dry-chemical pad-steam process was soon followed by the introduction of even simpler dyeing sequences such as pad-dry-steam and pad-steam. These sequences have been described to minimise bleeding and migration problems associated with second chemical pad methods [58].

The roller-type steamers are usually used for steam-fixation processes. They are designed to provide an air-free environment with a cold water exit seal (usually called 'water-lock'). Each commercial range of dyes requires an appropriate set of steaming conditions. However, saturated steam, i.e. wet temperature of 101–102°C and 100% moisture, is usually used for steam-fixation reactive dyeing of cotton. Bifunctional reactive dyes have been claimed to be more reproducible than monofunctional systems because they tend to self-compensate in the changing temperature and humidity conditions within a continuous dyeing range [59, 60].

1.6 Pad-steam dyeing

Pad-steam dyeing of cotton with reactive dyes is the simplest and most economical process of steam fixation processes for dyeing pale-medium shades [20, 52, 61]. This process was introduced by eliminating the intermediate drying from the pad-dry-steam sequence to avoid dye migration problems in dyeing of some pile fabrics. Today, pad-steam process is one of the most practiced continuous dyeing sequences. In this process, fabric is padded with a reactive dye solution containing inorganic electrolyte (for diffusion and subsequent levelness of the dyes into the fibre) and the appropriate alkali (to initiate the dye-fibre reaction) followed by 60–90 sec steaming for dye fixation [20, 52, 61]. Finally, the fabric is washed-off to remove unfixed dye and residual chemicals. The hot and humid treatment of wet fabric during steaming tends to cause excessive hydrolysis of the dye and thus lowers the colour yield. Therefore, dyes of moderate to high reactivity are suitable.

1.7 Reactive dyeing effluent

Generally, the wastes can be classified into two ways: the physical form, i.e. gas, liquid or solid, and their effect on the environment, i.e. toxicity and biodegradability [62]. Toxicity is the degree to which any substance is poisonous for life in any way. Biodegradability is discussed in the next section. The textile processing effluent wastes come under the liquid form and can be further classified as:

1. Toxic, nonbiodegradable
2. Toxic, biodegradable
3. Nontoxic, nonbiodegradable
4. Nontoxic, biodegradable

The reactive dyeing effluent is essentially composed of the left over dyebath solution, and the draining washing-off water containing the residual dye, inorganic electrolyte and inorganic alkali taken from the dyed fabric, and also the detergent [20, 31]. The use of large quantities of inorganic electrolyte poses the most serious problem [26]. This increases the salinity of the effluent to very high levels which adversely affects the life forms in water, and the life that consumes that water.

1.7.1 Biodegradability

It is the ability of any substance to be biodegradable. The substances which are biodegradable are broken down into simpler molecules by the digestive action of micro-organisms that are capable of using them as food. These simpler molecules are then excreted as waste, which may form a food source for some other organism, to be then converted into yet simpler molecules which are excreted, and so on.

All of the dissolved components in reactive dyeing effluent are more or less toxic to the environment. However, the major environmental concern is the inorganic electrolyte (sodium chloride or sodium sulphate) because it is classified as potentially toxic and nonbiodegradable [63]. Suitable alternative compounds, which are either nontoxic and biodegradable, or of low toxicity but biodegradable to nontoxic substance(s), can be used to reduce this problem. This current research forms a part of such efforts where inorganic electrolytes and alkalis are replaced by alternative biodegradable organic compounds.

1.7.2 Total Dissolved solids

This is a measure of the total amount of dissolved substances per unit volume of water. This is directly proportional to any characteristic parameter of the substances such as salinity and conductivity in the case of dissolved inorganic electrolytes. Thus, reduction in the total dissolved solids (TDS) content of an effluent would lead to reductions in other environmental concerns such as salinity, conductivity and oxygen demands. The TDS content of dyeing effluents was measured to compare the environmental impact of the proposed dyeing recipe formulations presented in this thesis.

Chapter 2

Environmental issues and developments in reactive dyeing of cotton

2.1 Introduction

Since ICI introduced the first commercial reactive dyes for cotton in the 1950s, this dye class has become increasingly popular [64]. This is mainly due to high levels of washing fastness, a wide gamut of bright colours, and versatility for different application methods. The high fastness to washing of reactive dyes is due to their unique reactive group(s), which form covalent bonds with the hydroxyl groups of the cotton cellulose under alkaline pH conditions (Section 1.4).

The dyes also react with hydroxide ions present in the aqueous dyebath under alkaline pH conditions. This produces nonreactive hydrolysed dye which remains in the dyebath as well as in the fibre. In order to obtain the required levels of washing fastness, it is necessary to remove all unreacted and hydrolysed (unfixed) dye from the cotton fibre. This is achieved by 'washing-off'; a series of thorough rinsing and 'soaping' steps. The dye fixation efficiency is typically in the range of 50–80% [65]; i.e. 20 to 50% of the dye necessary to achieve the desired depth of colour is discharged to the environment.

Reactive dyes are soluble anionic dyes which, in solution, are repelled by the negatively charged surface of the cotton fibre. An electrolyte such as sodium chloride or sodium sulphate is added to promote the dye transfer (exhaustion) and penetration (diffusion) into the fibre. The amount of the electrolyte can vary up to 100 g/l depending on the dye structure, depth of shade and dyeing method. Once sufficient dye is on the fibre, either by exhaustion (exhaust dyeing methods) or padding (pad dyeing methods), alkali such as sodium carbonate, sodium bicarbonate or sodium hydroxide is used to initiate the dye-fibre reaction. The quantities and composition of the alkali depend on the pH required for the particular type of reactive group of the dye and the dyeing method.

Irrespective of the dyeing method and the type of reactive group, almost all of the potentially toxic nonbiodegradable inorganic electrolyte [63], inorganic alkali and unfixed dye are discharged to dyeing effluent. This creates potential

environmental problems from a highly-coloured effluent with high levels of dissolved solids and oxygen demand [65-69].

Urea, which is often used in pad dyeing methods and in printing to increase dye solubility and yield of the dye-fibre reaction, is another environmentally undesirable chemical [69-71]. Urea, when used in the pad-dry-bake dyeing process, decomposes and increases the nitrogen content of the effluent.

There have been a number of developments for improving the quality of effluent for cotton dyeing systems with reactive dyes. The review on such developments is presented in this chapter under four principal areas;

- Development of reactive dyes (Section 2.2),
- Developments in dyeing machinery and processes (Section 2.3),
- Chemical modification of cotton fibre prior to dyeing (Section 2.4), and
- Use of organic compounds in place of inorganic chemicals (Section 2.5).

The discussion focuses primarily on how researchers and industry are addressing the issues of how to reduce the discharge amounts of inorganic chemicals (electrolyte, alkali and urea) and unfixed dye.

2.2 Development of reactive dyes

Since the original invention of cotton reactive dyes, a number of improved dye structures and mixtures have been developed. Most of the major advances for reducing effluent pollution are discussed below.

2.2.1 Bifunctional reactive dyes

The first commercial reactive dyes for cotton were based on the dichloro-s-triazine reactive group. Since then many other reactive groups have been developed. The most widely used reactive groups, in the order of increasing reactivity, are trichloropyrimidine, aminochloro-s-triazine, sulphatoethylsulphone, dichloroquinoxaline, aminofluoro-s-triazine, difluorochloropyrimide and dichlorotriazin (Table 1.3). The extent of dye-fibre reaction and the ultimate discharge of unfixed dye vary widely with the type of reactive group and the dyeing technology used.

The use of two reactive groups in a dye molecule results in higher fixation efficiencies [72]. For exhaust dyeing methods, fixation efficiency typically improves from the range of 50–60% to that of 70–80% [65]. Such dyes are known as bifunctional reactive dyes and are further classified as homo-bifunctional (e.g. the ICI Procion HE dyes with two aminochloro-s-triazine groups) and hetero-bifunctional (e.g. the Sumitomo Sumifix Supra dyes with aminochloro-s-triazine and sulphatoethylsufphone groups) [27]. Hetero-bifunctional dyes provide better fixation with more flexibility for the colouration method and the process parameters. Some bifunctional dyes are claimed to provide a fixation efficiency of up to 95% when applied on cotton by the pad-batch dyeing method [72, 73].

Such improvements in dye fixation efficiency result in significant reductions in the amount of unfixed dye in dyeing effluent. However, their use in industry is often limited by cost considerations.

2.2.2 Polyfunctional reactive dyes

The approach of having more than two reactive groups provides a minor influence on improving fixation efficiency [27, 74]. However, a careful combination of reactive groups can make polyfunctional dyes superior to traditional dyes. Cibacron Red C-2G and Remazol Red BS are commercially successful examples of trifunctional reactive dyes. Some tetrafunctional reactive dyes have also been reported but are not yet commercial [27, 29].

2.2.3 Dye mixtures

Commercial mixtures of selected reactive dyes have become popular because they provide an economic range of secondary and tertiary colours [27]. At the same time, the commercial mixtures can have improved dyeing properties and reduced sensitivity to dyeing variables such as temperature and pH. In turn, this can improve dye fixation efficiency.

2.2.4 Reactive dye fixable at neutral pH

Reactive groups containing a nicotinic acid residue can allow dye-fibre reaction at a neutral pH of 7–7.5 [75-77]. A typical aminonicotinotriazine reactive group is shown in Figure 2.1. This form of a reactive group was introduced by Nippon Kayaku with the name of Kayacelon React (Table 1.2). The Kayacelon React is a homo-bifunctional reactive dye range with the *bis*(aminonicotinotriazine) reactive system. The requirement of using inorganic alkali for dyeing cotton at pH of 10–12 becomes unnecessary and the amount of the alkali in dyeing effluent is substantially reduced. The Kayacelon React dyes are relatively expensive and not widely used in commercial dyehouses.

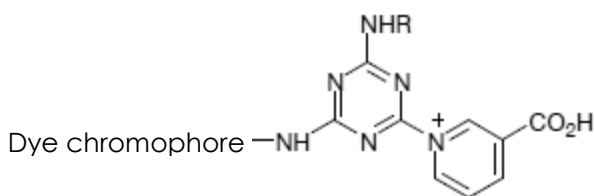


Figure 2.1: Aminonicotinotriazine reactive group (source: [20])

2.2.5 Acid fixing reactive dyes

Acid-fixing reactive dyes were developed for reducing the electrolyte requirement. Burlington Industries (USA) developed reactive dyes containing phosphonic acid and carboxylic acid reactive groups for dyeing without electrolyte [78]. However, the use of these dyes has been reported to cause tendering of cotton [79].

2.2.6 Low-salt reactive dyes

The 'low-salt' Cibacron LS reactive dyes developed by Ciba have allowed meaningful improvements to the discharge effluent [80]. DyStar introduced Remazol EF as its low-salt reactive dye range [27]. The requirement of reduced amount of electrolyte is due to the high affinity of such dyes to cotton. Most of these low-salt dyes are bifunctional and have high fixation efficiencies. Therefore, such dyes produce lower amounts of unfixed dye and electrolyte in the dyeing effluent. They are based largely, but not exclusively, upon *bis*(aminofluoro-s-triazine).

2.2.7 Cationic reactive dyes

Traditional reactive dyes, being anionic, require high concentrations of electrolyte to overcome the repulsion effects arising from the anionic charge on the surface of the cotton fibre in the dyebath. Cationic reactive dyes eliminate the requirement for an electrolyte [48, 81]. Such dyes offer the potential for dyeing of cotton using zero-salt but they are yet to be commercialised.

2.3 Developments in dyeing machinery and processes

2.3.1 Low liquor-to-fibre ratio dyeing

As per industrial dyeing practice, the concentrations of inorganic electrolyte and alkali are determined by the mass per unit volume of dyeing liquor. Thus, the total consumption of inorganic chemicals can be reduced by reducing the total volume of dyeing liquor. On the basis of this approach, a wide number of forms of low liquor-to-fibre ratio dyeing machines have been commercially introduced [67, 82, 83]. Industry has been motivated to move from 20:1 ratio dyeings to lower liquor ratios. The ultra low liquor ratio dyeing machines offer the opportunity to dye at ratios as low as 4:1. The reduction in liquor ratio reduces the chance of the reactive dye being repelled by cotton fibre [82]. Thus, a reduced concentration of electrolyte is needed for dye exhaustion. The use of less volume of water also decreases the possibility of dyebath hydrolysis. Other advantages of the development of low liquor-to-fibre ratio dyeing machinery are less water usage, reduced dye liquor wastage and lower steam consumption to heat the dyebath, thus, minimising air-pollution generated by steam boilers and reducing the heating costs.

2.3.2 Low padding trough volumes

In pad dyeing methods, the dyeing liquor left in the padding trough at the end of the dyeing process is drained to the effluent in its concentrated form. The volume of the liquor left depends on the padding trough capacity. Reduced trough volumes down to 10–15 litres provided meaningful reductions in such waste [67]. The new padders also benefit in reduced wastage of cotton fabric caused by 'tailing' [51, 84]. Tailing is the result of preferential dye uptake of one colour by cotton fibre when dyeing with combination colours. Industry is highly motivated to use such padders

which lead to cost savings through reduced liquor waste and reductions in off-specification fabric shades.

2.3.3 Hot washing-off

Washing-off is required to remove unreacted and hydrolysed dye from the cotton fibre at the end of the dyeing process. The washing-off steps normally recommended by dye manufacturers are a cold rinse, followed by a warm rinse, soaping at the boil, a warm rinse and finally a cold rinse. An approach of hot-washing, i.e. beginning with hot rinses and a final rinse at low temperature, has been reported to improve dyeing results and marginally reduce effluent chemical oxygen demand [50, 85].

2.3.4 Aftertreatments to fix hydrolysed dye on the fibre

A hydrolysed dye is not able to react with cotton and is removed by washing-off. A dye fixation efficiency of 99% is sometimes claimed for some reactive dyes with pad-batch dyeing processes [67]. However, there is still a need for washing-off to remove any residual hydrolysed dye on the fibre. The use of special aftertreatment agents to trap small amounts of hydrolysed dye in the fibre has been proposed for reducing the amount of unfixed dye in the discharge and to improve colour yields. Cationic aftertreatment agents have been studied for immobilising any unfixed dye present on the fibre after washing-off [86-88]. Improvements in colourfastness to washing were found. Many dye manufacturers market the cationic aftertreatment agents.

2.3.5 Urea- and electrolyte-free dyeing process

Urea is used in continuous pad-dry-bake dyeing processes to improve the yield of the dye-fibre reaction (Section 1.5.2). Inorganic electrolyte is used in the pad-steam dyeing method to improve dye levelness into the fibre, and also in the pad-dry-chemical pad-steam method to avoid dye bleeding during the second chemical padding step. A commercially viable dyeing machine jointly developed by BASF and Monforts, called 'Econtrol', eliminates the need for urea and electrolyte [89]. The machine is designed to inject humidity into the hot fixation chamber. The typical fixation conditions for a dichloro-s-triazine dyes have been reported as 120°C temperature and 20–25% relative humidity. Only small concentrations of alkali

(sodium bicarbonate) are required for these dyes. However, the machinery is very capital intensive and has high operating and maintenance costs. To date, there has only been limited interest from industry.

2.3.6 Polymerisation techniques for dye fixation

The polymerisation of dye molecules has been explored as a method for achieving 100% dye fixation [27]. Individual dye molecules react together in the dyebath forming a polymeric dye. The polymeric dye is then subjected to covalent fixation to cellulose through its conventional reactive groups. This approach offers many potential benefits including the prevention of coloured effluent and dyeing without using electrolyte. However, the concept has yet to result in a commercial product.

2.4 Chemical modification of cotton fibre prior to dyeing

The chemical modification of cotton to improve dyeing with direct, reactive, sulphur or vat dyes, is an emerging area. This research has focussed on the introduction of cationic groups to the cotton fibre [90, 91]. Such modifications, usually referred to as cationisation, are achieved by treating cotton with low molecular weight cationic chemicals or with cationic polymers (resins). Most of the cationic groups are quaternary, tertiary or secondary amino residues.

In the reactive dyeing of cationised cotton, the anionic dyes are attracted by the cationic charges on the fibre. As a result, higher fixation efficiency and reduced (or no) use of electrolyte can be achieved. Examples of reactive dyeing of modified cotton without using electrolyte and alkali have also been reported [92-94].

In reactive dyeing, cationisation of cotton has been shown to be capable of eliminating the use of inorganic electrolyte and alkali and leaving a reduced amount of unfixed dye. This offers significant environmental benefits. However, the technique has yet to be adopted by industry. This is mainly because cationisation is an additional process step and the treatment itself does not guarantee safer effluent. Natural polymers such as cationic starch and chitosan [95, 96] have been explored as cationising agents. They may make the cationisation process environmentally safer.

2.5 Use of organic compounds in place of inorganic chemicals

Using a reduced amount of urea with a dicyandiamide in the dyebath has been proposed to reduce the environmental impact [67]. Caprolactum products have been reported to have potential of achieving partial or complete substitution of urea in reactive dyeing and in the printing of cotton fabrics [97].

Use of selected organic compounds has been shown to be an effective alternative to inorganic electrolyte. This reduces effluent load [27, 98], as most of such compounds tend to be biodegradable. Betaine, an organic compound, has been reported to reduce the amount of inorganic electrolyte [99]. Organic surfactants have also been studied as inorganic electrolyte substitutes [100]. The use of a mixture of magnesium-based organic compounds in the dyeing of cotton with direct or reactive dyes has been patented [101]. The mixture is claimed to substitute inorganic sodium chloride or sodium sulphate that prevents the discharge of untreatable toxic wastewater. However, this could not be commercialised because magnesium ions cause water hardness and create problems with colour matching and dyeing process control [41, 42].

The sodium salts of organic acids have been explored as an alternative to sodium chloride and sodium sulphate. Prabu et al [68] have demonstrated the use of trisodium citrate as an alternative to traditional inorganic electrolytes for exhaust dyeing of cotton with reactive, direct and solubilised vat dyes. Salts of polycarboxylic acids have also been shown to be the most effective alternatives to inorganic electrolytes [98, 102]. An alkaline polycarboxylic sodium salt, tetrasodium ethylene diamine tetra-acetate (sodium edate) has been reported as an alternative to inorganic electrolyte (sodium sulphate) and alkali (sodium carbonate) in exhaust dyeing of cotton with reactive dyes [63]. However, the high alkalinity of sodium edate would cause reactive dye hydrolysis in the dyebath during dye exhaustion. This may result in the difficult control of dyeing and reduced dye fixation [102]. The use of organic salts in pad dyeing methods, where dye exhaustion is not required, has not been reported.

2.6 Proposed research objective

The primary objective of this research was to study the use of biodegradable organic salt alternatives to nonbiodegradable inorganic electrolytes and alkalis in the

pad-steam dyeing of cotton with reactive dyes, as a means for reducing effluent discharge loads. It was identified through a review of the literature that the alkaline polycarboxylic salts may be the most appropriate replacements. Two such alkaline salts, sodium edate and trisodium nitrilo triacetate (trisodium NTA), were initially identified as compounds with the potential to replace the inorganic chemicals used in pad-steam dyeing. An objective then became to develop supplementary theories for their mode of action when used in the reactive dyeing of cotton. Further details on the aims and objectives, research questions and hypotheses of this study are presented in the next chapter.

Research Proposal

Chapter 3

Research proposal and hypotheses

3.1 Aims and objectives

This research was undertaken to study the effectiveness of biodegradable alkaline polycarboxylic sodium salts as alternatives to traditional nonbiodegradable inorganic electrolytes and alkalis used in pad-steam dyeing of cotton with reactive dyes. The primary objective of the study was to develop improved environmentally sustainable dyeing systems. The basic aims and objectives for the study were:

1. To minimise the use of inorganic electrolytes and inorganic alkalis for pad-steam dyeing of cotton with reactive dyes.
2. To develop a new dyeing methodology based on organic salts which will reduce the environmental load of dyeing effluent.
3. To develop a theory for the effective utilisation of substitute organic salts.
4. To attempt to balance the total cost of dyeing taking into account the cost of discharge and the treatment of the effluent to improve water quality.

3.2 Research questions

The aims and objectives of this study were to be achieved by answering the following research questions;

1. What properties of organic salts are required so that they can replace the currently used inorganic electrolytes and alkalis?
2. Is it possible to substitute the inorganic electrolyte and alkali used in current reactive dyeing techniques with one organic compound?
3. How will new recipes be designed and researched for effectiveness?
4. How can the effectiveness of alternative organic salts be assessed for the critical dyeing parameters of dye diffusion and fixation and hence the final colour yield?
5. Will the size and chemistry of organic anions affect dye diffusion and fixation?

6. How will the different types of reactive group of the dyes function in the new dyebath chemistry?

3.3 Rationale

Globally, the textile dyeing industry is known to be a major contributor to environmental pollution [103, 104]. This is mainly due to heavy discharges of nonbiodegradable inorganic salts (electrolytes), alkalis, other processing aids and organic matter such as dyes to the dyeing effluent. The industry also consumes large volumes of clean water [66]. Effluent treatment and water-recycling play a significant role in reducing discharge pollution and providing reusable processing water [105]. However, these treatments are expensive. The better approach would obviously be to modify the textile processing technologies and chemistry to reduce the environmental discharge.

For apparel textiles, the predominant dye-fibre combination is that of reactive dyes and cotton [31]. Of all the dye-fibre combinations, cotton dyed with reactive dyes consumes the highest volume of water per kilogram of fibre. Moreover, this combination causes the highest discharge of inorganic electrolytes, alkalis and organic matter per unit fibre mass [67]. Per capita demand for apparel textiles is projected to continue to grow. Therefore, it becomes important to find solutions for reducing water use and the discharge of polluting chemicals.

The main challenge that the dyeing industry faces is to modify production techniques at a competitive price by using safer dyes and chemicals. This research work was a part of such challenge. It is aimed at researching current practices for pad-steam dyeing of cotton with reactive dyes.

Dyeing cotton with reactive dyes is widely practised mainly because the covalent bond that is formed between the fibre and the dye molecules which leads to excellent colourfastness to washing. However, considerable quantities of inorganic salt (such as sodium chloride and sodium sulphate), as electrolyte, and inorganic alkali (such as sodium bicarbonate, sodium carbonate and sodium hydroxide), as the dye-fibre reaction activator, are required (Chapter 1). In addition to that, low reactive dye fixation on the fibre can take place because of the potential dyebath hydrolysis. Irrespective of the dyeing method, almost all of the inorganic electrolyte,

inorganic alkali and unfixed dye is discharged to dyeing effluent. This leads to environmental problems concerning highly-coloured effluent with high levels of dissolved solids [65, 68].

There have been a number of developments for improving the quality of effluent for cellulose reactive dyeing systems [106]. A detailed discussion on such developments is presented in the previous chapter. Pad dyeing processes are recommended wherever possible to reduce or avoid the use of an inorganic electrolyte [44]. Nevertheless, pad dyeing of cotton with reactive dyes using steam fixation still requires a considerable amount of an inorganic electrolyte for dye levelness, dye diffusion and minimising dye bleeding [26]. The broad aim of this research work was to study the potential of biodegradable alkaline polycarboxylic salts, such as sodium edate, trisodium NTA and tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate (tetrasodium GLDA) [107-112], to improve effluent quality by replacing the inorganic electrolyte and alkali in the pad-steam dyeing of cotton with reactive dyes.

Steam fixation of reactive dyes padded onto cotton fabric is one of the most practised ways of continuous dyeing [61, 113]. There are a number of variations to this process such as pad-steam, pad-dry-steam and pad-dry-pad-steam. The pad-steam dyeing method was selected for simplicity.

3.4 Hypotheses

The following two hypotheses were developed at the outset of the study.

1. Selected biodegradable alkaline polycarboxylic salts (such as sodium edate, trisodium NTA and tetrasodium GLDA) can replace the use of nonbiodegradable inorganic electrolyte and alkali for pad-steam reactive dyeing of cotton.
2. The required concentration of alkaline polycarboxylic salts will be a function of their alkalinity and ionic strength.

Chapter 7 presents the findings of studies on using these biodegradable alkaline organic salts for pad-steam dyeing of cotton with reactive dyes.

As the research progressed, following fundamental studies were also carried out to achieve the aims and objectives.

- The assessment of the diffusion of reactive dye into the cotton fibre, and
- Determining the required concentration of alternative electrolyte.

Full details of these fundamental studies and the respective findings are presented in Chapters 5 and 6 respectively. The findings were then effectively used for studies presented in Chapter 7.

Experimental

Chapter 4

Materials, methods and measurements

4.1 Introduction

This chapter describes the cotton fabric, reactive dyes, dyeing auxiliaries, chemicals, dyeing methods, testing and evaluation methods used in this study.

4.2 Materials

4.2.1 Cotton fabric

A commercially scoured and bleached ready-to-dye cotton fabric (twill, 282 g/m²) was used. The fabric was free of fluorescent brightener. It was tested and found to have an absorbency of 1 sec (AATCC 79 – 1995), pH extract of 8.2 and a CIE whiteness index of 78.6.

4.2.2 Dyestuffs and chemicals

The dye selection criteria included process compatibility, commercial usage, and variety of reactive groups, functionality, dye-fibre reaction mechanisms and colours. The CI Reactive Red 147, a difluorochloropyrimidine dye (Drimarene Red K4BL, Clariant), and the CI Reactive Blue 250, a *bis*(sulphatoethylsulphone) dye (Remazol Navy RGB 150%, DyStar) were selected for this study. The two dyes are widely used colourants from each of these two classes of reactive group. The complete molecular structures of CI Reactive Red 147 and CI Reactive Blue 250 have not been disclosed by the manufacturers. However, the basic chemical identity of CI Reactive Blue 250 is 2,7-Naphthalenedisulphonic acid, 4-amino-5-hydroxy-3,6-*bis*[[4-[[2-(sulphooxy)ethyl]sulphonyl]phenyl]azo], tetrasodium salt (Appendix II).

A nonionic emulsifying detergent (Felosan RGN-S, CHT) was used for washing-off and Alginate NVS (CHT) was used as an antimigrant for pad-dry-bake dyeing. The sodium chloride, sodium sulphate, potassium chloride, potassium sulphate, sodium bicarbonate, sodium carbonate, potassium bicarbonate, potassium carbonate,

sodium hydroxide, sodium silicate, urea, sodium acetate, trisodium citrate, sodium edate, trisodium NTA and N,N-dimethyl formamide (DMF) were analytical grade. Dissolvine GL-47-S (Akzo Nobel), comprising $47 \pm 2\%$ w/w tetrasodium GLDA and $1.2 \pm 0.7\%$ w/w sodium hydroxide, was used as an alkaline polycarboxylic sodium salt.

4.2.3 Deionised water

Deionised water was used for laboratory dyeings, DMF treatment, effluent analysis and colourfastness testing. The use of deionised water was particularly necessary for studies into the dyebath ionic strength.

4.3 Methods

4.3.1 Dyeing methods

4.3.1.1 Pad-steam dyeing

Pad-steam dyeing is suitable for pale to medium depths of shade [61, 113]. After discussion with industrial dyers, a dye concentration of 20 g/l was selected as this was the generally recognised upper limit in commercial production. Fabric samples were dyed (20 g/l dye and the relevant salt and alkali) by padding (two dip-two nip, 70% liquor pick-up, Benz laboratory padder). The padded fabrics were then steamed (wet-temperature of 101–102°C, 100% moisture, Mathis laboratory steamer) for 60 sec. For the traditional dyeings, the alkali used was sodium bicarbonate for the CI Reactive Red 147 and sodium carbonate for the CI Reactive Blue 250. Dyeings were also carried out to study the effect of variation in the magnitudes of dye concentration (0–20 g/l), inorganic and organic chemical concentrations and steaming time (0–120 sec). Further details of chemicals and their concentrations used are given in the results and discussion part and Appendix I.

4.3.1.2 Pad-dry-bake dyeing

Pad-dry-bake dyeing was used as a part of the experimental plan for studies on dye diffusion presented in the next chapter. Fabric samples were padded (two dip-two nip, Benz laboratory padder, 70% liquor pick-up) using dyebaths containing 5, 10 and

20 g/l dye and dye manufacturer's recommended padding chemicals. The dyed fabrics were then dried (70°C, suspended in a Brownbuilt automatic oven dryer) followed by baking (160°C for CI Reactive Red 147 and 150°C for CI Reactive Blue 250, Mathis laboratory stenter) for 60 sec. The padding chemicals used were 100 g/l urea, 15 g/l sodium bicarbonate and 1 g/l antimigrant for CI Reactive Red 147 and 50 g/l urea, 15 g/l sodium carbonate and 1 g/l antimigrant for CI Reactive Blue 250. For investigating the effect of baking time, the samples dyed with 20 g/l dye were baked for 30, 60, 90 and 120 sec.

4.3.1.3 Pad-batch dyeing

Pad-batch dyeing was also carried out for the dye diffusion studies. Fabric samples were padded (two dip-two nip, BENZ laboratory padder, 70% liquor pick-up) using dyebaths containing 10, 20 and 30 g/l dye and dye manufacturer's recommended alkali systems. The dyed fabrics were then carefully rolled, wrapped in plastic and left to batch (ambient temperature, $25 \pm 2^\circ\text{C}$) for 12 hrs. The padding chemicals used were 8 ml/l sodium hydroxide (38°Bé) and 10 g/l sodium carbonate for CI Reactive Red 147 and 14 ml/l sodium hydroxide (38°Bé) and 70 g/l sodium silicate for CI Reactive Blue 250. For investigating the effect of batching time, the samples dyed with 20 g/l dye were batched for 6, 12 and 24 hrs. The results form a part of the next chapter.

4.3.1.4 Exhaust dyeing

Exhaust dyeing was conducted to study the effect of dyebath ionic strength on dye exhaustion. Dyebaths were prepared containing the selected electrolyte and 2% dye (o.m.f.) with liquor-to-fibre ratio of 10:1 and loaded to an Ahiba AG Turbomat CH-8305 laboratory dyeing machine. The fabric was immersed at 40°C, the temperature was raised to 50°C and the dyeing continued for 40 min (primary exhaustion phase). Then alkali was added (2.5% o.m.f. for CI Reactive Red 147 and 5 g/l for CI Reactive Blue 250), the temperature was raised to 60°C (CI Reactive Red 147) and to 80°C (CI Reactive Blue 250) and the dyeing was continued for a further 45 min. Sodium carbonate was used as an alkali when sodium salts were used,

likewise potassium carbonate was used with potassium salts. The details of electrolytes and their concentrations used are given in Chapter 6 and Appendix I.

4.3.1.5 Washing-off

Tap water was used for washing-off. For all dyeings (pad-steam, pad-dry-bake, pad-batch and exhaust), the dyed fabrics were rinsed with cold then hot water, soaped with 2 g/l nonionic detergent at the boil for 15 min, and then rinsed with hot water until no further colour desorbed. The fabrics were finally rinsed with cold water and dried.

4.3.2 DMF treatment

Washing-off does not remove all unfixed dye from the dyed fabric. Therefore, for measuring the extent of reactive dye fixation, the dyed fabric is further boiled with DMF or pyridine solution to strip any unfixed dye left on the fabric [47, 114, 115]. DMF treatment was preferred to pyridine treatment because of occupational health and safety limitations. The dyed and washed-off fabrics were boiled in a 50% aqueous solution of DMF (15 min, liquor-to-fibre ratio of 40:1, reflux condensation).

4.3.3 Industrial trial

In order to validate and compare the effectiveness of alkaline polycarboxylic salts under production conditions two 50 m lengths of bleached cotton fabrics (156 g/m², plain weave) were dyed (20 g/l CI Reactive Red 147) on a Benninger pad-steam range in an industrial dyehouse. The organic salt dyeing was carried out using sodium edate (100 g/l). The traditional dyeing was carried out with the mill's standard recipe of 30 g/l sodium chloride and 15 g/l sodium bicarbonate. Commercial grade chemicals were used for the trial. The fabric was padded (70% liquor pick-up, ambient temperature), steamed (wet-temperature of 100–102°C, 100% moisture, 60 and 120 sec), washed-off (see Table 4.1) and then dried. DMF stripping was not carried out on the fabrics of this trial. Therefore, the per cent dye fixation was calculated as $[(K/S_{\text{after washing-off}}) / (K/S_{\text{before washing-off}})] \times 100$, where ' $K/S_{\text{after washing-off}}$ ' was taken as the final colour yield.

Table 4.1: Washing-off conditions on Benninger dyeing range

Parameters	Washing tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6
Temp (°C)	35	80	90	90	90	35
Soaping	-	-	2 g/l detergent ‡	-	-	-
Flow rate (l/min)	40	30		30		

4.4 Measurements and testing

4.4.1 Colour yield

Colour strength (K/S) of two-folded samples was measured at the maximum absorption peak using a Datacolour 600 spectrophotometer. The specific measurement settings were: 30 mm sample aperture, illuminant D65, UV included, specular component included, reflectance mode and 1964 (10°) CIE Supplementary Standard Observer. The fabric samples were conditioned (30 min, ~25°C, ~65% relative humidity) before measuring the K/S value. The colour strength after DMF treatment (K/S_{DMF}) was obtained as the final colour yield. The only exception was a production trial where the colour strength after washing-off ($K/S_{after\ washing-off}$) was taken as the final colour yield.

4.4.2 Dye diffusion

The extent of dye diffusion (%D) was determined by using Equation 4.1. The equation was developed as a part of this study. The detailed discussion on this approach is presented in the next chapter.

$$\%D = 100 - [(K/S_{diffusion\ index}) / (K/S_{reference}) \times 100] \quad (4.1)$$

‡ slightly anionic (Perlavin RIS, Dr Petry)

Where;

' $K/S_{diffusion\ index}$ ' is the value obtained sometime later in the dyeing process after padding but before washing-off (and/or of the fabric padded with dye and auxiliaries, electrolyte, alkali, urea...etc), and

' $K/S_{reference}$ ' is the colour strength of fabric sample padded with dye only (not steamed, baked or batched).

4.4.3 Dye fixation

The approach for determining the extent of reactive dye fixation using K/S values, used by other researchers [115-118], was followed. The percentage of reactive dye fixed on the cotton fabric was measured using Equation 4.2.

$$\%F = [(K/S_{after\ DMF\ stripping}) / (K/S_{before\ washing-off})] \times 100 \quad (4.2)$$

4.4.4 Dye exhaustion

Two measures of dye exhaustion were obtained. The primary dye exhaustion (PE) was obtained before adding alkali. Total dye exhaustion (TE) was determined after addition of alkali and at the end of the dyeing process. The primary and total exhaustion values were calculated using Equations 4.3 and 4.4 respectively [63].

$$\%PE = [(A_0 - A_1) / A_0] \times 100 \quad (4.3)$$

$$\%TE = [(A_0 - A_2) / A_0] \times 100 \quad (4.4)$$

A_0 = maximum absorbance of dyebath before fabric immersion

A_1 = maximum absorbance of dyebath before adding alkali

A_2 = maximum absorbance of dyebath after dyeing

Maximum absorbance of dyebath solutions was measured on a Varian Cary 50 UV-Vis Spectrophotometer at ambient temperature.

4.4.5 Cross-sections of dyed cotton fibre

Diffusion of reactive dyes into the interior of fibres was assessed by visual observation of cross-sections of dyed cotton fibres. The sections of dyed yarn bundles were prepared on thin steel plate having 1mm holes. This was done by pulling the bundle of yarns through the hole, using a strong nylon yarn, so that the yarns were tightly packed. The cross-sections were then revealed by slicing them off on the metal surface. The microscopic observations were made at 500 times magnification using a Leica DM 2500M Microscope. The cross-sectional images of dyed fabrics are given in the study on dye diffusion presented in the next chapter.

4.4.6 Ionic strength of dye bath

The total ionic strength of dye solution was calculated by using Equation 4.5 [119].

$$\mu = \frac{1}{2} \sum [\text{molar concentration of compound} \times (\text{ionic charge})^2] \quad (4.5)$$

Two examples of using Equation 4.5 are given below.

1. Ionic strength of aqueous solution containing 50 g/l sodium chloride and 15 g/l sodium carbonate

Molecular mass of sodium chloride (NaCl) = 58.44

Molar mass of 50 g/l sodium chloride = $50 / 58.44 = 0.86$

Ionic mass of Na^+ in 50 g/l sodium chloride = $0.86 \times (+1)^2 = 0.86$

Ionic mass of Cl^- in 50 g/l sodium chloride = $0.86 \times (-1)^2 = 0.86$

Ionic strength of 50 g/l sodium chloride = $\frac{1}{2} (0.86 + 0.86) = 0.86$

Molecular mass of sodium carbonate (Na_2CO_3) = 106

Molar mass of 15 g/l sodium carbonate = $15 / 106 = 0.14$

Ionic mass of 2Na^+ in 15 g/l sodium carbonate = $2 \times 0.14 \times (+1)^2 = 0.28$

Ionic mass of CO_3^{2-} in 15 g/l sodium carbonate = $0.14 \times (-2)^2 = 0.56$

Ionic strength of 15 g/l sodium carbonate = $\frac{1}{2} (0.28 + 0.56) = 0.42$

Total ionic strength of aqueous solution containing 50 g/l sodium chloride and 15 g/l sodium carbonate = $0.86 + 0.42 = 1.28$

2. Ionic strength of 100 g/l sodium edate (dihydrate) solution

Molecular mass of sodium edate dihydrate ($\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$) = 416.21

Molecular mass of sodium edate ($\text{Na}_4\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$) = 380.18

Molecular mass of water molecules in sodium edate dihydrate = 36.03

Molar mass of water molecules in 100 g/l sodium edate dihydrate

$$= (36.03 / 416.21) \times 100 = 8.6 \text{ ml}$$

100 g/l sodium edate dihydrate means (100 – 8.6 = 91.4) g of sodium edate dissolved in 1008.6 ml of water. Thus, 100 g/l sodium edate dihydrate is actually 90.6 g/l sodium edate.

Molar mass of 90.6 g/l sodium edate = $90.6 / 380.18 = 0.24$

Ionic mass of 4Na^+ in 100 g/l sodium edate dihydrate = $4 \times 0.24 \times (+1)^2 = 0.96$

Ionic mass of $4(\dots\text{COO})^-$ in 100 g/l sodium edate dihydrate

$$= 4 \times 0.24 \times (-1)^2 = 0.96$$

Ionic strength of 100 g/l sodium edate dihydrate = $\frac{1}{2} (0.96 + 0.96) = 0.96$

4.4.7 Colourfastness

Colourfastness was tested on dyed and washed-off samples (not DMF treated). The samples for colourfastness testing were dyed and washed-off with 2 g/l nonionic detergent at boil for 30 min [115]. The specific tests were colourfastness to rubbing (AS 2001.4.3 – 1995), washing (AS 2001.4.15C – 2006) and light (AS 2001.4.21 – 2006).

4.4.8 Total dissolved solids (TDS)

The TDS was measured using a laboratory TDS meter (Oakton). Each optimum dyeing recipe was diluted 100 times as representative of the dyeing effluent discharged on a production scale.

4.4.9 FTIR analysis

Fourier transform infrared (FTIR) spectra of dyed cotton fabrics, undyed cotton fabric and the dye (CI Reactive Red 147 and CI Reactive Blue 250) were recorded on a Perkin Elmer Spectrum 400 FT-IR using the UATR diamond/ZnSe crystal method, at 4 cm⁻¹ resolution and scan speed of 0.2 cm/sec. For FTIR testing, fabric samples were boiled in deionised water for 30 min before and after dyeing to remove any residues. The spectra of undyed cotton and the dye were subtracted from that of the dyed cotton to compare the resultant spectra of the fabrics dyed using alkaline polycarboxylic sodium salts and the conventionally dyed fabrics.

4.5 Reproducibility of results and replicate experiments

Preliminary experiments were carried out to assess the reproducibility of the reflectance and colour strength (*K/S*) values of laboratory dyeings. Using the two selected dyestuffs, three to five dyeings for a number of different salt combinations were carried out. For each dyeing the reflectance, and hence also *K/S*, was determined as the average of three measurements. On the basis of replicate dyeing results, the individual steps and the timing between the steps were standardised, then the variation in results was within $\pm 2.5\%$. All subsequent dyeing experiments were carried out using standardised steps and timings followed by measuring colour strength as the average of at least three measurements on each sample. In this way, the reproducibility was maintained as $\pm 2.5\%$. As this is within the accepted limits of variability for cotton dyeings, no further analyses, including assessments of statistical significance, were made.

Results and Discussion

Chapter 5

Determining the diffusion of reactive dyes into cotton fibre in pad dyeings using K/S values

5.1 Introduction

Pad dyeing of cotton fabric with reactive dyes is a two stage process. First the dye is applied to the fabric by padding. The fabric is then subjected to a dye fixation step [51]. The dye commences to diffuse into the interior of the fibre when the fabric is padded. The diffusion continues till the subsequent fixation step. The extent of the diffusion depends mainly on the electrolyte concentration (steam fixation) or the urea concentration (bake fixation) and swelling of the fibre during fixation step [70]. Dye diffusion exerts a significant influence on dye fixation, colour yield and colourfastness of a dyed fibre [26, 53-55]. However, industrial dyehouses are not known to make measurements of dye diffusion. This may be because the currently available methods for determining dye diffusion are seen by industrial dyers to be time consuming and indirect. They also require the use of sophisticated laboratory techniques and equipment [120, 121]. The currently available methods for determining dye diffusion are:

- a) Examination of fibre or yarn cross-sections [120]. A cross-section of a bundle of dyed yarn is microtomed from a 'wax block' or from a thin 'punched card' having 1 mm holes. The dye diffusion into the fibres is then observed through microscopic examination of the thin section with the magnifications up to 500. The results are qualitative.
- b) Multilayer diffusion methods [122-124]. A clear polymer thin film of known mass is tightly wound round a cylindrical rod to form multiple layers and subjected to dyeing with known concentrations of dyes and chemicals. When the film is subsequently unrolled after dyeing, dye penetration from the top to inside layers can be observed and measured.
- c) The microdensitometer method [125]. This requires a parallel-sided block of polymer. The block is dyed and then is carefully sliced into thin transverse cross-sections. Dye diffusion is determined by measuring the decrease in

relative absorbance with distance from the surface of the slice using a microdensitometer.

Multilayer and microdensitometer methods are not carried out on the fibres. Therefore, they are only useful for quantitative determination of relative dye diffusions. Their practical application is limited.

- d) Rate of dyeing method [120]. This method provides an indirect indication of the rate of dye diffusion. This is based on the measurement of dye exhaustion using a spectrophotometer. The fibre is dyed in a very long liquor-to-fibre ratio dyebath (i.e. an 'infinite dyebath'). A curve is then obtained by plotting the ratio of the dye exhaustion at various dyeing times to the equilibrium exhaustion against square root of the dyeing time. The square of the slope of that curve is proportional to the relative diffusion rate of the various dyes tested. This method is time consuming and does not provide a direct measure of the dye diffusion.
- e) Laser scanning confocal microscopy (LSCM) method [126-128]. LSCM can provide high resolution three-dimensional images of the spatial distribution of dyes in fibres. A profile of the distribution of dye across the fibre and the total dye content of the fibre can be obtained. The laser scanning confocal microscope is an expensive and sophisticated instrument.

Reflectance spectrophotometers are now a basic feature in the laboratories of most industrial dyehouses. There they are used for colour matching and quality control. Fundamentally, such spectrophotometers provide the means to measure the reflectance of any surface across the visible spectrum. The surface reflectance value (*R*) can be further used for determining other primary colour measurement quantities such as tristimulus values (*XYZ*), CIE *L*a*b** values, total colour difference values and colour strength value (*K/S*) [129].

The colour strength of a dyed fabric is customarily expressed as its *K/S* value. '*K*' and '*S*' are absorption and scattering coefficients of the dyed fibre. The *K/S* value is calculated from '*R*' using the Kubelka-Munk Equation 5.1 [63, 94, 130].

$$K/S = (1 - R)^2 / 2R \quad (5.1)$$

'*R*' is preferably determined at the maximum absorption wavelength of the dyed fabric (λ_{\max}) [131]. The *K/S* value has been shown to be a direct measure of the

colour yield [132]. The value can also be used to determine other important dyeing factors such as dye uptake, migration index (MI) and dye fixation [43, 47, 131, 133, 134]. A relation between K/S value and the cross-sectional distribution of dye molecules in the dyed cellulosic fibres and yarns has been reported [135]. Based on this fact, studies were carried out for dye diffusion in pad dyeings which resulted in a new method of measuring reactive dye diffusion into cotton using K/S values.

5.2 Hypothesis

Immediately after padding a cotton fabric with a reactive dye, the dye is almost exclusively concentrated on the surface of the fibres and yarns within the fabric. As dye diffusion progresses, the number of dye molecules on the surface of the fibre becomes less and less. Consequently, the colour strength (K/S) value, being a measure of surface reflectance, commences to decrease. In other words there is an inverse relationship between the colour strength and diffusion. As the dyeing process continues, the diffusion of the dye will eventually approach an equilibrium and the dye will be uniformly distributed throughout the fibre. It was hypothesised that a measure of diffusion could be obtained through using K/S values obtained at various stages of the dyeing process. These measurements would need to be made before any washing-off because this removes unfixed dye from the surface and interior of the fibre. The base value for the measure of diffusion should ideally represent the colour strength of the dyed fabric where effectively no dye diffusion has occurred. For this purpose, if the fabric is padded with dyebath containing the dye only, the diffusion will be at minimum and there will be the maximum number of dye molecules on the surface of the fibre. The colour strength value measured at this point was taken as the base or reference value. That value is represented by ' $K/S_{reference}$ '. The colour strength value of a dyed fabric where certain diffusion has occurred because of either fixation step or using the auxiliaries (such as electrolyte, urea, alkali, antimigrant...etc) is represented by ' $K/S_{diffusion\ index}$ '. This value is obtained sometime later in the dyeing process after padding the fabric in a dyebath with or without auxiliaries before washing-off. Having known the $K/S_{reference}$ and $K/S_{diffusion\ index}$ values, a measure of diffusion can be calculated by using Equation 4.1, i.e. $\%D = 100 - [(K/S_{diffusion\ index}) / (K/S_{reference}) \times 100]$. Here, ' $(K/S_{diffusion\ index}) / (K/S_{reference}) \times 100$ ' represents the percentage of the dye remaining on the surface of the fibre after a

certain amount of dye diffusion has occurred. Ideally, $K/S_{diffusion\ index}$ will be equal to $K/S_{reference}$, when there is no dye diffusion.

There are three basic methods for fixation of the dye after padding cotton fabric with reactive dyes. These are steaming (saturated steam, 30–120 sec), baking (150–160°C, 30–90 sec) and batching (ambient temperature, 6–24 hrs). The hypothesis was examined for these three fixation methods. The specific dyeing processes selected for the study were pad-steam, pad-dry-bake and pad-batch.

5.3 Procedure for the proposed method of measuring diffusion

5.3.1 Determining $K/S_{reference}$

The fabric sample was padded with a known concentration of the dye (two dip-two nip, 70% liquor pick-up, Benz laboratory padder). The preparation of the dye solution and setting up the liquor pick-up were precisely done. The sample was then dried (15 min, 70°C, suspended in a Brownbuilt automatic oven dryer) and conditioned (30 min, 25°C and 65% relative humidity). Drying, in the absence of an electrolyte, urea or antimigrant, results in maximum number of dye molecules on the surface of the fabric because the dye solution migrates to the surface of the fabric as reported by Hunger [51]. The colour strength ($K/S_{reference}$) was then measured on a Datacolour 600 spectrophotometer at the maximum absorption.

5.3.2 Determining $K/S_{diffusion\ index}$

Having determined the ' $K/S_{reference}$ ', an undyed sample of the same fabric was padded with the dyebath containing the same concentration of the same dye together with known concentrations of the relevant auxiliaries in the same precised way. The colour strength ($K/S_{diffusion\ index}$) was then measured before and after the subsequent fixation steps (steaming, baking or batching). The fabric sample was conditioned in the same way before every spectrophotometric measurement. The pad-steam, pad-dry-bake and pad-batch dyeing methods carried out are described in the previous chapter.

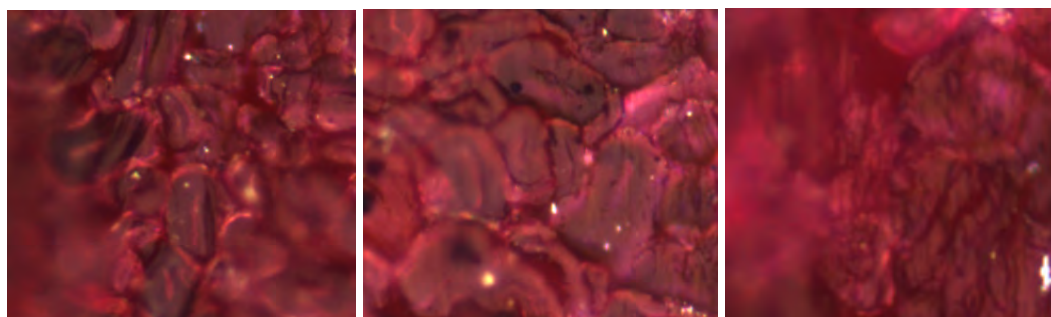
5.4 Validation of the new method

5.4.1 Effect of electrolyte concentration on dye diffusion (pad-steam dyeing)

In pad-steam dyeing, an electrolyte favours increased dye levelness in the fibre and the eventual colour yield [20, 52, 61]. This is because the electrolyte promotes dye diffusion and ultimately dye fixation [53]. Consequently, pad-steam dyeing results were obtained to determine the effect of electrolyte concentration on dye diffusion.

5.4.1.1 Microscopic analysis

Fibre cross-sections of the fabrics dyed with CI Reactive Red 147 showed that the core is more coloured with increasing electrolyte concentration (Figure 5.1). This confirms that the electrolyte promotes dye diffusion in pad-steam reactive dyeing of cotton [22, 26, 52, 53, 136, 137].



00 g/l sodium chloride 20 g/l sodium chloride 40 g/l sodium chloride

Figure 5.1: Fibre cross-sections of cotton fabrics dyed with 20 g/l CI Reactive Red 147 (before washing-off) at 60 sec steaming

5.4.1.2 New method for the extent of dye diffusion (%D)

Figure 5.2 shows relationship between the colour strength before washing-off ($K/S_{diffusion\ index}$) and the proposed measure of dye diffusion (see Equation 5.2). The figure also presents the effect of electrolyte concentration on dye diffusion. The figure shows an inverse relation between $K/S_{diffusion\ index}$ and %D. Figure 5.2 (b) shows that the dye diffusion increases with increasing sodium chloride concentration, at constant alkali concentration (15 g/l) and steaming time (60 sec). Maximum dye

diffusion was obtained at 50 g/l sodium chloride. It is well known that the addition of an electrolyte in a dyebath increases the degree of aggregation of the dye molecules [138]. Therefore, an optimum electrolyte concentration generally exists. Electrolyte concentrations higher than the optimum are avoided to minimise excessive dye aggregation. The CI Reactive Red 147 diffused more than CI Reactive Blue 250. The dye-fibre reaction and dye diffusion occur simultaneously in pad-steam dyeing. Therefore, CI Reactive Blue 250, being a bifunctional dye, may have higher relative rate of dye-fibre reaction to the rate of dye diffusion.

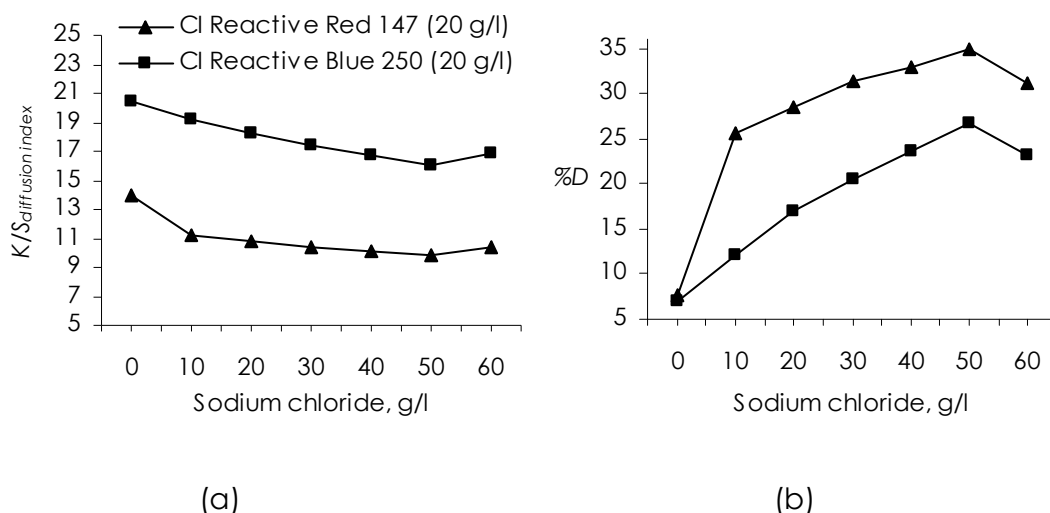


Figure 5.2: Effect of electrolyte concentration on dye diffusion

5.4.2 Dye diffusion vs dye fixation and colour yield (pad-steam dyeing)

Figure 5.3 shows that the dye fixation and colour yield increase with increasing sodium chloride concentration, at constant alkali concentration (15 g/l) and steaming time (60 sec). The maximum values were obtained at 50 g/l sodium chloride, after which a near-constant colour yield was observed with CI Reactive Red 147. The optimum dye diffusion was also obtained at 50 g/l sodium chloride; therefore, it can be postulated that the dye fixation and colour yield increase with the increase in dye diffusion. Further, the optimum dye fixation and colour yield can be obtained at optimum dye diffusion. Thus, the optimum electrolyte concentration can be determined by obtaining optimum dye diffusion instead of obtaining dye

fixation and colour yield. This saves time as washing-off procedures are not required for determining dye diffusion.

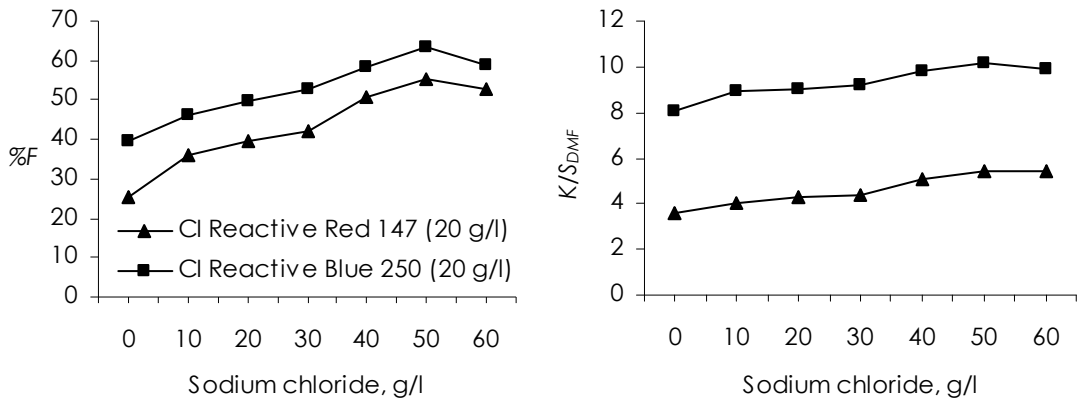


Figure 5.3: Effect of electrolyte concentration on dye fixation and colour yield

The relationship between the extent of dye diffusion and dye fixation (and hence colour yield) can be obtained through results presented in Figures 5.2 (b) and 5.3. The increase in dye diffusion is known to favour dye fixation and colour yield in pad dyeings [53]. Figure 5.4 shows that the proposed measure of diffusion is directly related to dye fixation and colour yield. This further confirms the validity of the new method for determining the extent of dye diffusion.

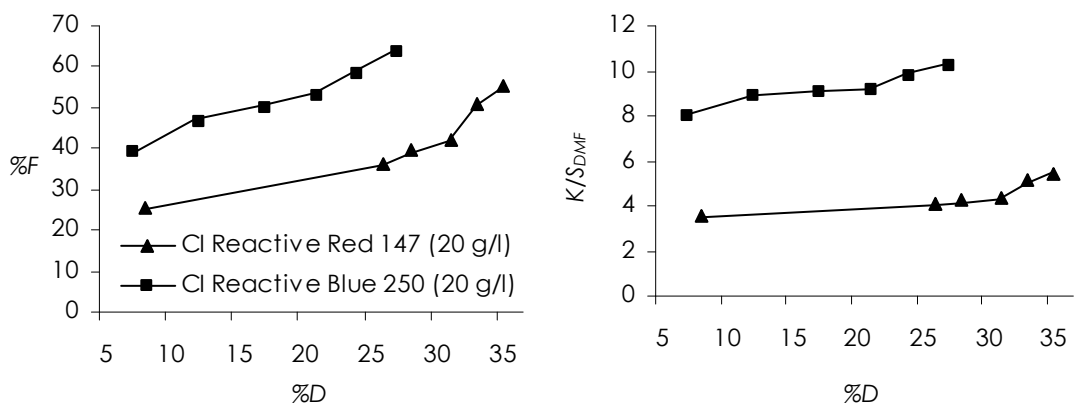


Figure 5.4: Dye diffusion vs dye fixation and colour yield

5.4.3 Rate of dye diffusion during steaming, baking and batching

Figure 5.5 shows the extent of dye diffusion achieved at a range of steaming times for CI Reactive Red 147 and CI Reactive Blue 250. For the CI Reactive Blue 250, over 95% of its diffusion occurred within the first 30 seconds of steaming. This implies that the dye has higher dye migration initially when the extent of dye-fibre reaction is low. The diffusion after the first 30 seconds of steaming appeared to increase up to a maximum at 60 seconds and slightly decrease at longer steaming time.

For the CI Reactive Red 147, a pronounced maximum value for %D was observed at 60 seconds of steaming time. This shows that the rate of diffusion of this dye, relative to CI Reactive Blue 250, was expedited more by steaming. The relative sizes of the chromophores of both dyes are not known. However, CI Reactive Blue 250 is a bifunctional dye. In such circumstances, it may be that the bifunctional dye has a lower rate of diffusion relative to its rate of reaction with the fibre.

The diffusion maxima may be due to excessive dye hydrolysis with increasing steaming time and the hydrolysed dye is relatively mobile within the fibre. The reasons for the maxima are not fully understood which may have industrial implications. The effect of dye size and the type and number of reactive groups, though beyond the scope of this thesis, may be worthy of further study.

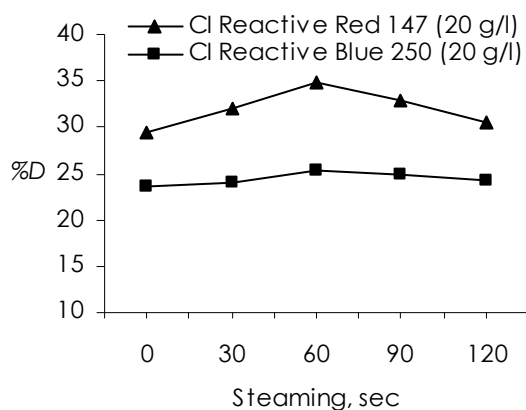


Figure 5.5: Rate and extent of dye diffusion during steaming

For the pad-dry-bake method, Figure 5.6 shows that the patterns of behaviour of dye diffusion with baking time are similar to those obtained with steaming time. For both dyes, the absolute values of diffusion at any time were less with baking than

with steaming. This implies the presence of water molecules in the cotton fibre at elevated temperatures has a marked effect on the rate and extent of diffusion.

For the CI Reactive Blue 250, dye diffusion continued to increase marginally with increasing baking time. The maximum value for this dye was not determined because the time exceeds the industrial practice. Whereas the diffusion of CI Reactive Red 147 increased up to 90 seconds of baking time and then decreased. As observed with steaming, the maximum value obtained for CI Reactive Red 147 suggests that the rate of dye hydrolysis is higher than that for CI Reactive Blue 250 at higher temperatures. As noted above, the reasons for the maximum values obtained with the CI Reactive Red 147 are not clear, which may have implications for industrial practice and are worthy of further investigation.

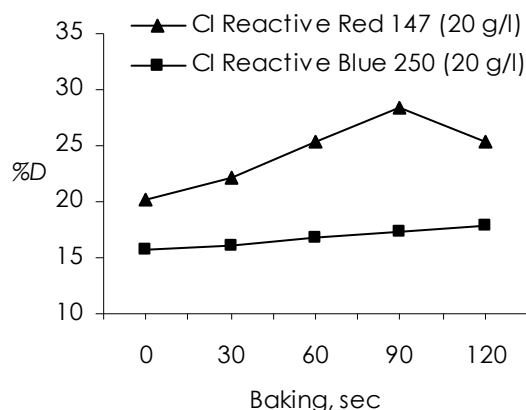


Figure 5.6: Rate and extent of dye diffusion during baking

Figure 5.7 demonstrates the applicability of the proposed method for determining diffusion to the pad-batch dyeing method. There, the extent of CI Reactive Red 147 dye diffusion increases then decreases with increasing batching time. The maximum value of diffusion was obtained at 12 hrs batching. For the CI Reactive Blue 250, diffusion continued to increase with increasing batching time. The maximum value for CI Reactive Blue 250 is of the order of 36 hrs of batching. As per the dye manufacturers' recommendations for optimum dyeing results, the batching time for CI Reactive Red 147 ranges from 4 to 14 hrs and that for CI Reactive Blue 250 is up to 36 hrs. The figure confirms that the dyeing results

significantly depend on the extent of dye diffusion and conforms to the dye manufacturers' recommendations.

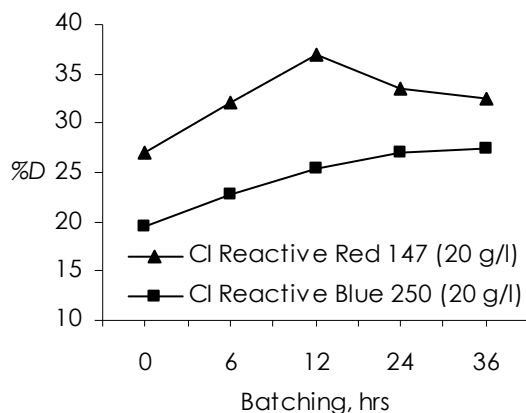


Figure 5.7: Rate and extent of dye diffusion during batching

It is clear from Figures 5.5, 5.6 and 5.7 that the dye diffusion is promoted by steaming, baking and batching. The CI Reactive Blue 250 diffuses more slowly than CI Reactive Red 147. This may be because of the molecular size and two reactive groups in the CI Reactive Blue 250 molecule.

Figure 5.8 shows that the optimum dye diffusion obtained in pad-steam and pad-batch dyeings was considerably higher than that obtained in pad-dry-bake dyeing. This reflects that the penetration of dye molecules is supported by the presence of water molecules which are not present in pad-dry-bake process.

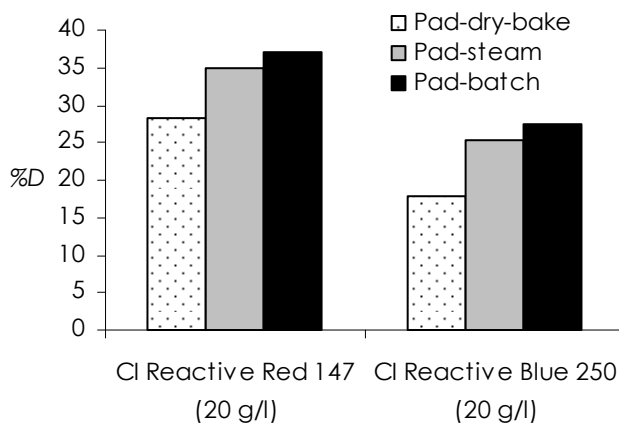


Figure 5.8: Optimum dye diffusion obtained with steaming, baking and batching

5.4.4 Effect of dye concentration on diffusion

The effect of dye concentration on diffusion was determined for the pad-steam and pad-batch processes as these processes showed a significant extent of dye diffusion. In kinetic studies, dye concentration dependence is an important factor because increasing the number of dye molecules results in increasing the competition for dye sites on the fibre. Most of such studies have been of theoretical nature where diffusion coefficients are demonstrated for exhaust dyeings [53, 123, 125, 139, 140]. In exhaust dyeing of cotton with anionic dyes, dye exhaustion gradually decreases with an increase in the concentration of dyes applied. This is due to the gradual build-up of the dye at the fibre surface, hence retarding the further adsorption of remaining dye from the dyebath [141]. The effect of dye concentration on the extent of dye diffusion as determined by the proposed equation for pad dyeings is shown in Figure 5.9. The results show that the dye diffusion decreases with increasing dye concentration in both pad-steam and pad-exhaust dyeings. In order to obtain optimum dyeing results, increased amounts of electrolyte may be used for increased dye concentrations. This is in line with dye manufacturers' recommendations.

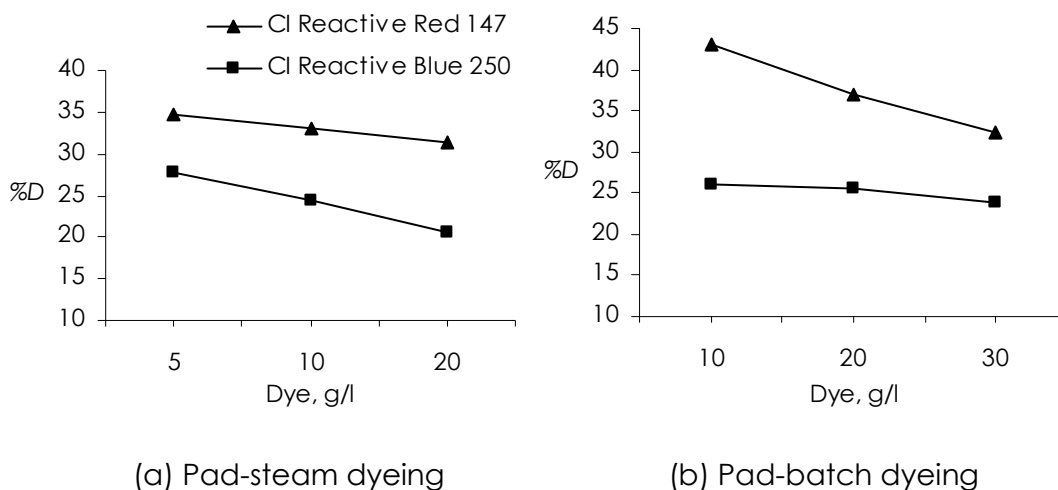


Figure 5.9: Effect of dye concentration on dye diffusion at constant electrolyte (50 g/l), alkali (15 g/l) and steaming time (60 sec)

5.5 Industrial applications

The selection of dyes and colour matching are the most critical processes in cotton dyehouses. Colour yield, the extent of dye fixation and colourfastness are the key results in these processes. However, the important goals are the shade reproducibility and right-first-time production [134, 142, 143], thus producing the required quality with minimum costs including the costs involved in production time and rehandling. It has been shown in this chapter that dye fixation and colour yield significantly depend on the extent of dye diffusion. Therefore, dye diffusion must be considered for dye selection and colour matching as one of the primary parameters. This should lead to reduce times needed for dye selection and colour matching time. It should also reduce production delays, rehandling, and improve reproducibility.

To date, industrial dyehouses have not considered measurement of dye diffusion as an everyday tool because the currently available methods are either time consuming, indirect or involve the use of sophisticated laboratory procedures. An easy, direct and industrially applicable method for determining the dye diffusion has been presented in this chapter. The new method requires only several hours to prepare the database reference colour strength values. Those values can be used for dye diffusion measurements repeatedly for the same dye and fabric. The diffusion measurement can be performed during the regular spectrophotometric measurements for dye selection and colour matching processes.

5.6 Conclusion

The new method for determining the extent of dye diffusion by using *K/S* values provides results consistent with established theories for pad dyeings. It also confirms dye manufacturers' recommendations for obtaining maximum colour yields. The method should be applicable to other dye classes, such as vat dyes and sulphur dyes. The new method can effectively be used in industrial dyehouses for precise determination of the dye efficiency and thus improve dyeing results and assist with cost reductions.

Chapter 6

Role of dyebath ionic strength in pad-steam dyeing of cotton with reactive dyes

6.1 Introduction

Sodium chloride (common salt) and sodium sulphate (Glauber's salt) are widely used electrolytes in the dyeing of cotton with anionic dyes [136]. However, these inorganic electrolytes increase the effluent pollution to a very high levels [65, 104]. Therefore, researchers and industry have been investigating alternative electrolytes which would result in improved dyeing efficiency and reduced environmental impact. Accordingly, studies into the role of cations and anions of electrolytes have been effectively made for exhaust dyeing of cotton with anionic dyes. The discussion on such studies is given in Chapter 1 (Section 1.4.11). This chapter presents studies into the role cations and anions of electrolytes and dyebath ionic strength in the pad-steam dyeing of cotton with reactive dyes. The studies were also extended to exhaust dyeing process.

For any alternative electrolyte, the concentration is always different from the concentration of the original electrolyte used in dyeing of cotton with anionic dyes [35]. This is because each electrolyte has its own electrolytic effect (ionic strength) depending on its cations and anions. In order to substitute one electrolyte with another, a series of laboratory dyeings must be conducted to determine the optimum concentration of the alternative electrolyte. This is a time and cost consuming task.

When an electrolyte concentration is known, the ionic strength of the electrolyte can be calculated by using Equation 4.5 (i.e. $\mu = \frac{1}{2} \sum [\text{molar concentration of compound} \times (\text{ionic charge})^2]$), and vice versa. On the basis of this fact, studies were made on a range of electrolytes of different cations and anions. These studies have resulted in a new theory for determining the required concentration of an alternative electrolyte in the dyeing of cotton. It was hypothesised that the required concentration of any alternative electrolyte can be calculated if the concentration of the original electrolyte is known. This saves laboratory experiments and thus a reasonable amount of time and the cost.

6.2 Hypothesis

Traditionally, industry and dye research laboratories have determined the optimum concentration for an electrolyte, in grams per litre, via laboratory sample dyeings. This hypothesis proposes that for a given cation the required concentration of an alternative electrolyte is determined by its ionic strength. In other words, having determined the optimum concentration for say sodium chloride, the optimum concentration of any other sodium salt is the concentration required to give the same ionic strength. These findings also lead to an improved understanding of pad dyeings. The driving force for transfer of dye onto the surface of the fibre and its subsequent diffusion through the fibre structure is the dyebath ionic strength.

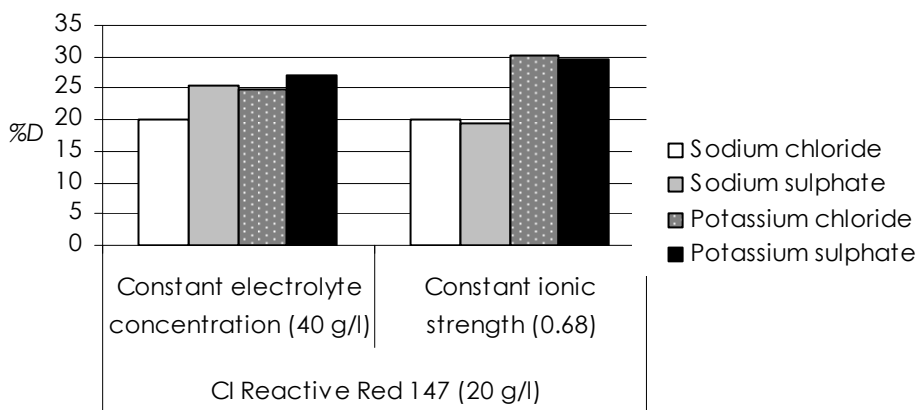
6.2 Selection of electrolytes for the study

A range of inorganic electrolytes of various cations and anions have been studied for their effectiveness into dyeing of cotton with anionic dyes. That included sodium chloride, sodium sulphate, potassium chloride, potassium sulphate, lithium chloride, caesium chloride, ammonium chloride, ammonium sulphate, magnesium chloride, magnesium sulphate, calcium chloride, aluminium chloride, aluminium sulphate and zinc chloride [10, 35, 37, 144-146]. For this study, four uni-univalent electrolytes of two different cations and two different anions, i.e. sodium chloride, sodium sulphate, potassium chloride and potassium sulphate, were selected. The sodium and potassium salts have very good aqueous solubility and are cost effective. Most of other inorganic electrolytes either have poor aqueous solubility or cause water hardness. For example, calcium and magnesium salts promote dye aggregation to a greater extent [40] and increase water hardness thus creating dyeing problems [41-43]. The studies into the effectiveness of dyebath ionic strength were extended to the use of organic salts in pad-steam dyeing of cotton with reactive dyes. Sodium acetate, a basic carboxylic sodium salt, was selected for this purpose.

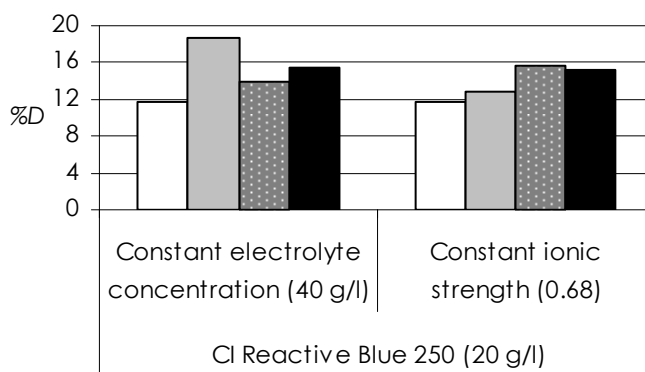
6.4 Effect of different inorganic electrolytes on dye diffusion (constant electrolyte concentrations vs constant ionic strength)

Fabric samples were dyed, without using alkali, in order to study the effect of different inorganic electrolytes on reactive dye diffusion into cotton at constant electrolyte concentration and constant dyebath ionic strength in pad-steam dyeing. The diffusion results were obtained after a steaming time of 60 sec and are shown in Figure 6.1. The figure shows that different extents of dye diffusion were obtained with the same concentration of different electrolytes. The difference between the diffusion obtained using sodium chloride and sodium sulphate was higher than that obtained using potassium chloride and potassium sulphate. At constant electrolyte concentration, the ionic strength of sulphate salts is higher than that of chloride salts (Table 6.1). Therefore, sulphate salts have shown higher dye diffusion than chloride salts. Table 6.1 shows the ionic strengths of different electrolytes at constant concentration and their concentrations at constant ionic strength calculated using Equation 4.5.

On the other hand, extents of dye diffusion obtained with same dyebath ionic strength using different salts of the same cation are closely comparable. This proves the hypothesis for the role of dyebath ionic strength in pad-steam dyeing of cotton with reactive dyes. That is to say, for a given cation, similar extent of dye diffusion is obtained using different electrolytes at constant ionic strength. Note that potassium salts gave considerably higher dye diffusion than sodium salts at constant ionic strength.



(a)



(b)

Figure 6.1: Effect of different electrolytes on dye diffusion at constant concentration and constant ionic strength

Table 6.1: Electrolyte concentration vs ionic strength

Constant concentration (40 g/l)		Constant ionic strength (0.68)	
Electrolyte	Ionic strength (μ)	Electrolyte	Concentration (g/l)
Sodium chloride	0.68	Sodium chloride	40
Sodium sulphate	0.85	Sodium sulphate	32.38
Potassium chloride	0.54	Potassium chloride	50.99
Potassium sulphate	0.69	Potassium sulphate	39.73
Sodium acetate	0.49	Sodium acetate	56.11

6.5 Total dyebath ionic strength

Inorganic alkali is used in conventional pad-steam dyeing of cotton with reactive dyes for activating dye-fibre reaction. The alkali, being a soluble compound, should exert an influence on dye diffusion as per the hypothesis because it also provides dissociated cations and anions in the dyebath. Figure 6.2 shows dye diffusion results obtained using an inorganic electrolyte (sodium chloride) with and without an inorganic alkali (sodium bicarbonate for CI Reactive Red 147 and sodium carbonate for CI Reactive Blue 250). The figure shows that the dye diffusion increases by adding alkali to the dyebath. This is because inorganic alkali dissociates in water and increases dyebath ionic strength. Thus, the total dyebath ionic strength is an ultimate driving force for dye diffusion in pad-steam dyeing of cotton with reactive dyes.

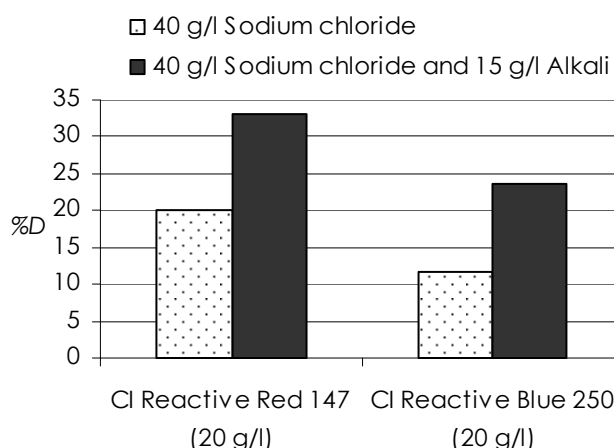
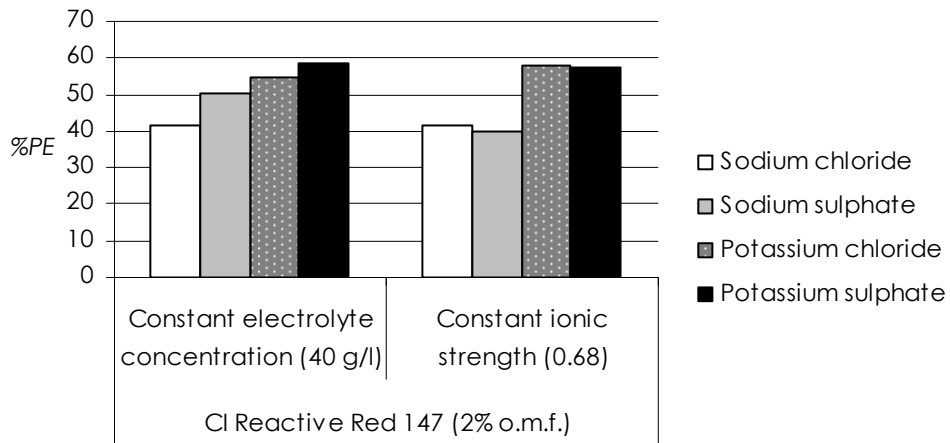


Figure 6.2: Effect of inorganic alkali on dye diffusion at 60 sec steaming

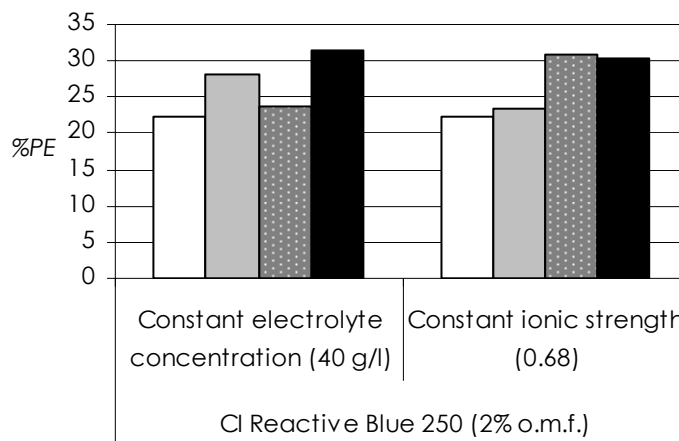
6.6 Testing the hypothesis for dye exhaustion (exhaust dyeing)

Figure 6.3 shows the effect of different inorganic electrolytes on reactive dye exhaustion onto cotton at constant electrolyte concentration and constant dyebath ionic strength. In order to study the effect of electrolytes (without alkali), primary dye exhaustion (PE) were determined. Similar to the results obtained for dye diffusion in pad-steam dyeing, different extents of primary dye exhaustion were obtained with the same concentration of different electrolytes. Similar extents of primary dye exhaustion were obtained with same dyebath ionic strength using different

electrolytes of the same cation. This extends the viability of the hypothesis to exhaust dyeing.



(a)



(b)

Figure 6.3: Effect of different electrolytes on dye exhaustion at constant concentration and constant ionic strength

Figure 6.4 shows that the total dye exhaustion is higher than primary exhaustion. This is due to further (secondary) dye exhaustion after addition of alkali to the dyebath [34, 48]. The secondary exhaustion is attributed to the increase in ionic strength from the added alkali. The lower primary exhaustion of Cl Reactive Blue 250 is because of its lower rate of initial exhaustion.

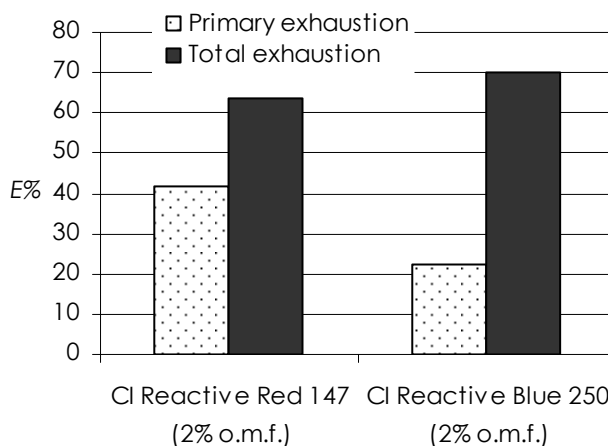


Figure 6.4: Effect of inorganic alkali on dye exhaustion

6.7 Testing the hypothesis for using an organic electrolyte in pad-steam dyeing

Figure 6.5 shows the effect of an inorganic electrolyte (sodium chloride) and an organic electrolyte (sodium acetate) at constant concentration and at constant ionic strength. The results support the hypothesis for organic electrolyte also. Lower dye diffusions were obtained with sodium acetate at constant electrolyte concentration. This is because the ionic strength of sodium acetate is lower than sodium chloride (Table 7.4).

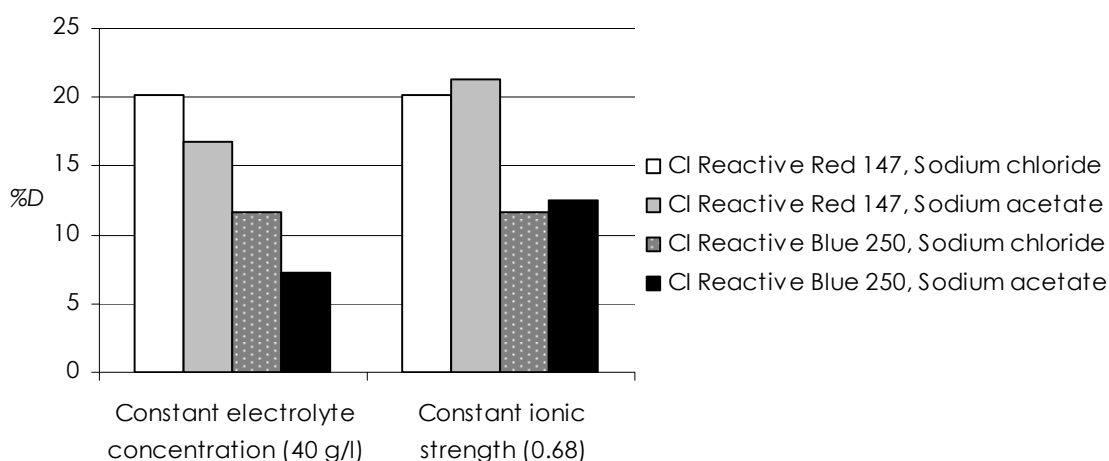


Figure 6.5: Effect of organic electrolyte on dye diffusion at constant concentration and constant ionic strength

6.6 Conclusion

It was found that the driving force for reactive dye exhaustion on cotton fibre and the dye diffusion into the fibre is dyebath ionic strength. Thus, a near approximation to the required concentration of any alternative salt can be calculated if the optimum concentrations of the original electrolyte and alkali of the same cation are known. The optimum concentrations of alternative alkaline polycarboxylic salts are studied in the next chapter.

Chapter 7

Use of alkaline polycarboxylic sodium salts in pad-steam dyeing of cotton with reactive dyes

7.1 Introduction

Organic compounds have been shown to be effective alternatives to inorganic electrolytes in exhaust dyeing [98, 100, 102]. Prabu and Sundrarajan [68] have demonstrated the use of trisodium citrate as an alternative to traditional inorganic electrolytes for exhaust dyeing of cotton with reactive, direct and solubilised vat dyes. Sodium edate, an alkaline polycarboxylic salt, has been reported as an alternative to inorganic electrolyte (sodium sulphate) and alkali (sodium carbonate) in exhaust dyeing of cotton with reactive dyes [63]. However, the high alkalinity of sodium edate can cause reactive dye hydrolysis in the dyebath during dye exhaustion. This can result in the difficult control of dyeing and reduced dye fixation [102]. Thus, the use of the alkaline organic salts in continuous dyeing of cotton with reactive dyes would be of interest and has not been reported.

On the basis of the theories established in the previous chapters, this chapter presents the findings of a study of using an alkaline polycarboxylic salt, such as sodium edate, trisodium NTA and tetrasodium GLDA (Figure 7.1), as an alternative to electrolyte and alkali in the continuous pad-steam dyeing of cotton with reactive dyes. These alkaline polycarboxylic sodium salts are biodegradable compounds [108-112] and commercially available as 'chelating agents'.

Alkaline polycarboxylic salts, as soluble salts, can act as the electrolyte and hence substitute the inorganic electrolyte. These salts provide an alkaline pH of 10–12 when dissolved in water. Thus, they are capable of activating the dye-fibre reaction. The reaction between dye molecules and cotton cellulose using these salts is believed to be the same as that using an inorganic alkali, i.e. a nucleophilic substitution mechanism in the case of the difluorochloropyrimidine reactive group (CI Reactive Red 147) and nucleophilic addition mechanism in the case of a sulphatoethylsulphone reactive group (CI Reactive Blue 250) [22, 26, 52]. This was verified by the FTIR analysis (Section 7.6.3).

7.2 Optimum inorganic electrolyte concentration

As discussed in Chapter 5, electrolytes promote dye diffusion in pad-steam dyeing of cotton with reactive dyes. Figure 7.2 shows that the optimum dye diffusion was obtained at 50 g/l sodium chloride for CI Reactive Red 147 and CI Reactive Blue 250.

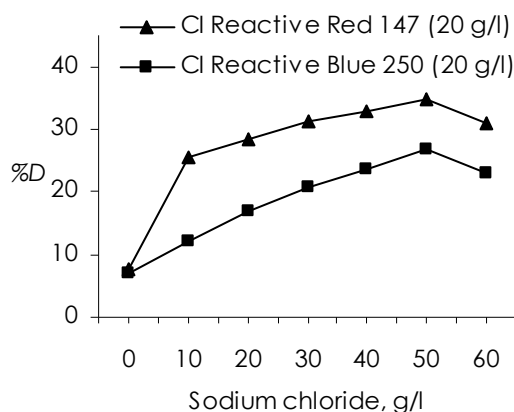


Figure 7.2: Effect of inorganic electrolyte concentration on dye diffusion at 60 sec steaming

7.3 Effect of inorganic alkali concentration

Under alkaline conditions (up to pH of 10–12), reactive dyes react with the hydroxyl groups of the cotton cellulose [20, 26, 52]. The dyes can also react with the hydroxide ions present in aqueous dyebath under alkaline pH conditions. This produces nonreactive hydrolysed dye. Therefore, excess alkali can act to increase dye hydrolysis at the expense of dye-fibre reaction. Figure 7.3 shows that 15 g/l was the optimum alkali concentration for CI Reactive Red 147 (sodium bicarbonate) and CI Reactive Blue 250 (sodium carbonate) with constant sodium chloride (50 g/l) at steaming time of 60 sec. The better fixation of CI Reactive Blue 250 may be because the dye is bifunctional and therefore has an increased opportunity to react with the cotton cellulose [20, 26].

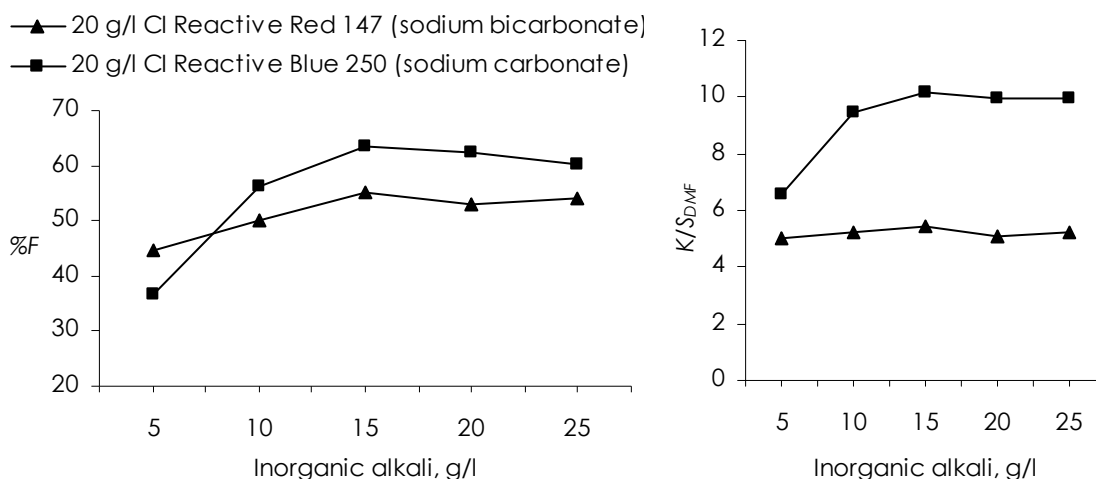


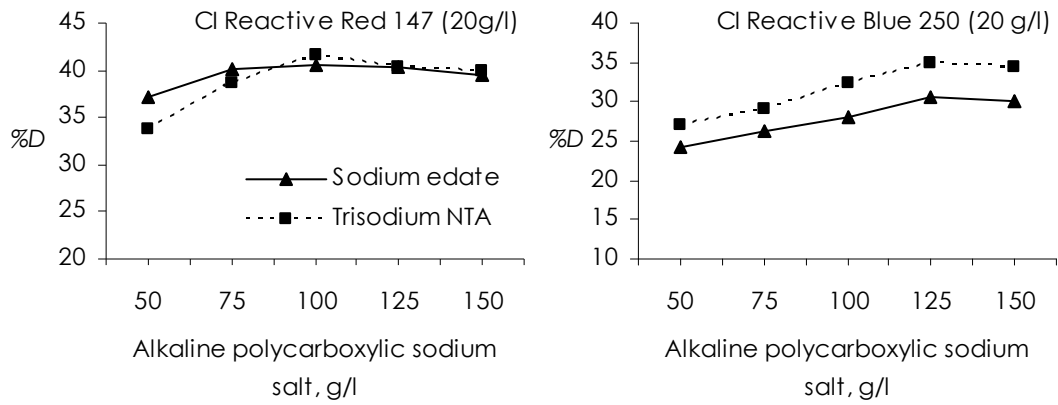
Figure 7.3: Effect of inorganic alkali concentration on dye fixation and colour yield

7.4 Determining optimum alkaline polycarboxylic sodium salt concentrations

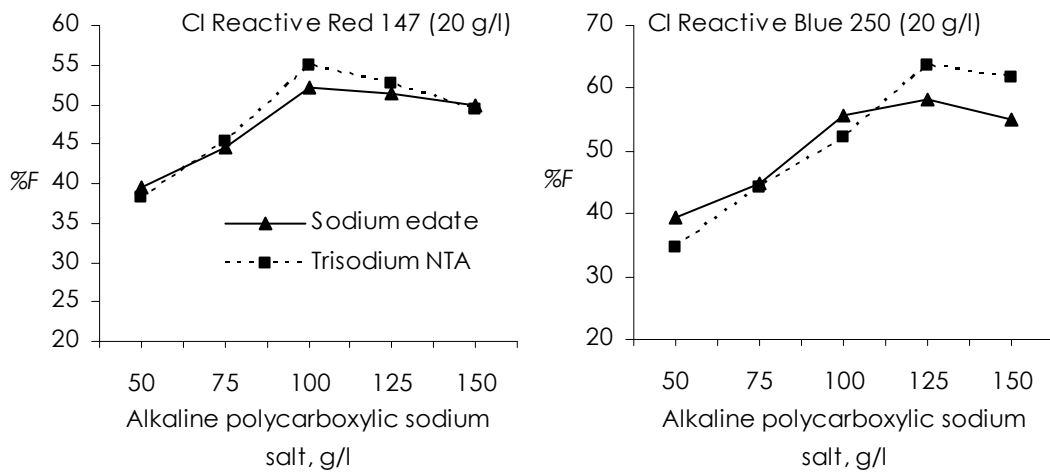
7.4.1 Via laboratory dyeings (industrial practice)

Figure 7.4 shows that the dye diffusion and fixation passed through maximum values with increasing concentration of sodium edate or trisodium NTA at a steaming time of 60 sec. These maxima may be due to the result of increasing dye aggregation and competing dye hydrolysis and dye-fibre reaction. The optimum values were obtained with 100 g/l of sodium edate or trisodium NTA for CI Reactive Red 147 and 125 g/l for CI Reactive Blue 250. The optimum concentrations of sodium edate and trisodium NTA (approx. 100–125 g/l) were higher than those of the inorganic electrolyte and alkali (approx. 50 g/l sodium chloride and 15 g/l sodium bicarbonate for CI Reactive Red 147 or 15 g/l sodium carbonate for CI Reactive Blue 250). This may be attributed to the ionic strength of sodium edate or trisodium NTA being lower than sodium chloride and sodium bicarbonate/sodium carbonate together [119]. Thus, more of the alkaline polycarboxylic sodium salt is needed to achieve the adequate level of electrolytic effect for dye sorption [20, 52, 53]. The higher concentration of the alkaline polycarboxylic sodium salt required for CI Reactive Blue 250 is due to higher dyebath ionic strength needed (Section 7.4.2). As found in the study using inorganic chemicals presented in Chapter 5, CI Reactive Red 147 diffused more than CI Reactive Blue 250 using alkaline organic salts. The dye diffusion and fixation obtained with optimum trisodium NTA were slightly better than those

obtained with sodium edate. This is because the dyebath ionic strength of trisodium NTA is slightly higher than that of sodium edate.



(a)



(b)

Figure 7.4: Effect of alkaline polycarboxylic sodium salt concentration on dye diffusion and dye fixation

Figure 7.5 shows that the effect of alkaline polycarboxylic sodium salt concentration on resultant colour yield is similar to that on dye diffusion and fixation.

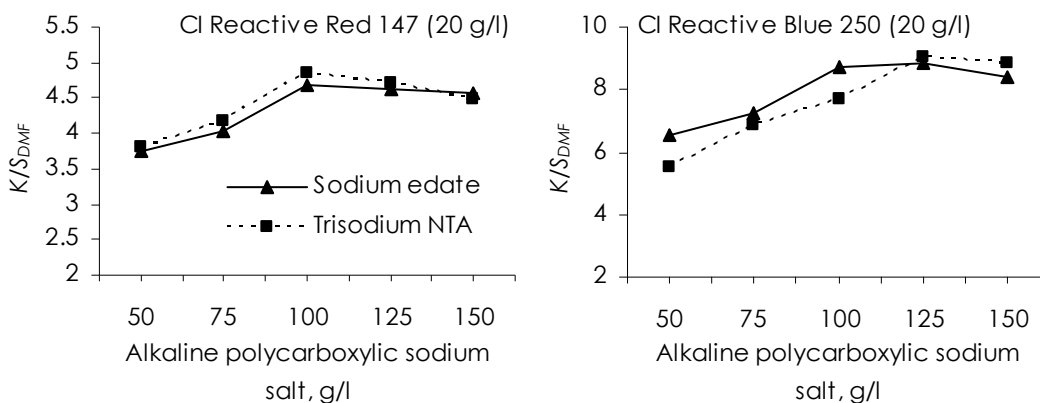


Figure 7.5: Effect of alkaline polycarboxylic sodium salt concentration on colour yield

7.4.2 Via calculating dyebath ionic strength

Table 7.1 shows the optimum alkaline polycarboxylic sodium salt concentration calculated on the basis of the dyebath ionic strength using Equation 4.5. The optimum concentration obtained from laboratory dyeings are very close to the concentrations calculated on the basis of total dyebath ionic strength. This shows that the new theory of the role of dyebath ionic strength is also applicable for alternative alkaline organic salts. The total dyebath ionic strength for CI Reactive Blue 250 was higher than that for CI Reactive Red 147 because the ionic strength of sodium carbonate used for CI Reactive Blue 250 is higher than that of sodium bicarbonate used for CI Reactive Red 147 in traditional dyeing.

Table 7.1: Optimum alkaline polycarboxylic sodium salt calculated on the basis of dyebath ionic strength

Dye	Optimum inorganic chemical concentration	Ionic strength	Total ionic strength of dyebath	Optimum alkaline polycarboxylic sodium salt
CI Reactive Red 147	50 g/l sodium chloride	0.86	1.04	109.2 g/l sodium edate
	15 g/l sodium bicarbonate	0.18		95.9 g/l trisodium NTA
CI Reactive Blue 250	50 g/l sodium chloride	0.86	1.29	135.7 g/l sodium edate
	15 g/l sodium carbonate	0.43		119.2 g/l trisodium NTA

7.5 Use of tetrasodium GLDA

Tetrasodium GLDA is another alkaline polycarboxylic sodium salt. This is claimed to be better than the salts of ethylene diamine tetra-acetate (EDTA) and NTA in terms of its biodegradability and eco-sustainability [112]. Dissolvine GL-47-S (Akzo Nobel) was used as tetrasodium GLDA. It is a $47 \pm 2\%$ w/w aqueous solution of tetrasodium GLDA and contains $1.2 \pm 0.7\%$ w/w sodium hydroxide. Figure 7.6 shows the effect of tetrasodium GLDA concentration on dye fixation and colour yield. Like sodium edate and trisodium NTA, the dye fixation and colour yield passed through maximum values with increasing concentration of tetrasodium GLDA at a steaming time of 60 sec. The optimum values were obtained with 75 g/l of tetrasodium GLDA for CI Reactive Red 147 and 100 g/l for CI Reactive Blue 250. More than 90% dye fixation was achieved for CI Reactive Blue 250, which is notably a significant increase compared to traditionally possible lower fixation levels because of excessive dye hydrolysis in pad-steam dyeing of cotton with reactive dyes [20]. This may be because the mixture of tetrasodium GLDA solution with a slight concentration of sodium hydroxide provides better stability at elevated pH for a bis(sulphatoethylsulphone) dye reaction with the fibre. The colour yield obtained for the same dye was also higher than that

obtained for any other electrolyte and the alkali. These results obtained with tetrasodium GLDA for the bis(sulphatoethylsulphone) dye are worthy of further study.

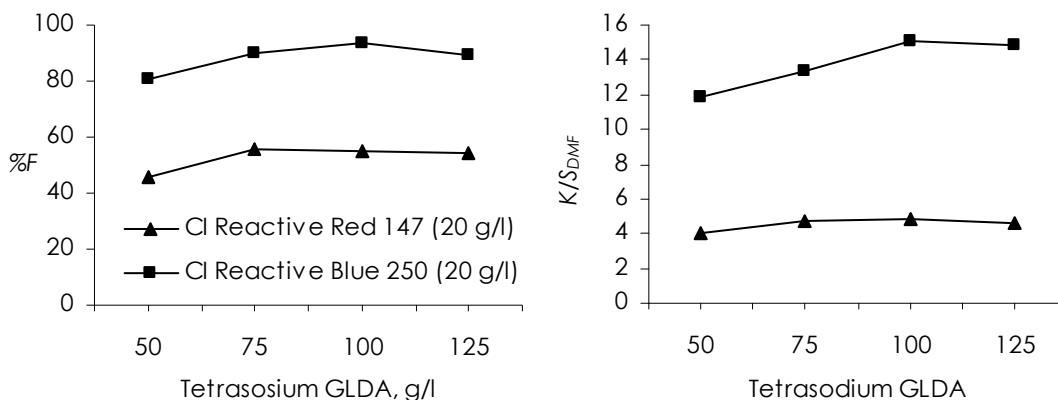


Figure 7.6: Effect of tetrasodium GLDA concentration on dye fixation and colour yield

7.6 Effect of steaming time using optimum concentration of alkaline polycarboxylic salts

Steaming of the fabric padded with reactive dye provides the high temperature under moist conditions to accelerate the dye-fibre reaction. The steaming conditions in traditional pad-steam dyeing are always fixed, i.e. temperature of 101–102°C and 100% moisture. Therefore, the key process parameter is steaming time. The fabric was padded with dye solution and then steamed for 60, 90 and 120 sec to determine the extent of dye fixation and colour yield. The steaming time range of 60–120 sec was selected because industrial pad-steam dyeing machines are generally designed to operate within this time range. The effect of steaming time on dye fixation and colour yield with the optimum concentrations of alkaline polycarboxylic sodium salts is shown in Figure 7.7. The figure shows that dye fixation and colour yield continued to increase with steaming time. Steaming time to maximum fixation and yield was not determined because the time exceeds standard industry practice. Similar to results obtained using inorganic chemicals (Chapter 5), over 95% of the CI Reactive Blue 250 diffused within the initial 60 sec of steaming. After which a very slight increase in the dye fixation and colour yield was obtained.

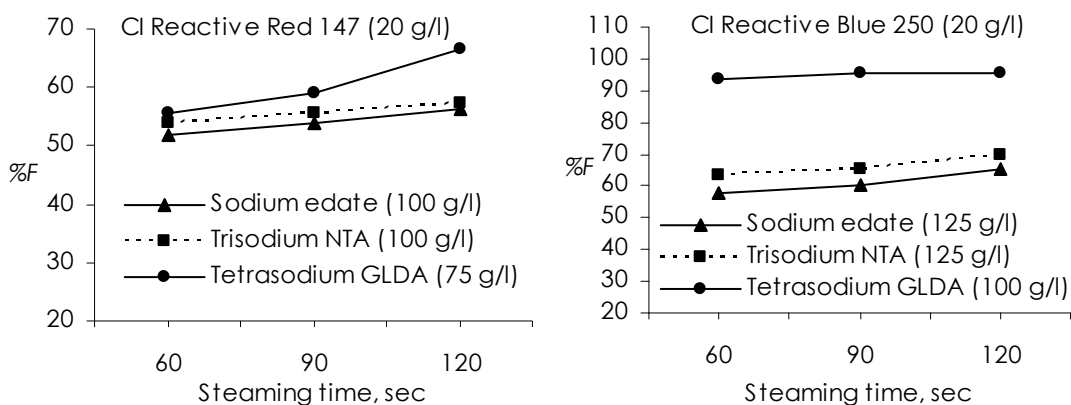


Figure 7.7 (a): Effect of steaming time on dye fixation using alkaline polycarboxylic sodium salts

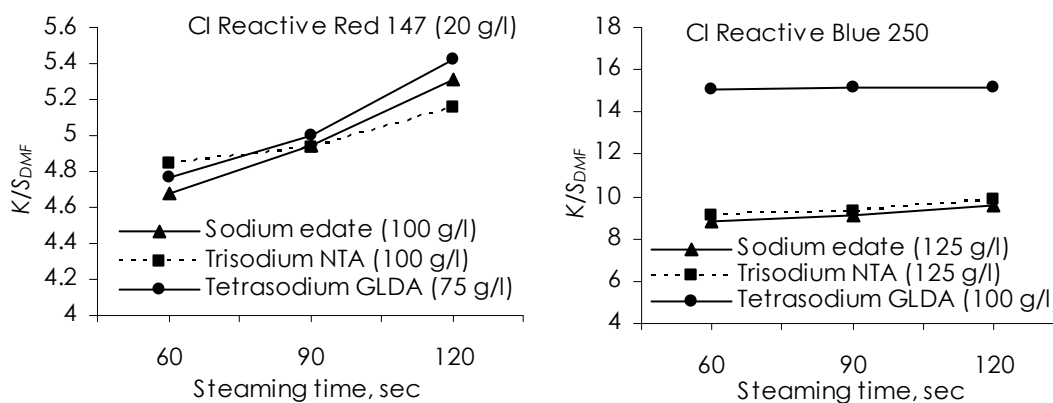


Figure 7.7 (b): Effect of steaming time on colour yield using alkaline polycarboxylic sodium salts

7.7 Comparison between traditional dyeing and dyeings using organic salts

7.7.1 Dye fixation and colour yield

Figure 7.8 shows that the fixation and yield results for the organic and inorganic electrolyte dyeings were closely comparable except for tetrasodium GLDA. The tetrasodium GLDA gave significantly higher dye fixation and colour yield with Cl Reactive Blue 250. With inorganic electrolyte and alkali, colour yield did not change when steaming was increased from 60 to 120 sec. However, with the alkaline polycarboxylic salts, small increases in the colour yield (averaging around 10%) were obtained at the longer steaming time. This suggests that the smaller inorganic ions

are slightly more effective as diffusion promoters. From the dye fixation results, over around 90% of the resultant dye-fibre reaction occurred within the first 60 sec of steaming. The tetrasodium GLDA was the most effective among polycarboxylic salts in causing dye fixation whereas sodium edate provided the lowest fixation. Note that the fixation of the CI Reactive Blue 250 with trisodium NTA was effectively identical to that obtained with the inorganic electrolyte and alkali at both 60 and 120 sec steaming times. The colour yield of the same dye obtained using tetrasodium GLDA was significantly higher than all other dyeing systems.

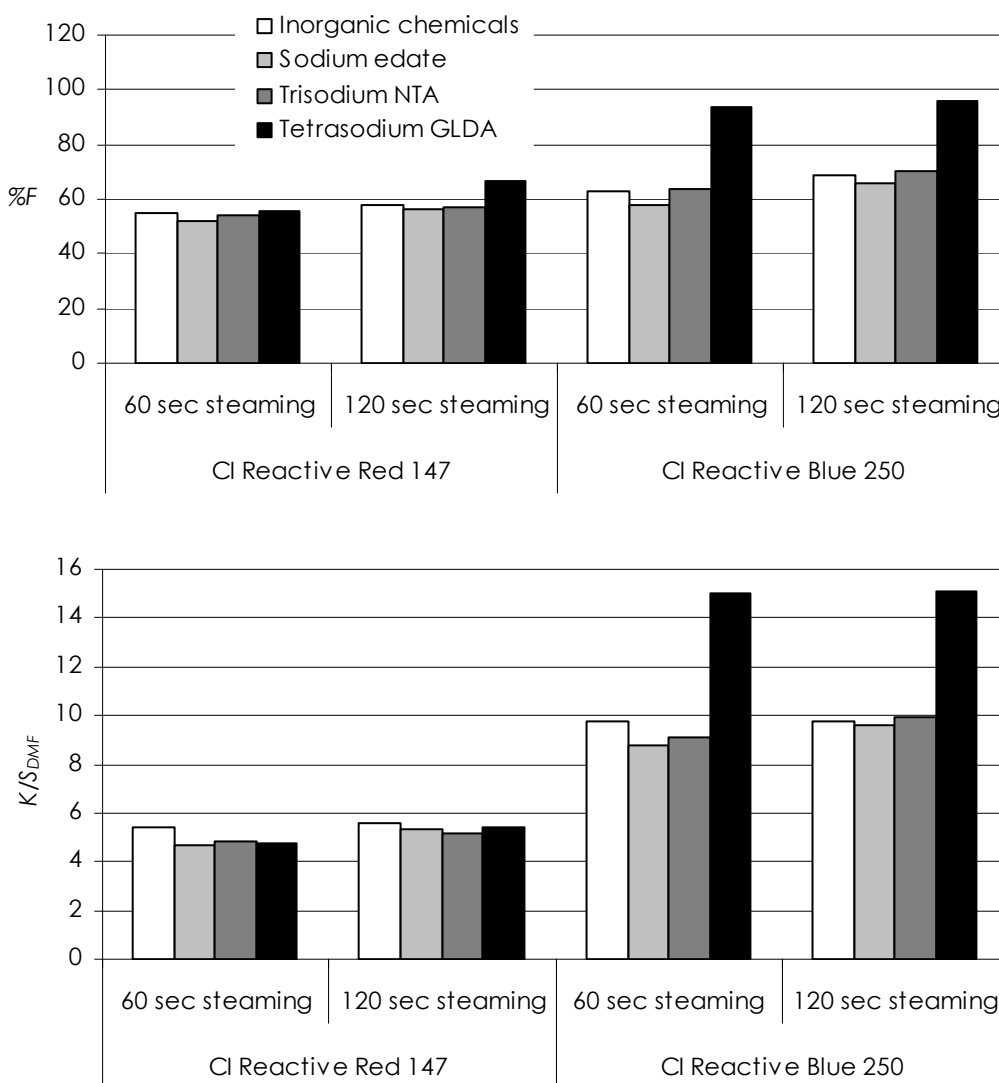


Figure 7.8: Dye fixation and colour yield of 20 g/l shade using optimum inorganic chemicals and alkaline polycarboxylic sodium salts

7.7.2 Colourfastness properties

As shown in Table 7.2, the colourfastness to rubbing, washing and light of the alternative dyeings are generally good to excellent and the same as those achieved with the traditional dyeing formulation containing inorganic electrolyte and alkali. Such identical colourfastness results are encouraging. The lower lightfastness of CI Reactive Blue 250 is the same produced on the dye manufacturer's pattern card. The rubbing and washing fastness of CI Reactive Blue 250 was slightly lower than CI Reactive Red 147 because of the higher colour yields. The concentration of tetrasodium GLDA used was 40 g/l (that was not optimum) for CI Reactive Blue 250 which gave the colour yield similar to other dyeings.

Table 7.2: Colourfastness of cotton fabrics dyed at 120 sec steaming

Dye (20 g/l)	Chemical concentrations	Colour yield (K/S after washing-off without DMF treatment)	Rubbing fastness		Washing fastness		Light fastness
			Dry	Wet	Change in colour	Staining on white **	Blue wool reference
CI Reactive Red 147	50 g/l sodium chloride 15 g/l sodium bicarbonate	5.85	5	4-5	5	5	6
	100 g/l sodium edate	5.65	5	4-5	5	5	6
	100 g/l trisodium NTA	5.54	5	4-5	5	5	6
	75 g/l tetrasodium GLDA (~ 190 g/l Dissolvine GL-47-S)	5.67	5	4-5	5	5	6
CI Reactive Blue 250	50 g/l sodium chloride 15 g/l sodium carbonate	10.34	4-5	4	4-5	4-5	3-4
	125 g/l sodium edate	10.12	4-5	4	4-5	4-5	3-4
	125 g/l trisodium NTA	10.27	4-5	4	4-5	4-5	3-4
	40 g/l tetrasodium GLDA (~ 93 g/l Dissolvine GL-47-S)	10.82	4-5	4	4-5	4-5	3-4

** Secondary cellulose acetate, cotton, polyacrylonitrile, polyester, polyamide and wool

7.7.3 Effluent analysis

Table 7.3 shows that sodium edate and trisodium NTA provided around 24–29% TDS reduction in the effluent of CI Reactive Red 147 and around 8–14% reduction in the case of CI Reactive Blue 250. The lower percent reduction in TDS for CI Reactive Blue 250 is due to the higher concentration of alkaline polycarboxylic salt needed to obtain optimum colour fixation and yield. Tetrasodium GLDA did not provide any significant reduction in the effluent TDS. This is because its solution (Dissolvine GL-47-S) contained sodium hydroxide that has high TDS content (see Table 7.4). However, Dissolvine GL-47-S is still safer in terms ecological footprint than sodium edate and trisodium NTA principally because of its better biodegradability [112]. Further, it provided higher dye fixation levels with significantly high level for CI Reactive Blue 250. This means the amount of unfixed dye washed-off to effluent will be reduced significantly.

Table 7.3: TDS of dyeing effluents

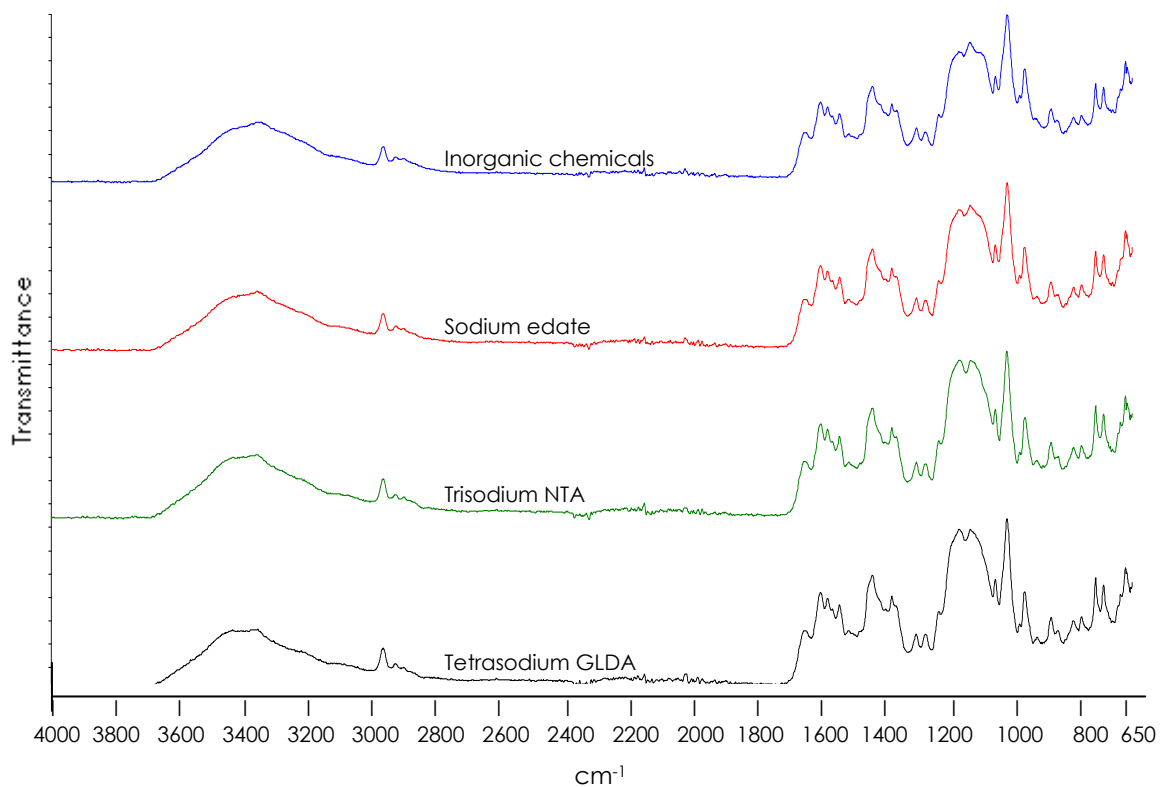
Dye (20 g/l)	Effluent samples (Dyebath recipes diluted 100 times)	TDS (mg/l)
CI Reactive Red 147	50 g/l sodium chloride 15 g/l sodium bicarbonate	1380
	100 g/l sodium edate	1010
	100 g/l trisodium NTA	1040
	75 g/l Tetrasodium GLDA (~ 190 g/l Dissolvine GL-47-S)	1370
CI Reactive Blue 250	50 g/l sodium chloride 15 g/l sodium carbonate	1400
	125 g/l sodium edate	1100
	125 g/l trisodium NTA	1230
	40 g/l Tetrasodium GLDA (~ 93 g/l Dissolvine GL-47-S)	1350

7.7.4 Economic considerations

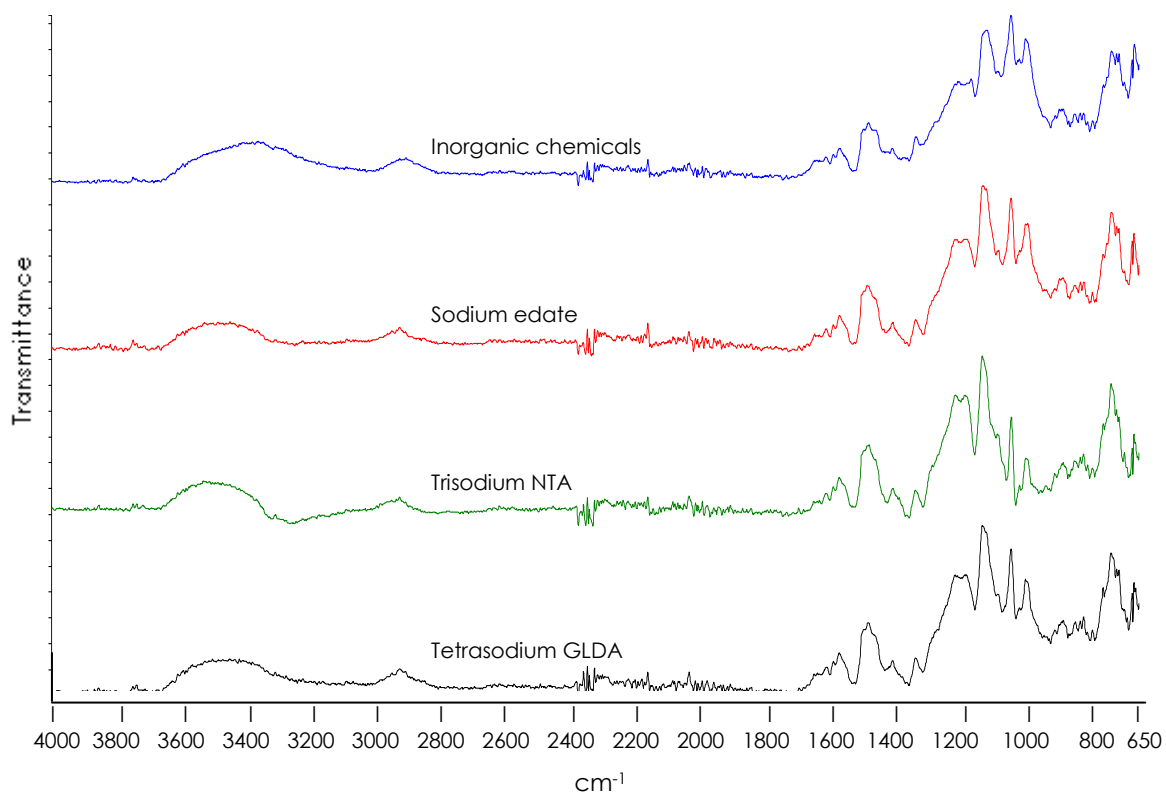
Governments and water authorities throughout the world are increasingly moving to load-based discharge permits, charges and penalties. Although the total cost of using alkaline polycarboxylic sodium salts is more than that of using inorganic electrolyte and alkali (see Table 7.4), the additional cost may be offset through lower discharge fees. Selected organic salts which provide higher levels of dye fixation and colour yield than inorganic based dyebath formulations may provide further offsets.

7.7.5 FTIR analysis

FTIR analysis was carried out to determine whether there is any new bond formed when an alkaline polycarboxylic sodium salt is used instead of inorganic electrolyte and alkali. For this purpose, the infrared transmittance spectra of undyed cotton and the dye was subtracted from the dyed cotton. The resultant spectra are shown in Figure 7.9 for comparison. The figure does not show any new peak for the spectra obtained for organic salts comparing to that obtained for inorganic chemicals. This indicates that the reactive dye reacted with cotton fibre, when using alkaline polycarboxylic sodium salts, in a similar manner to when using inorganic alkali.



(a) CI Reactive Red 147



(b) CI Reactive Blue 250

Figure 7.9: Spectra of dyed cotton subtracted by the spectra of undyed cotton and the dye

7.8 Selection of electrolyte and alkali for dyeing cotton with reactive dyes

Use of traditional salts is cheaper than using organic salts. However, organic salts offer reduction in effluent loads. If the required electrolyte concentration and pH for dyeing a cotton fabric with a reactive dye are known, a dyer can select a suitable electrolyte and alkali on the basis of dyebath ionic strength theory (Chapter 6) to suit his need for cost effectiveness, sustainability or certain combination of both. Table 7.4 can be used for such selection processes. The table can also be used for selection of a suitable electrolyte for other cotton dyes such as direct, sulphur and vat.

Table 7.4: Electrolytes and alkalis used for dyeing cotton with reactive dyes

Chemical (5 g/l)	Molecular Mass (g/mol)	Water of hydration	Ionic Strength (μ)	pH	TDS (mg/l)	Price †† (AUD/Kg)
Sodium chloride	58.44	Not hydrated	0.09	6.7	6900	1.34
Sodium sulphate	142.04	Not hydrated	1.06	6.4	4900	1.62
Sodium bicarbonate	84.01	Not hydrated	0.06	8.7	3700	1.75
Sodium carbonate	106.00	Not hydrated	0.14	11.3	6100	3.88
Sodium hydroxide	40.00	Not hydrated	0.12	12.6	22000	7.50
Sodium acetate	82.03	Not hydrated	0.06	8.0	2200	4.92
Trisodium citrate	294.10	Dihydrate	0.05	8.5	3100	4.25
Sodium edate	416.21	Dihydrate	0.05	11.3	2700	6.42
Trisodium NTA	275.11	Monohydrate	0.06	11.0	2900	6.53
10.8 g/l Dissolvine GL- 47-S (~ 5 g/l tetrasodium GLDA)	- NA -	- NA - (47% w/w tetrasodium GLDA and 1.2% w/w sodium hydroxide)	Approx. 0.063	11.82	5600	2.85

†† The commercial prices were obtained from local Australian suppliers (IMCD Australia and RPL Trading Pty Ltd).

7.9 Industrial dyeing

Figure 7.10 shows the results obtained from a large scale industrial trial. The results show the dye fixation and colour yield obtained with sodium edate were closely equivalent to those obtained with sodium chloride and sodium bicarbonate at 120 sec steaming. The fixation and yield values achieved under production conditions were higher than those obtained on a laboratory scale because the fabric used for production had a lower mass per unit area.

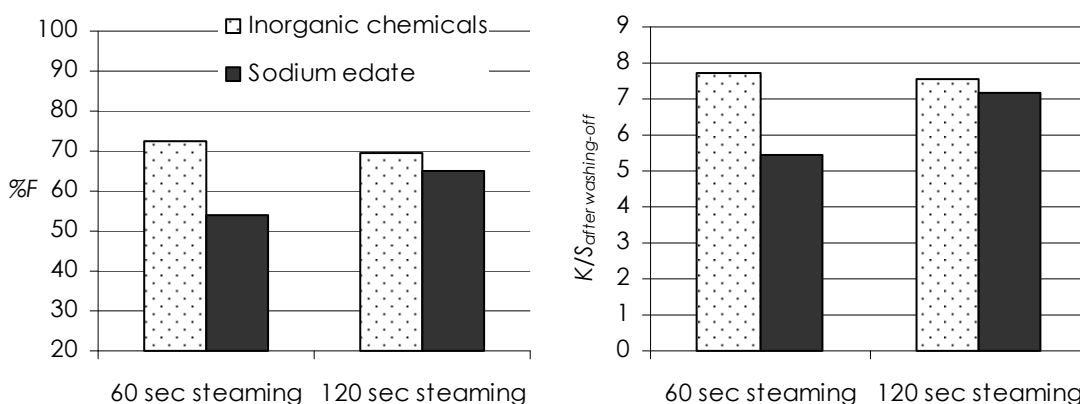


Figure 7.10: Dye fixation and colour yield of 20 g/l CI Reactive Red 147 using optimum inorganic chemicals and sodium edate on production scale

7.10 Conclusion

This chapter concludes that the selected biodegradable alkaline polycarboxylic sodium salts can be used for pad-steam dyeing of cotton with reactive dyes to replace inorganic electrolyte and alkali. Tetrasodium GLDA gave better dye fixation and colour yield than sodium edate and trisodium NTA. On the one hand, the proposed dyeing using organic salts is comparatively more expensive, but on the other hand, the effluent characteristics are improved.

Conclusions

Chapter 8

Overall conclusions and recommendations

8.1 Conclusions

This research has led to three principle outcomes;

- a) Pad-steam dyeing of cotton using biodegradable alkaline polycarboxylic sodium salts such as sodium edate, trisodium NTA and tetrasodium GLDA has been developed to improve effluent quality.
- b) A new theory on the role of dyebath ionic strength in dyeing of cotton with reactive dyes has been proven.
- c) A novel industrially applicable method for determining the extent of dye diffusion in pad dyeing of cotton with reactive dyes has been developed.

The investigation has shown that the alkaline polycarboxylic salts such as sodium edate, trisodium NTA and tetrasodium GLDA can effectively be used for pad-steam dyeing of cotton with reactive dyes to produce at least the same colour yields and colourfastness properties as obtained using traditional inorganic compounds. These organic salts offer the potential to reduce effluent discharge load through their biodegradability and reduction in TDS content. The dye-fibre reaction mechanisms for organic salts, namely nucleophilic substitution and nucleophilic addition, appear to be the same as using inorganic alkalis. This was confirmed by an FTIR analysis. Tetrasodium GLDA gave the best dyeing results among alkaline polycarboxylic salts. On one hand, the proposed dyeing using organic salts is comparatively more expensive, but on the other hand, the effluent characteristics are improved. It is suggested that refinements to the use of alkaline polycarboxylic salts may lead to opportunities for further reductions in effluent loads from cotton dyehouses.

The driving force for reactive dye exhaustion on cotton fibre and the dye diffusion into the fibre has been found to be dyebath ionic strength, which can be calculated as $\frac{1}{2} \sum [\text{molar concentration of compound} \times (\text{ionic charge})^2]$. On the basis of this fact and experimental evidences, it has been concluded that for a given cation, the required concentration of any alternative compound is the

concentration required to give the ionic strength of known optimum concentrations of the original electrolyte and alkali.

The extent of reactive dye diffusion into cotton can be calculated as $100 - [(K/S_{diffusion\ index}) / (K/S_{reference}) \times 100]$ by using a reflectance spectrophotometer. The new method can effectively be used in industrial dyehouses for precise determination of the dye efficiency and thus to improve dyeing results.

8.2 Recommendations for future research

This study has suggested a number of areas worthy of future research. These areas are:

- a) The use of trisodium NTA and tetrasodium GLDA for exhaust dyeing of cotton with reactive dyes.
- b) The use of biodegradable polycarboxylic salts for dyeing of cotton with other dyes such as direct, vat and sulphur dyes.
- c) The study of electrolyte ionic strength can be extended to the dyeing of cotton with other dyes such as direct, vat and sulphur dyes.
- d) The theory of determining dye diffusion using reflectance values can be further studied for other dye-fibre combinations and dyeing processes.
- e) The applicability of the polycarboxylic salts can be examined for other reactive groups.
- f) The significantly higher dye fixation and colour yield obtained with *bis(sulphatoethylsulphone)* dye and Dissolvine GL-47-S (tetrasodium GLDA solution) merits further study.

References

- [1] (7 July 2010). *The story of cotton*. Available: <http://www.cotton.org/pubs/cottoncounts/resources.cfm>
- [2] S. Gordon and Y.-L. Hsieh, *Cotton: Science and Technology*, First ed.: Woodhead Publishing Limited, 2007.
- [3] V. S. Borland, "King cotton: Here today and here tomorrow - From fiber to fashion, cotton weaves its way through the supply chain," *Textile World*, vol. 160, 2010.
- [4] B. Hembree, "World cotton demand remains strong," *Southeast Farm Press*, July 19 2010.
- [5] T. P. Nevell, "Cellulose: structure, properties and behaviour in the dyeing process," in *Cellulosics Dyeing*, J. Shore, Ed., First ed: Society of Dyers and Colourists, 1995, pp. 1-80.
- [6] E. P. G. Gohl and L. D. Vilensky, *Textile Science: An Explanation of Fibre Properties*, Second ed. Melbourne: Longman Cheshire, 1983.
- [7] "Natural cellulosic fibres," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 70-91.
- [8] Y. L. Hsieh, "Chemical structure and properties of cotton," in *Cotton: Science and Technology*, S. Gordon and Y.-L. Hsieh, Eds., First ed: Woodhead Publishing Limited, 2007, pp. 3-34.
- [9] "Union dyeing," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 411-426.
- [10] J. D. Hamlin, "Novel auxiliaries with reactive dyes to solve environmental problems," PhD, Department of Chemistry, UMIST, Manchester, 1999.
- [11] I. D. Rattee, "Reactive dyes in the coloration of cellulosic materials," *Journal of the Society of Dyers & Colourists*, vol. 85, pp. 23-31, January 1969 1969.
- [12] T. Vickerstaff, "Reactive Dyes for Textiles," *Journal of the Society of Dyers and Colourists*, vol. 73, pp. 237-245, 1957.
- [13] W. S. Hickman, "Preparation," in *Cellulosics Dyeing*, J. Shore, Ed.: Society of Dyers and Colourists, 1995, pp. 81-151.
- [14] J. Shore, *Cellulosics Dyeing*, First ed.: Society of Dyers and Colourists, 1995.
- [15] V. Ribitsch and K. Stana-Kleinscheck, "Characterizing textile fiber surfaces with streaming potential measurements," *Textile Research Journal*, vol. 68, pp. 701-707, 1998.
- [16] C. C. Cook, "Aftertreatments for improving the fastness of dyes on textile fibres," *Review of Progress in Coloration and Related Topics*, vol. 12, pp. 73-89, 1982.
- [17] J. Shore, "Dyeing with direct dyes," in *Cellulosics Dyeing*, J. Shore, Ed., First ed: Society of Dyers and Colourists, 1995, pp. 152-188.
- [18] A. I. Ahmed, "Reactive dyes development: a review," *Textile Dyer & Printer*, vol. 28, pp. 19-24, 1995.

- [19] C. F. Cross and E. J. Bevan, *Researchers on Cellulose*. London: Longmans, Green and Company, 1912.
- [20] "Reactive dyes," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 332-357.
- [21] D. M. Lewis, A. H. Renfrew and A. A. Siddique, "The synthesis and application of a new reactive dye based on disulfide-bis-ethylsulfone," *Dyes and Pigments*, vol. 47, pp. 151-167, 2000.
- [22] P. J. Dolby, "Dyeing of cellulosic fibres with reactive dyes," *Textile Chemist and Colorist*, vol. 9, pp. 264-268, 1977.
- [23] I. D. Rattee, "Reactive Dyes for Cellulose 1953–1983," *Review of Progress in Coloration and Related Topics*, vol. 14, pp. 50-57, 1984.
- [24] G. N. Mock, "A short history on fiber reactive dyes," *Textile Chemist and Colorist*, vol. 28, pp. 10-11, 1996.
- [25] "Dyes, General survey," in *Industrial Dyes*, K. Hunger, Ed., Third ed: Wiley-VCH, 2003, pp. 1-12.
- [26] J. Shore, "Dyeing with reactive dyes," in *Cellulosics Dyeing*, J. Shore, Ed., First ed: Society of Dyers and Colourists, 1995, pp. 189-245.
- [27] J. A. Taylor, "Recent developments in reactive dyes," *Review of Progress in Coloration*, vol. 30, pp. 93-107, 2000.
- [28] "Multifunctional reactive dyes," in *Reactive Dyes for Textile*, A. H. M. Renfrew, Ed., First ed: Society of Dyers and Colourists, 1999, pp. 105-138.
- [29] D. M. Lewis, "Colour and textile chemistry - a lucky career choice," *AATCC Review*, vol. 9, pp. 38-41, 2009.
- [30] H.-K. Rouette, *Encyclopedia of Textile Finishing*: Springer, 2000.
- [31] D. King, "Dyeing of cotton and cotton products," in *Cotton: Science and Technology*, S. Gordon and Y.-L. Hsieh, Eds., First ed: Woodhead Publishing Limited, 2007, pp. 353-377.
- [32] "An introduction to dyes and dyeing," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 174-196.
- [33] "Dyeing theory," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 197-214.
- [34] K. Imada, N. Harada and T. Yoshida, "Recent developments in optimizing reactive dyeing of cotton," *Textile Chemist and Colorist*, vol. 24, pp. 83-87, 1992.
- [35] A. O. Noah, C. M. O. A. Martin and J. A. Braimah, "The effect of electrolytes on direct dyes for cotton," *Journal of Applied Polymer Science*, vol. 32, pp. 5841-5847, 1986.
- [36] T. Vickerstaff, *The Physical Chemistry of Dyeing*, Second ed.: Oliver and Boyd, 1954.
- [37] L. N. Guo, M. Petit-Ramil, R. Gauthier, B. Chabert and A. Jacquet, "Interaction of vinylsulphone reactive dyes with cellulosic fabrics. I. Dyeing mechanism, fibre characterization and effects of alkaline electrolytes," *Journal of the Society of Dyers and Colourists*, vol. 109, pp. 213-219, 1993.

- [38] S. R. S. Iyer and G. Ramaseshan, "The influence of mixtures of electrolytes on the adsorption of Chlorazol Sky Blue FF on viscose fibres," *Journal of the Society of Dyers and Colourists*, vol. 103, pp. 170-171, 1987.
- [39] M. Nango, S. Ohta, H. Kimura, Y. Shinmen and N. Kuroki, "Effect of counterions and ureas on adsorption of direct dyes on cellulose," *Textile Research Journal*, vol. 54, pp. 598-602, 1984.
- [40] K. W. Yeung and S. M. Shang, "The influence of metal ions on the aggregation and hydrophobicity of dyes in solutions," *Journal of the Society of Dyers and Colourists*, vol. 115, pp. 228-232, 1999.
- [41] A. K. Patra and S. Gupta, "Recent developments in reactive dyeing of cotton," *Asian Textile Journal*, vol. 3, pp. 57-60, 1995.
- [42] A. K. Jain and K. S. Mehta, "Control water hardness to minimize colour matching variations," *ATIRA Communications on Textiles*, p. 4, 1991.
- [43] M. J. Bradbury, P. S. Cowllisaw and D. A. S. Phillips, "The excel concept for the dyeing of cellulose fibres with Procion H-EXL dyes," *Journal of the Society of Dyers and Colourists*, vol. 108, pp. 430-435, 1992.
- [44] S. R. Shukla, "Pollution abatement and waste minimisation in textile dyeing," in *Environmental Aspects of Textile Dyeing*, R. M. Christie, Ed., First ed: Woodhead Publishing Ltd, 2007, pp. 116-148.
- [45] D. M. Lewis and L. T. T. Vo, "Dyeing cotton with reactive dyes under neutral conditions," *Coloration Technology*, vol. 123, pp. 306-311, 2007.
- [46] M. Montazer, R. M. A. Malek and A. Rahimi., "Salt free reactive dyeing of cationized cotton," *Fibers and Polymers*, vol. 8, pp. 608-612, 2007.
- [47] D. P. Chattopadhyay, R. B. Chavan and J. K. Sharma, "Salt-free reactive dyeing of cotton," *International Journal of Clothing Science and Technology*, vol. 19, pp. 99-108, 03 2007.
- [48] K. Srikulkit and P. Santifuengkul, "Salt-free dyeing of cotton cellulose with a model cationic reactive dye," *Coloration Technology*, vol. 116, pp. 398-402, 2000.
- [49] K. Imada and N. Harada, "Recent developments in the optimized dyeing of cellulose using reactive dyes," *Journal of the Society of Dyers and Colourists*, vol. 108, pp. 210-214, 1992.
- [50] H. H. Knudsen and H. Wenzel, "Environmentally friendly method in reactive dyeing of cotton," *Water Science and Technology*, vol. 33, pp. 17-27, 1996.
- [51] "Textile dyeing," in *Industrial Dyes*, K. Hunger, Ed., Third ed: Wiley-VCH, 2003, pp. 339-357.
- [52] J. R. Aspland, "Practical application of reactive dyes," *Textile Chemist and Colorist*, vol. 24, pp. 35-40, 1992.
- [53] G. E. Krichevskii and I. M. Movshovich, "Use of methods of heterogeneous chemical kinetics and nonequilibrium thermodynamics for the quantitative evaluation of the rate of fixation of reactive dyes by fibrous materials," *Textile Research Journal*, vol. 40, pp. 793-802, 1970.
- [54] J. R. Aspland, "Reactive dyes and their application," *Textile Chemist and Colorist*, vol. 24, pp. 31-36, 1992.

- [55] J. Suss-Leonhardt, D. McKelvey and B. Pesch, "New developments in cold pad batch dyeing," *Melliand International*, vol. 12, pp. 233-235, 2006.
- [56] "Dyeing machinery," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 215-239.
- [57] R. Fortin, M. Lablanc and S. Raymond, "Impact of vacuum extraction on the continuous dyeing of cotton with reactive dyes," in *Book of Papers, National Technical Conference - AATCC*, Charlotte, NC, USA, 1987, pp. 50-59.
- [58] L. Bright, "One bath-pad short steam process," *American Dyestuff Reporter*, vol. 79, p. 46, 1990.
- [59] S. Abeta and K. Imada, "Bifunctional reactive dyes - their dyeing properties and application to polyester/cotton blends," in *Book of Papers, National Technical Conference - AATCC*, Montreal, Que, Can, 1985, pp. 112-115.
- [60] K. Imada, Y. Ishizuka and T. Yoshida, in *AATCC International Conference and Exhibition*, 1990, p. 274.
- [61] D. A. S. Phillips, "The dyeing of cellulosic fibres with reactive dyes," *Advances in Colour Science and Technology*, vol. 1, pp. 1-11, 1998.
- [62] D. L. Connell, "The environmental impact of the textiles industry," in *Chemistry of the Textiles Industry*, C. M. Carr, Ed., First ed Glasgow: Blackie Academic & Professional, an imprint of Chapman and Hall, 1995, pp. 333-354.
- [63] N. S. E. Ahmed, "The use of sodium edate in the dyeing of cotton with reactive dyes," *Dyes and Pigments*, vol. 65, pp. 221-225, 2005.
- [64] I. Holme. (2004) Dyeing Cellulosic Fibres. *Textiles*. 8-13.
- [65] B. Smith, "Wastes from textile processing," in *Plastics and the Environment*, A. L. Andrady, Ed., First ed: John Wiley and Sons, Inc., 2003, pp. 293 - 295.
- [66] B. R. Babu, A. K. Parande, S. Raghu and T. P. Kumar, "Cotton textile processing: waste generation and effluent treatment," *Journal of Cotton Science*, vol. 11, pp. 141-153, 2007.
- [67] D. Phillips, "Environmentally friendly productive and reliable: priorities for cotton dyes and dyeing processes," *Journal of the Society of Dyers and Colourists*, vol. 112, pp. 183-186, 1996.
- [68] H. G. Prabu and M. Sundrarajan, "Effect of the bio-salt trisodium citrate in the dyeing of cotton," *Coloration Technology*, vol. 118, pp. 131-134, 2002.
- [69] R. F. Hyde, G. Thompson and K. A. Stanley, "Commercial and environmental challenges in continuous dyeing with fiber reactive dyes," *Textile Chemist and Colorist*, vol. 28, pp. 25-29, 1996.
- [70] E. Kissa, "Urea in reactive dyeing," *Textile Research Journal*, vol. 39, pp. 734-741, 1969.
- [71] R. B. Chavan, "Environment-friendly dyeing processes for cotton," *Indian Journal of Fibre and Textile Research*, vol. 26, pp. 93-100, 2001.
- [72] J. Shore, "Chemistry of reactive dyes," in *Colorants and Auxiliaries*. vol. 1 (Colorants), J. Shore, Ed., Second ed: Society of Dyers and Colourists, 2002, pp. 356-443.
- [73] J. P. Luttringer, "New generation of reactive dyes for cotton," *Textile Chemist and Colorist*, vol. 25, pp. 25-29, 1993.

- [74] K. Hunger, "Reactive dyes," in *Industrial Dyes*, K. Hunger, Ed., Third ed: Wiley-VCH, 2003, pp. 113-133.
- [75] W. Czajkowski and J. Paluszkiwicz, "Reactive dyes for dyeing cellulose fibers in a neutral medium," *Przemysl Chemiczny*, vol. 83, pp. 374-378, 2004.
- [76] N. Morimura and M. Ojima, "New reactive dyes fixable at neutral pH," *American Dyestuff Reporter*, vol. 74, pp. 28-36, 1985.
- [77] D. M. Lewis, "New possibilities to improve cellulosic fibre dyeing processes with fibre-reactive systems," *Journal of the Society of Dyers and Colourists*, vol. 109, pp. 357-364, 1993.
- [78] A. H. M. Renfrew, "Acid fixing reactive dyes," in *Reactive Dyes for Textile Fibres*, A. H. M. Renfrew, Ed., First ed: Society of Dyers and Colourists, 1999, pp. 156-167.
- [79] P. O. Nkeonye and O. O. Olawande, *Colourage*, vol. 41, p. 33, 1994.
- [80] Anon, "Ciba introduces low-salt reactive dyeing," *Textile Industries Dyegest Southern Africa*, vol. 15, pp. 5-8, 1996.
- [81] D. Hinks, S. M. Burkinshaw, D. M. Lewis and A. H. M. Renfrew, "Cationic fiber reactive dyes for cellulosic fibers," *AATCC Review*, vol. 1, pp. 43-46, 2001.
- [82] C. B. Anderson, "Dyeing reactive dyes using less salt," *American Dyestuff Reporter*, vol. 83, pp. 103-105, 1994.
- [83] L. Wilbers and G. Seiler, "New concept for dyeing of cellulosic substrates at ultra low liquor ratios," *Melliand International*, vol. 8, pp. 66-67, 2002.
- [84] Z. Khatri, "Control of tailing and listing problems in continuous dyeing – a systematic and practical approach." www.colourclick.org: Society of Dyers and Colourists, 2007, pp. 1-4.
- [85] S. Sostar-Turk, R. Schneider, I. Petrinic and R. Fijan, "Ecological alternatives in the conventional process of dyeing with reactive dyes," *Tekstilec*, vol. 51, pp. 122-133, 2008.
- [86] M. R. Sampath, "Dyeing of reactives - Part IV," *Colourage*, vol. 49, pp. 90-94, 2002.
- [87] V. Vasileva and J. Jeleva. (2009) The influence of the cationic agents on the wet and the light fastnesses of dyeings with reactive dyes. *Magazine Textile and Clothing*. 11-15.
- [88] S. M. Burkinshaw and D. Katsarelis, "A study of the wash-off and aftertreatment of dichlorotriazinyl reactive dyes on cotton," *Dyes and Pigments*, vol. 29, pp. 139-153, 1995.
- [89] R. F. Hyde, "Review of continuous dyeing of cellulose and its blends by heat fixation processes," *Review of Progress in Coloration*, vol. 28, pp. 26-31, 1998.
- [90] D. M. Lewis and X. P. Lei, "New methods for improving the dyeability of cellulose fibres with reactive dyes," *Journal of the Society of Dyers and Colourists*, vol. 107, pp. 102-109, 1991.
- [91] D. M. Lewis and K. A. McIlroy, "The chemical modification of cellulosic fibres to enhance dyeability," *Review of Progress in Coloration*, vol. 27, pp. 5-17, 1997.

- [92] S. M. Burkinshaw, M. Mignanelli, P. E. Froehling and M. J. Bide, "The use of dendrimers to modify the dyeing behaviour of reactive dyes on cotton," *Dyes and Pigments*, vol. 47, pp. 259-267, 2000.
- [93] M. S. S. Kannan and R. Nithyanandan, "Salt and alkali free reactive dyeing on cotton," *ATA Journal*, vol. 17, 2006.
- [94] R. S. Blackburn and S. M. Burkinshaw, "Treatment of cellulose with cationic, nucleophilic polymers to enable reactive dyeing at neutral pH without electrolyte addition," *Journal of Applied Polymer Science*, vol. 89, pp. 1026-1031, 2003.
- [95] D. P. Chattopadhyay, "Cationization of cotton for low-salt or salt-free dyeing," *Indian Journal of Fibre and Textile Research*, vol. 26, pp. 108-115, 2001.
- [96] S. Zhang, W. Ma, B. Ju, N. Dang, M. Zhang, S. Wu and J Yang, "Continuous dyeing of cationised cotton with reactive dyes," *Coloration Technology*, vol. 121, pp. 183-186, 2005.
- [97] G. N. Sheth and A. A. Musale, "Substitute products for urea in application of reactive dyes to cotton fabrics," *Indian Journal of Fibre and Textile Research*, vol. 29, pp. 462-469, 2004.
- [98] J. W. Rucker and D. M. Guthrie, "Reduction of salt requirements in dyeing cotton with fibre reactive dyes," in *AATCC International Conference Exhibition, Book of Papers*, 1997.
- [99] L. J. Liu and J. B. Yao, "Application of betaine in low-salt dyeing of cotton fabric with reactive dyes," *Journal of Tianjin Polytechnic University*, vol. 28, pp. 53-57, 2009.
- [100] J. W. Rucker and D. M. Guthrie, "Salt substitute for dyeing cotton with fiber reactive dyes," *Sen-I Gakkaishi*, vol. 53, pp. 256-260, 1997.
- [101] S. B. Moore, "Low toxicity, biodegradable salt substitute for dyeing textiles: magnesium acetate in direct or reactive dyeing of cotton " USA Patent 5207800, 1993.
- [102] Y. Guan, Q. Zheng, Y. Mao, M. Gui and H. Fu, "Application of polycarboxylic acid sodium salt in the dyeing of cotton fabric with reactive dyes," *Journal of Applied Polymer Science*, vol. 105, pp. 726-732, 2007.
- [103] "Water treatment," in *Basic Principles of Textile Coloration*, A. D. Broadbent, Ed., First ed: Society of Dyers and Colourists, 2005, pp. 130-151.
- [104] M. Bide, "Environmentally responsible dye application," in *Environmental Aspects of Textile Dyeing*, R. M. Christie, Ed., First ed: Woodhead Publishing Ltd, 2007, pp. 74-92.
- [105] M. Bide, "Decolorisation of effluent and re-use of spent dyebath," in *Environmental Aspects of Textile Dyeing*, R. M. Christie, Ed., First ed: Woodhead Publishing Ltd, 2007, pp. 149-190.
- [106] A. Khatri, R. Padhye and M. White, "Developments in reactive dyeing of cotton to improve sustainability," in *ERE 2010 "Transitions to a Sustainable Future"*, CQ University, Rockhampton QLD Australia, 2010.
- [107] M. Ash and I. Ash, *Handbook of Green Chemicals*, Second ed.: Synapse Information Resources Inc., 2008.

- [108] R. D. Swisher, T. A. Taulli and E. J. Malec, "Biodegradation of NTA metal chelates in river water," *Trace Metals and Metal-organic Interactions in Natural Waters*, pp. 237-263, 1973.
- [109] G. Marengo, Y. Libert and E. M. Barban, "The biodegradability of NTA in aquatic ecosystems of different degrees of trophic," *Acqua Aria*, pp. 35-40, 1990.
- [110] F. Alan Andersen, "Final report on the safety assessment of EDTA, calcium disodium EDTA, diammonium EDTA, dipotassium EDTA, disodium EDTA, TEA-EDTA, tetrasodium EDTA, tripotassium EDTA, trisodium EDTA, HEDTA, and trisodium HEDTA," *International Journal of Toxicology*, vol. 21, pp. 95 - 142, 2002.
- [111] Dissolvine GL [Online]. Available: http://www.dewolfchem.com/pdf/Akzo_Nobel_GL_brochure.pdf
- [112] (27 September 2010). *Dissolvine GL*. Available: http://www.akzonobel.com/dissolvinegl/product_information/
- [113] Mahapatra, "Continuous dyeing of cellulose and its blends," *Colourage*, vol. 54, p. 74, 2007.
- [114] S. A. A. Farha, A. M. Gamal, H. S. Bekhiet, G. E. A. Mahmoud and L. F. M. Ismail, "Sodium edate and sodium citrate as an exhausting and fixing agent for in dyeing cotton fiber with reactive dyes and reuse of dyeing effluent," *Journal of American Science*, vol. 6, pp. 109-127, 2010.
- [115] N. S. E. Ahmed, Y. A. Youssef, R. M. El-Shishtawy and A. A. Mousa, "Urea/alkali-free printing of cotton with reactive dyes," *Coloration Technology*, vol. 122, pp. 324-328, 2006.
- [116] N. Bairagi, M. L. Gulrajani, B. L. Deopura and A. Shrivastava, "Dyeing of N-modified viscose rayon fibres with reactive dyes," *Coloration Technology*, vol. 121, pp. 113-120, 2005.
- [117] M. M. Kamel, R. M. El-Shishtawy, H. L. Hanna and N. S. E. Ahmed, "Ultrasonic-assisted dyeing: I. Nylon dyeability with reactive dyes," *Polymer International*, vol. 52, pp. 373-380, 2003.
- [118] C. Hyung-Min, "One-bath dyeing and nonformaldehyde durable press finishing of cotton using dialdehyde and a monochlorotriazinyl reactive dye," *Textile Research Journal*, vol. 72, p. 469, 2002.
- [119] J. A. Dean, "Electrolytes, electromotive force, and chemical equilibrium," in *Lange's Handbook of Chemistry*, J. A. Dean, Ed., Fifteenth ed: McGraw-Hill, Inc., 1999.
- [120] T. L. Dawson and J. C. Todd, "Dye diffusion - The key to efficient colouration," *Journal of Society of Dyers and Colourists*, pp. 417-426, 1979.
- [121] P. Rys and H. Zollinger, "Reactive dyeing: basic principles and their implications for the dyer," *Textile Chemist and Colorist*, vol. 6, pp. 35-40, 1973.
- [122] M. Sekido and K. Matsui, "Method of the determination of surface concentration and diffusion coefficient by cylindrical cellophane film roll," *Sen-i Gakkaishi*, vol. 20, p. 778, 1964.
- [123] H. Motomura and Z. Morita, "Diffusion with simultaneous reaction of reactive dyes in cellulose," *Journal of Applied Polymer Science*, vol. 21, pp. 487-499, 1977.

- [124] M. Hamoudeh and E. Schonpflug, "Prüfung der färberischen Eigenschaften und der Kombinierbarkeit der Palanil-Farbstoffe nach dem BASF-Kombi-Test," *Melliand Textilberichte*, vol. 52, pp. 1063-1068, 1971.
- [125] R. H. Peters, J. H. Petropoulos and R. McGregor, "A Study of the diffusion of dyes in polymer films by a microdensitometric technique," *Journal of Society of Dyers and Colourists*, vol. 77, pp. 704-712, 1961.
- [126] Y. Song, M. Srinivasarao and A. Tonelli, "Study of dye diffusion in fibers by laser scanning confocal microscopy," *Macromolecular Symposia*, vol. 148, pp. 395-402, 1999.
- [127] Y. Song, M. Srinivasarao, A. Tonelli, C. M. Balik and R. McGregor, "Laser scanning confocal microscopy study of dye diffusion in fibers," *Macromolecules*, vol. 33, pp. 4478-4485, 2000.
- [128] C. Wang, L. Zhu and Y. Qiu, "Laser scanning confocal microscope characterization of dye diffusion in nylon 6 fibers treated with atmospheric pressure plasmas," vol. 107: Wiley Subscription Services, Inc., A Wiley Company, 2008, pp. 1471-1478.
- [129] R. McDonald, *Colour Physics for Industry*, Second ed.: Society of Dyers and Colourists, 1997.
- [130] E. Mouxiou, I. Eleftheriadis, N. Nikolaidis and E. Tsatsaroni, "Reactive dyeing of cellulosic fibers: use of cationic surfactants and their interaction with reactive dyes," *Journal of Applied Polymer Science*, vol. 108, pp. 1209-1215, 2008.
- [131] B. Becerir, "A novel approach for estimating the relation between K/S value and dye uptake in reactive dyeing of cotton fabrics," *Fibers and Polymers*, vol. 6, pp. 224-228, 2005.
- [132] J. Suesat, "The influence of NaCl concentration on the build-up properties and aggregation of reactive dyes," *Kasetsart Journal - Natural Science*, vol. 42, pp. 558-568, 2008.
- [133] N. Ahmed, D. P. Oulton and J. A. Taylor, "The use of reflectance measurements in the determination of fixation of reactive dyes to cotton," *Color Research & Application*, vol. 31, pp. 117-121, 2006.
- [134] P. S. Collishaw, D. A. S. Phillips and M. J. Bradbury, "Controlled coloration: a success strategy for the dyeing of cellulosic fibres with reactive dyes," *Journal of the Society of Dyers and Colourists*, vol. 109, pp. 284-292, 1993.
- [135] P. Goswami, R. Blackburn, J. Taylor and P. White, "Dyeing behaviour of lyocell fabric: effect of NaOH pre-treatment," *Cellulose*, vol. 16, pp. 481-489, 2009.
- [136] A. D. Broadbent, *Basic Principles of Textile Coloration*, First ed.: Society of Dyers and Colourists, 2005.
- [137] I. Rusznak, J. Zobor and G. Levai, "Kinetic investigation of reactive dyeing," *Dyes and Pigments*, vol. 2, pp. 285-303, 1981.
- [138] J. D. Hamlin, D. A. S. Phillips and A. Whiting, "UV/Visible spectroscopic studies of the effects of common salt and urea upon reactive dye solutions," *Dyes and Pigments*, vol. 41, pp. 137-142, 1999.
- [139] S. Rosenbaum and F. L. Goodwin, "Concentration dependence in dye diffusion," *Journal of Applied Polymer Science*, vol. 9, p. 333, 1965.

- [140] S. H. Lin, "Concentration-dependent diffusion of dye in reactive dyeing systems," *Journal of Applied Polymer Science*, vol. 44, pp. 1743-1749, 1992.
- [141] D. M. Lewis, "Dyestuff-fibre interactions," *Review of Progress in Coloration and Related Topics*, vol. 28, pp. 12-17, 1998.
- [142] M. J. Bradbury, P. S. Cowlshaw and S. Moorhouse, "Reactive dye selection and process development for exhaust dyeing of cellulose," *Textile Chemist and Colorist*, vol. 27, pp. 19-23, 1995.
- [143] P. S. Collishaw, M. J. Bradbury, J. A. Bone and R. F. Hyde, "Controlled coloration using high performance reactive and disperse dyes," *Book of Papers, International Conf. and Exhibition AATCC, Atlanta, 1997*, pp. 353-365, 1997.
- [144] J. Mughal, A. Aleem, Q. Siddiqui and M. Iqbal, "The study of electrolytes on the dye uptake of bifunctional reactive red dyes on a cellulosic substrate (cotton K-68)," *Pakistan Journal of Scientific and Industrial Research*, vol. 49, pp. 371-372, 2006.
- [145] M. F. Arif, M. T. Butt, M. N. Khan and M. Ali, "Effect of electrolyte concentration on dyeing process of cotton," *Pakistan Journal of Scientific and Industrial Research*, vol. 50, pp. 159-164, 2007.
- [146] F. J. Carrion, "Influence of magnesium salts in the dyeing of cotton with reactive dyes," *Boletín Intexter (U.P.C.)*, pp. 29-33, 2004.

Appendix I

Dyeing results for calculating dye diffusion, fixation and exhaustion

The colour strength (K/S) - before washing-off in following tables is also the K/S - diffusion index.

Table A I.1: $K/S_{reference}$

Dye (g/l)	$K/S_{reference}$	
	CI Reactive Red 147	CI Reactive Blue 250
5	4.97	6.83
10	8.74	13.32
20	15.08	21.9
30	20.41	26.29

Table A I.2: Effect of sodium chloride concentration (pad-steam dyeing)

20 g/l dye, 15 g/l alkali, steaming time: 60 sec

Sodium chloride (g/l)	CI Reactive Red 147		CI Reactive Blue 250	
	K/S before washing-off	K/S after DMF stripping	K/S before washing-off	K/S after DMF stripping
0	13.92	3.57	20.38	8.04
10	11.22	4.05	19.26	8.93
20	10.80	4.28	18.18	9.03
30	10.34	4.36	17.39	9.18
40	10.10	5.12	16.76	9.79
50	9.82	5.42	16.06	10.20
60	10.39	5.47	16.84	9.90

Table A I.3: Effect of inorganic alkali concentration (pad-steam dyeing)

20 g/l dye, 50 g/l sodium chloride, steaming time: 60 sec

Inorganic alkali (g/l)	CI Reactive Red 147		CI Reactive Blue 250	
	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>
5	11.16	4.98	17.89	6.57
10	10.45	5.24	16.79	9.46
15	9.82	5.42	16.06	10.20
20	9.57	5.07	15.90	9.92
25	9.59	5.20	16.59	9.98
15 g/l Alkali Steaming time: 120 sec	9.60	5.58	14.1	9.75

Table A I.4: Effect of sodium edate concentration (pad-steam dyeing)

20 g/l dye, steaming time: 60 sec

Sodium edate (g/l)	CI Reactive Red 147		CI Reactive Blue 250	
	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>
50	9.47	3.74	16.58	6.53
75	9.02	4.02	16.16	7.25
100	8.97	4.68	15.75	8.75
125	8.99	4.63	15.18	8.82
150	9.14	4.56	15.30	8.41

Table A I.5: Effect of trisodium NTA concentration (pad-steam dyeing)

20 g/l dye, steaming time: 60 sec

Trisodium NTA (g/l)	CI Reactive Red 147		CI Reactive Blue 250	
	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>
50	9.99	3.82	15.97	5.55
75	9.24	4.18	15.55	6.89
100	8.81	4.84	14.78	7.70
125	8.98	4.72	14.28	9.07
150	9.05	4.47	14.36	8.84

Table A I.6: Effect of tetrasodium GLDA concentration (pad-steam dyeing)

20 g/l Dye, Steaming time: 60 sec

Tetrasodium GLDA (g/l)	CI Reactive Red 147		CI Reactive Blue 250	
	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>	<i>K/S before washing-off</i>	<i>K/S after DMF stripping</i>
50	8.86	4.08	14.62	11.82
75	8.60	4.77	14.84	13.38
100	8.73	4.80	16.06	15.03
125	8.54	4.61	16.64	14.81

Table A I.7: Effect of steaming time (using optimum sodium edate)

20 g/l dye

Steaming time (sec)	CI Reactive Red 147 100 g/l sodium edate		CI Reactive Blue 250 125 g/l sodium edate	
	K/S	K/S	K/S	K/S
	<i>before washing-off</i>	<i>after DMF stripping</i>	<i>before washing-off</i>	<i>after DMF stripping</i>
60	8.99	4.68	15.30	8.82
90	9.16	4.94	15.08	9.11
120	9.43	5.31	14.60	9.58

Table A I.8: Effect of steaming time (using optimum trisodium NTA)

20 g/l dye

Steaming time (sec)	CI Reactive Red 147 100 g/l trisodium NTA		CI Reactive Blue 250 125 g/l trisodium NTA	
	K/S	K/S	K/S	K/S
	<i>before washing-off</i>	<i>after DMF stripping</i>	<i>before washing-off</i>	<i>after DMF stripping</i>
60	8.96	4.84	14.28	9.07
90	8.85	4.93	14.27	9.30
120	8.99	5.16	14.13	9.89

Table A I.9: Effect of steaming time (using optimum tetrasodium GLDA)

20 g/l dye

Steaming time (sec)	CI Reactive Red 147 75 g/l tetrasodium GLDA		CI Reactive Blue 250 100 g/l tetrasodium GLDA	
	K/S	K/S	K/S	K/S
	<i>before washing-off</i>	<i>after DMF stripping</i>	<i>before washing-off</i>	<i>after DMF stripping</i>
60	8.60	4.77	16.06	15.03
90	8.47	5.00	15.89	15.16
120	8.12	5.42	15.83	15.12

Table A I.10: Effect of steaming time (using optimum inorganic electrolyte and alkali)

Steaming time (sec)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
00	10.64	16.73
30	10.26	16.65
60	9.82	16.36
90	10.12	16.44
120	10.47	16.57

Table A I.11: Effect of baking time (using optimum urea, alkali and antimigrant)

20 g/l dye		
Steaming time (sec)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
00	12.03	18.43
30	11.74	18.37
60	11.26	18.25
90	10.79	18.08
120	11.27	18.00

Table A I.12: Effect of batching time (using optimum sodium hydroxide and sodium carbonate/sodium silicate)

20 g/l dye		
Steaming time (sec)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
00	11.01	17.60
30	10.26	16.90
60	9.5	16.32
90	10.02	16.01
120	10.17	15.89

Table A I.13: Effect of dye concentration (pad-steam dyeing)

30 g/l sodium chloride, 15 g/l alkali, steaming time: 60 sec

Dye concentration (g/l)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
5	3.24	4.93
10	5.85	10.08
20	10.34	17.39

Table A I.14: Effect of dye concentration (pad-batch dyeing)

Sodium hydroxide (Batching time: 12 hrs)

Dye concentration (g/l)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
10	4.97	9.85
20	9.5	16.32
30	13.79	20

Table A I.15: Effect of different electrolytes at constant concentration (pad-steam dyeing)

20 g/l dye

Electrolyte (40 g/l)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
Sodium chloride	12.03	19.34
Sodium sulphate	11.23	17.78
Sodium acetate	12.55	20.30
Potassium chloride	11.36	18.83
Potassium sulphate	10.98	18.53

Table A I.16: Effect of different electrolytes at constant ionic strength (pad-steam dyeing)

20 g/l dye

Electrolyte ($\mu = 0.68$)	<i>K/S</i> <i>before washing-off</i>	
	CI Reactive Red 147	CI Reactive Blue 250
40 g/l Sodium chloride	12.03	19.34
32.38 g/l Sodium sulphate	12.14	19.07
56.11 g/l Sodium acetate	11.87	19.16
50.99 g/l Potassium chloride	10.52	18.46
39.73 g/l Potassium sulphate	10.62	18.55

Table A I.17: Effect of different electrolytes at constant concentration (exhaust dyeing)

2% dye (o.m.f.), Alkali (2.5% o.m.f. for CI Reactive Red 147 and 5 g/l for CI Reactive Blue 250)

Electrolyte (40 g/l)	Absorbance (λ_{\max}) of solutions diluted 100 times		
	A_0	A_1	A_2
Sodium chloride	0.318	0.185	0.115
Sodium sulphate	0.33	0.164	0.12
Potassium chloride	0.325	0.147	0.091
Potassium sulphate	0.316	0.131	0.099

Table A I.18: Effect of different electrolytes at constant ionic strength (exhaust dyeing)

2% dye (o.m.f.), Alkali (2.5% o.m.f. for CI Reactive Red 147 and 5 g/l for CI Reactive Blue 250)

Electrolyte ($\mu = 0.68$)	Absorbance (λ_{max}) of solutions diluted 100 times		
	A ₀	A ₁	A ₂
40 g/l Sodium chloride	0.318	0.185	0.115
32.38 g/l Sodium sulphate	0.32	0.192	0.079
50.99 g/l Potassium chloride	0.321	0.134	0.093
39.73 g/l Potassium sulphate	0.322	0.137	0.085

Table A I.19: Results of a cotton fabric dyed with 20 g/l CI Reactive Red 147 on production scale

Steaming time (sec)	30 g/l sodium chloride 15 g/l sodium bicarbonate		100 g/l sodium edate	
	<i>K/S before washing-off</i>	<i>K/S after washing-off</i>	<i>K/S before washing-off</i>	<i>K/S after washing-off</i>
60	10.68	7.72	10.04	5.42
120	10.91	7.56	11.00	7.14

Appendix II

Material safety data sheets

DRIMARENE RED K4BL CDG PRODUCT: 1203467

Page: 1 of 6
Date of Issue:
25 November 2005

1. Identification of the material and supplier

Product (material) name:
DRIMARENE RED K4BL CDG

Product Code:
1203467

Recommended Use:
Textile dye

Supplier:
Chemcolour Ind. (Aust) P/L.
ACN 125 602 271 ABN 70 125 602 271
19-25 Anne Street,
St. Marys NSW 2760
Australia

Telephone: +61 2 8801 8100 Facsimile: +61 2 9623 1594

Emergency Telephone Number: 1800 127 406 (24 Hours)

2. Hazards identification

Not classified as hazardous according to criteria of
ASCC.

Not classified as dangerous goods according to the Australian Code for
Transport of Dangerous Goods.

Safety phrases:
S22 Do not breathe dust.

3. Composition/information on ingredients

Chemical identity	CAS Number	Proportion
Azo dyestuff, reactive		

4. First aid measures

After inhalation:
Remove from the source of vapour/ dust/ spray/ fumes;
remove to open space or fresh air.

After contact with skin:
Wash the skin thoroughly with soap and water.

After contact with eyes:
Immediately rinse eyes thoroughly, including under eyelids,
with running water for at least 15 minutes.
Seek immediate medical advice.

After ingestion:
Seek medical advice immediately if swallowed.

Advice to Doctor:
Treat symptomatically.

DRIMARENE RED K4BL CDG
PRODUCT: 1203467

Page: 2 of 6
Date of Issue:
25 November 2005

5. Fire fighting measures

(Continued)

Suitable extinguishing media:

All extinguishing media are suitable.

Special protective precautions and equipment for fire fighters:

Use water spray to cool fire-exposed containers and metallic parts.

In case of fire, prevent by any means possible spillage from entering drains or water courses.

Hazchem Code: N/A

6. Accidental release measures

Emergency procedures:

Collect product and consider recycling.

In case of spillage prevent the material from entering drains, water courses or sewers.

Methods and materials for containment and clean up:

Remove mechanically using a shovel or any other suitable equipment.

Collect in a convenient manner to avoid formation of dust.

Take up into tightly closed containers.

Wash the residue and small amounts from the contaminated area with water.

7. Handling and storage

Precautions for safe handling:

The product should be stored, handled and used in accordance with good industrial hygiene practices and in conformity with government regulations.

No special precautions are necessary.

In principle, with organic products which are intentionally or unintentionally in powder form, the danger of a dust explosion should be kept in mind.

8. Exposure controls/personal protection

National exposure standards:

No exposure standards have been assigned by the Australian Safety and Compensation Council for any components of this product.

Engineering controls:

Use only in well-ventilated areas.

Personal protective equipment:

Eye/ face protection:

Avoid contact with the eyes.

Skin protection:

DRIMARENE RED K4BL CDG

PRODUCT: 1203467

Page: 3 of 6
Date of Issue:
25 November 2005

8. Exposure controls/personal protection

(Continued)

Avoid contact with the skin.
Wear suitable protective gloves.
Wear suitable protective clothing.

Respiratory protection:

Do not breathe vapour/ dust/ spray/ fumes.

Other protection:

Do not eat, drink or smoke until after washing.
Wash thoroughly after handling.
Persons sensitized to this material should not work with it or near it.

9. Physical and chemical properties

Appearance (colour, physical form, shape) / Odour:

Dark red granules/no odour

Vapour pressure : not appl.

Boiling point/ Melting Point (C) : MP >100

Solubility in Water (g/l) at 25 C : >100

Flash Point (C) and method of detecting flash point:
not appl.

Upper and lower flammable (explosive) limits (% Volume in air): no data

Additional Information:

Flammability:

Combustible solid.

Bulk Density : ca. 490 kg/m³

pH (100 g/l water) : ca. 5

10. Stability and reactivity

Reactivity Hazards:

No hazards are expected, if the material is handled, stored and used according to instructions & government regulations.
May form flammable/explosive dust-air mixture.

Hazardous decomposition products/ Hazardous Reactions:

Thermal decomposition: 200C (Long duration test, Heating rate 0K/min.; air open cup). Dynamic decomp'n: 230C (Heating rate 0.75K/min.; air open cup)

Hazardous products of combustion: oxides of carbon, nitrogen and sulphur; hydrogen chloride, hydrogen fluoride.

11. Toxicological information

Health Effects of Acute Overexposure:

If swallowed:

The product is of low acute oral toxicity in the rat.

If in eyes:

The material should not be allowed to contact the eyes.
Not expected to cause eye irritation.

If on skin:

The material should not be allowed to come into contact with the skin.

DRIMARENE RED K4BL CDG

PRODUCT: 1203467

Page: 4 of 6
Date of Issue:
25 November 2005

11. Toxicological information

(Continued)

Not expected to be irritating to the skin.

If inhaled:
Avoid breathing vapour/ dust/ spray/ fumes.
CDG products are dye preparations, which have proven dust-free under the strictest procedures for testing the dusting behaviour of dyestuffs. Sensitization of the respiratory tract caused by some powder reactive dyes on inhalation should therefore be largely excluded. Nevertheless, if feeling unwell or if asthma symptoms occur as a result of inhaling, it is recommended that a doctor be consulted.

Health Effects of Chronic Overexposure:
No information available.

Acute oral toxicity LD50 (mg/kg): >5000 Species: rat

12. Ecological information

Ecotoxicity:
Fish toxicity: LC0:>100 mg/l Testing Time(h): 48 Species: Rainbow trout
Toxicity to Bacteria in Effluent: IC50, >100 mg/l Test: OECD 209
Persistence and degradability:
Biodegradation: ca. 35 Parameter: TOC Method:

Additional Information:
Chemical oxygen demand: 2680 mg O₂/g
Aquatic, Air or Soil Environment Hazards:
Do not allow product to enter waste water, rivers or creeks.

13. Disposal considerations

Disposal methods and containers:
In accordance with government regulations for the disposal of special waste.
Consider recycling the product.

Special precautions for landfill or incineration:
Dispose of waste material via a licensed contractor.

14. Transport information

Australian Code for Transport of Dangerous Goods by Road and Rail:

DRIMARENE RED K4BL CDG

PRODUCT: 1203467

Page: 5 of 6
Date of Issue:
25 November 2005

14. Transport information

(Continued)

U.N. Number: N/A
U.N. Proper Shipping Name:
Not Applicable
Class: N/A
Subsidiary risk: N/A
Packing Group: N/A
Hazchem Code: N/A

Transport information:
Not classified as dangerous goods according to the
Australian Code for the Transport of Dangerous Goods
by Road and Rail.

15. Regulatory information

Poison schedule (SUSDP): None allocated

Regulatory Information:
All components of this product are listed on the Australian
Inventory of Chemical Substances (AICS).

16. Other information

Special precautions/ comments:
Composition: C (23,8%), Cl, F, H, N (4.7%), Na, O, S.
Toxicological and ecotoxicity information based on data for components.

Data sources/ references:
Clariant Produkte (Schweiz) AG, Switzerland
- Material Safety Data Sheet

Abbreviation(s):
N/A, Not appl. = Not applicable

Contact point:
For specialist advice in emergency - contact Emergency Response Co-ordinator
Chemcolour Industries (Australia) Pty. Limited
Tel: 1800 127 406
For non-emergency enquiries - contact Product Safety Manager
Chemcolour Industries Australia Pty. Limited
Tel: (03)8801 8100 Fax: (03)9623 1594

This MSDS summarises our best knowledge of the health and safety hazard
information of the product and how to safely handle and use the product in
the workplace. Each user should read this MSDS and consider the information
in the context of how the product will be handled and used in the workplace,
including in conjunction with other products.

If clarification or further information is needed to ensure that an
appropriate risk assessment can be made, the user should contact this company.

Our responsibility for products sold is subject to our standard terms and

DRIMARENE RED K4BL CDG
PRODUCT: 1203467

Page: 6 of 6
Date of Issue:
25 November 2005

16. Other information

(Continued)

conditions, a copy of which is sent to our customers and is also available on request.

Safety Data Sheet

REMAZOL NAVY RGB 150% Gran.

1. Identification of the Chemical/Mixture and the supplier

Product Name: REMAZOL NAVY RGB 150% Gran.
Other Names:
Supplier's Code:
Recommended Use: Textile dyeing. Reactive dye
Supplier: DYECHEM INDUSTRIES Pty. Ltd.
ABN: 16287780439
Street Address: 60 – 62 Kylta Road
Heidelberg West VIC 3081 Australia
Telephone: +61 (0)3 9457-5311
Facsimile: +61 (0)3 9457-5164
Emergency Numbers: +61 (0)3 9457-5311 (Monday – Friday, 8:00am – 5:00pm) | Transport & Spill
+61 (0)407-822-236 (After hours) | emergencies only

2. Hazards Identification

HAZARDOUS CHEMICAL / NON-DANGEROUS GOODS according to criteria of ASCC / ADG

GHS -

- Hazard Class/Category:** SENSITISATION - RESPIRATORY Category 1
SENSITISATION - SKIN Category 1
- Signal Word:** DANGER
- Hazard Statements:** May cause allergy or asthma symptoms or breathing difficulties if inhaled. H334

May cause an allergic skin reaction H317
- Precautionary Statements:**
 - Prevention – P261 Avoid breathing dust / mist.
P285 In case of inadequate ventilation wear respiratory protection (dust mask with particle filter).
P272 Contaminated work clothes should not be allowed out of the work place.
P280 Wear protective gloves.
 - Response – P304 + P341 - IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing.
P342 + P311 - If experiencing respiratory symptoms: Call a POISON CENTRE or doctor/physician.
P302 + P352 – IF ON SKIN: wash with plenty of soap & water.
P333 + P313 – If skin irritation or rash occurs: Get medical attention.
P363 – Wash contaminated clothing before reuse.
 - Disposal – P501 – Dispose of contents/container to authorised special waste disposal site or incineration plant.



NOHSC :1008 -

- Hazard Category:** Xn Harmful
- Risk Phrases:** R42 May cause sensitisation by inhalation.
R43 May cause sensitisation by skin contact.



- **Safety Phrases:**
 - S20/21 When using, do not eat drink or smoke.
 - S22 Do not breathe dust.
 - S24 Avoid contact with skin.
 - S28 After contact with skin, wash immediately with plenty of soap and water
 - S35/37 Wear suitable protective clothing and gloves.
 - S45 : In case of accident or if you feel unwell, seek medical advice immediately

ADG -

- **Class:** None allocated
- **Subsidiary Risk 1:** None allocated
- **Packing Group:** None allocated
- **Poisons Schedule:** Not scheduled

3. Composition/Information on ingredients

Chemical Identity	CAS No.	Proportion
- 2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis[[4-[[2-(sulfooxy)ethyl]sulfonyl]phenyl]azo]-, tetrasodium salt	17095-24-8	LOW
- Other ingredients determined to be non-hazardous	-	VHIGH

Proportion (% weight per weight): VHIGH >60, HIGH 30–60, MED 10–<30, LOW 1–9, VLOW <1

4. First Aid Measures**DESCRIPTION OF NECESSARY MEASURES ACCORDING TO ROUTES OF EXPOSURE**

For Scheduled Poisons, Poison Information Centres in each State capital city can provide additional assistance. Phone Australia 13 12 26

- Swallowed:** If the product is swallowed, the patient must immediately drink water repeatedly, if possible with the addition of activated carbon. If the patient feels unwell, seek medical advice.
- Eye Contact:** Contamination of the eyes must be treated by thorough irrigation with water for 15 minutes, with the eyelids held open. A doctor (or eye specialist) should be consulted immediately.
- Skin Contact:** Remove all contaminated clothing immediately. Thoroughly wash with plenty of water and soap, or other non-irritating cleansing agents.
- Inhalation:** Upon inhalation of dust, take the patient into the fresh air. If there is difficulty in breathing, medical advice is required.
- Advice to Doctor:** Treat symptomatically

5. Fire-fighting Measures

- Suitable Extinguishing Media:** Water jet, Foam, Powder, CO2
For safety reasons, do not use CO2
- Specific Hazards:** If burning, may produce oxides of sulphur and nitrogen and carbon monoxide.
- Hazchem Code:** None allocated
- Flammability:** Combustible solid
- Fire-fighting advice:** Fire-fighters must wear protective boots, overalls, gloves and goggles.
Fire-fighters must wear self-contained breathing apparatus.
- Fire residues and contaminated firefighting water must be disposed of in accordance with local regulations.

6. Accidental Release Measures

Persons responding to accidental spills or release of this product are advised to wear personal protective equipment as given in Section 8 of this SDS.

- Spills:** Risk of dust explosion. Eliminate all sources of ignition. Do not breathe dust.
Do not allow product to enter drains, sewers or waterways.
Avoid formation and deposition of dust. Take up spilled product with dust-binding material or suitable vacuum cleaner.
Fill into labelled, sealable containers.
- Disposal:** Unusable recovered product should be placed in sealed, labelled containers for disposal in accordance with instructions in section 13.
Wash away remaining traces with water.

7. Handling and Storage

- Industrial Hygiene:** Keep away from food and drink stuffs.
Wash hands after use and before eating, drinking, smoking or using toilet.
Remove contaminated clothing and protective equipment before entering eating areas.
- Precautions for Safe Handling:** Observe the usual precautionary measures required for chemicals with dust-explosive properties.
Do not breathe dust.
Wear personal protective equipment as given in Section 8 of this SDS.
In filling operations take precautionary measures against static discharges.
- Conditions for Safe Storage:** Avoid formation and deposition of dust. Keep containers tightly closed.
Store in a cool, dry place, out of direct sunlight.
Store away from oxidising agents.

8. Exposure Controls / Personal Protection

Do not breathe dust. Avoid contact with eyes and skin.
Remove all contaminated clothing immediately.

NOTICE: GRANULATE DYESTUFFS ARE FREE-FLOWING, SPECIALLY DEDUSTED REACTIVE DYESTUFF PREPARATIONS. BY CAREFUL HANDLING DUSTING CAN BE SUPPRESSED ALMOST COMPLETELY.

Inhalation of dust & aerosols MUST be prevented by either adequate ventilation or by a suitable mask.

Reactive dyestuff.

People with chronic respiratory problems should not work with reactive dyestuff powders.

If symptoms such as tightness in the chest or asthma occur while handling reactive dyestuff powders, a physician should be consulted as soon as possible.

If hypersensitivity is confirmed, all contact with reactive dyestuff powders must cease immediately.

Occupational Exposure Limits for this specific chemical

EXPOSURE STANDARDS

- Allocated by the ASCC: No exposure standard allocated.
However, NOHSC:3008 (1995) lists a value of 10mg/m³ for inspirable dust containing no asbestos and <1% crystalline silica.
- Allocated by other organisations: Not known

BIOLOGICAL LIMIT VALUES

- Allocated by the ASCC: No value allocated
- Allocated by other organisations: Not known

Occupational Exposure Limits for Ingredients

Ingredient	TWA	STEL	BLV	Notices
------------	-----	------	-----	---------

	ppm	mg/m ³	ppm	mg/m ³		
No Data Available	X	X	X	X	X	X

X = No data available

TWA – the Time Weighted Average airborne concentration over an eight-hour working day, for a five-day working week over an entire working life.

STEL - (Short Term Exposure Limit) – the average airborne concentration over a 15 minute period which should not be exceeded at any time during a normal, eight-hour, working day. According to current knowledge, these concentrations should neither impair the health of, nor cause undue discomfort to nearly all workers.

BLV - Biological Limit Value

'SK' notice – absorption through the skin may be a significant source of exposure. The exposure standard is invalidated if such contact should occur.

These exposure standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. Exposure standards should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity.

If the directions for use on the product label are followed, exposure of individuals using the product should not exceed the above standard. The standard was created for workers who are routinely, potentially exposed during product manufacture.

Engineering Controls

Ensure adequate ventilation to control airborne exposure. Good general ventilation should be sufficient; otherwise, provision of local exhaust ventilation is recommended.

Engineering controls, such as provision of local exhaust ventilation or containment, should always be implemented before personal protection equipment is necessary.

Personal Protection

Eye / Face Protection:



Wear safety glasses with eye shields or chemical goggles. Final choice of appropriate eye/face protection will vary according to individual circumstances. Eye protection devices should conform to AS/NZS 1337 - Eye Protectors for Industrial Applications.

Respiratory Protection:



Wear dust mask with particle filter. Wear an approved respirator if engineering controls and dust mask are not effective in controlling airborne exposure. For guidance on the selection, use and maintenance of Respiratory Protection Devices, refer to AS/NZS 1715 & AS/NZS 1716.

Gloves:



Wear impervious PVC or nitrile rubber gloves. If necessary, test gloves before use.

Clothing:



Wear suitable protective clothing such as overalls closed at neck and wrists.

9. Physical and Chemical Properties

Colour / Form:	dark blue granules.
Odour:	Odourless
pH:	4.5 - 5.0 (100g/l)
Melting Point:	Not available
Freezing Point:	Not applicable

Initial Boiling Point / Boiling Range:	Not applicable
Flash Point:	Not available
Evaporation Rate:	Not applicable
Flammability:	Combustible solid
Flammability Limits:	Not available
Vapour Pressure:	Not available
Vapour Density:	Not available
Relative Density:	Not available
Solubility:	30g/l @ 25°C
Partition Co-efficient:	n-octanol / water; Not available
Auto-Ignition Temperature:	Not available
Decomposition Temperature:	Not available
Viscosity:	Not available

10. Stability and Reactivity

Reactivity:	Will not react or polymerise. As with all dusty organic chemicals, the possibility of a dust explosion should be considered.
Chemical Stability:	Stable under normal ambient and anticipated storage and handling conditions of temperature and pressure.
Conditions to Avoid:	Avoid temperatures above 100°C.
Incompatible Materials:	Strong alkalis, oxidising agents and reducing agents destroy the product.
Hazardous Decomposition Products:	At temperatures above 150°C, may liberate toxic gases consisting of oxides of sulphur and nitrogen, and carbon monoxide.

11. Toxicological Information

Toxicity Data

(PRODUCT = Chemical identified in Section 1)

- | | | |
|-------------------------------------|----------------|--|
| • ACUTE TOXICITY | - Product | : ORAL LD50 > 5,000 mg/kg (rat) |
| | - Ingredients: | ORAL LD50 > 2,000 mg/kg (rat) (*) |
| • SKIN CORROSION / IRRITATION | - Product | : non-irritant (rabbit) |
| | - Ingredients: | non-irritant (rabbit) |
| • SERIOUS EYE DAMAGE / IRRITATION | - Product | : non-irritant (rabbit eye) |
| | - Ingredients: | non-irritant (rabbit eye) |
| • RESPIRATORY OR SKIN SENSITISATION | - Product | : In the guinea-pig the product has a sensitising effect (OECD 406; GPMT according to MAGNUSSON-KLIGMAN). |
| | - Ingredients: | Possible respiratory sensitiser (*)
Skin sensitiser (*) |
| • GERM CELL MUTAGENICITY | - Product | : Salmonella/microsome test (Ames test): No indication of mutagenic effects. |
| | - Ingredients: | In Vitro Ames Test (with and without metabolic activation)
Result: Negative
Species: salmonella typhimurium
Concentration: 4 - 5,000 micrograms (*) |
| | | |
-

• CARCINOGENICITY	- Product : No data available - Ingredients: No data available
• REPRODUCTIVE TOXICITY	- Product : No data available - Ingredients: Teratogenicity: NOEL = 1,000mg/kg (rat) (*)
• STOST; SINGLE EXPOSURE	- Product : No data available - Ingredients: No data available
• STOST; REPEATED EXPOSURE	- Product : No data available - Ingredients: No data available
• ASPIRATION HAZARD	- Product : No data available - Ingredients: No data available

HEALTH EFFECTS - ACUTE

Swallowed:	May cause mild irritation of digestive tract if ingested in large quantities.
Eye Contact:	Non-Irritant. May cause temporary redness / mild irritation.
Skin Contact:	Non-Irritant. May cause temporary redness / mild irritation.
Inhalation:	High dust concentration may result in irritation of the mucous membranes (eyes or respiratory tract.).

HEALTH EFFECTS - CHRONIC:

Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity.
Repeated exposure to high dust concentration of some reactive dyestuff POWDERS containing this dyestuff has very sporadically caused respiratory hypersensitivity.

12. Ecological Information

The following data is derived from test results of an analogous product.

Environmental Fate:	No data available
Ecotoxicity:	Fish toxicity : LC50 >100 mg/l (96 h, Brachydanio rerio) Method : 92/69/EEC, C.1 Bacteria toxicity : EC50 > 100 mg/l (3 h, activated sludge micro-organism) Method : OECD 209
	Chemical oxygen demand (COD) : 690 mg/g
	Biochemical oxygen demand (BOD5): < 30 mg/g
Persistence / Degradability:	Biodegradability : < 10 % Method : static test.
	If regulations are followed when introducing effluent into biological waste water treatment plants, no adverse effect on the degradation activity of activated sludge is to be expected.
Bioaccumulative Potential:	No data available
Mobility:	No data available
Other Data:	Product does not add to the AOX-value of the sewage. (DIN EN 1485) The product does not contain heavy metals in concentrations of concern for waste water. The product does not release nitrogen which can contribute to eutrophication. The product does not contain phosphates or organophosphorus compounds.

13. Disposal Considerations

If utilisation or recycling of product is not possible, product should be disposed of in accordance with local regulations, at an authorised incineration plant or special waste disposal site.

Contaminated packaging should be emptied as much as possible and may be re-used after appropriate cleaning. Packaging that cannot be cleaned should be disposed of as for product.

14. Transport Information

UN Number:	None allocated
Proper Shipping Name:	None allocated
ADG Class:	None allocated
Subsidiary Risk 1:	None allocated
Packing Group:	None allocated
Hazchem Code:	None allocated
EPG:	None allocated
Segregation Dangerous Goods:	None allocated
Marine Transport:	None allocated
Air Transport:	None allocated

15. Regulatory Information

All the constituents of this chemical are listed on the Australian Inventory of Chemical Substances (AICS).

Water Hazard Class (Ger.): WGK 2 - impairment of water quality WGK = Classification in accordance with the German Water Resources Act Annex 2 VwVwS (Germany) dated May, 17th 1999

16. Other Information

Prepared in accordance with:

Draft National Code of Practice for the Preparation of Safety Data Sheets - December 2006 including hazard categories and statements (see Section 2 of this SDS) according to NOHSC:2011(2003).

Date of Preparation:

Date of Revision: 27/08/2007

Reason(s) for Issue:
- Change of SDS format
- Update data in Sections 11

Safety Data Sheets are updated frequently. Please ensure that you have a current copy.

Literary References / Data Sources:

- Supplier SDS: Remazol Navy RGB 150% Gran. (Dystar GmbH) - unless otherwise noted.
- (*) European Chemicals Bureau - IUCLID Dataset

Legend to Abbreviations and Acronyms:

<	less than
>	greater than
°C	degrees Celsius
ACGIH	American Conference of Governmental Industrial Hygienists
ADG	(ADG Code) Australian Code for the Transport of Dangerous Goods by Road and Rail.
ADN	European Agreement concerning the International Transport of Dangerous Goods by Inland Waterways.
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road.
AICS	Australian Inventory of Chemical Substances
approx.	approximately
AS	Australian Standard
ASCC	Australian Safety and Compensation Council (succeeded NOHSC 7/02/2005)
BLV	Biological Limit Value
BOD	Biological Oxygen Demand

CAS	Chemical Abstracts Service (number)
CO2	Carbon Dioxide
COD	Chemical Oxygen Demand
EC No/ EC#	EC No and EC# refer to the seven-digit code allocated by the Commission of the European Communities.
EPG	Emergency Procedure Guide
g	gram
g/cc	grams per cubic centimetre
g/l	grams per litre
GHS	Globally Harmonised System
HSIS	Hazardous Substance Information Service
IATA-DGR	International Air Transport Association - Dangerous Goods Regulations
ICAO-TI	International Civil Aviation Organisation - Technical Instructions on Safe Transport of Dangerous Goods by Air.
IMDG	International Maritime Dangerous Goods Code.
IUCLID	International Uniform Chemical Information Database
kg	kilogram
kg/m3	kilograms per cubic metre
LC50	LC stands for "Lethal Concentration". LC50 is the concentration of a chemical in air which causes the death of 50% (1/2) of a group of test animals. The chemical is inhaled over a set period of time, usually 1 or 4 hours.
LD50	LD stands for "Lethal Dose". LD50 is the amount of chemical, given all at once, which causes the death of 50% (1/2) of a group of test animals.
mg	milligram
mg/m³	milligrams per cubic metre
mm	millimetre
NOEL	No Observable Effect Limit
NOHSC	National Occupational Health and Safety Commission (succeeded by ASCC)
NZS	New Zealand Standard
ppm	parts per million
PVC	polyvinyl chloride
RID	European Agreement concerning the International Carriage of Dangerous Goods by Rail.
R Phrase	Risk phrase
S Phrase	Safety phrase
STOST	Specific Target Organ Systemic Toxicity
UN	United Nations (number)
w/v	Weight by volume
w/w	Weight by weight

This SDS summarizes our best knowledge of the health and safety hazard information of the product and how to safely handle the product in the workplace. Each user should read this SDS and consider the information in the context of how the product will be handled and used in the workplace, including its use in conjunction with other substances.

We have reviewed any information contained herein, which was received from sources outside DYECHM INDUSTRIES Pty Ltd. However, no warranty or recommendation, expressed or implied, is made as to the accuracy or completeness of the data and information contained in this data sheet.

Health and safety precautions and environmental advice noted in this data sheet may not be accurate for all individuals and/or situations. It is the user's obligation to evaluate and use this product safely and to comply with all applicable laws and regulations. No statement made in this data sheet shall be construed as a permission, recommendation or authorization, given or implied, to practise any patented invention without a valid licence.

DYECHM INDUSTRIES Pty Ltd shall not be responsible for any damage or injury resulting from: abnormal use of the chemical; any failure to adhere to recommendations; any hazards inherent in the nature of the chemical.

DYECHM INDUSTRIES Pty Ltd expressly disclaims that the SDS is a representation or guarantee of the chemical specifications for the product.

End of SDS

Ethylenediaminetetraacetic Acid Tetrasodium Salt MSDS

Section 1: Chemical Product and Company Identification	
<p>Product Name: Ethylenediaminetetraacetic Acid Tetrasodium Salt</p> <p>Catalog Codes: SLE2284</p> <p>CAS#: 10378-23-1</p> <p>RTECS: AH5075000 (For CAS no. 64-02-8 known as EDTA Tetrasodium salt, anhydrous)</p> <p>TSCA: TSCA 8(b) inventory: No products were found.</p> <p>CI#: Not available.</p> <p>Synonym: Versene, Kalex, Hampene, Dissolvine; EDTA tetrasodium salt dihydrate; Tetrasodium EDTA dihydrate; Tetrasodium salt EDTA dihydrate; Tetrasodium salt of EDTA, dihydrate; Tetrasodium salt of ethylenediaminetetraacetic acid, dihydrate; Sodium salt of ethylenediaminetetraacetic acid, dihydrate; Sodium ethylenediaminetetraacetate, dihydrate; Sodium ethylenediaminetetraacetic acid, dihydrate; Sodium EDTA, dihydrate; Edetate sodium dihydrate; Edetic acid tetrasodium salt, dihydrate; Endrate tetrasodium; Ethylenebis(iminodiacetic acid) tetrasodium salt, dihydrate; Ethylenediaminetetraacetic acid, tetrasodium salt, dihydrate; Edathaniltetrasodium, dihydrate; N, N'-Ethylenediaminediacetic acid tetrasodium salt.</p> <p>Chemical Name: Acetic acid, (ethylenedinitrilo)tetra-, tetrasodium salt, dihydrate</p> <p>Chemical Formula: C10H12N2Na4O8.2H2O</p>	<p>Contact Information:</p> <p>Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396</p> <p>US Sales: 1-800-901-7247 International Sales: 1-281-441-4400</p> <p>Order Online: ScienceLab.com</p> <p>CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300</p> <p>International CHEMTREC, call: 1-703-527-3887</p> <p>For non-emergency assistance, call: 1-281-441-4400</p>

Section 2: Composition and Information on Ingredients		
Composition:		
Name	CAS #	% by Weight
Ethylenediaminetetraacetic acid tetrasodium salt	10378-23-1	100
Toxicological Data on Ingredients: Ethylenediaminetetraacetic acid tetrasodium salt: ORAL (LD50): Acute: >2000 mg/kg [Rat].		

Section 3: Hazards Identification

Potential Acute Health Effects: Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects: CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to upper respiratory tract, skin, eyes. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact: Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

Skin Contact: Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation: If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion: Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-ignition Temperature: Not available.

Flash Points: CLOSED CUP: Higher than 93.3°C (200°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO₂), nitrogen oxides (NO, NO₂...). Some metallic oxides.

Fire Hazards in Presence of Various Substances: Slightly flammable to flammable in presence of heat. Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances: Slightly explosive in presence of open flames and sparks. Non-explosive in presence of shocks.

Fire Fighting Media and Instructions: SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: As with most organic solids, fire is possible at elevated temperatures

Special Remarks on Explosion Hazards: Fine dust dispersed in air in sufficient concentrations, and in the presence of an ignition source is a potential dust explosion hazard.

Section 6: Accidental Release Measures

Small Spill: Use appropriate tools to put the spilled solid in a convenient waste disposal container. If necessary: Neutralize the residue with a dilute solution of acetic acid. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill: Use a shovel to put the material into a convenient waste disposal container. Neutralize the residue with a dilute solution of acetic acid. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions: Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe dust. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents, metals.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8: Exposure Controls/Personal Protection

Engineering Controls: Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection: Safety glasses. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill: Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Crystalline solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 416.23 g/mole

Color: White.

pH (1% soln/water): 11.3 [Basic.]

Boiling Point: Not available.

Melting Point: Not available.

Critical Temperature: Not available.

Specific Gravity: Bulk Density: 0.77 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.
Dispersion Properties: See solubility in water.
Solubility: Soluble in cold water.

Section 10: Stability and Reactivity Data

Stability: The product is stable.
Instability Temperature: Not available.
Conditions of Instability: Not available.
Incompatibility with various substances: Reactive with oxidizing agents, metals.
Corrosivity: Non-corrosive in presence of glass.
Special Remarks on Reactivity: Avoid contact with aluminum, copper, copper alloys, zinc, and nickel, and strong oxidizers.
Special Remarks on Corrosivity: Not available.
Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Absorbed through skin. Eye contact. Inhalation. Ingestion.
Toxicity to Animals: Acute oral toxicity (LD50): >2000 mg/kg [Rat].
Chronic Effects on Humans: May cause damage to the following organs: upper respiratory tract, skin, eyes.
Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.
Special Remarks on Toxicity to Animals: Not available.
Special Remarks on Chronic Effects on Humans: Not available.
Special Remarks on other Toxic Effects on Humans: Acute Potential Health effects: Skin: May cause skin irritation. Eyes: May cause eye irritation. Inhalation: May cause irritation of the respiratory tract. Ingestion: May cause gastrointestinal tract irritation. The toxicological properties of this substance have not been fully investigated.

Section 12: Ecological Information

Ecotoxicity: Ecotoxicity in water (LC50): 760 mg/l 96 hours [Bull gill sunfish]. 59.8 mg/l 96 hours [Fathead Minnow].
BOD5 and COD: Not available.
Products of Biodegradation: Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.
Toxicity of the Products of Biodegradation: The product itself and its products of degradation are not toxic.
Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal: Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations: No products were found.

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC): This product is not classified according to the EU regulations. Not applicable.

HMIS (U.S.A.):

Health Hazard: 1

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment: Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Safety glasses.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/09/2005 05:29 PM

Last Updated: 11/28/2005 01:09 PM

The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the

information for their particular purposes. In no event shall ScienceLab.com be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if ScienceLab.com has been advised of the possibility of such damages.

Nitrilotriacetic acid, Trisodium salt MSDS

Section 1: Chemical Product and Company Identification	
<p>Product Name: Nitrilotriacetic acid, Trisodium salt</p> <p>Catalog Codes: SLN1531</p> <p>CAS#: 18662-53-8</p> <p>RTECS: AJ1070000</p> <p>TSCA: TSCA 8(b) inventory: No products were found.</p> <p>Cl#: Not available.</p> <p>Synonym: NTA, sodium hydrate; Trisodium nitrilotriacetate monohydrate; Nitriooacetic acid trisodium salt monohydrate; Glycine, N,N-bis(carboxymethyl)-, trisodium salt monohydrate; N,N-Bis(carboxymethyl)glycine trisodium salt monohydrate</p> <p>Chemical Name: Nitrilotriacetic Acid, Trisodium Salt, Monohydrate</p> <p>Chemical Formula: C6-H6-N-06-Na3.H20</p>	<p>Contact Information:</p> <p>Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396</p> <p>US Sales: 1-800-901-7247 International Sales: 1-281-441-4400</p> <p>Order Online: ScienceLab.com</p> <p>CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300</p> <p>International CHEMTREC, call: 1-703-527-3887</p> <p>For non-emergency assistance, call: 1-281-441-4400</p>

Section 2: Composition and Information on Ingredients		
Composition:		
Name	CAS #	% by Weight
Nitrilotriacetic acid, Trisodium salt	18662-53-8	100
Toxicological Data on Ingredients: Nitrilotriacetic acid, Trisodium salt LD50: Not available. LC50: Not available.		

Section 3: Hazards Identification
<p>Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.</p> <p>Potential Chronic Health Effects: CARCINOGENIC EFFECTS: Classified 2B (Possible for human.) by IARC. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. Repeated or prolonged exposure is not known to aggravate medical condition.</p>

Section 4: First Aid Measures

Eye Contact:

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention.

Skin Contact:

In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:

Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO₂), nitrogen oxides (NO, NO₂...). Some metallic oxides.

Fire Hazards in Presence of Various Substances:

Slightly flammable to flammable in presence of heat.

Non-flammable in presence of shocks.

Explosion Hazards in Presence of Various Substances:

Risks of explosion of the product in presence of mechanical impact: Not available.

Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:

SMALL FIRE: Use DRY chemical powder.

LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:

Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by

spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:

Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system.

Section 7: Handling and Storage

Precautions:

Keep locked up.. Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:

Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid.

Odor: Not available.

Taste: Not available.

Molecular Weight: 275.1 g/mole

Color: Not available.

pH (1% soln/water): Not available.

Boiling Point: Not available.

Melting Point: >320°C (608°F)

Critical Temperature: Not available.

Specific Gravity: Not available.

Vapor Pressure: Not applicable.

Vapor Density: Not available.
Volatility: Not available.
Odor Threshold: Not available.
Water/Oil Dist. Coeff.: Not available.
Ionicity (in Water): Not available.
Dispersion Properties: Not available.
Solubility: Not available.

Section 10: Stability and Reactivity Data

Stability: The product is stable.
Instability Temperature: Not available.
Conditions of Instability: Excessive heat, incompatible materials, dust generation
Incompatibility with various substances: Reactive with oxidizing agents.
Corrosivity: Not available.
Special Remarks on Reactivity: Not available.
Special Remarks on Corrosivity: Not available.
Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.
Toxicity to Animals:
LD50: Not available.
LC50: Not available.
Chronic Effects on Humans:
CARCINOGENIC EFFECTS: Classified 2B (Possible for human.) by IARC.
MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells.
Other Toxic Effects on Humans: Hazardous in case of skin contact (irritant), of ingestion, of inhalation.
Special Remarks on Toxicity to Animals: Not available.
Special Remarks on Chronic Effects on Humans:
May cause cancer.
May affect genetic material (mutagenic)
Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects:
Skin: No information was found regarding skin irritation.
Eyes: May cause eye irritation.
Inhalation: May cause respiratory tract irritation.
Ingestion: May be harmful if swallowed. May cause gastrointestinal tract irritation.
The toxicological properties of this substance have not been fully investigated.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:

California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer, birth defects or other reproductive harm, which would require a warning under the statute:

Nitritotriacetic acid, Trisodium salt

California prop. 65 (no significant risk level): Nitritotriacetic acid, Trisodium salt: 0.07 mg/day (value)

California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer which would require a warning under the statute: Nitritotriacetic acid, Trisodium salt

Massachusetts RTK: Nitritotriacetic acid, Trisodium salt

Other Regulations: Not available.

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):

R22- Harmful if swallowed.

R40- Possible risks of irreversible effects.

S28- After contact with skin, wash immediately with plenty of water

S36/37- Wear suitable protective clothing and gloves.

S45- In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

HMIS (U.S.A.):

<p>Health Hazard: 2</p> <p>Fire Hazard: 1</p> <p>Reactivity: 0</p> <p>Personal Protection: E</p> <p>National Fire Protection Association (U.S.A.):</p> <p>Health: 2</p> <p>Flammability: 1</p> <p>Reactivity: 0</p> <p>Specific hazard:</p> <p>Protective Equipment: Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Splash goggles.</p>
--

Section 16: Other Information
<p>References: Not available.</p> <p>Other Special Considerations: Not available.</p> <p>Created: 10/10/2005 11:00 AM</p> <p>Last Updated: 10/10/2005 11:00 AM</p> <p><i>The information above is believed to be accurate and represents the best information currently available to us. However, we make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use. Users should make their own investigations to determine the suitability of the information for their particular purposes. In no event shall ScienceLab.com be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if ScienceLab.com has been advised of the possibility of such damages.</i></p>

DISSOLVINE GL-47-S

1. IDENTIFICATION OF THE SUBSTANCE OR PREPARATION AND THE COMPANY/UNDERTAKING

Product label name Glutamic acid, N,N-diacetic acid, tetrasodium salt, 47% aqueous solution	
Supplier Akzo Nobel Functional Chemicals bv Stationsstraat 77 PO Box 247 NL-3800 AE Amersfoort Tel.: +31 334676767	
E-mail address of person responsible for safety data sheet SDS_chelates@AkzoNobel.com	
Emergency telephone T +31570679211 F +31570679801 AkzoNobel Chemicals-Deventer-NL	
Intended use chelating agent	
Date of last issue / Revision number 2009/05/11 / 0.00	

2. HAZARDS IDENTIFICATION

Irritating to eyes and skin.

3. COMPOSITION/INFORMATION ON INGREDIENTS

This product is to be considered as a preparation in conformance to EC directives			
Information on hazardous ingredients			
Chemical description Glutamic acid, N,N-diacetic acid, tetrasodium salt, 47% aqueous solution			
Composition / information on ingredients			
Number	% w/w	CAS-number	Chemical name
1	45 - 49	051981-21-6	Tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate
2	0.5 - 1.9	001310-73-2	Sodium hydroxide

	Index-No.	EC-number	Symbol(s) (EU classification)	Risk-phrase(s)
1		257-573-7		none
2	011-002-00-6	215-185-5	C	R35

Other information Balance: water
--

4. FIRST AID MEASURES

Symptoms and effects No typical symptoms and effects known.
First aid
General In all cases of doubt, or when symptoms persist, seek medical attention.

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

Inhalation Not likely to occur. Move to fresh air, rest, half upright position, loosen clothing.
Skin Take off contaminated clothing immediately. Wash immediately with soap and water. Launder clothes before reuse.
Eye Rinse thoroughly with plenty of water. Eyelids should be held away from the eyeball to ensure thorough rinsing. Seek medical advice.
Ingestion Rinse mouth, give water to drink. Do NOT induce vomiting. Seek medical advice after significant exposure

Advice to physician
Symptomatic treatment is advised.

5. FIRE-FIGHTING MEASURES

Extinguishing media waterspray, foam, Carbon dioxide, dry chemical powder
Unsuitable extinguishing media none known.
Hazardous decomposition / combustion products Nitrous gases may be produced
Protective equipment Use self-contained respiratory equipment.
Fire and explosion hazard In case of fire and/or explosion do not breathe fumes.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions For personal protection see Section 8
Environmental precautions Collect as much as possible in a clean container for (preferable) reuse or disposal.
Methods for cleaning up Flush remainder with water (Absorb the remainder with e.g. vermiculite). See also Section 13.

7. HANDLING AND STORAGE

Handling The usual precautions for handling chemicals should be observed.
Fire and explosion prevention No specific recommendations
Storage requirements Avoid contact with: aluminium, nickel, zinc, copper and copper alloys. Store in: PVC, PE, Stainless steel, Bituminized tanks.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls No specific recommendations
Personal protection

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

Respiratory No specific recommendations
Hand For permanent (>480 minutes), full contact use, 100% Viton gloves conforming to EN 374, e.g. KCL Vitoject 890 are recommended. If used under conditions other than given above it is recommended that a supplier of CE approved gloves is contacted. These recommendations are only applicable to the chemical as supplied by Akzo Nobel; if mixed with or dissolved in other substances please contact a supplier of CE approved gloves (e.g. KCL International +49 66 59870, fax +49 6659 87155).
Eye Wear eye/face protection.
Skin and body light protective clothing, suitable materials

Sodium hydroxide	
Short Term Exposure Limit (STEL)	2 mg/m ³

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance liquid (25 °C)
Colour light yellow
Odour slightly ammonia like
Boiling point/range 105 - 110°C
Melting point/range not applicable
Flash point not applicable (aqueous solution)
Flammability not applicable
Explosive properties not applicable
Oxidising properties no
Vapour pressure same as water (aqueous solution)
Density 1150 - 1380 kg/m ³
Bulk density not applicable
Solubility in water Completely miscible
Solubility in other solvents not determined

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

pH value 11 - 12 (1 % solution)
Partition coefficient n-octanol/water Log Pow < 0
Relative vapour density (air=1) same as water
Viscosity not determined
Autoignition temperature not applicable
Explosion limits not applicable
Other information Crystallization point/range < -15°C

10. STABILITY AND REACTIVITY

Conditions to avoid
Reaction with strong oxidising agents
Stability Stable under recommended storage and handling conditions (see section 7)
Incompatibles aluminium, nickel, zinc, copper and copper alloys. Formation of: Hydrogen.
Hazardous decomposition products Emits toxic fumes under fire conditions (nitrous gases (NOx)).

11. TOXICOLOGICAL INFORMATION

No experimental toxicological data on the preparation as such available. The following data are applicable to the ingredient(s) listed below:

Tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate
Acute toxicity
Oral LD50 >2000 mg/kg (rat) (Akzo Nobel E-file)
Irritation
Skin Non-irritating (Akzo Nobel E-file)
Eye Non-irritating (Akzo Nobel E-file)
Sensitization Not sensitizing (Akzo Nobel E-file)
Genotoxicity No evidence of genotoxic effects in vivo (Akzo Nobel E-file). No evidence of genotoxic effects in vitro (Akzo Nobel E-file). Not mutagenic (Akzo Nobel E-file).
Sodium hydroxide
Acute toxicity
Oral LD50 No data available

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

Irritation
Skin Highly corrosive
Eye Corrosive
Respiratory Corrosive

12. ECOLOGICAL INFORMATION

No experimental ecological data are available on the preparation as such. The following data are applicable to the ingredient(s) listed below:
Tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate
Ecotoxicity
fish 96h LC50 >100mg/l (Oncorhynchus mykiss) (Akzo Nobel E-file)
daphnia 48h EC50 >100mg/l (Daphnia magna) (Akzo Nobel E-file)
algae 72h EC50 >100 mg/l (Akzo Nobel E-file)
Fate
Degradation Biotic Readily biodegradable (Akzo Nobel E-file)
Bioaccumulation Log Pow <3
Sodium hydroxide.
Ecotoxicity
fish 96h-LC50: 33 to 189 mg/l (various species).
Fate
Degradation Biotic not applicable
Bioaccumulation Not expected to bioaccumulate
Other information The product increases the pH (water, soil). Harmful effect due to pH shift is possible.

13. DISPOSAL CONSIDERATIONS

Product According to local regulations.
Contaminated packaging According to local regulations.

14. TRANSPORT INFORMATION

<i>Land transport</i>

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

Class 8
Classification Code C7
RID class 8
Packing group III
Hazard Identification No. 80
Substance Identification No. 3267
TREM-Card or ERG number CEFIC TEC(R)- 80GC7-II+III
UN number 3267
Proper Shipping Name CORROSIVE LIQUID, BASIC, ORGANIC, N.O.S. (Glutamic acid, N,N-diacetic acid, tetrasodium salt)

<i>Sea transport (IMO / IMDG-code)</i>
Class 8
Packing group III
UN number 3267
EMS F-A, S-B
Marine pollutant no
Proper Shipping Name Corrosive liquid, basic, organic, n.o.s. (Glutamic acid, N,N-diacetic acid, tetrasodium salt, 38% solution)

<i>Air transport (ICAO-TI / IATA-DGR)</i>
UN number 3267
Class 8
Packing group III
Proper Shipping Name Corrosive liquid, basic, organic, n.o.s. (Glutamic acid, N,N-diacetic acid, tetrasodium salt, 38% solution)

15. REGULATORY INFORMATION


According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

Product label name Glutamic acid, N,N-diacetic acid, tetrasodium salt, 47% aqueous solution
Labelling according to EC directives
EC-number See section 3

R(isk) phrase(s) (EU classification)	
Code	Description
R36/38	Irritating to eyes and skin

S(afety) phrase(s) (EU classification)	
Code	Description
S24/25	Avoid contact with skin and eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S37/39	Wear suitable gloves and eye/face protection
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

Symbol(s) (EU classification)	
	
IRRITANT	

German Water Hazard Class (WGK) German: Non-hazardous to waters (NWG) (VwVwS Anhang 4 Nr. 3)
--

16. OTHER INFORMATION

R-phrase information		
Chemical name	R(isk) phrase(s) (EU classification)	
Tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate	none	none
Sodium hydroxide	R35	Causes severe burns

According to Regulation (EC) No. 1907/2006

DISSOLVINE GL-47-S

History
Date of printing/ pdf file generated 2009/07/01
Revision 0.00
Composed by R. Borgmann-Strahsen A. Reichwein
<small>This information only concerns the above mentioned product and does not need to be valid if used with other product(s) or in any process. The information is to our best present knowledge correct and complete and is given in good faith but without warranty. It remains the user's own responsibility to make sure that the information is appropriate and complete for his special use of this product.</small>