

**INNOVATIONS IN DYEING OF COTTON
WITH INDIGO AND OTHER VAT DYES
USING IRON(II) SALT AND ITS COMPLEXES**

by

J. N. CHAKRABORTY

DEPARTMENT OF TEXTILE TECHNOLOGY

Submitted in fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



INDIAN INSTITUTE OF TECHNOLOGY , DELHI

JULY , 2000

Dyest
dyeing - Textile fibre

TH
677.027
CHA-1

I. I. T. DELHI.
LIBRARY
No. 2764

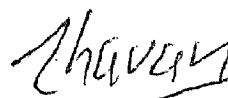
I. I. T. DELHI
LIBRARY
PROCESSED

**DEDICATED
TO
MY BELOVED MOTHER**
WHOM I LOST DURING THIS RESEARCH

CERTIFICATE

This is to certify that the thesis entitled " INNOVATIONS IN DYEING OF COTTON WITH INDIGO AND OTHER VAT DYES USING IRON(II) SALT AND ITS COMPLEXES " being submitted by Mr. J.N.Chakraborty , to the Indian Institute of Technology , Delhi , for the award of the degree of Doctor of Philosophy in the Department of Textile Technology is a record of bonafide research work carried out by him. Mr. J.N. Chakraborty has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis .

The results contained in this thesis have not been submitted , in part or in full , to any other University or Institute for the award of any degree or diploma .



(DR. R.B.CHAVAN)
Professor & Head,
Department of Textile Technology
I.I.T., New Delhi - 110016 .

ACKNOWLEDGEMENTS

I wish to express my heartiest regard to Prof. R.B.CHAVAN for his excellent and valuable guidance, in spite of his busy schedule as Head , Department of Textile Technology , throughout the course of this research work .

I am thankful to the authority of Dr. B.R.Ambedkar Regional Engineering College , Jalandhar , for sponsoring me for this research programme .

I gratefully acknowledge the financial support provided for this research programme by the Ministry of Human Resource and Development , Govt. of India , under Quality Improvement Programme .

My sincere thanks are due to Mr. V.A.Passi , Mr. Rajendra Prasad , Mr. Shiv Charan and others in Textile Chemistry Laboratory as well as Mr. Rajkumar Tejanian of Computer Laboratory for their immense help , cooperation and cordial behaviour during the period of my research .

I am also thankful to the staff members of various other Laboratories in the Textile Department for their time to time help and cooperation .

I appreciate the cooperation extended by other research scholars of this department, especially Mr. Shirish Kumar , who helped to solve different chemical aspects .

At the end , I offer my heartiest thanks to my wife Neeta , daughter Ananya and son Amit for their understanding , encouragement and constant cooperation throughout the period of this research .

Dated : July , 2000


(J.N.CHAKRABORTY)

ABSTRACT

The study reported in the present thesis consists of

1. Pretreatment of cotton with metal salts to enhance indigo uptake.
2. A system consisting of iron (II) salt and a single ligand as a replacement of $\text{Na}_2\text{S}_2\text{O}_4$ in the dyeing of cotton with indigo, and
3. The use of iron (II) salt and two ligands as a replacement of $\text{Na}_2\text{S}_2\text{O}_4$ in dyeing of cotton with vat dyes other than indigo.

The philosophy of pretreating cotton with metal salt before indigo application by conventional 6-dip 6-nip technique was to impart a positive charge on the fibre surface to enhance the attraction of negatively charged dye anions . Among the various metal salts, viz. Ferrous Sulphate, Cobaltous Sulphate, Nickel Sulphate, Copper Sulphate, Aluminium Sulphate, Magnesium Sulphate , Manganous Chloride , Zinc Sulphate and Stannous Chloride , pretreatment with FeSO_4 was found to give satisfactory results and increase in colour yield was to an extent of 25% , higher compared to untreated cotton . The possible mechanism for enhancement of colour yield is suggested.

$\text{Na}_2\text{S}_2\text{O}_4$, though universally used as a reducing agent for application of vat dyes including indigo , however , recently there have been criticism on the environmental friendliness of $\text{Na}_2\text{S}_2\text{O}_4$. Use of various alternative reducing agents for the replacement of $\text{Na}_2\text{S}_2\text{O}_4$ have been suggested in the literature . In the present thesis , the detailed investigation on the use of iron (II) salt complexed with single ligand , such as triethanolamine, tartaric acid, citric acid, gluconic acid and a combination of ligands, such as triethanolamine and tartaric acid or triethanolamine and citric acid have been reported.

Indigo can be reduced at low reduction potential (-700 mV and above). This requirement is met by the use of iron (II) salt - triethanolamine system, iron (II) salt - tartaric acid system, iron (II) salt - citric acid system and iron (II) salt - gluconic acid system (single ligand systems) ; whereas vat dyes other than indigo require much higher reduction potential (-850 mV and above) for their reduction . It has been established that such vat dyes could be reduced only when a double ligand system was used for the complexing of iron (II) salt with combination of either triethanolamine and tartaric acid or triethanolamine and citric acid . The advantage of such iron (II) complexes was that it was possible to reduce and dye with vat dyes at room temperature . A tentative mechanism for the complex formation among iron (II) salt and single ligand as well as combination of ligands have been suggested .

CONTENTS

	<u>Page</u>
CERTIFICATE	(i)
ACKNOWLEDGEMENT	(ii)
ABSTRACT	(iii)
LIST OF FIGURES	(x)
LIST OF TABLES	(xii)
CHAPTER 1 : GENERAL INTRODUCTION AND LITERATURE SURVEY ON DYEING WITH INDIGO	
1.1 INTRODUCTION	1
1.2 APPLICATION OF INDIGO	2
1.2.1 Dyeing methods with indigo	2
1.3 CHEMISTRY OF INDIGO DYEING	7
1.3.1 Reduction of indigo and other vat dyes	7
1.3.2 Factors influencing indigo uptake	17
1.4 TECHNIQUES TO ENHANCE INDIGO UPTAKE	27
1.4.1 pH control	27
1.4.1 Pretreatment of cotton	29
1.5 COST EFFECTIVE PRODUCTION IN INDIGO DYEING	30
1.6 QUANTITATIVE ESTIMATION OF INDIGO AND OTHER VAT DYES	31
1.6.1 Colorimetry of leuco indigo	32
1.6.2 Turbidity of indigo in oxidised form	33
1.6.3 Colorimetry of sulphonated indigo	33
1.6.4 Solvent technique	34
CHAPTER 2 : ENHANCEMENT OF INDIGO UPTAKE BY PRETREATMENT OF COTTON WITH METAL SALTS	
2.1 INTRODUCTION	37
2.2 MATERIALS AND EXPERIMENTAL METHODS	38
2.2.1 Materials	38

2.2.2	Machines / Instruments	40
2.2.3	Preparation of pad liquor	40
2.2.4	Treatment of cotton with various metal salts followed by dyeing	41
2.2.5	Evaluation of dyed samples	42
2.2.6	Quantitative estimation of indigo on dyed samples	42
2.2.7	Estimation of iron on dyed samples	43
2.3	RESULTS AND DISCUSSION	45
2.3.1	Pretreatment of cotton with metal salts followed by padding with indigo	45
2.3.2	Methods of application of FeSO_4	47
2.3.3	Optimisation of FeSO_4 concentration in dry and wet methods	48
2.3.4	Comparison of colour yield in different methods of pretreatment	52
2.3.5	Comparison in dye uptake in different methods of pretreatment	54
2.3.6	Comparison in colour yield values in absence of iron in dyed Samples	56
2.3.7	Change in pH during various dips	58
2.3.8	Mechanism of dyeing	59
2.3.9	Influence of iron content on colour yield / dye uptake	62
2.3.10	Stability of $\text{Fe}(\text{OH})_3$	64
2.3.11	Influence of $\text{Fe}(\text{OH})_2$ on colour yield	65
2.3.12	Merits of FeSO_4 treatment	66
2.4	CONCLUSIONS	67

CHAPTER 3 : IRON (II) COMPLEXES FOR DYEING OF COTTON WITH INDIGO

3.1	INTRODUCTION	68
3.2	MATERIALS AND EXPERIMENTAL METHODS	70
3.2.1	Material	70
3.2.2	Machines / Instruments used	71
3.2.3	Determination of alkali equivalence of acidic ligands	71
3.2.4	Calculations on molar ratios between FeSO_4 and ligand	72
3.2.5	Calculation on total NaOH requirement	73
3.2.6	Preparation of dyebath	74
3.2.7	Padding of samples	74
3.2.8	Measurement of pH	74
3.2.9	Measurement of redox potential	74
3.2.10	Evaluation of samples	75
3.2.11	Estimation of soluble iron in bath	75
3.2.12	Calculation of iron in FeSO_4	75

3.3	RESULTS AND DISCUSSION	76
3.3.1	Reduction of indigo with FeSO ₄ and NaOH	76
3.3.2	Influence of ligand on reduction potential of bath , colour yield and iron content of samples	81
3.3.3	Optimisation of concentration of FeSO ₄ in presence of triethanolamine	87
3.3.4	Optimisation of NaOH concentration in presence of triethanolamine	89
3.3.5	Influence of various chemicals as ligands on dyeing with indigo	91
3.3.6	Dyeing of cotton with indigo in presence of effective ligand systems	95
3.3.7	Stability of Fe(OH) ₂ bath in presence of ligands	100
3.4	CONCLUSIONS	104

CHAPTER 4 : INTRODUCTION AND LITERATURE SURVEY ON DYEING WITH VAT DYES

4.1	INTRODUCTION	106
4.2	REDUCTION OF VAT DYES	107
4.3	DYEING OF COTTON WITH VAT DYES	109
4.3.1	Fundamental aspects	109
4.3.2	Practical aspects	112
4.4	AFTERTREATMENT OF DYEINGS	119
4.5	FASTNESS PROPERTIES OF DYEINGS	120
4.6	ECO-ENVIRONMENTAL ASPECTS	121
4.6.1	Vat dyes and Ecology	121
4.6.2	Reducing agents and Ecology	122
4.6.3	Waste-water load from exhausted dyebath	124
4.6.4	Preventive measures to reduce waste-water load	124

CHAPTER 5 : IRON(II) COMPLEXES FOR DYEING OF COTTON WITH VAT DYES : EXHAUST METHOD

5.1	INTRODUCTION	127
5.2	MATERIALS AND EXPERIMENTAL METHODS	127
5.2.1	Material	127

5.2.2	Instruments used	131
5.2.3	Preparation of reduction bath	131
5.2.4	Dyeing of samples	132
5.2.5	Calculation of molar ratios of FeSO ₄ and ligand	132
5.2.6	Determination of NaOH equivalence of acidic ligands	132
5.2.7	Calculation of NaOH concentration required	132
5.2.8	Calculation of total iron in reduction bath	132
5.2.9	Measurement of K/S of dyed samples	133
5.2.10	Estimation of soluble iron in bath	133
5.2.11	Determination of fastness properties	133
5.3	RESULTS AND DISCUSSION	134
5.3.1	Dyeing of cotton with anthraquinoid vat dye using iron(II) complex (single ligand system)	134
5.3.2	Two ligand systems	142
5.3.3	Optimisation of dyebath recipe in new reducing systems	144
5.3.4	Stability of reduction baths	158
5.3.5	Dyeing with different vat dyes	162
5.3.6	Dyeing with blue dyes	172
5.3.7	Dyeing with black	173
5.3.8	Fastness properties of dyed samples	174
5.4	CONCLUSIONS	176

CHAPTER 6 : IRON (II) COMPLEXES FOR DYEING OF COTTON WITH VAT DYES : PAD - DEVELOP METHOD

6.1	INTRODUCTION	178
6.2	MATERIAL AND EXPERIMENTAL METHODS	179
6.2.1	Material	179
6.2.2	Instruments / Machine used	180
6.2.3	Preparation of reduction bath	180
6.2.4	Preparation of dye solution	180
6.2.5	Padding of fabric	180
6.2.6	Intermediate drying of padded samples	180
6.2.7	Development of shade	181
6.2.8	Evaluation of dyed samples	181
6.3	RESULTS AND DISCUSSION	181
6.3.1	Colour yield on padding using iron (II) complexes	182
6.3.2	Padding with different vat dyes	186
6.4	CONCLUSIONS	190

**CHAPTER 7 : MECHANISM OF FORMATION OF IRON(II) COMPLEXES
FOR REDUCTION OF INDIGO AND OTHER VAT DYES**

7.1	INTRODUCTION	191
7.2	MECHANISM OF FORMATION OF COMPLEX IN SINGLE LIGAND SYSTEM	191
7.2.1	Tartaric acid system	192
7.2.2	Citric acid system	193
7.2.3	Triethanolamine system	194
7.2.4	Gluconic acid system	194
7.3	DOUBLE LIGAND SYSTEM AND REDUCTION OF VAT DYES OTHER THAN INDIGO	198
7.4	THERMAL STABILITY OF REDUCTION BATHS	210
7.5	CONCLUSIONS	212
	CHAPTER 8 : SUMMARY AND CONCLUSIONS	214
	REFERENCES	216
	PUBLICATIONS	(xvi)
	CURRICULUM VITAE	(xvii)