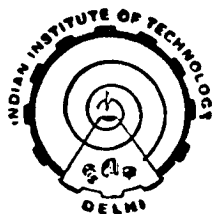


STUDIES IN SODIUM CHLORITE BLEACHING

by
R. VENKATRAJ

A thesis submitted to the
Indian Institute of technology, Delhi
for the award of the degree of

DOCTOR OF PHILOSOPHY



Department of Textile Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
JANUARY, 1988

*dedicated to my
supervisor*

CERTIFICATE

Certified that the dissertation entitled "STUDIES IN SODIUM CHLORITE BLEACHING", which is being submitted to the Indian Institute of Technology, Delhi, by R. Venkatraj, in fulfilment for the award of the Degree of DOCTOR OF PHILOSOPHY is a record of the student's own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for the award of any degree or Diploma.



(M.L. Gulrajani)
Professor and Head,
Department of Textile Technology,
Indian Institute of Technology, Delhi,
New Delhi-110016.

ACKNOWLEDGEMENT

I bow my head to express sincere gratitude to my supervisor, Prof. M.L. Gulrajani, the Head of Textile Technology Department, Indian Institute of Technology, for his personal involvement and constant encouragement in this work. Without his help, this work would not have been possible. I also gratefully acknowledge the assistance rendered by him for the computation part of this study.

I sincerely thank Mr. P. Chandrasekaran, Research Scholar, Department of Computer Science, University of Houston, U.S.A., Mr. S.R. Pandian, Research Scholar, Department of Electrical Engg., I.I.T. Delhi and Mr. M. Karuppasamy of Tata Energy Research Institute, New Delhi for assisting me in the computer programming at various stages.

I am very much thankful to all my research colleagues, especially to Dr. N. Sukumar, Dr. P. Balasubramanian, Mr. R. Ananda Kumar, Dr. Manjeet Bhatia and Ms. M. Surya Kumari, who have contributed some form of help during the course of the study.

I wish to record my appreciation for Mr. Rajesh K. Arora for his meticulous typing, supporting staffs of the Textile Chemistry Laboratory, Mr. K.G. Padam who did all the tracings in an excellent manner and Mr. Didarmal, Store Superintendent, who arranged the required materials in time.

I offer my thanks to Dr. K. Murugesan and Dr. Radha Murugesan of All India Institute of Medical Sciences and Mr. K. Nagarajan of NTPC, for their affection during my stay in Delhi as local guardians.

I finally would like to thank my fiance Ms. K. Nagasumathy and my parents for their encouragement and wishings over the years.


R. Venkatraj

ABSTRACT

ABSTRACT

Sodium chlorite was introduced by Mathieson Alkali Works of U.S.A in 1939 as a safe bleaching agent for cotton and linen fabrics. Its use subsequently spread to France, Germany, the U.K. and other European countries. Though, expensive, than the more established bleaching agents (for instance sodium hypochlorite and hydrogen peroxide), sodium chlorite was preferred for shorter and safer bleaching operation. In some instances, it was possible to bleach unscoured cotton, since bleaching with sodium chlorite obviated the need for kier boiling operation.

The use of sodium chlorite raised problems of corrosion of equipment and evolution of undesirable chlorine dioxide gas. In order to overcome these problems, use of special quality stainless steel, containing molybdenum was recommended along with corrosion inhibiting chemicals and auxiliaries. However, strict pollution control regulation resulted in the ouster of sodium chlorite as general purpose textile bleaching agent.

Subsequently, introduction of synthetic fibres gave an impetus to the use of sodium chlorite, since it is the only bleaching agent which is able to effectively bleach these fibres.

In most of the bleaching processes, acidified sodium chlorite is used at high temperature. This results in excessive evolution of chlorine dioxide. A search is on for an activator which could decompose sodium chlorite at a lower temperature and thereby overcome the problem of chlorine dioxide evolution. Scores of chemicals have been patented which are claimed to activate sodium chlorite at low temperature. Some of them are :

formaldehyde, chloral hydrate, organic esters, acid liberating salts, sodium dichloroisocyanurate etc.

In the present study, two compounds namely triethanolamine hydrochloride (TEA.HCl) and sodium dichloroisocyanurate have been evaluated for their effectiveness as low temperature activators for sodium chlorite bleaching. Furthermore, in order to work out a cost effective process, the scouring and the bleaching steps have been combined.

The first part of the work (Part 3 of the thesis) has been framed to study the possibility of combining scouring and bleaching of desized cotton fabric at low temperature by using an emulsifiable solvent formulation as scouring agent and TEA.HCl activated sodium chlorite as bleaching agent.

For this study, enzymatically desized cambric cotton fabric has been used. The process variables namely scouring agent concentration, sodium chlorite concentration, activator concentration, treatment temperature and treatment time have been varied at 5 levels. The response surface methodology has been applied to correlate the effect of variables upon the properties of the scoured/bleached fabric. Three important properties namely whiteness index, wetting time and per centage loss in strength have been measured. The process variables have been optimised using canonical analysis. The necessary computer program developed for the analysis was run on an ICL 2960 mainframe computer. The optimum treatment conditions from the statistical analysis worked out to be : Scouring agent 4.5%, sodium chlorite 1.4%, activator 0.6%, treatment temperature 60°C and treatment time 330 to 390 min.

The kinetics of decomposition of triethanolamine hydrochloride catalysed sodium chlorite on a cotton fabric has been investigated at 50 °C for various concentration of triethanolamine hydrochloride ranging from 0.25 to 1.00%. From this study it has been observed that the decomposition of sodium chlorite follows a first order kinetics for 0.25% and 0.50% triethanolamine hydrochloride concentrations. The kinetics of decomposition of sodium chlorite in presence of triethanolamine hydrochloride in aqueous medium at various temperature and pH has also been investigated. The decomposition products of the reaction have been analysed for the presence of aldehyde and carboxylic groups. It has been observed that the by-product contains only aldehyde groups. The extent of aldehyde group formation increased with increase in concentration of activator. From these observations, it is proposed that, in order to effectively utilise sodium chlorite for bleaching, the activator concentration should be kept below 0.5% owf.

In spite of its being fibre-gentle, sodium chlorite works out to be expensive and hence it is not generally used for bleaching 100% cotton fabric. However, it is the most satisfactory bleaching agent for polyester. The scouring/bleaching process, optimised in the first part has been subsequently tried on a desized polyester/cotton (67/33) blended fabric in the second part of the study (Part 4 of the thesis). The study has been conducted on similar lines using a three variable and five level response design. The process variables namely, bleaching

agent concentration, temperature and treatment time have been optimised by canonical analysis.

The optimised recipe has been worked out, taking the whiteness index, wetting time and percentage strength loss of conventionally prepared fabric as standard. The results obtained with the optimised recipe are almost identical to those, achievable in a commercial preparatory process. The optimum treatment conditions for the above mentioned fabric are: scouring agent concentration 2% owf, bleaching agent concentration 0.8% owf, activator concentration 0.4% owf, time of treatment 7-8 h, treatment temperature 55°C.

As stated earlier, various organic compounds have been patented which can activate sodium chlorite at low temperatures. These compounds either get oxidised into acids or liberate acids on hydrolysis. One such compound which has been very recently patented is sodium dichloroisocyanurate.

In the third part (Part 5 of the thesis), a low temperature combined scouring/bleaching process for two different varieties of desized, polyester/cotton blend fabrics (48/52 and 67/33) has been worked out using sodium dichloroisocyanurate activated sodium chlorite. The effect of process parameters namely, bleaching agent concentration, activator concentration and treatment temperature on whiteness index of the treated fabrics have been investigated using a response surface methodology. Since the best fitted regression equation is of a third order polynomial, the canonical optimisation is not possible. Hence the optimisation has been carried out by penalty function method. By this method, the optimum treatment conditions can be obtained within

the feasible region and the other advantage of penalty function optimisation is that, the function itself can be taken as a constraint. The program developed has been run on the ICL 2960 mainframe computer to obtain the most economic recipe.

The kinetics of decomposition of sodium chlorite in presence of sodium dichloroisocyanurate has been investigated and it seems to follow first order reaction kinetics. The activator is susceptible to hydrolysis at room temperature (20-30 °C). On hydrolysis, hydrochloric acid is liberated. The liberated hydrochloric acid causes quaternisation of nitrogen atom, which increases its electrophilic character and hence accelerates the hydrolysis. The reaction is thus autocatalytic. During the course of hydrolysis, the first chlorine atom reacts at lower temperature and the second chlorine atom is replaced at or above 60°C, which has been substantiated by higher rate constants.

In the fourth part of the present study (Part 6 of the thesis), a recipe for combined scouring/bleaching of polyester/cotton blended fabric has been worked out using a foamed scouring/bleaching composition. The foam padded fabrics were processed in a laboratory model Vaporloc machine.

The fabric selected for investigation is a desized polyester/cotton 67/33 blend. For this process, a composition was prepared by emulsifying nonylphenol 10 EO condensate (non-ionic emulsifier), perchloroethylene, sodium chlorite and formic acid together. This composition was then converted into a foam with a derivative of sodium lauryl sulphate (SLS) based foaming agent and applied onto the fabric in a vertical mangle. The

padded fabric was steamed in a laboratory model Vaporloc machine for different time periods to achieve required whiteness.

The effect of three process variables namely, bleaching agent concentration, residence time inside pressure chamber and treatment temperature upon whiteness index have been optimised by using Box and Behnkan response surface design methodology.

The salient features of the investigation have been summarised in the last part of the thesis (Part 7).

CONTENTS

ABSTRACT

PART 1	INTRODUCTION AND REVIEW OF LITERATURE	1
1.1	COTTON	1
1.1.1	Adventitious Impurities	2
1.1.2	Removal of Adventitious Impurity	4
1.2	SCOURING	5
1.2.1	Alkali Boiling	5
1.2.2	Scouring Assistants	6
1.2.3	Scouring Methods	7
	1.2.3.1 Kier Boiling	7
	1.2.3.2 Processing in J-boxes	8
	1.2.3.3 Pad-roll Steam Process	8
	1.2.3.4 Scouring on Jiggers	9
	1.2.3.5 Continuous Pressure Steamers	9
	1.2.3.6 Continuous Roller and Combination Steaming Processes	9
	1.2.3.7 Steam-purging System	9
1.2.4	Solvent Scouring	10
1.2.5	The Solvent Assisted Scouring Process	10
1.3	BLEACHING	11
1.3.1	Bleaching with Hypochlorite	12
1.3.2	Bleaching with Hydrogen Peroxide	13
1.3.3	Bleaching with Sodium Chlorite	14
	1.3.3.1 Properties of Sodium Chlorite	15
	1.3.3.2 Advantages and Disadvantages of Chlorite Bleaching	16
	1.3.3.3 Mechanism of Chlorite Bleaching	16

1.3.3.4	Machinery Modification/Developments for Sodium Chlorite Bleaching	19
	Batch-wise Bleaching	
	Semi-continuous Machines	
	Continuous open-width bleaching plant	
1.3.3.5	Activated Chlorite Bleaching	20
	Formaldehyde and Formaldehyde Adducts	
	Chloral Hydrate	
	Hydrolysable Organic Esters	
	Sodium Salts	
	Ammonium Salts	
	Peroxygen Compounds	
	Sodium Dichloroisocyanurate	
	Acid Liberating Salts of Aliphatic Amines	
1.4	POLYESTER	27
1.4.1	Preparation Process for Polyester/Cellulosic Blends	29
1.4.1.1	Desizing of Polyester/Cellulosic Blends	29
1.4.1.2	Scouring of Polyester/Cellulosic Blends	30
1.4.1.3	Bleaching of Polyester/Cellulosic Blends	31
1.4.2	Single-stage Preparatory Processes for Polyester/Cotton Blends	32
1.5	RECENT TRENDS IN FABRIC PREPARATION	33
1.5.1	Two-stage Combined Preparatory Processes	34
1.5.2	Single-stage Combined Preparatory Processes	36
1.5.3	Low Temperature Preparatory Processes	39
1.6	SUMMARY	42
PART 2	STATISTICAL METHODOLOGY	44
2.1	FACTORIAL DESIGN	45
2.2	CENTRALLY ROTATABLE COMPOSITE DESIGNS	46
2.2.1	Yates Algorithm	52
2.3	INCOMPLETE BLOCK DESIGN	52
2.4	GENERAL CRITERIA OF THE FITTED MODEL	58

2.5	MATRIX METHODOLOGY	62
2.5.1	Analysis of Variance	63
2.5.2	Fisher F-ratio	64
2.5.3	Multiple Correlation Coefficient	64
2.5.4	R Squared Bar	64
2.5.6	Estimation of Significant b Coefficients (Students' t-test)	66
PART 3	LOW TEMPERATURE SCOURING/BLEACHING PROCESS FOR COTTON USING TEA.HCl ACTIVATED SODIUM CHLORITE	68
3.1	EFFECT OF pH	68
3.2	EXPERIMENTAL	70
3.2.1	Materials	70
3.2.2	Desizing	71
3.2.3	Chemicals	71
3.3	TEST METHODS	72
3.3.1	Evaluation of Whiteness Index	72
3.3.2	Wettability Measurement	72
3.3.3	Measurement of Tensile Strength	72
3.3.4	Estimation of Sodium Chlorite Content on Fabric	73
3.3.5	Colourimetric Estimation of Aldehyde Groups	74
3.4	FABRIC TREATMENT	75
3.5	EXPERIMENTAL DESIGN	75
3.5.1	Canonical analysis	79
3.5.2	Optimisation	85
3.6.	RESULTS AND DISCUSSION	86
3.6.1	Whiteness Index	91
3.6.2	Wetting Time	94
3.6.3	Fabric Strength	99

3.7	MECHANISM AND KINETICS OF DECOMPOSITION OF TEA.HCl ACTIVATED SODIUM CHLORITE SYSTEM	99
3.8	CONCLUSION	109
PART 4	PROCESS FOR COMBINED SCOURING/BLEACHING OF POLYESTER/ COTTON BLENDED FABRIC AT LOW TEMPERATURE	111
4.1	SCOPE OF THE WORK	112
4.2	EXPERIMENTAL	113
4.2.1	Fabric	113
4.2.2	Chemicals	113
4.3	TEST METHODS	114
4.3.1	Whiteness Measurement	114
4.3.2	Wettability Measurement	114
4.3.3	Tensile Strength Measurement	114
4.4	SAMPLE PREPARATION AND EXPERIMENTAL DESIGN	114
4.5	RESULTS AND DISCUSSION	118
4.5.1	Whiteness Index	122
4.5.2	Fabric Strength	126
4.5.3	Wetting Time	130
4.6	OPTIMISATION	132
PART 5	A LOW TEMPERATURE COMBINED SCOURING/BLEACHING PROCESS FOR POLYESTER/COTTON BLENDED FABRICS USING SODIUM DICHLOROISOCYANURATE ACTIVATED SODIUM CHLORITE SYSTEM	134
5.1	SCOPE OF THE WORK	135
5.2	MATERIALS	135
5.2.1	Fabrics	135
5.2.2	Desizing	136
5.2.3	Chemicals	137
5.2.4	Pad-bath Formulation	137

5.3	TESTING PROCEDURE	137
5.3.1	Whiteness Measurement	137
5.3.2	Wetting Time Measurement	138
5.4	EXPERIMENTAL PLAN	138
5.5.	OPTIMISATION PROCEDURE	142
5.6	RESULTS AND DISCUSSION	146
5.6.1	General Observations	146
5.6.2	Optimisation	147
	5.6.2.1 Fabric 1	147
	5.6.2.2 Fabric 2	152
5.7	DECOMPOSITION OF SODIUM CHLORITE IN PRESENCE OF SODIUM DICHLOROISOCYANURATE	159
PART 6	COMBINED SCOURING/BLEACHING PROCESS USING FOAMED SODIUM CHLORITE COMPOSITION	165
6.1	FOAM PROCESSING	165
6.1.1	Historic Developments of Foam Processes	166
6.1.2	Advantages of Foam Processing	166
6.1.3	Foam Formulation	167
6.1.4	Classification of Foams	167
6.1.5	Principl of Foam Generators	167
6.1.6	Physical Properties of Foam	168
6.1.7	Half Life of Foam	168
6.1.8	Bubble Size	169
6.1.9	Foam Processing Machines	169
6.1.10	Dynamic Absorption Rate	171
6.2	OPEN WIDTH PROCESSING MACHINES	171
6.2.1	Combination Steamers	172

6.2.2	Pressure Steamer	172
6.3	SCOPE OF THE PRESENT WORK	173
6.4	MATERIALS AND METHODS	174
6.4.1	Fabric	174
6.4.2	Desizing	174
6.4.3	Bleaching Agent	174
6.4.4	Scouring Formulation	175
6.4.5	Foaming Agent	175
6.4.6	Foam Preparation	175
6.4.7	Vaporloc Machine Particulars	176
6.5	TESTING PROCEDURE	176
6.6	EXPERIMENTAL PLAN	178
6.7	RESULTS AND DISCUSSION	178
6.8	OPTIMISATION	187
PART 7	CONCLUSIONS	188
	REFERENCES	193
	LIST OF PUBLICATIONS	
	APPENDICES	