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TEXTILE SCIENCE AND TECHNOLOGY

S.R. KARMAKAR

CHEMICAL TECHNOLOGY IN THE PRE-TREATMENT PROCESSES OF TEXTILES

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CHEMICAL TECHNOLOGY IN THE PRE-TREATMENT PROCESSES OF TEXTILES

BY

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PREFACE

Textile chemical processing today, particularly the pre-treatment processes require a highly sophisticated technology and engineering to achieve the well known concepts of "Right first time, Rigtht everytime and Right on time" processing and production. Chemical pre-treatment may be broadly defined as a procedure mainly concerned with the removal of natural as well as added impurities in fabric to a level necessary for good whiteness and absorbancy by utilising minimum time , energy and chemical as well as water.

This book discusses the fundamental aspects of chemistry, chemical technology and machineries involved in the various pre-treatment process of textiles before subsequent dyeing, printing and finishing. With the introduction of newer fibres, specialty chemicals, improved technology and sophisticated machineries developed during the last decade, all attempts have been made to fill a gap in this area of technology. New chapters are integrated and introduced to upgrade the information and the subject matter and contents are so chosen that it will permit the teacher to rearrange units to suit the needs of individual groups of students. Efforts are also made to provide an in-depth exposition of the topic with a review of the most exciting recent developments in the rapidly moving field. But the real strength of this book is its clear perception of ample background description , which will enable to understand most current journals empowering the reader to stay abreast of the latest advances in the field.

The interplay between fibre structure, morphlogy and chemistry is an integral part of all pre-treatment processes and in Chapter 1 an attempt is made to cover the most up-to-date information regarding all the principal classes of fibres, viewed in the light of research and commercial exploitation. Chapter 2 is devoted to mechanical fabric preparation before chemical processing commences to achieve smooth and trouble free results in subsequent dyeing and finishing. Chapter 3 discusses the chemistry of different sizing agents with respect to their removal from the fabrics. Chapter 4 covers a purifying treatment of textiles to reduce the amount of natural impurities sufficiently to enable level and reproducible dyeings and finishing to be produced. Specialty chemicals have very high value in the chemical processing of textiles and the applications of chemical auxiliaries are included in the relevent processes. Chapter 5 describes the various machineries that have been developed

for the purifying operations. Chapter 6 deals with the detailed understanding of various bleaching agents and their mechanisms or mode of action on various fibres. The chemistry, technology and care guides are included seperately for each fibre and blended fiber fabrics . New machineries have been developed for the bleaching of textiles and Chapter 7 looks at the machineries involved in such process. Recent technological advances of mercerizing and heat-setting of textiles are included in Chapters 8 and 9 respectively. Textile fibres do not appear perfectly white even after chemical bleaching and Chapter 10 describes the chemistry and mechanism of optical brightening agents as well as their applications to various kinds of fibers. All serious efforts have been directed in Chapter 11 towards shortened or combined pre-treatment processing in order to minimize energy consumption. Chemical degradation or damages caused by improper application of processes, erroneous concept of procedure, faulty operation of machines and chemicals are critically reviewed in Chapter 12. A changing concern in matters relating to environmental pollution from pre-treatment processes involved in textile mills and processing house in particular is increasingly demanded and thus all these varied developments in legislation , in analysis and standards and in treatments are included in Chapter 13. Pre-treatment or surface modification of textiles with low temperature glow-discharges or plasma is of great interest in near future and Chapter 14 discusses its application as an alternative to conventional techniques. Enzymatic pre-treatment (a biological approach) is becoming an important commercial process and Chapter 15 contains the development in the field of enzyme treatments for textiles. Testing, analyses and evalutation of the efficiency of processes present the time domain approach to modern process control, which allows for the formation of precise performance objectives that can be examined. Thus, Chapter 16 will be a valuable resource for practicing process control technologists and students.

I hope the reader will find the book interesting and useful with suggested references in each chapter along with simplified flow diagrams showing various processes and machineries involved in pre-treatment technology of textiles. No single text can be sufficient unto itself . Any constructive suggestions and comments are therefore welcome for future revesions and corrections.

Serampore,Hooghly, West Bengal,
(India), April 1999.

Samir Ranjan Karmakar

CONTENTS

Preface v

Chapter 1 **Kinds of fibres** **1**

1.1 Introduction 1

1.2 Classification of fibres 1

1.3 Chemical composition, morphology and structure of cotton 3

1.3.1 Cotton impurities 5

1.4 Natural protein fibres 8

1.4.1 Molecular structure of wool fibres 8

1.4.2 Impurities in raw wool 13

1.4.3 Morphology and chemical structure of silk 14

1.5 Long vegetable fibres 16

1.5.1 Flax (linen) 17

1.5.2 Remie 18

1.5.3 Hemp 19

1.5.4 Jute 19

1.6 Regenerated natural fibres 22

1.6.1 Cuprammonium rayon 22

1.6.2 Viscose rayon 22

1.6.3 Acetate fibres 25

1.6.4 Regenerated protein fibres 26

1.7 Synthetic fibres 27

1.7.1 Polyester 27

1.7.2 Nylon 29

1.7.3 Acrylic fibres 34

1.7.4 Olefin fibres 37

1.8 Miscellaneous synthetic fibres 38

1.8.1 Chlorofibres 39

1.8.2 Poly(vinyl alcohol) fibres 39

1.8.3 Elastomeric fibres 40

1.8.4 Carbon fibres 41

1.8.5 PTO fibres (Enkatherm) 42

1.8.6 Other synthetic fibres 42
References 44

Chapter 2 **Preparation before chemical processes** **49**
2.1 Introduction 49
2.2 Inspection 49
2.3 Sewing 51
2.4 Mechanical cleaning of fabrics 52
2.4.1 Brushing 52
2.4.2 Cropping and shearing 52
2.5 Singeing 55
2.5.1 Singeing different kinds of fibres fabrics 56
2.5.2 Plate singeing machine 57
2.5.3 Rotary cylinder machine 58
2.5.4 Gas singeing machine 58
2.5.5 Singeing circular knit fabrics 63
2.6 Process sequence 65
2.6.1 Cotton fabric on kier 65
2.6.2 Cotton fabric on J-Box 66
2.6.3 Cotton fabric on pad-roll/thermoreaction chamber (T.R.C.) 66
2.6.4 Cotton fabric on Jumbo jigger 66
2.6.5 Knitted cotton goods 66
2.6.6 Woollen fabrics 67
2.6.7 Silk fabrics 67
2.6.8 Polyester fabrics 67
2.6.9 Nylon fabrics 67
2.6.10 Polyester/cotton blends 67
2.6.11 Polyester/viscose blends 68
2.6.12 Polyester/wool blends 68
2.6.13 Diacetate/viscose blends 68

Chapter 3 **Desizing** **69**
3.1 Introduction 69
3.2 Methods of desizing 71
3.2.1 Rot steeping 72

3.2.2 Acid desizing 72
3.2.3 Enzymatic desizing 72
3.2.4 Desizing with oxidising agents 75
3.3 Desizing of synthetic fabrics and their blends 77
3.4 Desizing machineries 79
References 84

Chapter 4 **Scouring** **86**
4.1 Introduction 86
4.2 Mechanism of removal of impurities 87
4.3 Scouring of cotton in alkaline agents 89
4.3.1 The lime-soda boil 89
4.3.2 The caustic soda boil 89
4.3.3 The soda-ash boil 90
4.3.4 The mixture of caustic soda and soda-ash boil 90
4.3.5 The soap/detergent-soda-ash boil 90
4.3.6 Sequestering agents 91
4.3.7 Builders 93
4.3.8 Fibre protecting reducing agents 94
4.3.9 Mild oxidising agents 94
4.3.10 Water insoluble solvents 94
4.4 Surfactants 94
4.4.1 Anionic surfactants 95
4.4.2 Cationic surfactants 96
4.4.3 Non-ionic surfactants 97
4.4.4 Amphoteric surfactants 98
4.4.5 Blends of surfactants 99
4.4.6 Surfactants as wetting agent 99
4.4.7 Surfactants as detergent (scouring agent) 101
4.4.8 Emulsion scouring 103
4.5 Solvent scouring 106
4.6 Scouring of raw wool 107
4.6.1 Emulsion scouring 108
4.6.2 Suint scouring 109
4.6.3 Solvent extraction scouring 109
4.6.4 Refrigeration process 109

4.7	Scouring wool yarn and fabric	109
	4.7.1 Setting and scouring of wool yarn	109
	4.7.2 Crabbing (setting) of woollen fabric	110
	4.7.3 Potting of woollen fabric	110
	4.7.4 Scouring of wool fabric	113
4.8	Carbonising of wool	113
4.9	Degumming of silk	114
	4.9.1 Degumming in water	116
	4.9.2 Degumming with alkali and acid	116
	4.9.3 Degumming with soap	116
	4.9.4 Degumming with synthetic detergents	116
	4.9.5 Enzymatic degumming	117
	4.9.6 Foam degumming	117
	4.9.7 Partial degumming	117
	4.9.8 Washing of degummed silk	118
4.10	Degumming of remie	118
4.11	Scouring of linen	119
4.12	Scouring of jute	120
4.13	Scouring of synthetic-polymer fibres	120
	4.13.1 Polyester	121
	4.13.2 Nylon	121
	4.13.3 Polyacrylonitrile fibres	122
	4.13.4 Acetate fibres	123
	4.13.5 Regenerated cellulose	123
	4.13.6 Texturised fabrics	123
4.14	Scouring of blended fibre fabrics	125
	4.14.1 Polyster/cotton	125
	4.14.2 Polyester/wool	126
	4.14.3 Polyester/acrylic	122
	4.14.4 Acrylic/wool	127
	4.14.5 Acrylic/cellulosics	127
	4.14.6 Acetate/wool	128
	4.14.7 Blends containing viscose	128
	4.14.8 Polyester/silk	129
	4.14.9 Blends containing casein	129
References		129

Chapter 5 **Scouring machineries** **132**
5.1 Introduction 132
5.2 Batch type (rope) scouring machines 132
5.2.1 Low pressure kier 132
5.2.2 High pressure kier 133
5.2.3 Jafferson-Walker's kier 134
5.2.4 Gebauer kier 135
5.3 Batch type (open-width) scouring machines 135
5.3.1 Mather and Platt horizontal kier 135
5.3.2 Jackson kier 136
5.3.3 Jig process 137
5.4 Semi-continuous scouring machines 138
5.4.1 Padd-roll system 138
5.4.2 Padd-steam-roll system 138
5.4.3 Padd-roll on perforated cylinder 138
5.5 Continuous scouring machines 138
5.5.1 Saturator J-Box-rope washer 138
5.5.2 Open-width roller steamer 139
5.5.3 Batch or re-batching system 139
5.5.4 Vaporloc system 140
5.5.5 High pressure Klienewefer roller steamer 141
5.5.6 Conveyer storage steamer system 142
5.5.7 Roller-bed steamer with pre-swelling time 142
5.5.8 Continuous relaxing/scouring machines 142
5.5.9 Solvent scouring machines 144
5.6 Wool scouring machines 145
5.6.1 Raw wool scouring machines 145
5.6.2 Wool hank scouring machines 147
5.6.3 Wool fabric scouring machines 147
5.6.4 Carbonising range for woollen fabric 150
5.6.5 Crabbing and decatising machines 152
5.7 Silk degumming machines 156
5.7.1 Yarn degumming machines 156
5.7.2 Piece goods degumming machines 156
References 158

Chapter 6 **Bleaching of textiles** **160**
6.1 Introduction 160
6.2 Bleaching with hypochlorites 161
6.2.1 Calcium hypochlorite (bleaching powder) 161
6.2.2 Sodium hypochlorite 162
6.2.3 Lithium hypochlorite and chlorinated trisodium phosphate 163
6.2.4 Factors effecting hypochlorite bleaching operations 164
6.2.5 Accelerated hypochlorite bleaching 166
6.2.6 Advantages of hypochlorite bleaching over bleaching powder 167
6.2.7 Disadvantages of sodium hypochlorite bleaching over bleaching powder 168
6.3 Bleaching with peroxides 168
6.3.1 Mechanism of peroxide bleaching 170
6.3.2 Stabilisers for peroxide bleaching 170
6.3.3 Parameters in peroxide bleaching operations 172
6.4 Bleaching of wool with hydrogen peroxide 173
6.4.1 In alkaline hydrogen peroxide 174
6.4.2 In acidic hydrogen peroxide 174
6.4.3 Alkaline peroxide followed by hydrosulphite treatment 175
6.4.4 Mordanting and peroxide bleaching 175
6.4.5 Sequential oxidative and reductive bleaching 176
6.4.6 In emulsion of hydrogen peroxide 178
6.5 Bleaching of silk with hydrogen peroxide 178
6.6 Bleaching of synthetic fibres with peroxide 180
6.6.1 Regenerated cellulose 180
6.6.2 Acetate fibres 180
6.6.3 Acrylic fibres 180
6.7 Advantages and disadvantages of peroxide over hypochlorite bleaching 181
6.8 Bleaching with sodium chlorite 182
6.8.1 Mechanism of bleaching 182
6.8.2 Bleaching of cotton 183
6.8.3 Bleaching of polyester 184
6.8.4 Bleaching of nylon 184

	6.8.5 Bleaching of acetate fibres	185
	6.8.6 Bleaching of polyacrylonitrile	185
	6.8.7 Bleaching of polyvinyl alcohol	186
	6.8.8 Problem of corrosion and its prevention	186
	6.8.9 Merits and demerits of chlorite bleaching	187
6.9	Bleaching with peracetic acid	188
	6.9.1 Cotton	190
	6.9.2 Nylon	190
	6.9.3 Cellulose acetate	191
	6.9.4 Acrylics	191
	6.9.5 Merits and demerits	191
6.10	Reductive bleaching of wool	192
	6.10.1 Sulphur dioxide	192
	6.10.2 Sodium bisulphite	193
	6.10.3 Sodium hydrosulphite	193
	6.10.4 Thio-urea bleaching of wool	194
	6.10.5 Photo-bleaching of wool	194
6.11	Bleaching of silk with reducing agents	194
6.12	Reductive bleaching of nylon	195
6.13	Peroxygen bleaching compounds	196
6.14	Bleaching of jute	196
	6.14.1 Hypochlorite	197
	6.14.2 Hydrogen peroxide	197
	6.14.3 Sodium chlorite	198
	6.14.4 Peracetic acid	198
	6.14.5 Drawbacks in bleaching of jute	199
	6.14.6 Causes of yellowing and improvement of photostability of bleached jute	199
6.15	Bleaching of linen	201
6.16	Bleaching of blended fabrics	203
	6.16.1 Polyester/cotton	203
	6.16.2 Polyester/wool	206
	6.16.3 Nylon/cellulose	206
	6.16.4 Nylon/wool	207
	6.16.5 Acrylic/cellulose	207
	6.16.6 Acrylic/wool	208

6.16.7 Acetate/cellulose 208
6.16.8 Polyester/linen 208
6.16.9 Wool/viscose 209
6.16.10 Viscose/cotton 209
6.17 Bleaching of cotton weft knitted fabrics 209
References 211

Chapter 7 **Bleaching and washing equipment** **217**
7.1 Introduction 217
7.2 Batch bleaching process machineries 217
7.3 Semi-continuous bleaching process machineries 222
7.4 Continuous bleaching by J-Box systems 224
7.5 Continuous open-width bleaching equipment 230
7.5.1 Steamers without plaited storage 232
7.5.2 Conveyer steamer without pre-steeping zone 232
7.5.3 Conveyer steamer with pre-steeping zone 234
7.5.4 Pressureless or Combi-steamers 236
7.5.5 Submerged bleaching systems 238
7.6 Washing equipment 240
7.6.1 Rope washing machines 241
7.6.2 Open-width washing machines 247
References 257

Chapter 8 **Heat-setting** **259**
8.1 Introduction 259
8.2 Thermal behaviour of synthetic fibres 259
8.3 Stages of heat-setting 260
8.4 Methods of heat-setting 261
8.4.1 Contact method 261
8.4.2 Steam-setting method 261
8.4.3 Hydro-setting method 262
8.4.4 Heat-setting using tenter frame 263
8.4.5 Selective infra-red emitters method 266
8.5 Heat-setting conditions for different kinds of fibres 267
8.5.1 Polyester fabrics 267
8.5.2 Nylon fabrics 267

8.5.3 Texturised fabrics 268
8.5.4 Acrylic and modacrylic fabrics 269
8.5.5 Cationic dyeable polyester 269
8.5.6 Triacetate fibres 269
8.5.7 Polyvinyl chloride fibres 270
8.5.8 Elastomeric fibres 271
8.6 Heat-setting of blended fibre fabrics 271
8.6.1 Polyester/cotton 271
8.6.2 Polyester/wool 271
8.6.3 Polyester/linen 272
8.6.4 Polyester/silk 272
8.6.5 Polyvinyl chloride/cellulosics 272
8.7 Effect of heat-setting on properties of synthetic fibres 272
8.7.1 Structural changes 272
8.7.2 Dimensional stability 273
8.7.3 Stiffness 275
8.7.4 Crease recovery 275
8.7.5 Dyeability 276
References 277

Chapter 9 **Mercerization** **279**
9.1 Introduction 279
9.2 Conditions for mercerization 279
9.3 Changes in properties of cellulose on mercerization 288
9.3.1 Swelling and shrinkage 281
9.3.2 Structural modification 285
9.3.3 Increased lustre 286
9.3.4 Gain in strength 288
9.3.5 Increased moisture absorption 288
9.3.6 Increased dye absorption 289
9.3.7 Increased reactivity 290
9.3.8 Removal of immature cotton 290
9.3.9 Physical compactness 290
9.4 Mercerization of remie and flax fibres 290
9.5 Mercerization of blended fibre fabrics 291
9.6 Mercerizing machineries 292

9.6.1 Cloth (woven) mercerizing machines 293
9.6.2 Yarn mercerizing machines 302
9.6.3 Knit goods mercerizing machines 303
9.7 Hot mercerization 306
9.8 Liquid ammonia mercerization 309
References 315

Chapter 10 **Optical brightening agents** **320**
10.1 Introduction 320
10.2 Chemical constitution of optical brighteners 321
10.3 Mechanism of fluorescent whitening 323
10.4 Factors influencing the functions of optical whiteners 323
10.4.1 Substrate 324
10.4.2 Saturation 324
10.4.3 Method of application 324
10.4.4 Time 324
10.4.5 Temperature 324
10.4.6 pH 325
10.4.7 Salt 325
10.5 Application of optical brighteners 325
10.5.1 Cellulose fabrics 326
10.5.2 Woollen fabrics 327
10.5.3 Silk fabrics 328
10.5.4 Polyester 328
10.5.5 Nylon 329
10.5.6 Polyacrylonitrile 330
10.5.7 Cationic dyeable polyester 331
10.5.8 Polyvinyl chloride 332
10.5.9 Other synthetic polymers and plastics 332
10.5.10 Blended fibre fabrics 332
References 334

Chapter 11 **Combined pre-treatment processes of textiles** **336**
11.1 Introduction 336
11.2 Combined scouring and desizing 336
11.3 Combined scouring and bleaching 337

11.4 Combined desizing, scouring and bleaching 339
References 342

Chapter 12 Degradation of fibres associated with chemical pre-treatment processes 344
12.1 Introduction 344
12.2 Degradation of cotton during desizing 344
12.3 Degradation of cotton during scouring 346
12.4 Degradation of cotton during bleaching 350
12.4.1 Hypochlorite bleaching and damage 350
12.4.2 Peroxide bleaching and damage 353
12.5 Damage of wool during pre-treatment processes 354
12.6 Damage of silk during pre-treatment processes 356
12.7 Damage of polyester during pre-treatment processes 357
References 357

***Chapter 13* Conservation of energy and water, economy and effluent control in pre-treatment processes 360**
13.1 Water consumption in textile industry 360
13.2 Impurities in water 361
13.3 Water purification 363
13.3.1 Soda-alum process 363
13.3.2 Lime-soda process 363
13.3.3 Base exchange process 364
13.4 Economy through energy conservation 364
13.4.1 Efficient generation of energy and minimum consumption 365
13.4.2 Mechanical removal of water before drying 365
13.4.3 Increased efficiency of drying and heat-setting 365
13.4.4 Reduced liquor to material ratio 366
13.4.5 Efficient heat recovery 366
13.4.6 Heat recovery from process effluents 367
13.5 Economy through water conservation 367
13.5.1 Minimising liquor to material ratio 367
13.5.2 Minimising wash liquor 367
13.5.3 Re-using rinsing bath water 367

13.5.4 Direct steam injection 368
13.6 Economy through process modification 368
13.6.1 Vaporloc bleaching 368
13.6.2 J-Box bleaching 368
13.6.3 Solvent scouring 368
13.6.4 Cold bleaching 369
13.6.5 Combined processing 369
13.6.6 Shortening of process sequence 369
13.7 Pollution aspects in pre-treatment processes of textiles 370
13.7.1 Water and air pollution 370
13.7.2 Parameters for assessment of harmful materials in waste water 372
13.8 Pollution load and pre-treatment processes 374
13.8.1 Desizing effluents 376
13.8.2 Scouring effluents 377
13.8.3 Bleaching effluents 378
13.8.4 Auxiliary effluents 379
13.9 Waste water treatment from pre-treatment plants 380
13.10 Protective measures for ultra-violet radiation 390
References 391

Chapter 14 **Pre-treatment of textiles under plasma conditions** **395**
14.1 Introduction 395
14.2 The concept of plasma 395
14.2.1 Corona discharge 396
14.2.2 Glow-discharge 396
14.3 Generation of plasma and its action 397
14.3.1 Machine performance for producing plasma 398
14.3.2 The interaction of plasma with substrate 404
14.4 Surface modification of fabrics under plasma treatment 407
14.4.1 Plasma treatment of wool 407
14.4.2 Plasma treatment of other fabrics 410
14.5 High energy radiation of textiles 412
References 414

Chapter 15 **Application of bio-technology in the pre-treatment processes of textiles** **418**
15.1 Introduction 418
15.2 Enzymes for textile application 418
15.2.1 The chemistry of enzymes 418
15.2.2 Mechanism of enzyme action on cotton 420
15.2.3 Parameters governing the cellulase treatments 422
15.2.4 Structural and morphological changes of fibres by enzymatic hydrolysis 423
15.2.5 The use and advantages of enzymatic processing 424
15.3 Treatment of cotton with enzymes 425
15.3.1 Enzymatic desizing of cotton and silk 426
15.3.2 Use of enzymes in mercerization 426
15.3.3 Enzymatic scouring and bleaching processes 426
15.3.4 Bio-polishing 428
15.3.5 Effect of cellulase treatment in washing processes 431
15.3.6 Stone washing 431
15.4 Treatment of protein fibres with enzyme 432
15.4.1 Wool carbonising 433
15.4.2 Wool bleaching 433
15.4.3 Shrink-proofing and modification of wool 434
15.5 Bio-technology and effluent treatment 435
References 436

Chapter 16 **Analysis and testing in preparatory processes** **441**
16.1 Introduction 441
16.2 Analysis of water 441
16.2.1 Suspended matter 442
16.2.2 Total soluble salts 442
16.2.3 Total hardness 442
16.2.4 Calcium hardness 443
16.2.5 Magnesium hardness 443
16.2.6 Temporary and permanent hardness 443
16.3 Analysis of non-cellulosic residues 443
16.3.1 Ash content (mineral matter) 443
16.3.2 Silicate and phosphate 444

16.3.3 Calcium and magnesium 444
16.3.4 Iron and copper 445
16.4 Evaluation of wax content in cotton 445
16.5 Evaluation of lubricants 446
16.5.1 Total fatty matter 446
16.5.2 Saponification value of an oil 447
16.5.3 Unsaponification matter 447
16.6 Determination of moisture content 447
16.7 Tests and analyses of sizes 448
16.7.1 Identification of sizes 449
16.7.2 Percentage size by ordinary method 451
16.7.3 Total size by Soxhlet method 451
16.7.4 Total size by enzyme method 451
16.8 Determination of the efficiency of scouring 452
16.8.1 Measurement of weight loss 452
16.8.2 Measurement of residual wax content 452
16.8.3 Practical test of absorbancy 452
16.8.4 Removal of motes (kitties) 453
16.9 Testing and evaluation of bleaching agents 453
16.9.1 Bleaching powder 455
16.9.2 Sodium hypochlorite 456
16.9.3 Sodium chlorite 456
16.9.4 Hydrogen peroxide 456
16.9.5 Stabilisers for peroxide bleach 457
16.9.6 Sodium hydrosulphite 457
16.9.7 Sodium bisulphite 457
16.9.8 Sodium silicate 458
16.10 Assessment of damage of cellulose 458
16.10.1 Determination of fluidity 458
16.10.2 Determination of Copper Number 460
16.10.3 Methylene Blue absorption test 461
16.10.4 Silver nitrate test 462
16.10.5 Determination of acidic groups by iodometric method 462
16.11 Assessment of damage of wool 463
16.11.1 Microscopic test 463
16.11.2 Swelling test 463

16.11.3 Solubility test 463
16.11.4 Spectrophotometric test 464
16.12 Determination of degree of mercerization 464
16.12.1 Deconvolution count 464
16.12.2 Swelling index 465
16.12.3 Benzopurpurine test 465
16.12.4 Sodium hydroxide spotting test 465
16.12.5 Goldthwait red-green test 466
16.12.6 Staining test 466
16.12.7 Barium activity number 466
16.12.8 Determination of lustre 467
16.12.9 X-ray analysis 467
16.12.10 Infra-red analysis 468
16.13 Evaluation of whitening efficiency of optical brighteners 468
16.13.1 Visual assessment 468
16.13.2 Extraction method 468
16.13.3 Instrumental analysis 469
16.14 Determination of degree of heat-setting 469
16.14.1 Shrinkage test 469
16.14.2 Crease recovery angle 469
16.14.3 Assessment of handle 469
16.14.4 Iodine absorption method 470
16.15 Determination of biodegradability of surfactants 470
16.15.1 Methylene Blue method 471
References 472

Subject index **474**

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Chapter 1

KINDS OF FIBRES

1.1 Introduction

Textile fibers consist of polymers. Polymers are long chain molecules which are formed by chemically joining the monomers and the process is known as polymerisation. The length of the chain is represented by degree of polymerisation (DP). If a polymer is formed from two or more monomers, it is called copolymer. To improve the properties of the fibre sometimes additional monomer is grafted on to the polymer chain.

With the introduction of new fibres during the last decade and increasing consumption of fibre blends it has become necessary to look at general fibre chemistry as the pre-treatment technology of one fibre is different to that of another. Table 1.1 gives some of the global textile fibre consumption data. The consumption of

TABLE 1.1

Global Fibre Demand

(Unit : 1000 tons : share % in consumption)

Fiber Type	1994	2000	Annual Growth (%)
Cotton	15160 (41.3)	16530 (31.2)	1.5
Wool	1520 (4.1)	1720 (4.1)	2.1
Cellulosic	2320 (6.3)	2280 (5.4)	-0.3
Synthetic	17720 (48.2)	21640 (51.3)	3.4

Source : The Japanese Ministry of International Trade & Industry.

cellulosic fibres is expected to decline marginally at the rate of 0.3%. The interplay between fibre structure, morphology and chemical composition is an essential part of all pre-treatment processes and thus, it is necessary to know the differences in the structures of different polymers and their effects on the properties of the fibres. There are many good books on this subject and hence only general fibre chemistry and manufacturing processes are presented in reference form and then proceeded to discuss how preparatory processes are chosen for use as fibre processing.

1.2 Classification of Fibres

Though textile fibres are classified by many systems, it is only in 1960, the Textile Fibre Products Identification Act (TFPIA) became effective. The classification shown in Table 1.2 is based on the principal origin of the fibre (natural or

TABLE 1.2
Classification of Textile Fibres [1]

Fibre

Natural Cellulosic Fibres	Natural Protein Fibres	Regenerated Natural Fibres	Synthetic Fibres
1. **seed hairs :** (a) cotton (b) milk weed (c) kapok (d) cattail	1. **animal hair fibres :** (a) wool (sheep) (b) specialty hair fibres like alpaca, Camel, Cashmere, guanaco, Ilama, mohair (angora goat), vicuna (c) fur fibres like mink, muskrat, angora, rabbit.	1. **rayon :** (a) Cuprammonium Bemberg (b) Viscose rayon like regular & high tenacity, high wet modulus, hollow fibires.	
2. **bast fibres :** (a) flax (b) remie (c) hemp (d) jute (e) sunn (f) kenaf (g) urena	2. **animal secretion :** (a) silk fibre like cultivated, dupioni, tussah, wild (b) spider silk.	2. **acetate :** (a) secondary acetate (b) tri-acetate.	
3. **leaf fibres :** (a) abaca (b) pineapple (c) agave (sisal, henequen)(d) palm (e) New Zeland flax (f) yucca (g) palma istle		3. **protein :** (a) casein (b) zein (c) peanut (d) soyabean.	
4. **fruit :** coir		4. **Miscellaneous :** (a) alginate (b) rubber.	
5. **mineral :** asbestos			

1. **condensation polymer fibres :**	2. **addition polymer :**	3. elastomers :	4. manmade **mineral :**	5. **other :**
(a) nylon 6,6, nylon 6, nylon type 11, 6, 10, aromatic type (Quina), bicomponent nylon (b) aramid like Kevlar and nomex (c) Polyester.	(a) anidex (b) acrylics (c) modacrylic (d) novoloid (e) nytril (f) olefin fibres like polyethylene, polypropylene (g) Saran (h) Vinal (i) Vinyon.	(a) Spandex (b) rubber (c) lastrile.	(a) glass (b) metallic.	(a) alginate (b) inorganic like Avceram, Fibrefax, Thornel (c) Organic like PBI, Teflon (d) biconstituent.

man-made), chemical type (cellulosic, man-made cellulosic), generic term (seed, hair, rayon) and common names and trade names of the fibres (cotton, viscose, rayon). However, this list of fibres under such category is not complete and for complete list books are to be referred [2,3].

1.3 Chemical Composition, Morphology and Structure of Cotton

The apparel industry is pre-dominantly cotton based and the share of cotton in total fibre consumption is about 70-75%. The cotton productivity of major countries is depicted in Table 1.3.

TABLE 1.3

Cotton Productivity 1992-'93

Country	Kg/Hectares
India	304
Brazil	384
Pakistan	550
China	660
USA	728
CIS (Formerly USSR)	728
Israel	1830

Source : Indian Textile Commissioner Statistics.

Cotton is single cell fibre and develops from the epidermis of the seed [4]. An elongation period continues for 17-25 days after flowering. Cotton consists of cellulosic and non-cellulosic material. A morphological structure of the cotton fibre is given in Fig. 1-1. The outer most layer of the cotton fibre is the cuticle, covered by waxes and pectins, and this surrounds a 'primary wall', built of cellu-

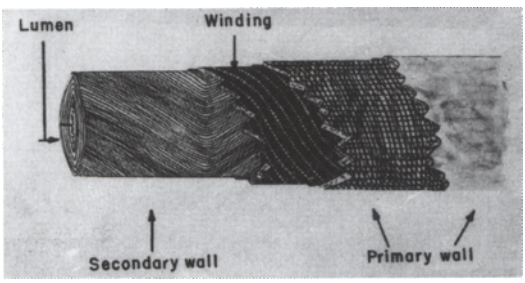


Figure 1-1. Concept of an idealized cotton fibre [5].

lose, pectins, waxes and proteinic material [6]. The inner part of the cotton fibre

comprises the 'secondary wall', subdivided into several layers of parallel cellulose fibrils, and the lumen. The smallest unit of the fibrils is the elementary fibril, consisting of densely packed bundles of cellulose chains [7], for which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions in a longitudinal direction. Inside the microfibrils a microcapillary system is developed [8]. These two capillary systems are responsible for swelling and absorption processes which are important for the pre-treatment of cotton [9]. The primary and secondary wall cellulose result from different polymerisation mechanisms [10].

Cotton consists of practically pure cellulose and may be chemically described as poly (1, 4-B-D- anhydroglucopyranose) (Fig. 1-2). The helical reversal struc-

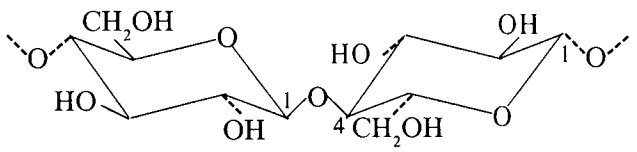


Figure 1-2. Molecular structure and configuration of cellulose [11].

ture of natural cellulose shows the constantly recurring cellobiose unit, consisting of two glucose units each with six carbon atoms. The length of unit cell along the fibre axis is 10.4Å calculated for the cellobiose unit. In natural cellulosic fibres there are 3000 - 5000 C_6 or glucose units joined together. This corresponds to a molecular weight of the order of 300,000 -500,000.

When cotton fibres dry from their initial fully swollen state, the cell wall collapse to give a typical kidney-shaped (Fig. 1-3) cross-sections and the different

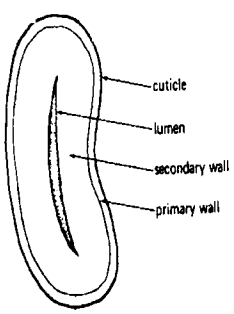


Figure 1-3. Diagram of a cotton fibre, cross-section.

regions of the cross-section have important differences in structure [12]. This is commonly referred to as 'bilateral structure' of the cotton fibre. The fibre is more

accessible to liquids on the concave side of the fibre, which could lead to uneven penetration. The spiral arrangement of microfibrils reverses direction on rotation periodically along the length of the fibre [13,14]. Accordingly, some relationship between convolution angle and fibre strength is established [15].

In the crystalline part, the cellobiose units are closely packed to form Cellulose I in native cellulose fibres and Cellulose II in regenerated cellulose fibres. In Cellulose I the chain molecules are parallel to one another [16]. The folded chain occurs at Cellulose II, in the crystalline regions the chain molecules are anti-parallel. Thus, the basis for helical structure for Cellulose I is preferably extended to the structure of Cellulose II [17].

1.3.1 Cotton impurities

The impurities in cotton fibre can range from 4 to 12% (o.w.f.) and the overall composition of cotton fibres are indicated in Table 1.4. Even after mechanical

TABLE 1.4
Composition of Mature Cotton Fibres

Constituents	Percentage by dry weight
α-cellulose	88.0 – 96.5
Protein	1.0 – 1.9
Wax	0.4 – 1.2
Ash (inorganic salts)	0.7 – 1.6
Pectins	0.4 – 1.2
Others (resins, pigments, hemi-cellulose, sugars, organic acids, incrusted ligneous substance)	0.5 – 8.0

ginning process, certain amount of seed-coat fragments, aborted seeds and leaves etc., clinge (adhere) to the fibre and these impurities are called 'motes'. The impurities in cotton fibre vary according to the fibre maturity [18] (Table 1.5). Cotton impurities are located largely on the outer side of the fibre (Table 1.6). The non-cellulosic material is mainly situated in the primary wall and the secondary wall is mainly composed of cellulose. Their quantity is higher when the fibre is finer, that

TABLE 1.5.
Influence of Maturity on the Impurities of Cotton Fibres (in percent of dry weight) [19]

Constituents	U. S. Cotton	
	Mature	Immature
Waxes	0.45	1.14
Proteins	1.01	2.02
Ash	0.71	1.32
Pectins	0.58	1.26

TABLE 1.6.
Proportion of Cellulosic and Non-cellulosic Material in Whole of Cotton Fibre and in Primary Wall [20]

Constituents	Proportion (wt. %)	
	Of the whole fibre	Of primary wall
Cellulose	88 – 96	52
Pectins	0.7 – 1.2	12
Waxes	0.4 – 1.0	7
Proteins	1.1 – 1.9	12
Minerals	0.7 – 1.6	3
Other organic compounds	0.5 – 1.0	14

is to say when the specific surface area is large [21]. Other factors which influence the impurities in raw cotton are : geology of the cultivation area, soil constitution, weather conditions during the maturing period, cultivation technique, raw cotton treatment etc.

The proteins are situated in the central cavity of the fibre and are therefore relatively inaccessible to chemical attack. About 14% (on dry weight) proteins are concentrated in the primary wall of the cotton fibre, but their presence in the lumen are also reported [22]. The elements of protein components generally found to be are : leucine, valine, proline, alanine, oxyproteine, threonine, glutamic acid, glycine, serine, aspertic acid, aspergine, lysine and arginine [23]. The yellowish or

brown discolouration of the cotton fibre is related to the protoplasmic residues of protein [24,25] and the flavone pigments of cotton flowers [26].

Natural oils and waxes are mostly mixtures of fatty alcohols, fatty acids and esters of these carbohydrates [27]. Wax content varies greatly among the different varieties of cotton and also same variety grown in different locations. The wax is located on the outside of the cotton fibre and the quantity increases with surface area of cotton [28]. The composition and removal properties of cotton wax are given in Table 1.7. Cotton wax contain carbon (80.38%), hydrogen (14.51%) and

TABLE 1.7
Composition of Removal Properties of Cotton Wax [27]

Component	Content (%)
Wax ester	22
Phytosterols	12.14
Polyterpenes	1 – 4
Hydrocarbons	7 – 8
Free Wax alcohols	42 – 46
Saponifiable	36 – 50
Non-saponifiable	50 – 63
Inert	0 – 3

oxygen (5.11%) [30]. The linkage between cellulose and waxes are mainly due to phosphatides [31] and amino acids, glucose and wax acids [32]. Melting points of cotton waxes vary between 68 to 80°C.

The inorganic matters (residual ash) in cotton contain cation (K^+, Na^+, Ca^{2+}, Mg^{2+},Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, $Cu^{2+}$and others) and anions (Cl^-, CO_3^-, PO_4^{3-}, SO_4^{2-} plus Fe, Mg, Ca as insoluble pectinates) [19]. The alkaline earth elements vary from fibre varieties and require appropriate treatments to reduce their presence on the fibre as far as possible. Any residue present in the fibre will lead to the formation of insoluble alkaline earth carbonates or hydroxides during alkaline scouring. These salts change the soft water to hard water rendering certain dyes insoluble which may be attached to the fiber surface [33].

Pectin is the name applied to impure methyl pectate. Pectins (0.4 - 1.2%) are

present in cotton as a poly -D - galacturonic acid in the form of insoluble salts of Ca, Mg and Fe [34, 35].

Chemically hemicelluloses are arabane, xylene, galactane, mannan, galactomannan, arabinomannan, as well as monosaccharides, disaccharides and digosaccharides. Hemicelluloses are easily soluble in alkali and hydrolysed by acids. Other substances are reducing sugars such as hexoses, pentoses, free glucose etc., constitute the base units of hemicellulose. Citric and malic acid, encrusted ligneous substances are coloured pigments.

1.4 Natural Protein Fibres

Natural protein fibres are generally obtained from animal hairs and animal secretions. Protein fibres have higher moisture regain and warmthness than natural cellulosic fibres. Natural protein fibres have poor resistance to alkalies but have good resiliency and elastic recovery. A good precaution is necessary during the chemical pre-treatment of natural protein fibres (except silk) due to its low strength.

1.4.1 Molecular structure of wool fibres

Wool fibre grows from the skin of sheep. It is composed of protein known as keratin. Major varieties of wool come from Merino, Lincoln, Leiester, Sussex, Cheviot and other breeds of sheep. Different species of sheep produce different types of wool in fibre length, diameter and other characteristics. The modification of the fibre properties during growth by dietary additives to produce purpose-grown wools is possible. Generally fine wool fibres are 1.5 -5" in length and 14 - 40μ in width. Wool fibres are roughly oval in cross-section and grows in a more or less wavy form with a certain amount of twist. The waviness is called crimp (Fig 1 - 4). The finer the wool the more is the crimp.

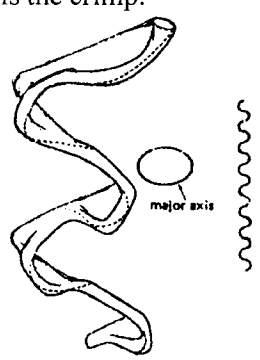


Figure 1-4. Diagram of wool fibre crimp and three-dimensional diagram of wool fibre, showing crimp.

The histological structure of wool fibre comprises consisting three layers : the scaly covering layer (cuticle), the fibrous fibrillar layer (cortex) and medullary layer (medulla). Fig. 1 - 5 shows the diagarm of wool fibre showing fibre morphology

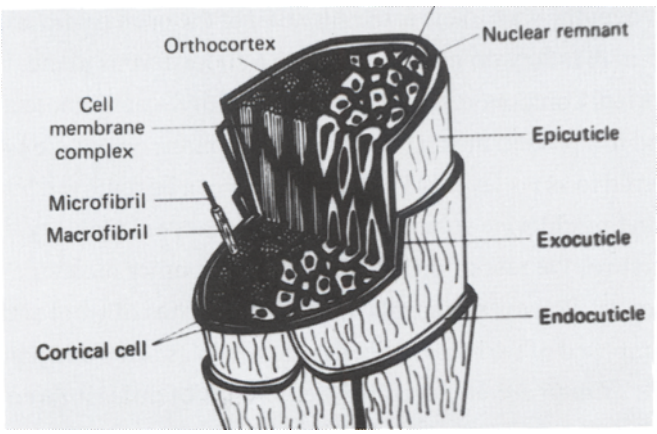


Figure 1-5. Diagrammatic representation of the morphological components of a wool fibre.

(medulla is not shown). The cuticle is sub-divided into two main layers, exocuticle (with A- and B- layers) and endocuticle, and has an outermost membrane called epicuticle. Beneath the epicuticle, there is a layer of flat, scale like cells which overlap like shingles on a roof.

Fig. 1 - 6 shows the longitudinal section of a wool follicle [36]. The sebaceous

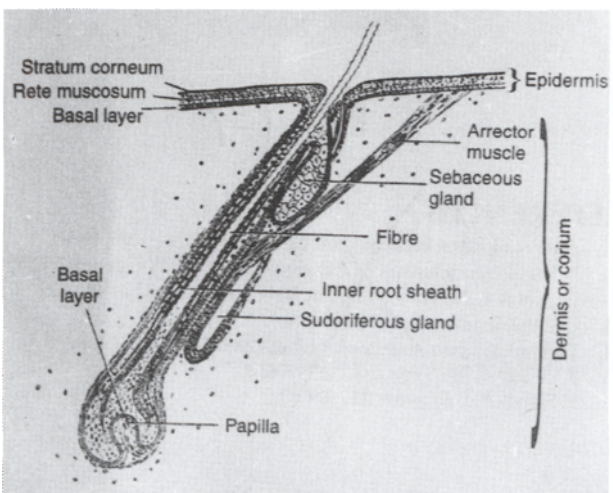


Figure 1-6. Longitudinal section of a wool follicle [36].

gland is beleived to produce the wax [37-39], and the sudoriferous gland the suint [37, 39]. As the opening of the sebaceous gland is placed below that of the sudoriferous gland, the wax is deposited directly onto the growing fibre while the suint is deposited over the wax. This is the situation of the primary fibres; the secondary fibres differ in that they do not usually have a sudoriferous gland.

An important component of cuticle is 18 - methyl - eicosanoic acid [40]. Fatty acid is bound to a protein matrix, forming a layer in the epicuticle [41, 42], and this layer is referred to as F - layer [43]. The F - layer can be removed by treatment with alcoholic alkaline chlorine solution in order to enhance wettability. The cuticle and epicuticle control the rate of diffusion of dyes and other molecules onto the fibre [44]. The cortex, however, controls the bulk properties of wool and has a bilateral structure composed of two types of cells referred to as ortho and para [45, 46]. The cortical cells of both are enclosed by membranes of at least three distinct layers within which the microfibrils fit. Cells of intermediate appearance and reactivity designated meso - cortical have also been reported [47]. Cortical cells on the ortho side are denti-cuticle and thin, those on the para side are polygonal and thick [47]. Fig. 1-7 illustrates the bilateral structure which is responsible for the crimp of the

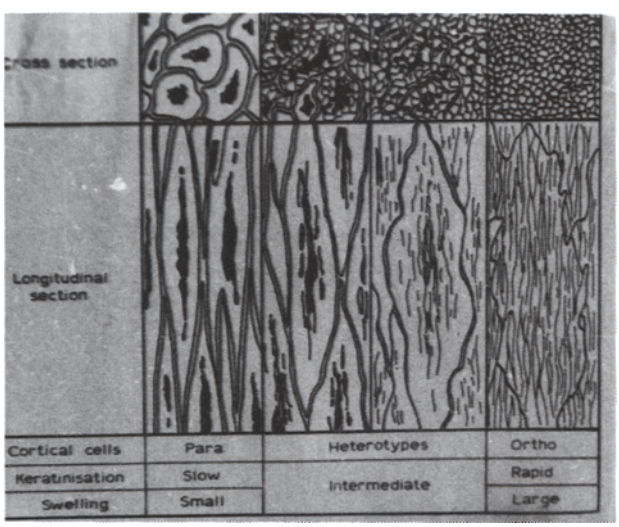


Figure 1-7. Comparison of cortical cells (Courtesy of l' Institut Textile de France).

fibre. The two cells differ in chemical composition and density and can be differ-

entiated under the microscope using polarised light and also by selective staining techniques. The ortho cortex are chemically more reactive and have a greater receptivity to certain dyes. In the centre of the wool is the medulla, which consists of spiral-shaped, air-filled cells. The finer wools, having no medulla, absorbs dyes more rapidly. Medulla contains pigment that gives colour to fibre.

Keratin is of amphoteric in nature and is composed of 16 to 18 different α - amino acids. The amino acid residues join together to give a polypeptide chain. There are two types of structure postulated for wool fibre : one is folded form of keratin (α - form) [Fig. 1-8] and the other is helical or spiral structure (Fig. 1-9).

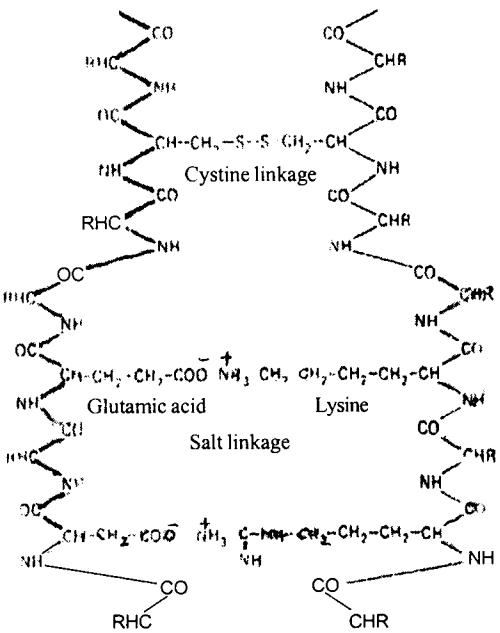


Figure 1-8. Folded chain characteristic of α-keratin (After Asbury).

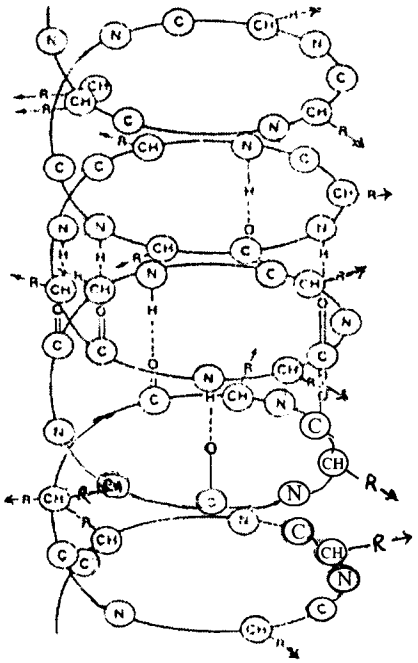
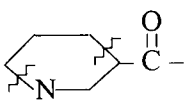
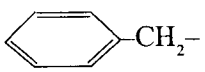
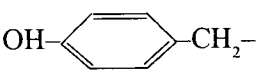
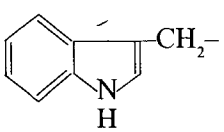
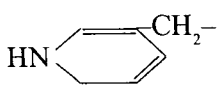


Figure 1-9. Helical or spiral structure of wool (After Pauling and Curey).

When the fibre is stretched, the coil extends to give β- keratin and on releasing the keratin back into α-form [48]. The amino acid and sequence in wool varies with the variety of wool [49]. The average amino acid contents for major varieties of wool and silk are given in Table 1.8. R represents relatively large side chains which contain amino, carboxyl, sulphide groups and relatively 50% of the weight of wool

TABLE 1.8
Amino Acid Content in Wool Keratin

R	Amino acid	Wool content (g/100 g fibre)	Fibrion content (g/100 g fibre)
H –	Glycine	5 – 7	36 – 43
CH_3 –	Alanine	3 – 5	29 – 35
$(CH_3)_2CH$ –	Valine	5 – 6	2 – 4
$(CH_3)_2CHCH_2$	Leucine	7 – 9	0 – 1
CH_3CH_2CH	Isoleucine	3 – 5	0 – 1
	Proline	5 – 9	0 – 1
	Phenylalanine	3 – 5	1 – 2
	Tyrosine	4 – 7	10 – 13
	Tryptophan	1 – 3	0 – 1
$HOCH_2$ –	Serine	7 – 10	13 – 17
CH_3CH – OH	Threonine	6 – 7	1 – 2
$-CH_2SSCH_2-$	Cystine	10 – 15	0
$CH_3SCH_2CH_2$ –	Methionine	0 – 1	0
$NH_2\overset{NH}{\overset{\|\|}{C}}NH(CH_2)_3-$	Arginine	8 – 11	0 – 2
	Histidine	2 – 4	0 – 1
$NH_2(CH_2)_4$ –	Lysine	0 – 2	0 – 1
$HOOCCH_2$ –	Aspartic acid	6 – 8	1 – 3
$HOOC(CH_2)_x$ –	Glutamic acid	12 – 7	1 – 2

is in the side chains. The cystine linkage and intermediate hydrogen bonding are

responsible for the shaping and setting characteristics of wool fibres and fabrics. Cystine linkages can occur within and between wool polymers. 35% of the exocuticle A- layer is made up of cystine residues and in addition to normal polypeptide bonds, the cuticle is cross-linked by isodipeptide bonds [ε – (γ – glutamyl) lysine]. The polymer system of wool is extremely amorphous as it is about 25 - 30% crystalline and 70 - 75% amorphous. Modern views [50, 51] assert that two or three protein chains (some of which are α - helical in structure) coil round to form a protofibril, a dozen of which aggregate to form micro-fibrils. These are located in close array within a matrix of protein material rich in cystine but with little structural regularity, para cortex containing more of the martix. This two phase structure gives rise to the micro-fibrils observed in the cortex and points to the existence of more than one protein in wool.

1.4.2 Impurities in raw wool

Raw wool is dirty and about 50% of its weight consists of natural and other impurities (Table 1.9). In general, the finer wools such as merino contains a higher

TABLE 1.9.
Impurities in Raw Wool (in %)

Type	Fat and suint	Sand and dirt	Vegetable matter	Wool fibre
Fine	20-50	5-40	0.5-2	20-50
Medium	15-30	5-20	1.5	40-60
Long	5-15	5-10	0.2	60-80

proportion of natural impurities than the coarse wool. The contaminants also vary according to breed, neutrition, environment and position of wool on the sheep. Wax, suint and dried perspiration are natural and dirt (adventitious), grass, seeds, straw, burrs, brambles, sticks etc. (vegetable matter) are acquired impurities. The presence of proteinaceous contaminant layer (PCL) is also found [50].

Chemically wool wax is a complex mixture of esters, diesters and hydroxy esters of high molecular weight lanolin alcohol and acids. The lanolin alcohol consists of three main types - aliphatic alcohols, sterols (such as cholesterol) and trimethyl sterols (such as lanosterols). The lanolin acid consists of four main types - normal, iso, anteiso and hydroxy acids. On exposure to the environment wool readily undergoes auto-oxidation. The reaction product (oxidised wool wax) be-

haves differently from unoxidised material [51]. The differences manifest themselves in the scouring process of wool.

Suint is mainly water soluble constituents of raw fleece and is normally neutral or slightly alkaline in reaction. It contains potassium and to a certain extent sodium ions.

The cellulosic materials are finely entangled with the wool fibre and require chemical treatments for their removal. As well as the cellulose the wool burrs also contain hemi-cellulose and lignin.

1.4.3 Morphology and chemical structure of silk

Silk fibre is a fine continuous strand unwound from the cocoon of a moth caterpillar known as silkworm. The silkworm as a means of self-protection spins a cocoon around its body by extruding the contents of the two silk glands through a spinnerette at its mouth. The two filaments solidify on coming in contact with air and form a composite thread. The silkworms are generally cultivated. There are mainly four varieties of silk e.g. Mulbery, Tassar, Eri and Muga and each variety is produced by feeding on the leaves of certain plants. All the species of silk have four stages in their life cycles namely, the egg, larva, pupa and moth. The mulbery silkworm belongs to the species Bombyx mori and about 95% of the world's production is of this species. The other three varieties are produced by the worm Antheraea mylitta and are termed as wild silk. They are stiffer and coarser than mulbery silk. Raw silk thread is obtained from silk cocoons by reeling after boiling the cocoons in water. Several such threads are doubled together and twisted into a strong yarn necessary for weaving and knitting.

The morphological structure of raw silk fibre is given in Fig. 1-10. The actual fibre protein is called fibrion and the protein sericin is the gummy substance that holds the filament together. The average composition of raw silk is 70-75% fibrion ($C_{15}H_{23}N_5O_8$), 20-25% sericin, 2-3% waxy substances extractable by ether and alcohol and 1 to 1.7% mineral matter. Sericin is amorphous and dissolves in hot soap solution. Fibrion is the form of a filament thread and dissolves in 5% sodium hydroxide solution at boil.

Both fibrion and sericin are protein substances built up of 16-18 amino acids, out of which only glycine, alanine, serine and tyrosine make up the largest part of the silk fibre (see Table 1.8) and the remaining amino acids containing bulky side groups are not significant. The chemical structure of fibrion and sericin for four

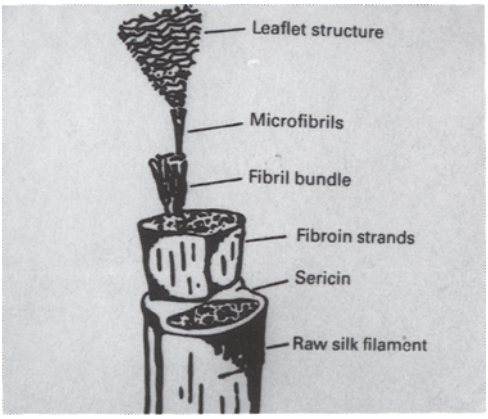


Figure 1-10. The structure of raw silk fibre.

amino acids is shown in Table 1.10. Fibrion contains hardly any sulphurous amino

TABLE 1.10
Amino Acid Composition of Sericin and Fibrion

Amino acids	Side groups	Sericin (% mol)	Fibrion (% mol)
Glycine	H –	14.75	45.21
Alanine	CH_3 –	4.72	29.16
Serine	CH_2 (OH) –	34.71	11.26
Tyrosine	$OHC_6H_4CH_2$ –	3.35	5.14

acids (cystine) and also only a minimal amount of amino acids as side chains. The low number of large side groups enables silk to be densely packed. The crystalline structure of the polypeptide chains in silk fibrion is shown in Fig. 1.11. Silk polymer occurs only in β-configuration. The important chemical groupings of the silk polymer are the peptide groups which give rise to hydrogen bonds, the carboxyl end amine groups which give rise to salt linkages and the Van der Waals' forces. It has high degree of molecular orientation which accounts for the excellent strength of the silk fibres. However, the polymer system of silk is now considered as being composed of layers of folded, linear polymer as shown in Fig. 1-12. Such a polymer system explains why silk is essential to be about 65-70% crystalline. The DP of silk fibrion is uncertain, with DP of 300 to 3000 having been measured in different solvents. Silk fibres are smooth surfaced and translucent with some irregularity

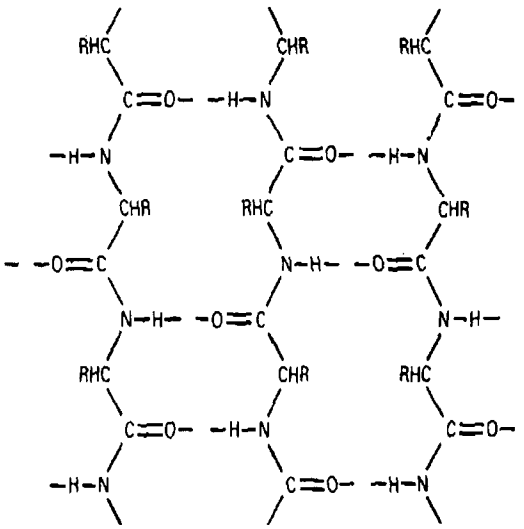


Figure 1-11. Crystalline structure of polypeptide chains in fibrion.

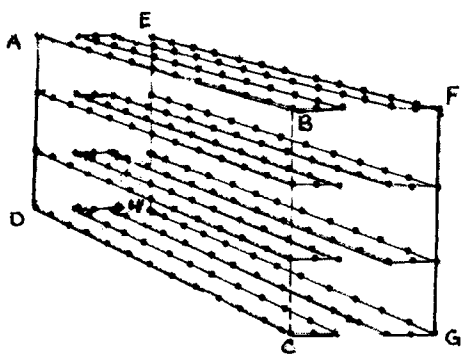


Figure 1-12. Laminated structure of silk.

in diameter along the fibre. The fibres are basically triangular in cross-section with rounded corners. The isoelectric point of silk is about 5.

1.5 Long Vegetable Fibres

The long vegetable fibres include various bast fibres, leaf fibres and fruit fibres. Among the bast fibres flax, remie, jute are the most important fibres. These fibres, which are used in cordage have suffered along with abaca, coir, henequeen and sisal fibres as they are unable to withstand the onslaught of synthetic fibre cordage technology. Thus, the long vegetable fibres with their limited and fluctuating growth rates, cannot cope with rapid rise in global demand for industrial textiles. The advantage of these fibres is that they are eco-friendly fibres.

1.5.1 Flax (linen)

Flax is a bast fibre used to manufacture linen textiles. It is obtained from plant Linium Usitatissimum by a complicated process to separate fibre from the woody core. This process known as retting and can be done by dew retting [52], pool retting, tank retting, steam retting [53-55], chemical [56-59] and biochemical retting. After retting is complete, the stack is bundled together and passed between flutted rollers that breaks the outer woody covering into small particles. It is then subjected to scutching process, which seperates the outer covering from the unusuable fibre. After scutching, the flax fibres are hackled or combed to separate the short fibres (tow) from the long fibres.

Flax is considered to be the oldest fibre in the Western world and CIS (formerly USSR) grows most of the flax fibre. Linen has been gradually loosing its position as an apparel fabric since 1950s, but the emergence of linen as a component of blends has stimulated considerable interest.

Flax fibres are multicellular, with each cell having tapering ends and a narrow lumen. The fibres show longitudinal striations and nodes (Fig. 1-13). The ultimate



Figure 1-13. Cross-section of flax fibre (E.I.DuPont de Nemours & Co.).

fibres are composed of elementary fibrils (microfibrils), which are spirally arranged [60]. The fibrils are held together by a bonding or gummy substances.

Cellulose is the main constituents of flax fibre (Fig. 1-14). The unretted flax contains about 16.7% hemicellulose, 1.8% pectins, 2% lignin and 1.5% fats and waxes. The polymer of flax consists with a degree of polymerisation of about 18000 cellobiose units. Flax is an assembly of ultimates cemented together within the fibres and an assembly of these fibres into bundles. These assemblies are prone

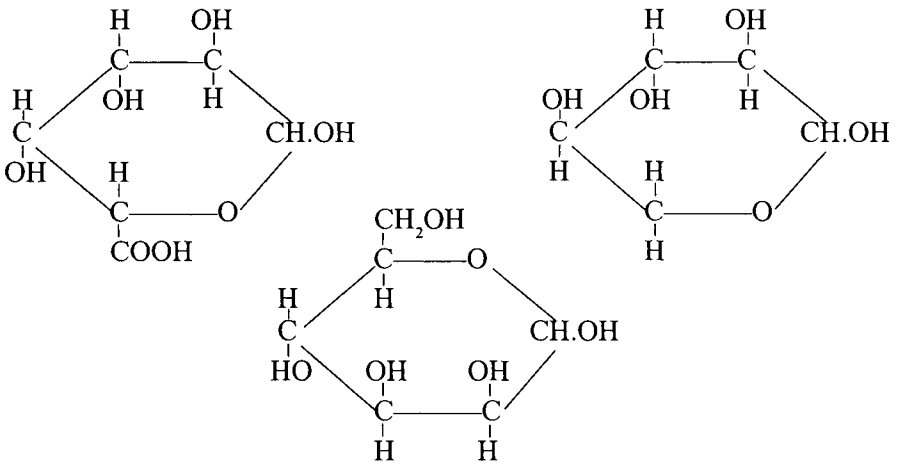


Figure 1-14. Chemical constitution of flax.
(64% Cellulose + 16% Hemi-cellulose).

to discolouration [61]. It is the structure which makes linen feel like linen. Flax has relatively high strength. Disruption of structure by, for example, scouring referred to as cottonisation.

1.5.2 Remie

Remie fibre is white and lustrous and often referred to as china grass. Remie has been grown in Brazil to substitute flax. The fibre is stiff and fairly coarse like canvas. This fibre comes from plants Boehmeria nivea or Boehmeria tenacissema which belong to a family of stingless nettles. The remie fibres are removed from the stalks by the process of decortication . The fibres are released from ribbons or strands in which they are held together by natural gums. Commercial degumming is carried out by treating the fibres with caustic soda solution for 4 h. The use of mixed bacterial cultures [62] and enzymes[63] are also reported to remove the gum from remie fibre.

Purified remie fibre is composed of a single cellulose with wall with an S-spiral 6^0 to the axis [64,65]. Remie has the highest degree of both polymerisation and birefringences. The high strength of remie is attributed to its highly ordered structure. The crystalline areas increase in lateral size and decrease in crystalline orientation as the gum is removed from the intercrystalline areas [66].

Remie fibres tend to have a hairy feel which reduces their cohesion. They are smooth and cylindrical, with thick wall. The surface of the cell is marked by little

ridges. The cell of the fibre is long and the cross-section irregular in shape. The lumen narrows and disappears towards the ends of the cell. Remie fibre absorbs water rapidly and fabrics made from it will launder easily and dry quickly.

1.5.3 Hemp

Hemp comes from the plant, Cannabis Sativa, an annual of the family Moraceae, which grows to a hight of 10 feet or more. The most important hemp producing countries are C.I.S., Yugoslavia, Rumania and Hungary. Fibre is freed from woody matter by a retting process, followed by breaking and scutching. This is then softened by pounding it mechanically or by hand. Hemp has cellulose content of about 67% and contains about 16% hemicellulose. Strands of hemp fibre may be 6 feet or more in length. The individual cell is, on average between 0.5 and 1 inch long. They are cylindrical in shape with joints, cracks, swelling and other irregularities on surface. Like flax, the cells of hemp fibre are thick walled, they are polygonal in cross-section. The central canal or lumen is broader than that of flax, however, the ends of the cells are blunt.

The fibre will not bleach easily and generally employed in the manufacture of ropes, twines, sacking, carpets, nets and tarpaulins. In addition, hemp also serves today as a raw material for paper industry. Cottonised hemp does not spin easily alone, but it gives useful yarn, when mixed with cotton (up to 50% hemp).

1.5.4 Jute

Jute is also a lignocellulosic bast fibre and is cultivated in a manner similar to that of flax. Jute is mainly grown in India, Bangladesh and Thailand. Jute fibre comes from herbaceous annual plant which grows as high as 20 feet. Jute fibres are extracted from the stem by retting which usually consists two stages : physical stage at which water is imbibed, swelling occurs, soluble substances are extracted and the microbial stage. Jute tends to be brown in colour due to about 20% lignin present in the fibre, but does have a silk like lustre.

The individual cells of jute are very short. Table 1.11 compares the dimension of ultimate from several sources. The cross-section of jute fibre is polygonal, usually with five or six sides. It has thick walls and a broad lumen of oval cross-section. By contrast with the regular lumen of flax, that of jute is irregular ; it becomes narrow in places quite suddenly. The lengths of various vegetable fibres varies considerably, whereas the diameter is moderately constant from fibre to fibre.

TABLE 1.11
Comparison of the Dimensions of Long Vegetable Fibres [67]

Fibre	Length (mm)	Diameter (nm)	Aspect ratio
Marino	4.6-5.2	17.0-21.4	255
Coir	0.9-1.2	16.2-19.5	60
Flax	27.4-36.1	17.8-21.6	1600
True Hemp	8.3-14.1	17.0-22.8	560
Sunn Hemp	3.7-6.0	23.0-35.0	170
Jute (Capsularis)	1.9-2.4	16.6-20.7	115
Jute (Cor. Olitorius)	2.3-3.2	15.9-18.8	160
Kenaf	2.0-2.7	17.7-21.9	120
Remie	12.5-12.6	28.1-35.0	4000
Mesta	2.6-3.3	18.5-20.0	150
Sisal	1.8-3.1	18.3-23.7	120
Urena	2.1-3.6	15.6-16.0	180

In flax the ultimates are much longer than those in jute, sisal and coir. The implication of this observation is that the 'cement' can be removed from the flax with little effect on tensile strength as hydrogen bonding still occurs over the large contact areas of the ultimates. In the case of fibres with short ultimates, such bonding does not occur and removal of the cement causes massive strength loss.

Jute fibres are bundles of fibrous material held together by a gummy substance of proteinaceous character. Chemically, jute fibres are composed of mainly polysaccharides and lignin, although the number of minor components, such as waxes, pectin, inorganic salts, nitrogeneous substances, colouring matter etc., are also found. Table 1.12 compares the constitution of cotton with flax and jute. The total carbohydrate material is usually designated as holocellulose, which is further divided into two groups, namely α-cellulose (true cellulose) and hemicellulose. Certain fractions of the hemicellulose may be chemically linked with the true cellulose. The formation of mixed crystals is postulated. Lignin is generally regarded as a

TABLE 1.12
Comparison of the Chemical Constitution of Jute with Flax and Cotton

Chemical constitution	Cotton average	Flax		Jute
		Retted	Unretted	
Cellulose	88-96	55.4	65.1	58-63
Hemicellulose	--	15.4	16.7	21-24
Pectins	0.7-1.2	2.5	1.8	0.2-15
Lignin	--	2.5	2.0	12-15
Proteins	1.1-1.9	--	--	0.8-1.8
Fats & Waxes	0.4-1.6	--	--	0.4-0.8
Ash (%)	--	--	--	0.6-1.2

three-dimensional polycondensate of dehydrogenation products of hydroxy and methoxy cinnamyl alcohols. The existance of ester-linkage between carboxyl groups in uronic acid of hemicellulose and hydroxyl groups of lignin is found. In general plant lignin resists the action of acids to a great extent. Coir with highest lignin content (35%) is most resistant to chemicals and micro-biological attack. Various properties of jute fibres are compared with flax in Table 1.13. Jute is not as strong

TABLE 1.13
Properties of Jute and Flax Fibres

Property	Evaluation	
	Flax	Jute
Lustre	High	Silky
Strength (tenacity)	6.5 g/d	3.5 g/d
Resiliency	Poor	Low
Density	1.54	1.50
Moisture absorption at 20°C	12%	13.7%

as flax or hemp. Jute fibres are stiff, but does have an unusually high moisture regain. Sunlight does not damage jute.

1.6 Regenerated Natural Fibres

There are three types of regenerated natural fibres - rayon, acctate and protein - the first two are derived from cotton linters or pine wood. Wool like protein based artificial fibres may be regenerated from animal and vegetable proteins.

1.6.1 Cuprammonium rayon

The preparation process of cuprammonium rayon is shown in Fig. 1-15. In

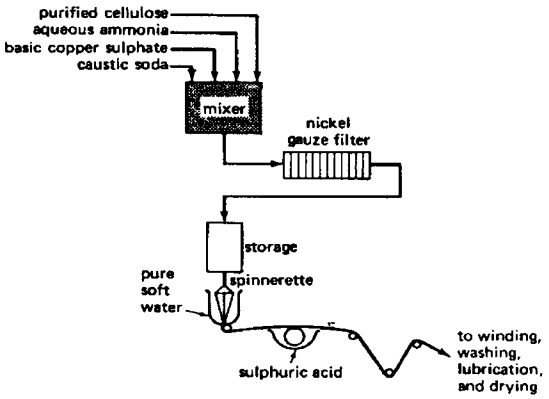


Figure 1-15. Flowchart showing process of cuprammonium manufacture.

order to make a spinning dope the basic copper sulphate is dissolved in ammonia, giving a solution of cupritetrammino hydroxide and sulphate in the molecular ratio of 3 : 1 and purified linters are added. Caustic soda is then added to convert the sulphate to corresponding hydroxide and filtered [68]. The chemical reactions are given in Fig. 1-16.

$$C_6H_7O_2(OH)_3 + Cu(NH_4OH) \rightarrow C_6H_7O_2(OH) : Cu(NH_4OH)$$
$$\downarrow H_2SO_4$$
$$C_6H_7O_2(OH)_3$$

Figure 1-16. Formation of cuprammonium rayon.

The spinning solution is pumped through the spinnerette into a funnel through which soft water is running. The movement of water stretches the newly formed filament. The fibres then move to spinning machines, where they are washed, put through a mild acid bath to remove any adhering solution, rinsed and twisted into yarns.

1.6.2 Viscose rayon

Purified bleached wood pulp or sheets of cellulose are steeped in an alkali solu-

tion (17.5%) until the cellulose is converted to soda-cellulose. The alkali pulp is then shredded into alkali cellulose crumb, which is aged for specific time. The crumbs are then treated with carbon disulphide and produce sodium cellulose xanthate. This is dissolved in dilute sodium hydroxide and forms a honey coloured liquid and aged till required viscosity is obtained. The viscous solution is pumped to the spinning tanks, delivered to the spinning machines, forced by pump through a spinnerette into a dilute acid bath (Fig. 1-17). The method of making fibre is

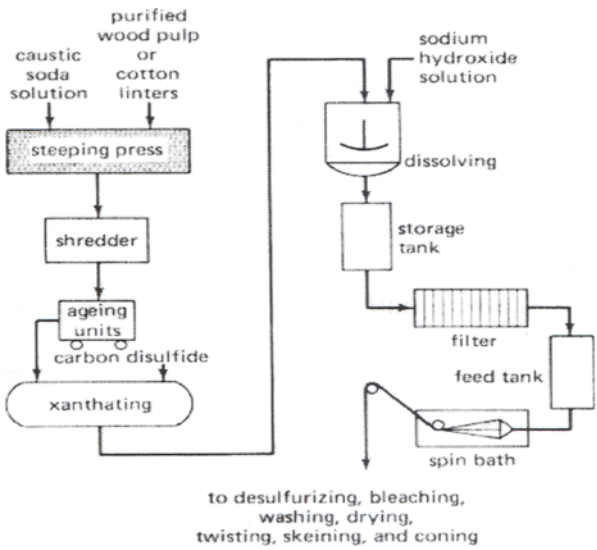
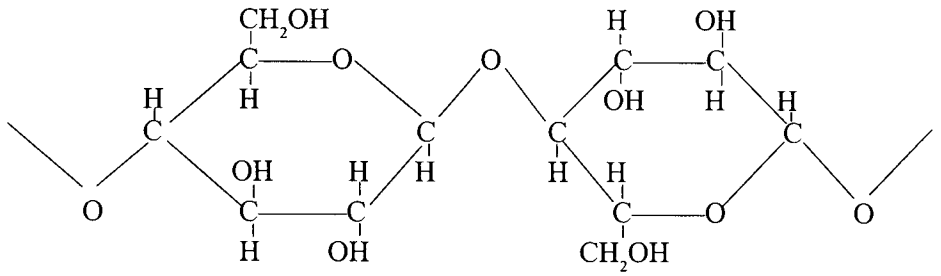
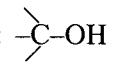


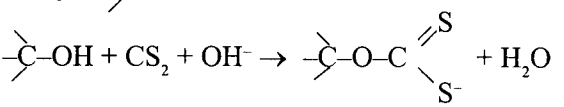
Figure 1-17. Viscose rayon manufacturing process.

called wet-spinning. The chemical changes that occured in the process are outlined in Fig. 1-18. In the mid-1960s fibres with higher wet stretch, low wet extensibility and a high wet modulus (HWM) are produced and known as 'polynosic' or 'modal' type fibres. HWM fibres are generally produced [69,70] by adding modifiers, e.g. various amines or poly (ethylene) glycol to the viscose to control the rate of regeneration of the filament in the coagulation bath. They are usually produced as staple fibre.

Viscose and modified viscose are composed of cellulose and like cotton they are polymer of anhydroglucose unit. The significant physical differences between various regenerated cellulose and cotton polymers are listed in Table 1.14. HWM viscose rayon may appear nearly round in cross-section. Viscose polymers are very amorphous and have high moisture absorption capacity of 11 to 16%. Vis-



Each hydroxyl group is represented by : 

Formation of xanthate ester : 

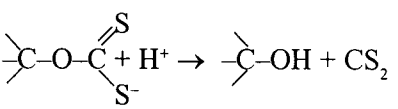
Regenerated viscose rayon : 

Figure 1-18. Viscose process.

TABLE 1.14
Significant Physical Differences Between Rayon and Cotton

Polymer	Approx. no. of cellobiose units	Approx. polymer length (mm)	Approx. polymer thickness (nm)	Approx. degree of polymesisation
Viscose	175	180	0.8	175
Polynosic	300	310	0.8	300
Cuprammonium rayon	250	260	0.8	250
Cotton	5000	5000	0.8	5000

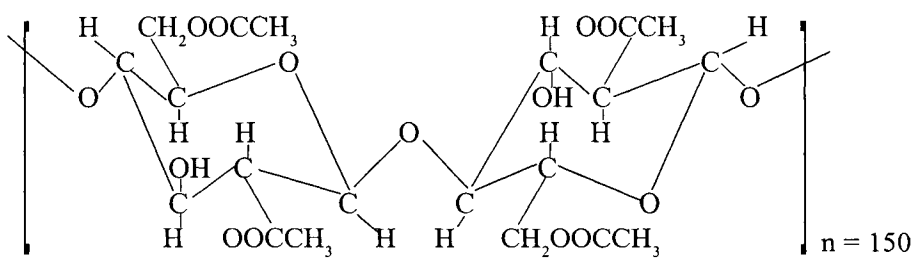
cose shows no discernible micro-structure, but polynosic shows a distinct fibrillar structure similar to cotton. Viscose fibres show longitudinal striations (tiny grooves), but cuprammonium and polynosic are coagulated much more slowly on extrusion, do not develop any striations. Folded chains model have been proposed [71] for the fine structure of viscose rayon (Cellulose II). The difference between Cellulose I and Cellulose II families appears in the arrangement of polarity of folded chains produced from the cellulose molecules [72].

1.6.3 Acetate fibres

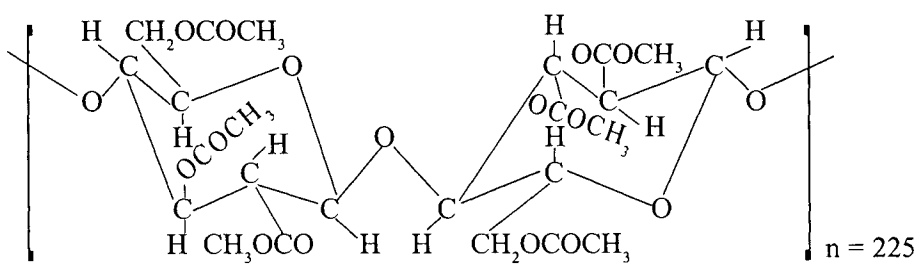
In this group there are two fibres : secondary cellulose acetate and triacetate fibres. Acetate fibres are produced from cotton linters or purified wood pulp, which are acetylated at temperature up to 50°C with acetic anhydride in presence of glacial acetic acid and concentrated sulphuric acid. It is then aged or ripened in presence of water and hydrolysis occurs during the ripening and results in the formation of secondary acetate. The flakes are then dissolved in acetone containing 4% water as the solvent to form the spinning dope, which is filtered and then forced through the spinnerette into a warm-air chamber and the method of spinning is called dry-spinning. Triacetate is manufactured from the same raw materials as secondary acetate, but the ripening stage in which hydrolysis occurs is omitted in triacetate production. To produce spinning solution, dried acetate flake is dissolved in methylene chloride and dry-spun into a warm-air chamber.

The chemical structure of acetate fibres are shown in Fig. 1-19. In secondary

$$(\text{Cellulose}) - OH + (CH_3CO)_2O \xrightarrow{H_2SO_4} (\text{Cellulose}) - O.CO.CH_3 + CH_3COOH$$



Secondary cellulose acetate



Triacetate fibre

Figure 1-19. Formation of cellulose acetate fibres.

acetate polymer, it is the methylol hydroxyl group that is acetylated and one of the other hydroxyl group. Theoretically between 2.3 to 2.4 acetyl or acetal groups per glucose unit occur in secondary cellulose acetate polymer.

Both types of acetate fibres have a polymer "backbone" of hexagonal units. The macro structure of acetate fibres is very similar to that of viscose and displays no discernible micro-structures. Acetate fibre complicates close packing because of bulky structure. Both the fibres are amorphous (60% or less) and are held together by Van der Waals' forces. Triacetate has certain properties that are different from secondary acetate fibres (Table 1.15). Secondary acetate is about 160 nm

TABLE 1.15
Comparison of Physical Properties of Acetate Fibres

Property	Secondary acetate	Triacetate	
Tenacity, g/den	1.2-1.5	1.2-1.4	
Elongation, %	25-45	25-45	(filament)
Recovery (at 4% elongation), %	45-65	50-65	(at 5% stretching)
Moisture regain, %	6-6.5	2.5-3.0	
Specific gravity	1.32	1.32	
Melting point, °C	240	300	

long and about 2.3 nm thick, whilst the triacetate is about 240 nm long and about 2.6 nm thick. Triacetates have much better resistance to boiling water and alkali. Triacetate is more expensive than secondary acetate. Both the fibres can be blended with cellulosic fibres to obtain special styling and performance characteristics. Tendency of acetate fibres to delustre in aqueous bath above 80°C force to dye these fibres at 75-80°C, giving poor wet-fastness properties. This short-coming of acetate has been removed recently (Xtol fibres) [73, 74].

1.6.4 Regenerated portein fibres

The raw materials used for the preperation of regenerated protein fibres may be milk, soyabeans, peanuts and zein. Sometimes alkaline solutions of gelatin, albumin and other raw materials like waste wool, silk and feathers may be used. Fibrolane (Great Bretain) and Merineva (Italy) are made by dissolving casein in sodium hydroxide, and then by extrusion into an acid/salt bath. The fibres formed in this way

is stretched as tow and partially stabilised by treatment with formaldehyde (Fig. 1-20).

$$R\text{–}NH_2 + HCHO + H_2N\text{–}R \rightarrow \underset{\text{Casein}}{RNHCH_2NHR}$$

$$[-NH+CH_2O+NH-]\rightarrow\underset{\text{Vicara ®}}{[-H\overset{+}{N}-CH_2O-\overset{+}{N}H-]}$$

Figure 1-20. Regenerated protein fibres.

The general properties of regenerated portein fibres include the wool like attributes of resilience, warmth and soft handle. The strength is lower than wool. These fibres do not contain cystine linkage, which results in more open structure. These fibres are far less successful than hoped and never seriously challanged wool.

1.7 Synthetic Fibres

The classic researches of Wallace Hume Carothers on polymer synthesis started in the Du Pont (USA) in 1928 and bulk scale production of nylon 6 and nylon 6,6 started in 1939. J.R.Whinfield and J.T.Dickson discovered polyester in 1941 and was commercially manufactured by 1954. Yarn texturising and spin draw yarns produced at super high speeds have further increase the popularity of synthetic fibres [75, 76]. Polyster fibre accounts for more than 50% of the total synthetic fibre production.

1.7.1 Polyester

Terephthalic acid or dimethyl terephthalate and ethylene glycol polymerise by condensation reaction to form the polyester polymer (Fig. 1-21). After

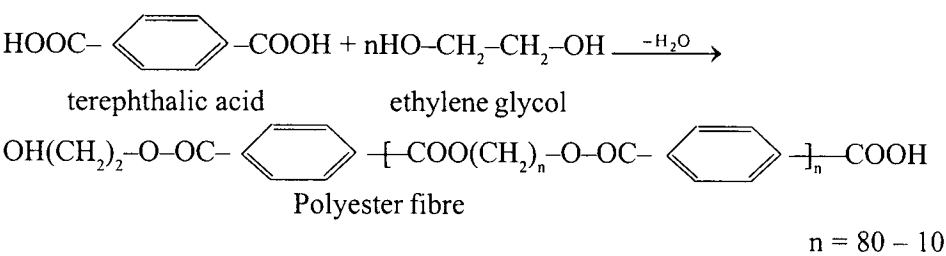


Figure 1-21. Chemical reactions in polyester formation.

polymerisation they are extruded in the form of ribbon, then cut into chips. The chips are dried and conveyed to a hopper, from which they are fed to the melt-spinning tank (Fig. 1-22). The hot solution is fed through the spinnerette and so-

lidifies into fibre form upon contact with air. It is stretched while hot to obtain strength.

Polyester is made up of fully extended planer chains and repeat unit along the chain is 10.75Å and the successive ester groups are essentially in the trans configuration of each other (Fig. 1-23). The polymer is held together mainly by Van der

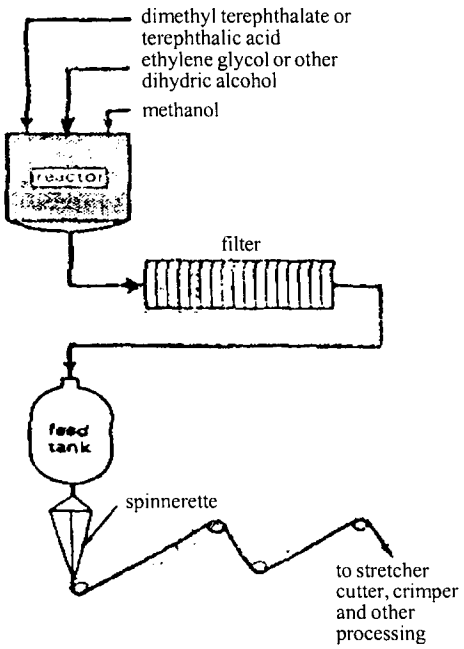


Figure 1-22. Flow diagram of polyester manufacturing process.

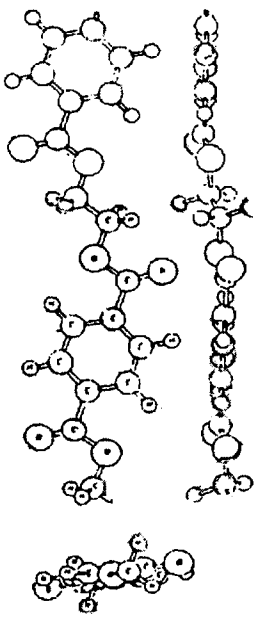


Figure 1-23. Structure of polyethylene terephthalate.

Waals' forces and to a lesser extent some weak hydrogen bonds. The polymer system is estimated to be about 65 to 85% crystalline.

The physical properties of polyester is given in Table 1.16. This fibre has high tensile strength, low moisture regain, high initial modulus and good crease recovery. Strong caustic alkalies at high temperatures hydrolyse and degrade the fibre and concentrated sulphuric acid disintegrates the fibre. Polyester dissolves in hot m-cresol, tri-fluoro acetic acid and o-chlorophenol.

The chemical modifications of polyester is mainly intended to overcome some of the inherent drawbacks of the fibre such as low dyeability, low moisture regain, static accumulation, soiling tendency, pilling property and flammability. Develop-

TABLE 1.16
Physical Properties of Polyester

Property	Range
Tenacity, g/den	2.5-6.0
Elongation, %	12-15
Elastic recovery, %	90-96 at 2% extension
Average stiffness, g/den	8-25
Specific gravity	1.38
Moisture regain (standard condition), %	0.4

ments of both homo - and co-polyesters have continued and many modified polyesters have appeared with improved properties. The repeating units of some of the modified polyester are given in Fig. 1-24. Kodel II is based on 1,4 - dimethylcyclohexane terephthalate and give increased stability to hydrolysis. A-Tell is polyethyleneoxybenzoate (PEB) and has a silk like handle and drape, good wrinkle resistance and easy care properties. The self polymer of poly (pivalolactone) has better resistance to hydrolysis and a much higher melting point than the original aliphatic polyester. Polybutylene terephthalate (PBT) is a carrier free dyeable polyester with lower glass-transition temperature(Tg). Vycron (USA) is a modified polyester where terephthalic acid is partly reduced by isophthalic acid to open up the compact structure. Sulphonic acid group is introduced additionally into the isophthalic acid to dye with basic dye (CDPET). Similarly anionic dyeable polyester is also introduced containing nitrogenous compounds (polyamines) which offer basic group as sites for the adsorption of acid dyes. Thermotropic 'liquid crystal' philosophy has developed a fully aromatic polyesters like polyallylate fibres with very high tensile modulus (of the order of 100 Gpa). The cross-section of the regular polyester is round, of dacron (Du Point) is trilobal, of Fortel and Encron is T-shape, of Trevira (Hoechst) is pentalobal and of Kodel is trilateral. Changes that occur the cross-section produce fibres with different hand and appearance.

1.7.2 Nylon

The most popular of the aliphatic polyamides are nylon 6,6 and nylon 6. Nylon

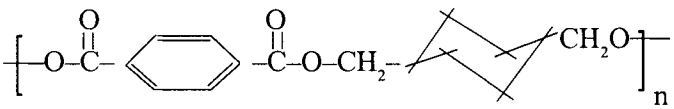
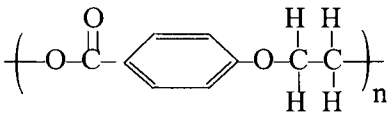
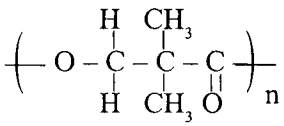
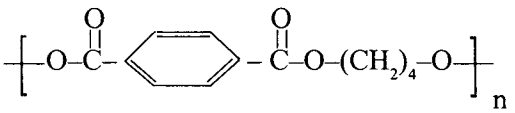
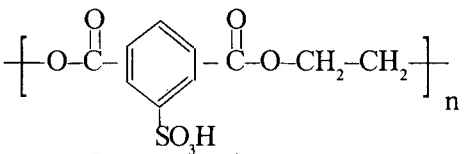
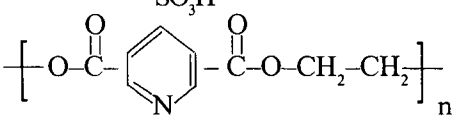
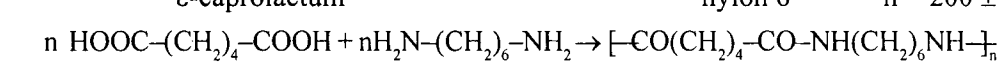
Repeating unit	Fibre
	Kodel II (Eastman Kodak)
	A – Tell (Japan)
	poly (pivalolactone)
	polybutylene terephthalate
	Cationic dyeable polyester (CDPET)
	Anionic dyeable polyester

Figure 1-24. Repeating units of some modified polyester [77].

6 is the polymerisation product made form ε - caprolactum and nylon 6,6 is produced by polycondensation from adipic acid and hexamethylene diamine (Fig. 1-25). The 6,6 designation simply implies that each of the two raw materials



ε-caprolactum nylon 6 n = 200 ±



adipic acid hexamethylene diamine nylon 6, 6 n = 50 – 80±

Figure 1-25. Chemical reactions in nylon 6 and 6, 6 manufacture.

contains 6 carbon atoms. Fig. 1-26 gives the flow chart showing steps in the manu-

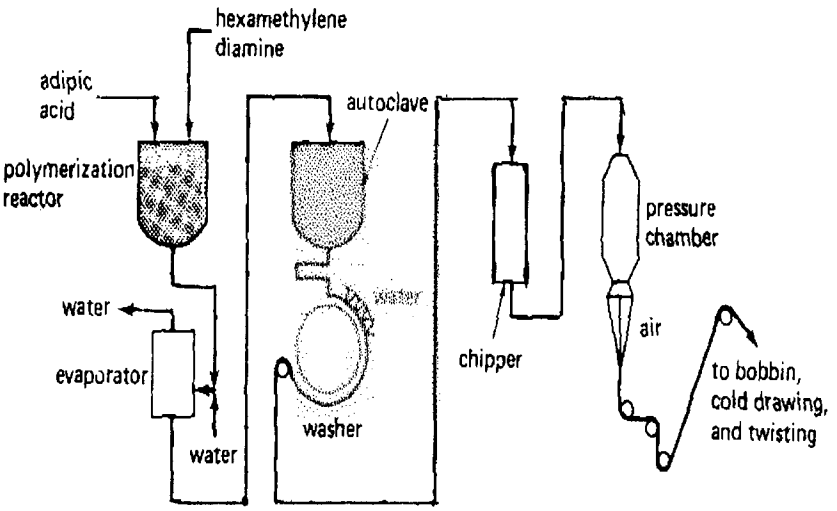


Figure 1-26. Flowchart showing steps in the manufacture of nylon 6, 6.

facture of nylon 6,6. Specific amounts of the two chemicals are combined in solution to form nylon salt. The salt is purified, polymerised, extruded in ribbon form and chipped into small flakes or pellets. The polymer is then melted and extruded through a spinnerette into cool air, where the filaments are formed. The filaments are then stretched or cold drawn to develop desired properties. Nylon staple is obtained by crimping filament tow and then cutting into short uniform lengths.

The estimated polymer length of nylon varies from 90 to 140 nm with polymer thickness of 0.3 nm. The amide linkage (-CO-NH-) ows its polarity to the slightly negative charge on its hydrogen atom, that is imino hydrogen. Many other nylons are synthesised (Fig. 1-27), amongst them 6, 10, 7, 11 etc. are marketed to some extent. Nylon filaments are smooth and shiny. When viewed in cross-section, nylon is usually perfectly round. They are highly resistance to alkalies and relatively less resistance to acids. The noteble feature of various nylons is their moisture sorption and melting point (Table 1.17). The photochemical behaviour of nylon is less favourable and the fibre turns yellow on heat and oxidising agent treatments. Apart from these textured nylons are very popular.

The modified nylons can take several forms : changing cross-section of shape

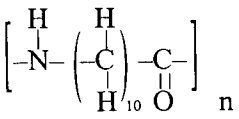
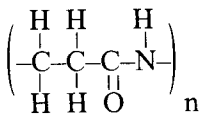
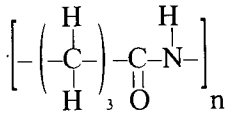
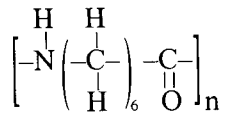
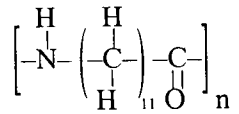
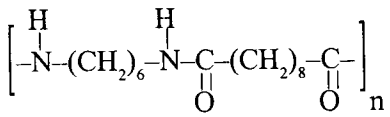
Repeat unit	Fibre
	Nylon 11
	Nylon 3
	Nylon 4
	Nylon 7
	Nylon 12
	Nylon 6, 10

Figure 1-27. Repeat units of various nylons.

TABLE 1.17
Moisture Sorption of Various Nylons

Fibre	Moisture sorption (%) at 65% r.h.at 20°C	Sp. gr.	M. Pt. (°C)
Nylon 6	3.5-5.0	1.14	210
Nylon 6,6	3.8-4.5	1.14	250
Nylon 11	1.18	1.04	189
Nylon 4	Higher than cotton	--	--
Nylon 6,10	2.6	--	214

and changing the physical and chemical properties to improve dyeability, handle, tenacity, heat stability etc. The repeat units of some of the modified nylons are

given in Fig. 1-28. Both nylon 6T and Nomex have very high thermal resistance.

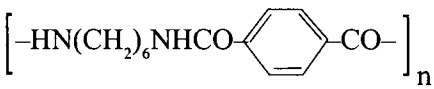
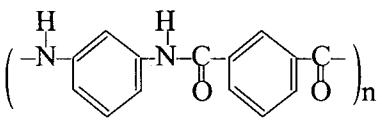
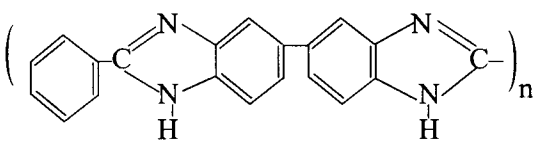
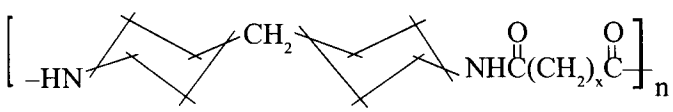
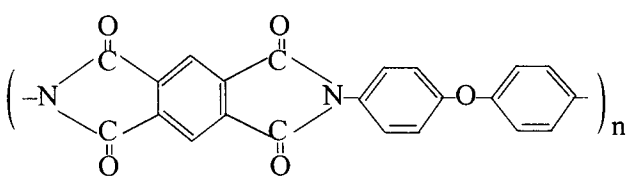
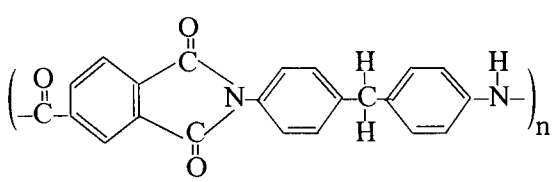
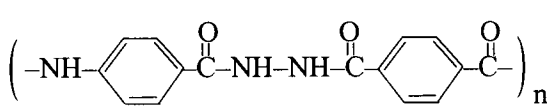
Repeat unit	Fibre
	Nylon 6T
	Nomex, Kevlar (Du Pont)
	PBI (Celanese Corpn.)
	Quina (Du Pont)
	Polyimide
	Kermel (Rohne-Poulene)
	X-500 (Monsanto)

Figure 1-28. Repeat units of some modified nylons [78].

Nylon 6T melts at 370°C, Nomex is practically flameproof. Kevlar, poly (p-phynyleneterephthalamide) represents a break-through in high modulus aromatic polyamide fibre and mainly used as reinforcement tyres, conveyers belt etc., PBI is

obtained by reacting diaminobenzidine and diphenylisophthalate and is used as an alternate to asbestos in high temperature filtration and thermal protection clothing. Its moisture regain is high at 14.4%, which permits high degree of comfort [79]. Quina, with a trilobal cross section, is a polycondensate of diaminodiphenylmethane and decane dicarboxylic acid. It is distinguished by its silk-like handle and regarded as synthetic substitute for pure silk. Kermel is a polyamide-imide fibre made from either trimillitic anhydride chloride and a diamine or a diisocyanate. These polymers have reasonable thermal stability, very resilient and have excellent flame-resistance. The Monsanto's X-500 class of fibre, of which that prepared from polyamide-hydrazide is typical. Developments in melt-spinning have led to filaments with novel cross-sections or containing cavities to obtain improved properties, such as increased cover, a crisp, silk-like, firm hand, reduced pilling, increased bulk, sparkle effects and heightened resistance to soil. Generally, normal nylon has a rounded cross-section and Quina has trilobal cross-section. Cadon (Monsanto) has a rounded square cross-section with four cavities [80].

1.7.3 Acrylic fibres

Polyacrylonitile (PAN) is a long chain polymer containing acrylonitrile [-CH_2-CH(CN)] as repeating unit in the polymeric chain and are formed by addition polymerisation. Acrylic fibre contains 15% or less copolymer. The modacrylic fibres are comprised of less than 85% but at least 35% by weight of acrylonitrile. The comonomers are added to increase the polymer thermoplasticity, solubility, dyeability, moisture regain, etc.

Thus, the molecular structure of copolymer of acrylonitrile and comonomer is represented as

$$-\left[-(CH_2-\underset{\underset{CN}{|}}{CH})_m-(CH_2-\underset{\underset{y}{|}}{\overset{\overset{x}{|}}{C}}-)_p-\right]_n$$

n = 150 to 200 units

where m and p are number of monomer and comonomer units respectively in the polymer chain, n is the degree of polymerisation and x and y are the substituted groups of the comonomer. In general, there are three stages for the production of acrylic fibres, i.e., polymerisation, dope preparation and spinning (Fig. 1-29). Acrylonitrile is polymerised either by the suspension system in which water is used or

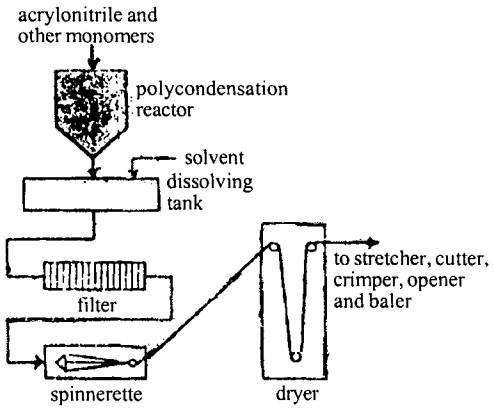


Figure 1-29. Stages for the production of acrylic fibres.

by the solution system where a solvent is used in the presence of suitable catalyst at appropriate temperature and time. The solution is then filtered and spun by the wet or dry-process. The yarn is drawn to increase the strength, twisted and coned. For the production of staple fibre tow is drawn, crimped, relaxed and cut into desired length and dried. Wet-spinning is preferred for large denier staple. Dry-spun fibres usually have a dog-bone cross-section and wet-spun have a round or bean shape.

Acrylic fibres have certain undesirable properties. To overcome such problems modifications of acrylics are made either chemically or physically (Table 1.18). Many vinyl compounds are listed in the literature [82]. The compounds possess a double bond which permits polymerisation by cleavage.

The acrylic polymer has a highly ordered structure in an oriented fibre, but only in lateral direction. The formation of radial pores during spinning has been attributed to the syneresis (or contraction forces) operating in the filament during coagulation. There is no evidence for a regular molecular arrangement along their lengths. Acrylic polymers are held together by Van der Waal's forces and it cannot be described as crystalline.

Acrylic fibres possess a very pleasing, warm and soft handle; fabrics made from it exhibit a silk-like lustre, hand and drape. An outstanding property of acrylic fibres is the comparatively low density which provides bulk and good coverage. The fibre has only 1.5% moisture regain and hence susciptible to static electricity. It has no definite melting point, it yellows on heating at 300°C and decomposes at

TABLE 1.18
Modification of Acrylic Fibres [81]

Modification	Means of Modification	Fibre obtained
Chemical modification	By comonomers	Enhanced dissolution and dyeing, Flame resistance, Antistatic, Improved hydrophilicity, Dyeing simultaneously with acid and basic colours.
	By polymer mixture	Graft polymerisation, Bicomponent fibres, Fibres from polymer mixture.
	Incorporation of additives	Enhanced whiteness and thermal stability, Flame retardant, Anti-soiling, Antistatic, Anti-pilling.
Physical modification	At polymerisation stage, dope preparation and spinning condition.	Hi-bulk fibres, Hollow fibres, Change of surface structure, Extreme denier fibre.

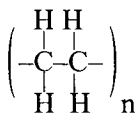
350°C. It has glass-transition between 85 and 100°C which appears to vary with molecular weight. It has poor resistance to strong acids, alkalies and to a few polar organic solvents. Its resistance to sunlight is good.

The modacrylic fibres have similar properties to those of acrylics and are flame resistant..Mostly this fibre is based on a 60/40 or 50/50 copolymer of acrylonitrile with vinylidine chloride ($CH_2 = CCl_2$) together with small proportion of ternary monomer to improve ionic dyeability or hydrophilicity. The better known modacrylic fibres have a ribbon-shaped or pea-nut shaped cross-section. One problem encountered with modacrylic fibre is loss of lustre at the boil [83, 84]. This fibre is used for apparel, home furnishing, wigs etc.

1.7.4 Olefin fibres

Polyethylene and polypropylene fibres are both used as fibre-forming for textile purposes. They are widely used in industrial fabrics. These two fibres can be bonded into non-woven fabric form and used as the base for tufted carpeting. Olefin fibres are relatively low in cost, but both the fibres have low melting points, low glass-transition temperatures and poor dyeability.

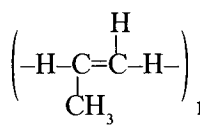
The polyethylene fibre is produced by either high pressure polymerisation of ethylene with a peroxide-catalysed process or low pressure polymerisation of ethylene using new catalysts systems. The molecular structure of polyethylene is a linear polymer of ethylene units with repeat unit of



n = c.550.

Oridinary polyethylene of molecular weight ca 10^4 is drawn up to ten times in length but the gel-spinning method produces the fibre that can be drawn over thirty times and can yeild a Young's modulus of 90 GPa. Fabrics made from this material possess high impact strength, high weather resistance and can be used for making bullet proof clothing, protective wear, filter, sailing cloth, parachutes etc.

The filaments of polypropylene fibre are produced from propylene using special catalysts. The polymerisation process involved is addition, as the double bond is broken in the propylene molecule, the monomer or single molecules join or add together. The filaments are produced by the melt-spinning process in a similar manner to polyester. The repeat unit of polypropylene is



n = c.1800.

When the propylene (monomer) polymerises, the pendent CH_3 can lie in either direction.The randomly disposed CH_3 group (atactic form) does not form good fibre. In the isotactic form the methyl groups are on the same side of the polymer backbone, but in syndiotactic arrangement the methyl groups lay atternately on either side of the polymer chain (Fig. 1-30). To produce this form of polypropylene, special catalysts are used.

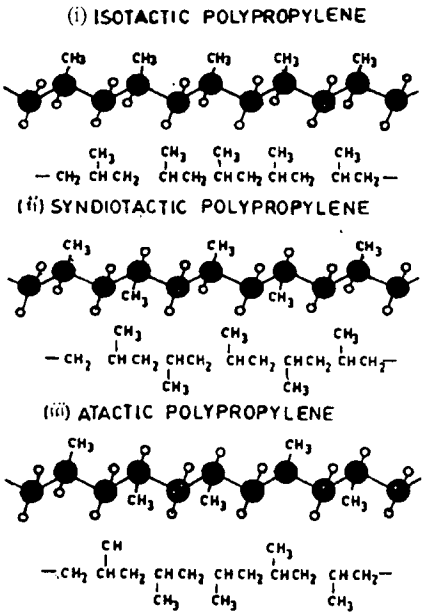


Figure 1-30. Stereostructures of polypropylene chain.

Unmodified polypropylene is highly crystalline. The absence of interchain hydrogen bonding effectively results in the fibre being a permanently swollen state. Stabilisation of polypropylene to heat, oxidation and light, particularly to ultraviolet radiation is extremely important and the patent literature on this subject is extensive. The unmodified polypropylene fibre is difficult to dye and extensive attempts have been made to modify the fibre structure by the introduction of dye-receptive sites [85-89]. Moisture absorption of polypropylene is virtually zero. The fibre has high tensile strength and good resistance to acids and alkalies. With a specific gravity of about 0.9, the fibre is the lightest fibre group. The melting point of polypropylene is 176°C. Polyolefin fibres resemble glass rod in longitudinal and cross-sectional view. The monofilament polypropylene is mainly used in outdoor furniture webbing, in car seat covers, swimming pool covers, filter fabrics, in the ropes and cordage fields etc. The multifilament yarns can be used as blankets, upholstery fabrics, sweaters, carpets, pile fabrics, stockings and can play a major role in non-woven fabrics.

1.8 Miscellaneous Synthetic Fibres

There are many other synthetic fibres have been developed over the years in

many countries, but only a few of them are used for apparel as well as commercial and industrial use. Though these fibres are not widely used but the science and technology of these fibres are briefly discussed from the academic point of view.

1.8.1 Chlorofibres

Poly (vinyl chloride) fibre used for textiles is manufactured from acetylene and hydrogen chloride which is dissolved in mixtures of carbon disulphide and acetone for dry-spinning of normal vinyl chloride (PVC) homopolymer. The fibres are copolymer of vinylchloride / vinyledine chloride and vinyl cyanide or vinyl acetate. The fibre is stretched to varying degrees as it leaves the spinning jet to give different types of filaments. The repeat units of some of the chlorofibres are shown in Fig. 1-31. The water absorption of these fibres are extremely low, softening

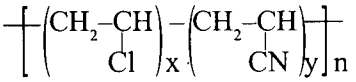
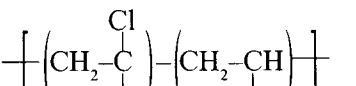
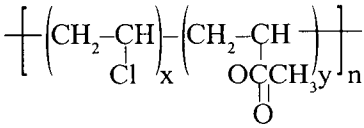
Fibre	Repeat unit
Dynel ® (Union carbide)	 x = 60%, y = 40%
Saran ® (Dow Chem. Corpn.)	 x > 80%, y < 20%
Vinyon ® (Avtex Fibres Inc.)	 x = 85%, y < 15%

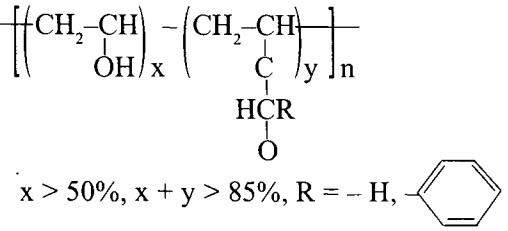
Figure 1-31. Repeat units of some chlorofibres.

temperature is low with considerable shrinkage at 70°C and have poor dyeability at moderate temperatures. These fibres are mainly used in filter cloths, flying suits (in which their property of non-flammability is an asset), curtains (owing to their resistance to degradation of light) and fishing nets (owing to their resistance to water). These fibres have regular round, dogbone or dumbell shaped cross-section and transparent, even and smooth. They are highly lustrous and silky in hand.

1.8.2 Poly (vinyl alcohol) fibres

Polyvinyl alcohol is manufactured indirectly by the hydrolysis of poly (vinyl

acetate). The polyvinyl alcohol is solution-spun to form the fibres and hot stretched at 200°C. As extruded, the fibre is water soluble and must be treated with formaldehyde to make them insoluble. The repeat unit of Vinal® is



x > 50%, x + y > 85%, R = – H,

The crystalline poly (vinyl alcohol) has a kinked chain with three monomer per repeat [90]. This fibre possesses good resistance to acids, alkalies and most organic solvents except formalin, phenol, cresol and formic acid above 60°C. It can be blended with cellulosic fibres and dyed. Vinal does not support combustion; it softens at 200°C and melts at 220°C. Allied Inc. of USA has developed high modulus high tenacity super high molecular weight PVA fibre by gel-spinning and the properties of PVA are similar to those of Aramid fibres. This fibre is employed in protective apparel-rain coats, jackets, hats, umbrellas, suiting and lining fabrics, socks and gloves. Industrial uses include fishing nets, filter fabrics, tyre cord, tarpaulins and bristles.

1.8.3 Elastomeric fibres

Spandex is the generic term applicable to all elastomeric fibres in which the fibre forming substance consists of at least 85% of a segmented polyurethane. The first elastomeric fibre, Lycra was developed by Du Pont around 1958. The fibres are characterised by extremely high elongation and outstanding elastic recovery. The chain molecules are made up of hard segments - crystalline, high melting polyurethane - and of soft segments-low melting, amorphous polyester or polyethers. Hydrogen bonds are mainly formed between the hard segments [91.92]. Elastic hard fibres may be prepared from polypropylene, poly (3-methylbut-1-ene), poly (oxymethylene) [93] and poly (isobutene oxide) [94] and largely based on 4, 4' - methylenebis (4-phenylisocyanate), utilising diamine or glycol extenders. Fig. 1-32 provides a simplified outline of commercial chemistries and Fig. 1-33 shows an overview of dry-spinning process of Spandex.

Spandex fibres have dogbone to rounder cross-section and tend to be larger in

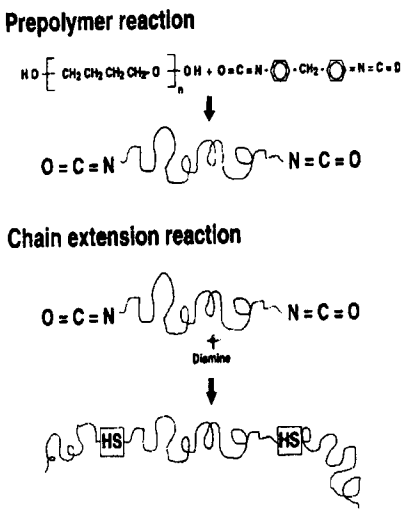


Figure 1-32. Prepolymer reaction, chain extension reaction.

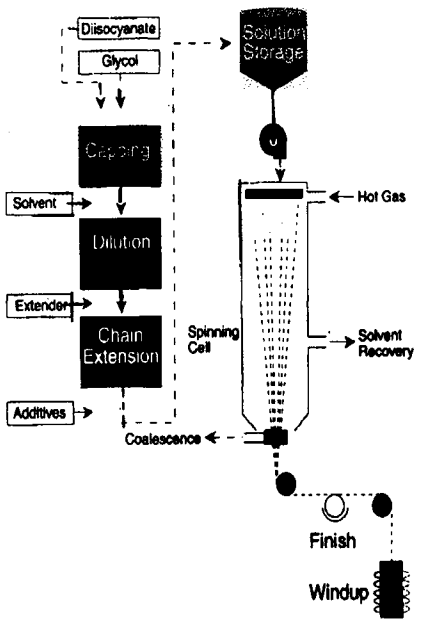


Figure 1-33. Dry-spinning process of Spandex.

diameter. Spandex have a density of 1.0 -1.2g/cm^3, moisture absorption is 0.3 - 3%, while elongation at break amounts 450 - 900% and 95% elastic recovery from 200% extension. This fibre has glass-transition temperature below 0^{0}C, so that soft components have a considerable freedom of movement at room temperature and above. Elastomeric fibres are resistant to dilute and cold acids, and also to alkalies. They can be ironed safely at temperatures below 150^{0}C. They are used for such purposes as swimwear, foundation garments , sports wear, hosiery, bras, sock tops and medical products requiring elasticity.

1.8.4 Carbon fibres

Carbon fibres are manufactured from rayon and polyacrylonitrile. Carbon fibres can be heated up to 1500^{0}C and contains up to 95% of elemental carbon. Graphite fibres can be heated above 2500^{0}C with 99% carbon. The formation of carbon fibres from polyacrylonitrile is outlined in Fig. 1-34. Carbon fibres are used in the aerospace industry, in compressor blade to jet engines, helicopter rotor- blades, aircraft fuselage structures, golf-club shafts, cross-bows for archery and in high speed reciprocating parts in loom.

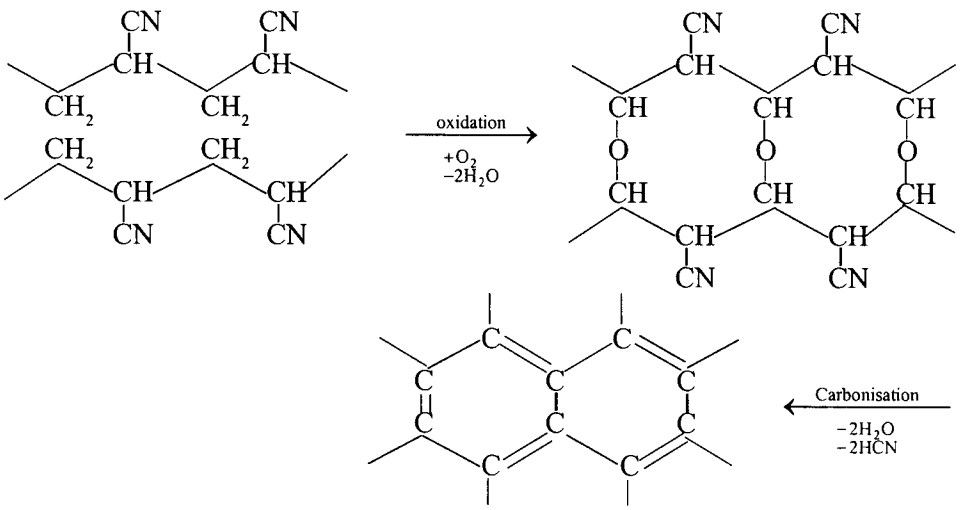


Figure 1-34. Formation of PAN based carbon fibres [95].

1.8.5 PTO fibres (Enkatherm)

Enkatherm, a high temperature flame-proof fibre is based on poly (terephthaloyl oxalic-bis-amidrazone) (PTO). This fibre is produced by wet-spinning and then drawn [96,97]. The formula of PTO and chelated forms of PTO is shown in Fig. 1-35.

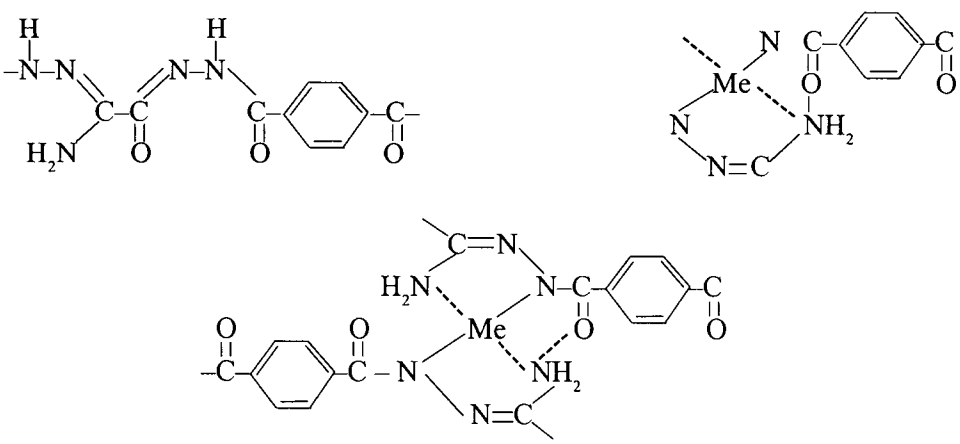


Figure 1-35. Formula of repeat unit of PTO fibre, showing possible chelated form.

1.8.6 Other synthetic fibres

Many other synthetic fibres are found in the literature, the trade names of some of them are Novoloid, PBI, Polycarbonate, Alginate, Flurocarbon (Teflon), min-

eral fibres like glass, ceramic and asbestos fibres, bicomponent and biconstituent fibres etc.

Novoloid is the designation assigned for a class of flame retardant fibre made from cross-linked phenol formaldehyde polymers. Polybenzimidazole, or PBI is nonflammable, comfortable, flexible and used in apparel for space and for drogue chutes and undersuit for astronauts. Polycarbonate fibres are linear polyesters of aliphatic or aromatic dihydroxy compounds with carbonic acid [98] and has excellent resistance to heat and weathering. The raw materials for glass fibre are primarily silica, sand and lime stone with modifiers like aluminium hydroxide, sodium carbonate, and borax [99]. Major uses of the fibre are in window curtains, tablecloths, ironing board covers, lampshades screens etc. The production of electrically conductive fibres [100 - 102] and metallised fibres [103,104] are reported. In perfumed fibres (Mistubishi Rayon) the essence is captured in four pedal-like cavities arranged radially in a hollow fibre. The essence is gradually released through the fibre cross-section produces the refreshing effect typical of deep forests and induces good sleep. Apart from these, textile fibres for medical applications, artificial skin, fibres produced by bacterias like bacterial cellulose, polyester and Bioplastics and carbon fibres from wood, optical fibres and new polytetramethylene ether glycol (PTMEG) from tetrahydrofuran (THF) for elastomeric material (Tetrathene by Du Pont) etc. are the recent advances in the field of fibre science and technology.

Bicomponent fibres are synthetic fibres composed of two firmly but separately combined polymers of different chemical and physical structures. The structure of the bicomponent depends on the shape of the spinnerette orifice (side-by-side, sheath core, matrix - fibril and multi-fibrillary) and the type of spinning method. Due to the structural differences, the two components shrink differently on heat treatment and form crimp and greater bulk in the fibre. The first fully synthetic bicomponent was an acrylic (Sayelle, Orlon 21). The use of sheath-core fibres composed of nylon 6,6 and nylon 6 (Heterofil, ICI) for floor coverings is described.

Biconstituent fibres consisting fibrils of a polymer aligned parallel to the fibre length interspersed in a continuous matrix of another polymer and their structure, resembles the bilateral structure of wool. Clearly fibrillar-matrix ratio and the nature and relative dimension of the components can be altered to vary the physico-

chemical properties. Some of the important biconstituent fibres are Monvelle (Nylon/Spandex), Source (Polyester/Nylon), Chinon (Acrylonitrile/Casein), Mirafi 140 (Nylon / Olefin), Polychlal (Polyvinyl chloride/ Polyvinyl alcohol) etc. New and improved types of bicomponent and biconstituent fibres continue to find increasing application in kintting, hosiery and carpeting [105,106].

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Chapter 2

PREPARATION BEFORE CHEMICAL PROCESSES

2.1 Introduction

After the grey fabrics have been received in the grey room by the finishing enterprises, the bales are opened and inspected, a process which is increasingly mechanical, but much of it remains subjective. The most important point is to obtain fabrics "free from exterior impurities" in order to achieve smooth and trouble free results in the subsequent finishing systems.

2.2 Inspection

It is checked whether the grey fabrics are in conformity with standards, and all weaving faults are marked out. Fabric inspection involves three possible steps : perching, burling and mending. Perching is a visual inspection and the name derives from the frame, called a perch, of frosted glass with lights behind and above it. The fabric passes through the perch and is inspected (Fig. 2-1). Flaws, stains or



Figure 2-1. Perches used for inspection of fabric (Courtesy of Springs Mills).

spots, yarn knots and other imperfections are marked. Burling is the removal of yarn knots or other imperfections from the fabric. The faults are then mended and any knots in the material are then pushed to the back. Mending, is obviously, the actual repair of imperfections. Knotting should be done carefully and thoroughly so that the repair or holes is not visible.

The recent innovation is the cloth inspection by the use of laser beams. Stains, holes, thick and thin places, and warp or weft thread breaks are detected. The apparatus works by the on-line system and eliminates human error caused by tiredness, thus ensuring constantly uniform fabric quality. Such apparatus operates on three different principles, namely, the coaxial, remission and transmission methods. In the coaxial method the scanner light beam is reflecteed back to its source (retro-reflection) onto a receiver situated in the optical hand. In the remission method the emitted light beam is received at a freely adjustable angle by a light guide system and conducted to the signal converter. The transmission method uses a receiver system located below the path of the fabric which measures the light passing through the web. A system for surface monitering of woven and knitted fabrics is shown in Fig. 2-2. The light source (1) is a heliumneon laser or a xenon high pressure lamp,

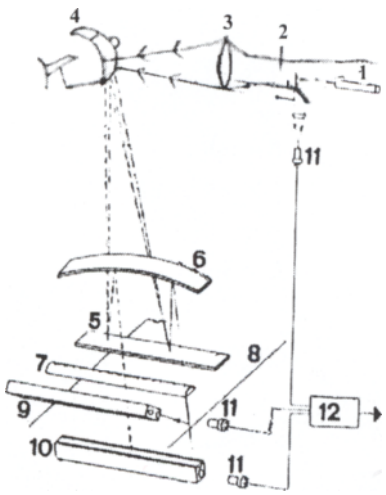


Figure 2-2. Cloth inspection by laser beams using the "Sick-Scan-System Ko-Re-Tra" (Courtesy of E.Sick, GmbH).

the light beam from which passes through an optical system (2) onto a lens (3). From here the light beam is projected onto a fast-rotating multiplanar mirror wheel (4). The light beam becomes a travelling beam by the rotation of the mirror wheel

and is deflected through the planar mirror (5) onto a parabolic reflector with axes parallel and focussed by the cylinder lens (7) onto the web path (8). The beam guiding system ensures that the light beam always strikes the cloth path at the same angle. The light receiver in the remission and transmission methods is a photoconductor [(9) for remission, (10) for transmission] which consists of an optically high grade light conducting material of high homogenity and low absorption. The photoconductor is attached at the front surface to a planar mirror and at the other end to a photoreceiver (11) which converts the amount of light into signals. The fault signals pass from the monitering apparatus through an amplifier to a central electronic unit to which may be connected to a data input, a display unit, a recorder, a counter with acoustic alarm, a marking device, a data store and/or a printer.

2.3 Sewing

After the goods have been inspected, checked and classed in the grey room, according to quality and stamped, they are sewn together, end to end, by sewing machines especially constructed for this purpose. There are various types of sewing machines [Fig. 2-3(a) & (b)]. The fabrics are usually sewn on circular machine.

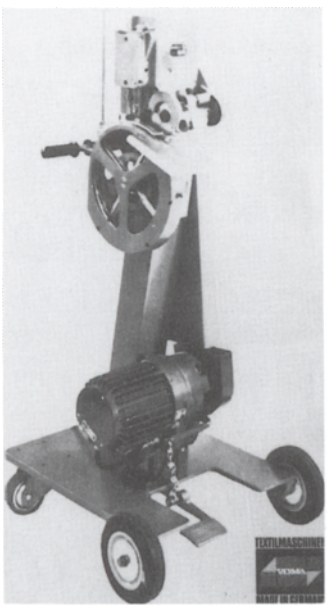


Figure 2-3(a). Portable sewing machine (Courtesy of Gebr. Dohle GmbH & Co.).

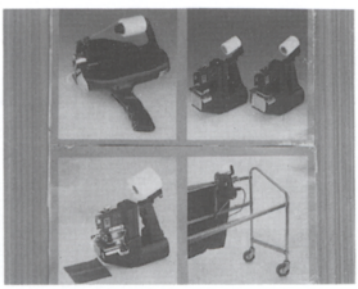


Figure 2-3(b). Overlocking machines for joining piece lengths of fabric (Courtesy of Metalplast, Italy).

The portable Rotary Sewing Machine is very handy. The main difficulties are bent selvedges. Stitching should be done in such a manner that the creases in fabric at the time of stitching should be avoided. The use of proper stitching thread is necessary to avoid stitch marks during colour padding. For heavy fabrics intended for mercerizing and continuous operations, the seam should be wider (15 mm) and stronger. Sometimes, glueing or bonding of fabrics to bind the end pieces by fusing polymer films under the action of high temperature is used instead of sewing to reduce the amount of rags. Goods of similar weight, width and construction and the goods which will receive a similar treatment is batched together and each lot is given a number.

2.4 Mechanical Cleaning of Fabrics

The pre-cleaning of grey fabrics may be carried out in a seperate unit just before cropping and shearing operations. The efficiency of pre-cleaning is the foundation of good cropping and shearing. The pre-cleaning operation is achieved with :

(i) Thorough grinding of the cloth surface by emery covered rollers.

(ii) Scraping with suitable designed and located scraping blades.

(iii) Efficient brushing on both sides of the cloth.

With the progress of grinding and scraping action, the cloth surface gets covered with thread ends, dust, fluff, dirt etc., thus the pre-cleaning unit should have a good dust exhausting system.

2.4.1 Brushing

The purpose of brushing is to remove the short and loose fibres from the surface of the cloth. It also removes husk particles clinging to the cloth. Brushing is mainly done to fabrics of staple fibre content, as filament yarns usually do not have loose fibre ends. Cylinders covered with fine bristles rotate over the fabric, pick up loose fibres, and pull them away by either gravity or vacuum. The raised fibre ends are cut off during shearing operation. Brushing before cropping minimise pilling.

2.4.2 Cropping and shearing

Shearing is an operation consists of cutting the loose strands of fibres from either surface of a fabric with a sharp edged razor or scissors. By manipulating the shearing it is also possible to cut designs into pile fabrics. Good cropping is perhaps, the simplest way of reducing the tendency of blended fabrics to 'pill'. In the case of cotton fabrics, in particular, care should be taken to see that the shearing

blades do not scratch the surface of the fabric, which otherwise can cause dyeing defects during subsequent dyeing.

Fig. 2-4 shows a four-cutter shearing machine and Figs. 2.5 and 2.6 show the

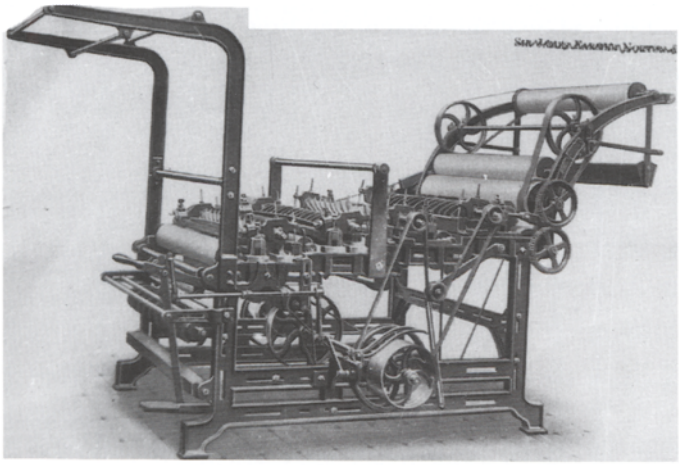


Figure 2-4. 4-cutter shearing machine (Courtesy of Farmer Norton & Co. Ltd.).

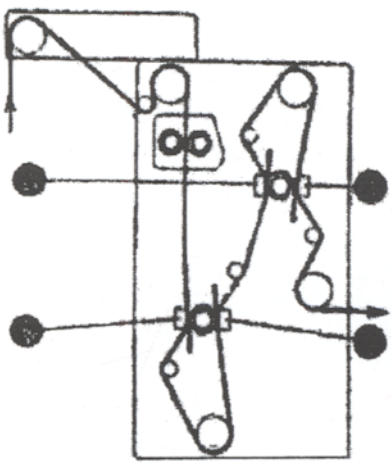


Figure 2-5. Typical 2-cutter cropping machine.

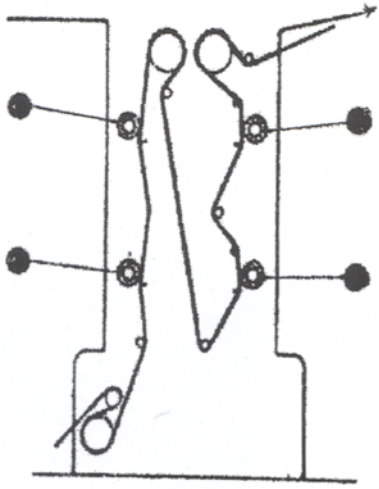


Figure 2-6. Typical 4-cutter cropping machine.

simplified line diagrams of 2 and 4-cutter machines which illustrate the shearing and cropping. The machine consists of a strong framing carrying four revolving cutters fitted with left and right hand spiral blades. A 4-cutter machine has four cutting points, two for the face and two for the reverse side. The term 'cutting

point' denotes the contact line between the spiral shearing cylinder and the ledger blade, over which the fabric has to pass during cropping and shearing operation. Each cutter is provided with adjustable ledger blade. Before leaving the machine, the cloth is brushed by a spiral revolving brush. The machines are of totally enclosed construction with exhaust channels. Although there have been no major changes in the latest cropping and shearing machines, a modern fully automatic shearing range (Fig. 2-7) has the following features :

(i) Fabric feeding device (electronically controlled) ensuring the entry of crease free fabric.

(ii) A soft bed under the cutters so that the blades which cut the fibres close to the surface do not damage the fibres in the yarn.

(iii) Seam joint sensors (electronic) which lift the shearing rolls away from the fabric surface when a seam passes.

(iv) Magnetic metal detectors sense the iron particles embedded with the cloth and activate the limiting switch, so that the machine stops, the concerned particles are removed and the machine restarted.

(v) Hydraulic speed gear system has been replaced by suitable DC drives. Modern shearing machine can operate up to a speed of 100m/min. The units have been made more modular, in order to facilitate quick installation.

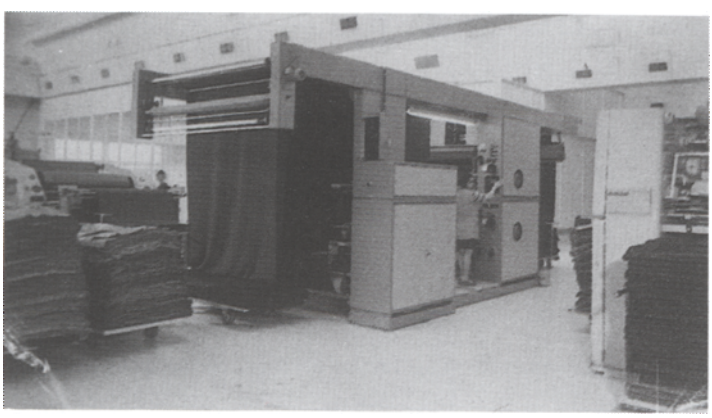


Figure 2-7. Fully automatic shearing range [Courtesy of Swiss Association of Machinery Manufacturers (VSM)].

Shearing machines fitted with serrated blades have been found satisfactory for

the cutting of polyester materials. Polyester staple fibre fabrics are cropped and singed mainly to control the pilling tendency. For polyester/wool blended fibre fabrics a good cropping is essential if the fabric is not to be milled. If it is desired to finish simulating wool, loose polyester should first be removed by brushing, cropping and singeing and then the fabric is soap-milled to produce a wool cover, which can be cropped to give the required appearance and handle.

2.5 Singeing

The aim of singeing is to burn-off the protruding fibres and hairs from the fabric surface. The spinning process produces hairiness of the yarn and lower the yarn counts (Ne 26/1 – 36/1) greater is the degree of hairiness. Therefore the reasons for singeing should be considered more closely.

(i) Singeing improves the end use and wearing properties of texiles.

(ii) The burning-off of protruding fibres results in a clean surface which allows the suructure of the fabric more clear.

(iii) Singeing reduces the fogginess caused by differing reflection of light by the projecting fibre and the dyed fabrics appear brighter.

(iv) Singeing is an effective means of reducing pilling in blended fabrics containing synthetic fibres.

(v) Unsinged fabrics soil more easily than singed fabrics.

(vi) A closely singed fabric is essential for printing fine intricate patterns.

(vii) Singeing process facilitates and speeds up desizing, if the fabric is impregnated with desizing liquor immediately after singeing.

On the other hand there are singeing faults which are not visible and once occurred can no longer be repaired. They are :

(i) Uneven singeing effect can cause streaks when the fabric is dyed, or bubbles when the fabric is finished.

(ii) In the cotton system singeing is done on the grey cloth, but for blended fabrics containing synthetic fibres grey state singeing is not advisable because small globules of melted synthetic fibres absorb dye preferentially, giving cloth a speckled appearance.

(iii) There is a possibility of thermal damage to temperature sensitive fibres, for instance polyester.

(iv) Stop-offs can cause heat bars on fabrics. Creasing produces streaks which is magnified when dyed.

(v) Protruding fibres are firmly bound by singeing on the surface by the sizing agent by hardening of the size and can lead to difficulties in desizing.

(vi) When singeing is done after dyeing, heat can cause colour loss from polyester portion of the blend because of sublimation of dye.

(vii) There may be reduction of tear strength due to oversingeing of the fabric.

Generally, singeing is done on both sides of the fabric. No chemical change occurs in the fabric during singeing and the reaction is basically one of oxidation. Singeing and desizing can be frequently combined by passing the singed cloth through the water bath which include enzymes. The enzymes digest the various sizing agents, making it easy to remove them during the scouring operation. The combined process also prevents possible latent damage to fabric from the singeing flame or heated plates.

2.5.1 Singeing different kinds of fibres fabrics

In singeing the short fibres are burnt off from the surface of the fabric by direct or indirect heating systems without damage to the cloth by scorching or burning. The thermal behaviour of different kinds of fibres are different and singeing at higher temperature is naturally associated with greater hazards on excessive contact period and may cause thermal degradation of the fibre.

In case of vegetable fibres, grey singeing is necessary as it leads to slight yellowing which needs subsequent bleaching to get high degree of whiteness. Grey singeing is also economical as singeing at any other stages of processing requires additional washing and drying. Vegetable and regenerated fibres fabrics can be singed very strongly with maximum burner intensity to obtain good results. Regenerated fibres normally burn to a little less easily than natural fibres.

Wool has poor combustion properties and are very sensitive to temperatures and hence woollen materials are not subjected to intense flame like cotton. In woollen fabric flame is not generally allowed to penetrate the material and this can be obtained by blowing air through the fabric from the opposite side of the flame so that the flame will be restricted only on the surface of the fabric. Alternatively, the fabric can be guided to water cooled guide rollers allowing the flame to heat the cloth. When the flame strikes the fabric it is reflected by air/steam cushion created within the material.

Amongst the synthetic fibres polyester has the greatest significance. It melts at

280-290°C, but does not burn till about 500°C. 'Reflector' or 'refractory' singeing machines produce smears of fused polymer on the surface of the polyester cloth and therefore unsuitable for polyester material. Thus flame singeing machine with a powerful flame is needed and also helps in overcoming the problems of oligomers i.e. the small chain polymers that come to the surface. High temperature singeing process may sometimes change the glass-transition temperature (T_g) of synthetic fibres that lead to uneven dyeing.

For blended fibre fabrics singeing conditions are to be selected depending on the sensitiveness of the kinds of fibres to heat, blend composition, weight of fabric and fabric geometry. For example, singeing should be carefully conducted to avoid heat damage of the acetate component of the accetate/viscose blended fibre fabrics. Though singeing improves the restistance to pilling of the polyester/wool blended fabrics, but should not be carried out on low weight fabrics because of risk of damage. In the case of 80/20 polyester/cotton blended fabrics or fabrics with dented pattern, sometimes, the cloth gets weekened only in the thinner or shadow portion. This is not detected until the material reaches to finish folding. If singeing is carried out after dyeing the sublimation fastness of disperse dyes used must be adequate to withstand the singeing conditions.

Singeing machineries are mainly based on direct and indirect singeing systems. The cloth is first passed over one or more steam-heated copper drying cylinders to remove the moisture and to raise the nap. The direct singeing may be done either on a hot plate, or on a rotary cylinder, or on a gas singeing machine or on a machine combining plates and gas burners. The special features of indirect singeing systems are no flame contact, uniform singeing, heat retention zone and singeing by means of heat radiations. The indirect system produces fabrics which have a softer touch as compared to other methods. Gas singeing is more convenient, more economical and more effective than other methods and is well accepted commercially. The plate singeing and roller singeing machines are now out of date. Clean singeing of potentially troublesome synthetic fibres can be achieved by using the scavenger tubes which are specifically designed to avoid thermoplastic melt (beading) problems.

2.5.2. Plate singeing machine

The machine consists of two copper plates of about 1-2" thick. The plates are

heated to bright red from the opposite side. The furnaces are fired by heavy petroleum oil, which is vaporised through special nozzles, by the action of steam, into a fine spray. The properly dried cloth passes over the plates at speeds up to 200 yards per minute, according to quality. A special traversing arrangement for the cloth is supplied to prevent local cooling of the hot plate. The singed cloth is then run through water to extinguish the spark, passed through a padding mangle and delivered to a winch or plaiter. The machine is driven by electric motor, steam engine or belt pulleys.

2.5.3. Rotary cylinder machine

In this type of singeing machine the cloth passes over a hollow cylinder which revolves slowly in the opposite direction of the goods. The hollow cast iron or copper cylinder may be fired internally. The cloth is drawn through the machine by a powerful squeezer nip, singed, run through water bath and plaited.

2.5.4 Gas singeing machine

Old singeing machines are often used which in their time worked acceptably when only pure cotton materials were singed, but which, however are no longer suitable for singeing of newer fibres and their blends. New technologies and techniques have been developed to suit the modern requirements.

In gas singeing machine, the singeing flame must have the capacity to loosen the fibre ends from the body of the sized yarn to such an extent that the flame envelopes them to be burnt off. When the flame at a temperature of around 1300°C touches the cold and moist material, an air/steam buffer zone results between the material and the flame. This buffer zone hinders singeing down to the base of the material unless the singeing flame has certain features. The singeing flame has thermal and high mechanical energy. To burn the material energy is needed. Metering is only possible by controlling the energy supply within a given time. The problem of singeing gets even more difficult as one has to distinguish between two types of pyrolysis i.e. exothermic pyrolysis of cotton and endothermic pyrolysis of polyester. Polyester ignites only at a temperature of 480-500°C, while starts melting at a temperature of 250-270°C. So, in order to avoid the polyester starts melting before it gets ignited the energy has to be supplied in a shock form and the pyrolysis has to be like an explosion, igniting the protruding fibre end over all its length. Another area of development in the gas singeing machine are the burners, together

with the supply and control units for the gas/air mixture. The gas/air mixture supplied to the burner is prepared in a proportional mixing valve, which means that the ratio of gas and air is always in accordance with the stoichiometric value independent of the quality of the mixture supplied to the burner.

Figs. 2.8 and 2.9 illustrate 4-burner and 2-burner gas singeing machines respec-

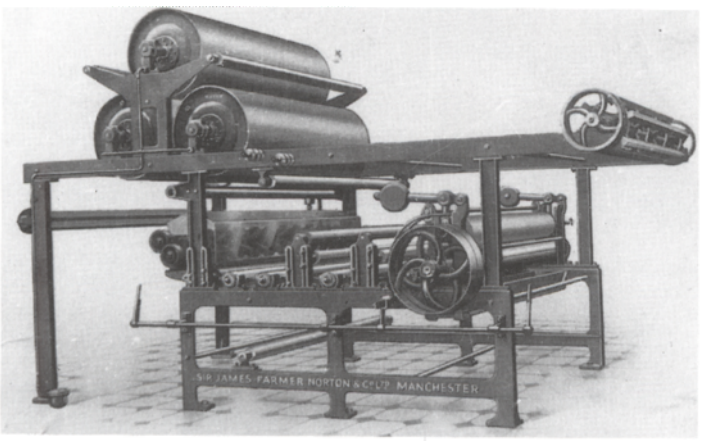


Figure 2-8. 4-burner gas singeing machine (Courtesy of Farmer Norton Co. Ltd.).

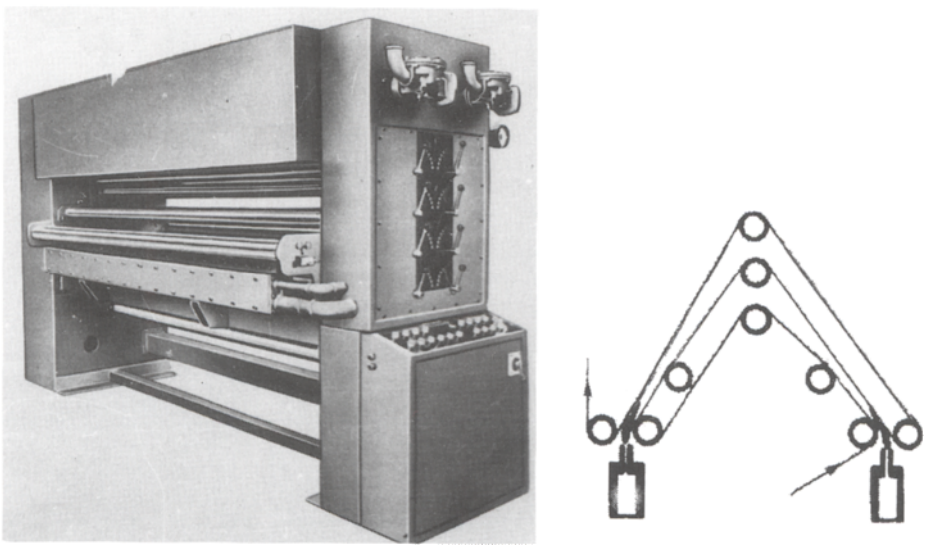


Figure 2-9. Two burner gas singeing machine (Courtesy of Ernest Turner (Parex) Ltd.).

tively. In order to avoid singeing streaks gas burners may be used for singeing with indirect system. In the indirect singeing, the temperature reaches the goods via heat stores-mainly infra-red radiation. Any variations arising from the burners are absorbed there and are compensated.

The schematic diagram of a modern metal burner ribbon type singer showing its component and fabric travel is shown in Fig. 2-10. In all types of burners, the gas

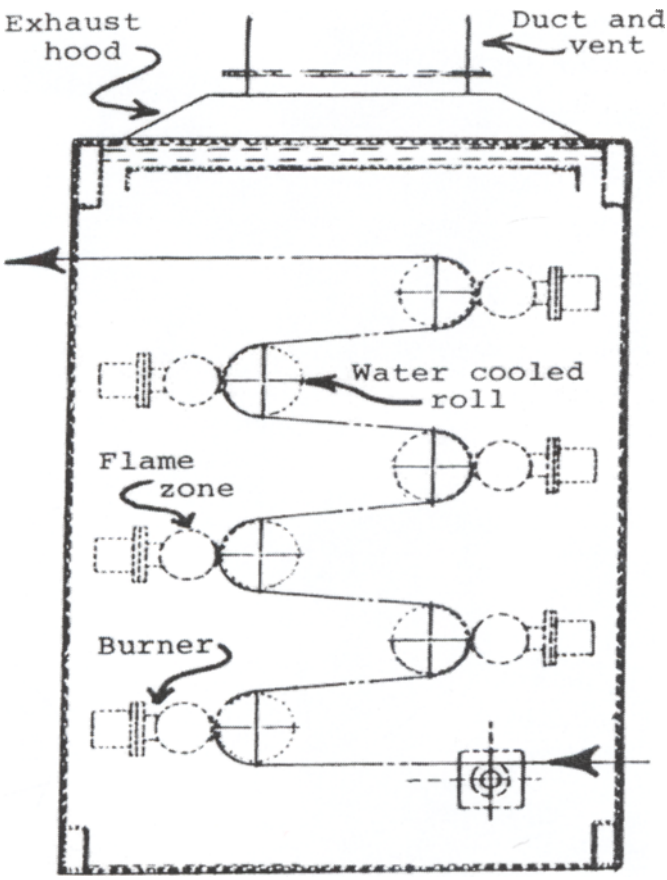


Figure 2-10. A typical singer showing its component and fabric travel (Courtesy of Menzel Inc.).

singeing machine is equipped with mechanical threading devices. The cloth is passed over tension rails, adjustable tensioner and then over gas burners. The fabric passes

the burners at a distance of 6-8 mm, and depending on fabric weight and fibre blend. The speed varies between 50 and 160 m/min, thus leading to a short contact time between flame and material. The flame because of its high thermal energy supplies them with sufficient heat to simultaneously ignite the entire surface and burn away the protruding unanchored fibres. A gas jet singer contains a series of small openings or jets mounted on a gas supply pipe. The jets are spaced 1 to 2 inches apart on the pipe which is parallel to the cloth and perpendicular to the warp direction. The length of the slit may be adjusted according to the width of the cloth. Recently, a burner design is modified to give a higher temperature, say up to 1300°C and fully combusted flue is used instead of flame produced by gas-air mixture. The method gives a light blue to almost colourless flame.

The position of the burner must be taken into consideration according to the fabric to be singed (Fig. 2-11). There are three different methods of applying flame to the material by changing the position of the flame to offer :

(i) Tangential singeing [Fig. 2-11(a)].

(ii) Singeing onto water cooled rollers [Fig. 2-11(b)].

(iii) Singeing into the fabric [Fig. 2-11(c)].

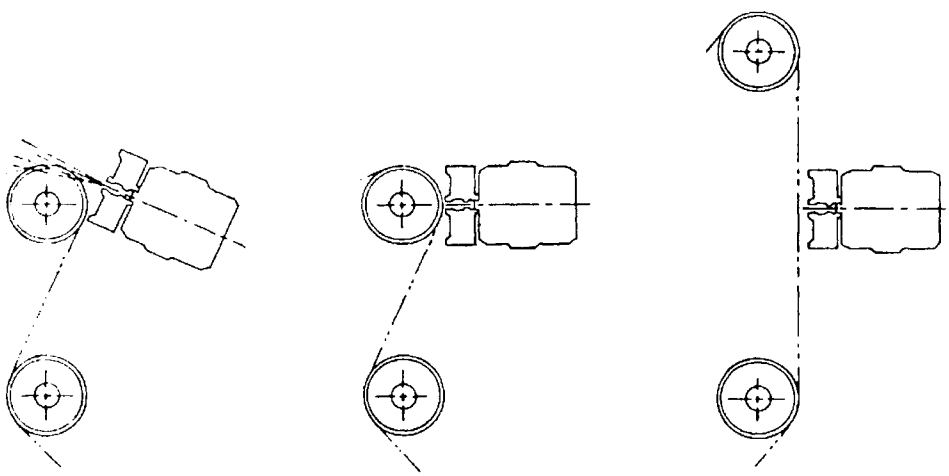


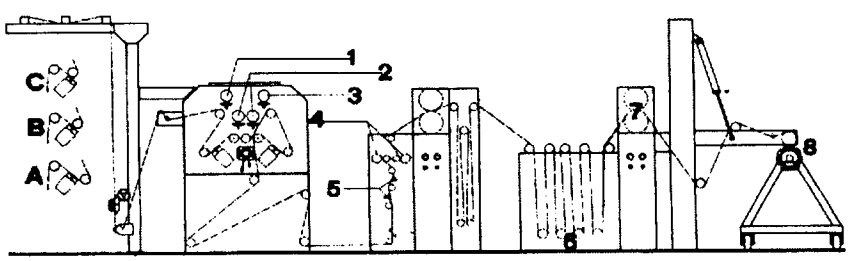
Fig 2-11(a) Fig 2-11(b) Fig 2-11(c)

Figure 2-11. Position of the burner depending on the fabric.

In the tangential singeing position the flame touches the passing fabric only tangentially. Only the protruding fibres are burned-off, while the fabric itself has hardly any contact with the flame. This position is specially suitable for the singeing of light weight and sensitive fabrics as well as for the levelling of fabrics with broken filaments.

In the singeing on to a water-cooled roller, as indicated in the accompanying sketches in Figs. 2-9 and 2-11(b), the flame hits the fabric at a right angle, but the fabric itself lies flat on the off-side on a water cooled roller. An elastic steam and air cushion is formed inside the fabric structure which resist any possible penetration of flame into the fabric. The flame is thus effective only on the surface. In view of the cold water in the water-cooled roller, the fabric remains relatively cooled during the singeing process and temperature sensitive fabrics are thus protected from heat. This position is well suited for all blended and synthetic fibres fabrics as well as those with open design.

In singeing on to the free-guided fabric position [Fig. 2-11(c)] the flame hits also at a right angle the free-guided fabric and also passes through the fabric whereby even the interstices gets good singeing. The arrangement is well suitable for fabrics made from natural and regenerated fibres and for heavy technical materials made of all types of fibre blends. Fig. 2-12 shows the line diagram of a modern singeing machine disposing three singeing positions which can be pre-selected.



1 air pressure
2 burner inside pressure
3 gas pressure
4 brushing rollers
5 beater rollers
6 impregnation compartment
7 squeezing rollers
8 giant batcher
A–C various singeing positions

Figure 2-12. Line diagram of a gas singeing machine used for all kinds of fabric qualities (Courtesy of Osthoff KG, Germany).

The singeing machine is provided with a control over flame height. The flame height may become irregular due to clogging of nozzles. Flame intensity indicates energy, of the singeing flame, which is applied on a unit area of the fabric per unit

time. This depends on the speed of the flame and heat capacity of the flame. It is usually measured in millimeter head water of the combustible mixture of the burner. The actual flame intensity for singeing lies between 5 and 20 mbars which can be set steplessly in the described manner.

The burner should be capable of individual swivelling to and from the cloth. The swivelling mechanism is connected to the gas supply system, whereby the burners are automatically ignited or extinguished. Dust and gaseous combustion products are exhausted through a ventilation hood arranged above the singeing machine. Singeing room should be well ventilated, spacious and fire-proof.

Modern singeing machines include pneumatic adjustable firing position, ultra-violet flame scanner, built-in flame extraction system, flame shearing effect, improved guiding system, high frequency burners and variable speed and adjustable burners. The use of double jet burner initiates singeing by means of an intense concentrated and homogeneous flame and snagmetic control system for controlling all flame parameters. Singeing machine is equipped with meter counters, speedometer and a thermocouple with a stationary multivoltmeter for measuring the temperature of singed surface. All modern singeing machine is electronised, with added device of warning noise or fire alarm in the case of a fire. As an added precaution, wet sprinklers and unburnt gas detectors have also become necessary due to stringent safety regulations. Apart from these features, singeing machineries should also have steam quenching for those sorts of fabric which are not to be wetted, e.g. grey mercerized fabrics.

2.5.5. Singeing circular knit fabrics

As with woven fabrics, hairiness of the face of knitted fabrics is seldom desirable. There are various ways to avoid this problem. The yarn quality, uniform face appearance and proper yarn count are important factors where the quality of knitted fabric is concerned. The quality can be further improved by additional process stage such as, for instance, singeing.

The singeing machine for circular knit fabric differs from the well-known singeing machine for woven fabrics only in guiding and transport of the fabric. The real problem consists in properly opening out the tubular fabric. The distance between burner and fabric must be exactly the same at every point. The burner must be so designed that there is an uniform flame intensity over the entire tube circumfer-

ence. The burner may be ring-shaped, and the tubular fabric too must be opened out in a circular form. A high capacity double jet burners can also be used. Based on the automatically adjustable system, Dornier (Germany) and other manufacturers like Rimmer, Brazzoli, Osthoff etc. have developed a circular singeing concept to singe knit goods in tubular form without edge marks. The fabric is guided to the circular expander via turntable and detwister (Fig. 2-13). The fabric runs through

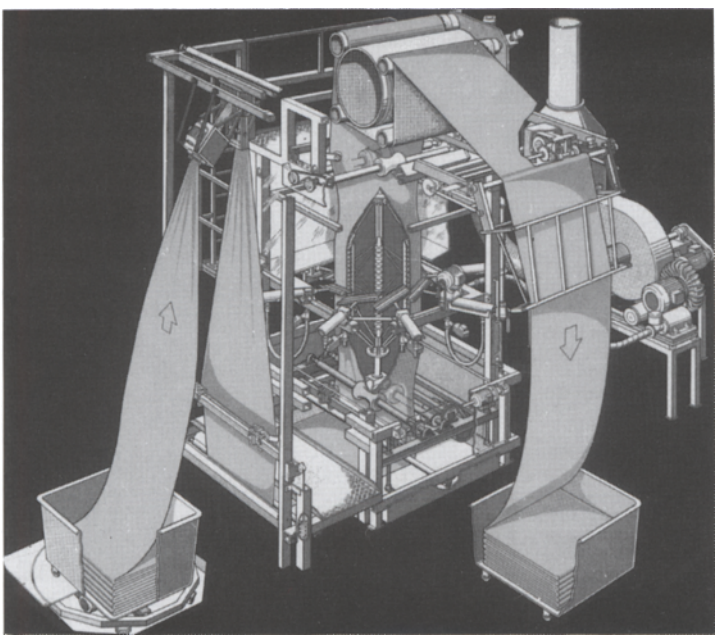


Figure 2-13. Singeing machine for circular knit fabric (Courtesy of Dornier Gassellschaft mbH).

the machine in an upward movement, thereby aiding the effect of the exhaust device, which is also fitted above the burner in circular arrangement. The expander applies tension, while eight swivelling burners are arranged on a ring in such a manner that, even with width adjustments, the full width of the flame of each segment is applied to the fabric. In the gas singeing process, the flame intensity of 70 to 100 mm water column is suitable. In the singeing area there is practically no longitudinal tension. After leaving the guide expander the fabric is then taken over by the driven spark extinguishing and plaiting unit. All data such as diameter, burner distance, burner intensity and speed are controlled from a computer terminal. Singeing and cellulase enzyme treatment to defuzz and improve the visual appearance is thus a best choice to give the consumer a value-added quality of knit fabrics.

2.6 Process Sequence

The selection of correct process sequence has a direct bearing on the quality of further processing operations such as dyeing, printing, finishing etc. Some 60% of all the problems occuring in subsequent processing generally originate from a wrong and inadequate selection of process sequence. Precise requirements of fabric preparation depend on the kind of fibre and its proportion contained in the blends, fabric construction, size type and loading and the end use. Cotton knitted fabrics are subjected to a modified routine in which singeing and desizing stages are sometimes omitted, whereas for woven fabrics desizing cannot be omitted. Synthetic fibres are produced under controlled conditions and contain only added impurities, their cleaning is comparatively easy. However, when they are used in admixture with natural fibres, the problems aggravate. Preparation of fabric also depends on the end requirement. For example, ''full white bleach'' is done in the case of goods which are to be supplied white, 'half bleach' for over dyeing or whenever big blotch and fully covered designs are to be printed and 'full bleach' whenever pastel shades are to be dyed. Cotton fabrics to be dyed in deep shades will most likely require mercerization in order to improve their dyeability.

Fabric preparation is a costly series of energy consuming processes. Economic consideration, thus, have led to considerable modification of the existing processing sequences. The traditional sequence of pre-treatment is shortened by single stage bleaching, where kiers are still in use. It is therefore necessary to balance the cost of preparation by optimizing the process sequence, conditions and development of shorter routes. Furthermore, several new types of machineries and newer processes have been evolved to meet the requirement of efficient but economical and rapid preparation of cloth. All these factors necessitate the alteration of process sequence to get the optimum results and the technologists can decide as and when any of the stages are to be by-passed without compromising the quality of the goods. The sequence given in this chapter, therefore, serves only a general guidence.

2.6.1 Process sequence for cotton fabric on kier

Method A : For white/printing : (Poplin, Cambric, Rubia, Mulls etc.) Grey mercerize → Scour in kier → Rinse in kier → Wash → Chemicking in Cistern → Wash → Open boil in kier using H_2O_2 → Rinse in kier → Wash → Scutch → Dry.

Method B : For dyeing : (Poplin, Cambric, Rubia, Mulls, Sheetings etc.) Grey

mercerize → Desize in Cistern → Wash → Scour in kier under pressure → Wash → Open boil in kier using H_2O_2 → Rinse in kier → Wash → Scutch → Dry.

2.6.2 Process sequence for cotton fabric on J-Box

Method A : For white/printing : Grey mercerize → Desize in J-Box Cistern → Wash → Caustic Saturator → Steam in J-Box → Wash → Chemick Saturator → Store in J-Box → Peroxide Saturator → Steam in J-Box → Wash → Scutch → Dry.

Method B : For dyeing : Grey mercerize → Wash → Caustic Saturator → Steam in J-Box → Wash → Chemick Saturator → Store in J-Box → Wash → Antichlor → Wash → Neutralise → Scutch → Dry.

2.6.3 Process sequence for cotton fabric on Pad-Roll/Thermoreaction Chamber (T.R.C.)

Method A : For white/printing : Singeing cum Desizing → Wash → Scour on Pad-Roll (T.R.C.) → Wash → Dry → Mercerize → Bleaching on Pad-Roll (T.R.C.) → Steaming → Wash → Dry.

Method B : For dyeing : Grey mercerize → Scour on Pad-Roll (T.R.C.) → Wash → Bleach on Pad-Roll (T.R.C.) → Wash → Dry.

2.6.4 Process sequence for cotton fabric on Jumbo Jigger

Method A : For white goods : Grey mercerize → Scour on Jigger → Wash → Chemicking → Wash → Peroxide Boil → Wash → Neutralise → Unload.

Method B : For dyeing : Grey mercerize → Scour at boil → Wash → Chemicking → Wash → Antichlor → Wash → Neutralise → Unload.

Method C : For coloured woven sorts : Grey mercerize → Desize → Wash → Chemicking → Wash → Peroxide Boil → Wash → Neutralise → Dry → Mercerize → Dry.

2.6.5 Process sequence for knitted cotton goods

Method A : For white goods : Hypochlorite Bleach → Reduction or Peroxide Bleach + Fluorescent Whitening Agent (FWA).

Method B : For white goods : Demineralization acid medium (metals) → Peroxide Bleach + FWA.

Method C : For white goods : Alkaline treatment + Demineralization (oils, paraffin spots + metals) → Peroxide Bleach + FWA.

2.6.6 Process sequence for woollen fabric

Method A : For dyeing in the worsted routine : Greasy wool → Scouring → Carding → Gilling → Combing → Combed Tops → (Top Dyeing) → Gilling → Recombing → Drawing and Spinning (Yarn Dyeing) → Weaving/Knitting → Fabric Dyeing → Finishing.

Method B : For dyeing in the woollen routine : Greasy wool → Scouring (loose stock dyeing) → Oiling → Willeying → Carding → Spinning → (Yarn dyeing) → Weaving → Scouring and Milling → Fabric Dyeing → Finishing.

2.6.7 Process sequence for silk fabric

Method A : Grey Inspection & Stitching → Singeing → Washing →Degumming → Bleaching → Dyeing → Padding mangle (apply some adhesive also) → Stentering → Felt Calendering → Curing → Decatising (to impart fluffy & soft feel).

2.6.8 Process sequence for polyester fabric

Method A : Heat setting → Scouring → Bleaching → Weight reduction → Dyeing → Drying on stenter.

2.6.9 Process sequence for nylon fabric

Method A : Ordinary woven fabric : Heat-set → Desizing & Scouring → Bleaching → Fluorescent Whitening → Pre-setting.

Method B : Hard twisted woven fabric (Gorgette) : Embossing → Creping (relaxing) → Desizing & Scouring → Bleaching→ Fluorescent Brightening → Pre-setting.

Method C : Knitted goods : Desizing and Scouring → Bleaching→ Fluorescent Whitening → Pre-setting.

2.6.10 Process sequence for polyester/cotton blends

Method A : For yarn : Scouring → Bleaching → Dyeing → Anti-static finishing.

Method B : For White goods : Desize → Scour → Mercerizing → Heat-set → Anti-pilling i.e. Brushing, Cropping and Singeing → Bleaching and Optical Whitening → Stentering or Sanforizing.

Method C : For deying : Desizing → Scouring → Mercerizing→ Heat-setting → Bleaching → Dyeing → Anti-pilling i.e. Brushing, Cropping and Singeing → Stentering or Sanforizing.

Grey singeing of polyester/cotton blended fabrics may be carried out only on

goods that are to be dyed by continuous processes or by high temperature batch processes using non-critical dyes. If the warp is heavily sized, singeing will be ineffective in the beginning and inset later in the routine. Goods that are to be prepared on J-Box range in rope form, may be heat-set in the grey state if they are reasonably free from loom stains. Unmodified sizes are also difficult to be removed from the fabric after heat-setting.

2.6.11 Process sequence for polyester/viscose blends

Method A : Desizing → Washing → Heat-setting → Singeing → Drying.

Method B : Singeing → Desizing → Washing → Drying → Heat-setting.

The process of mercerizing is omitted when viscose is present in the blends. Sometimes singeing operation is done after dyeing to avoid sooty appearance or dye specks arisen from melted beads of polyester.

2.6.12 Process sequence for polyester/wool blends

Method A : General : Grey Inspection → Removal of stains → Scouring → Pre-setting (Setting of wool component by crabbing) → Drying → Heat-setting → Dyeing → Brushing & Cropping → Singeing → Light scour (if necessary) → Steam or Damp → Decatising or Pressing.

Method B : Knitted goods (Crisp handle) : Open steam (allowing full relaxation) → Light brushing → Close Cropping on face side of fabric → Decatising.

Method C : Knitted goods (Soft handle) : Heavy Scour → Cropping on face side of fabric → Open Steam → Decatising.

A worsted polyester/wool blended fabric is prepared by crabbing or blowing and then Scoured → Dry → Heat-set (on pin stenter) → Brushed and Cropped → Press or Decatise.

If it is desired to finish a simulating wool, the loose fibre from the surface of the blended fabric is first removed by brushing, cropping and singeing and then soap milled to produce a wool cover, which can be cropped to give required appearance and handle. Heat-setting after milling is an optional process.

2.6.13 Process sequence for diacetate/viscose blends

Most blends for shirtings consists of 50% each of diacetate and viscose in plain weaves and the sequence of operations may be as follows :

Singeing (where necessary) → Contraction or relaxation → Scouring and Desizing → Dyeing → Finishing.

Chapter 3

DESIZING

3.1 Introduction

Desizing is the process in which the size applied to the warp yarn before weaving is removed to facilitate the penetration of dyes and chemicals in the subsequent wet processing operations. About 65% of the cotton used for textiles is made into woven fabric. The purpose of sizing is to form coating of sufficiently strong and elastic film around the cotton warp yarns so as to stand the tension during weaving and reduce the breakage. The surface coating of sizes are stiff, hard, smooth and less absorbant to water. Apart from film forming materials, the size recipe many a time also contains other additions such as humectants, binders and lubricants. Traditionally, starch-and tallow based lubricants (triglycerides) have been used as sizing components for cotton, being readily available, relatively cheap, and based on natural, sustainable materials. The removal of hydrophobic part of the sizes (the lubricants) is often especially problemetic. These are not removed during desizing, but are expected to be stabilised or emulsified in the alkaline scouring. The total material present in the cotton fibre is up to 20% of the fibre weight including that of 4-12% natural impurities. In the process of desizing, not only sizing agents, but also some natural impurities are eliminated from fibres.

About 75% of the sizing agents used throughout the world today consist of starch and its derivatives because of its low cost. Chemically starch is composed of amylose and amylopectin. Amylose molecule is in the form of helix with six glucose units per turn (Fig. 3-1). The low molecular weight of amylose is water soluble

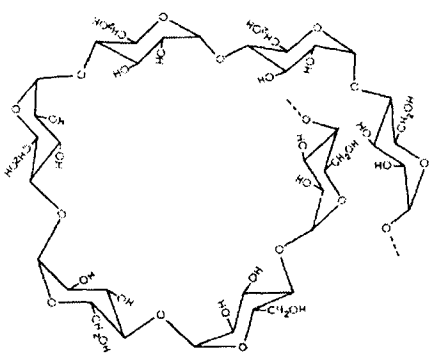


Figure 3-1. Helical structure of amylose [1].

straight chain polysaccharides of glucose whereas amylopectin (70-80%) being water insoluble is difficult to remove from cotton due to its higher molecular weight and branches chain (Fig. 3-2). Apart from starch, modified starches such as

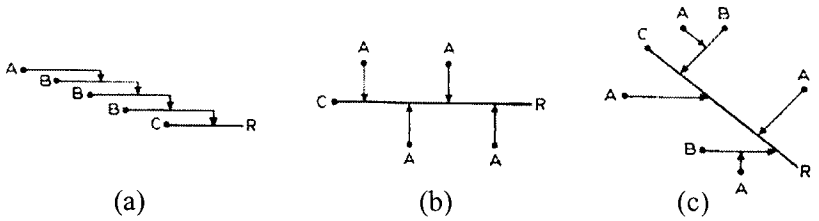


Figure 3-2. Schematic representations of amylopectin [2].
R = Reducing end.
A = Non-reducing end of singly connected chain.
B = Non-reducing end of multiply connected chain.
C = Non-reducing end of chain which carries a reducing end.

hydroxyethyl starch, carboxymethyl cellulose (CMC) and natural gums are also used. The other size ingredients particularly used in the case of regenerated cellulose fibres are protein based glue, gelatin etc.

In synthetic fibres the nature of sizes and sizing ingredients are different. Synthetic yarns are stronger and hence increasing strength by sizing is not the aim and adhesion of the sizing material to the yarn is also difficult. Starch sizing of man-made fibres possess many problems when yarns are slashed and fabrics are woven. Furthermore, with the introduction of textured synthetic fibre yarns, blended fibre fabrics, introduction of jet looms, system of dyeing and sizing together, permanant application of sizing, solvent sizing etc., change the pattern of sizing with conventional sizing ingredients. The demand for increasing the warp speed has also led to the development of special synthetic polymers and paraffin-based lubricants. The main synthetic sizes comprise of polyvinyl alcohol (PVA), polyacrylic acid, CMC, series of plasticised acidic vinyl acetate and acidic methyl acrylate polymers.

PVA is the oldest and best known group of synthetic sizes. PVA dries to form a tough to hard film of poor flexibility. The bars due to stoppages in sizing of pure cotton are dreaded and cause difficulties in dry splitting. The solubility of PVA can be impaired by heat applied during sizing, grey fabric heat-setting or singeing, an important point which influences desizing. The various grades of PVA can be differentiated depending on the degree of hydrolysis (of acetate groups of polyvi-

nyl acetate into hydroxy groups) and/ or the degree of polymerisation (viscosity).

There is a very wide variety of acrylic monomers that can be synthesised by various processes to yield products of different properties. They are derived from acrylic acid and from acrylic esters. The chemical structure thus decides the solubility of an acrylic sizes in water or whether it is so resistant to water that it is suitable for jet looms. Under high humidity conditions, many of the acrylic copolymer sizes absorb water and become tacky causing blocking on the beam, preventing the unwinding of the warp. Polyacrylates are compatable with other sizing agents like starch, CMC or PVA and sometimes give rise to synergistic effects. If acrylates are mixed with starch, good condition can be assured for effluent treatment. The adhesion of PVA can be controlled by CMC or acrylic sizing agents.

CMC and water dispensible polyester based size materials are also used for sizing of synthetic fibre materials. They are insoluble in acidic form and soluble in the presence of dilute alkali and can be removed from the fabric at about 60°C. They are, however, precipitated in presence of metal ions in the washing bath and hence the addition of chelating agent is recommended to nullify its effect. Synthetic detergents of either anionic or non-ionic type may be used to remove the polyester size from the fabric. The CMC can be reclaimed, recycled and reapplied from other size material.

In many cases efficiency of one type of size is inadequate and they must therefore be combined with other sizing agents to accomodate good adhesion, film flexibility, viscosity, compatibility with salts in hard water, abrasion resistance, washing out properties and possibilities of removal of the size and recycling the size from the effluent. By using synthetic polymers not only the quality of weaving is improved, but also reduce the amount of sizing additive, thus reducing the pollution and improvement in handle. Solvent soluble sizes are, however, a development for the future. Further, the easily removable sizing materials are preferred as the milder desizing and scouring treatments are required for synthetic fibres.

3.2 Methods of Desizing

Desizing of cotton fabric can be accomplished by physical, chemical or combination of physical and chemical mechanism, namely rot steeping, acid steeping, treatment with enzyme and oxidising agents. In desizing, the starches and polymers that are applied which are insoluble, are converted into water soluble com-

pound to ease their removal. This is accomplished by transferring the starch into their simple sugars or simple water soluble polymers. The synthetic sizes used for man-made fibres are generally water soluble and they are removed during the scouring operation.

3.2.1 Rot steeping

In this method grey cotton fabric is steeped in water in suitable box at a temperature of about 30-40°C. During the storage micro-organisms develop excreting enzymes which attack the starch. The swollen and hydrolysed starch is thus partially converted into soluble state which are then removed from the fabric by normal washing with water. The main problems in this method are low efficiency due to longer treatment time and degradation of cellulose due to cross-infections of mildew if the fermentation process is not properly controlled.

3.2.2 Acid desizing

In this method cotton fabric is treated with dilute sulphuric acid with a concentration of 5-10 g/l at a temperature of about 40°C for 3-4 h. Dilute acid attacks the polymer chain of starch and due to chain cleavage of starch molecule short water soluble or dispersible chain segments are formed. With sulphuric acid higher than 10 g/l and above 50°C there is always the possibility of weakening the cloth or causing holes [3,4]. The treated cloth must not be allowed to dry at all otherwise degradation of cotton will occur at the dried area. Rise in temperature increases the rate of reaction, but at the same time there is possibility of attacking the cellulose chain. Generally, the rate of reaction doubles for each 10°C rise in temperature. The acid-steeping method is particularly suitable for cotton varieties containing large metal contents as the mineral acid converts the metals to their corresponding sulphate which are water soluble. The degraded starch is removed from the fabric by normal washing treatment.

3.2.3 Enzymatic desizing

The word enzyme is from Greek words for 'in yeast' and was coined in 1876 by the German biochemist Willey Kuhne [5]. Enzymes are organic biocatalysts highly specific both in the reaction catalysed and their choice of reactants (substrate). Physically enzymes are colloidal nature and chemically they are of the nature of protein. Enzymes are complex and have high molecular weights [6]. Today enzymes are produced by biotechnological processes in great amount of constant quality, and are therefore applicable to large-scale processes. Advances in the field

of genetic engineering allow enzyme manufacturers to design specific enzymes for specific processes (with regard to temperature stability or an optimum pH, for example).

Enzymes can originate from animal or vegetable sources. Around 1900, the German Diamalt Co. of Munich introduced Diastafor, the commercial desizing compound, to the trade. Around 1912 enzymes extracted from slaughter house wastes became available. Generally, these contained four enzymes two of which reacted primarily with albumin and casein, one decomposed and reacted with starch. In 1919 bacterial diastase became available under the trade name Rapidase (Wallerstein & Co.), which rapidly liquified starch to dextrin. The main enzymatic development within starch desizing has so far been the introduction of amylase products (Diastafor) optimised to different temperature ranges. Malt amylases fall into two categories and are named the α (alpha) and β (beta) species which are found to be present in the ratio of 1.5 to 1.6. α-amylases are capable of hydrolysing starch molecules at random present in the sizing preparation, transform starch to dextrins, breaking them down to soluble sugars thus helping in eventual desizing. β-amylase attacks straight chains, cleaves the units and produces maltose, so that molecular chain of starch is shortened gradually. When an α-amylase is applied to a starch solution, it is found that viscosity of the solution decreases rapidly, but for β-amylase the viscosity drops slowly. Thus it is clear that the proportion of α and β-amylases in a desizing mixture determines the period (time) of effective desizing. It is also clear that the molecular structure of cotton is unaffected by amylases.

The other size ingredients namely glue, gelatin etc. being protein in nature can be hydrolysed using proteolytic enzymes such as Gelatase, Trypsin etc. The possibility of improving amylase desizing of woven cotton greige at medium/high temperatures with the help of a thermostable lipase is reported [7]. Starch and lubricants (glycerides) are known to form insoluble complexes and the lipase is expected to help break these complexes thus making the removal of starch much easier.

The enzyme process of desizing is very easy to use and is adaptable to any type of equipment. In actual practice the grey cloth is first passed through hot water to approximately 100% pick-up and then padded with the desizing mixture containing 0.5-2% malt extract and non-ionic wetting agent at 60-70^{0}C. Wetting agent helps the enzyme to penetrate the size film. The optimum conditions required for

different enzyme desizing processes are compared with rot and acid-steeping in Table 3.1. The length of time for digestion will vary with the concentration of

TABLE 3.1.
Comparison of Process Conditions for Desizing [8].

Process	Concentration (g/l)	Time (hour)/pH	Temperature (°C)
Rot-steeping	–	10-16 h	30-40
H_2SO_4-steeping	5-10	3-4 h (pH)	40
Malt Diastase	3-20	4.5-5.5	50-60
Pancreative Diastase	1-3	6.8-7.5	50-60
Bacterial Diastase	0.5-1	6.5-7.5	60-70

enzyme used, the temperature of the desizing bath, the types of goods being desized and by the methods depending on the batch or continuous process. Compared to pancreative enzyme, the malt enzyme has a lower action even with the addition of more amount of enzyme. The use of greater amount of enzyme than the optimum will not itself convert the starch. When the goods are padded with desizing mixture, digestion of the starch is a matter of time and temperature. At lower temperature the desizing efficiency is also lower. Malt enzyme is more strongly dependent upon temperature than other enzymes. Even some enzymes are available which can now be worked at 100°C so that high temperature desizing is a reality. Enzymes are quite specific in their response to pH and require close control (Table

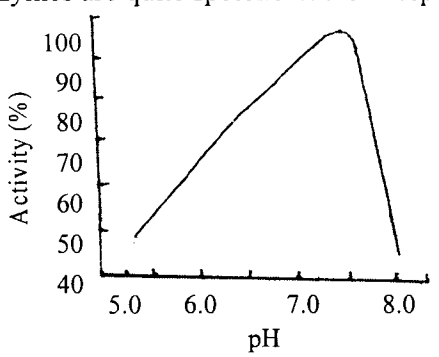


Figure 3-3. Effect of pH on enzyme activity (Courtesy of Graham Fisher, G.B. Fermentation Ind.).

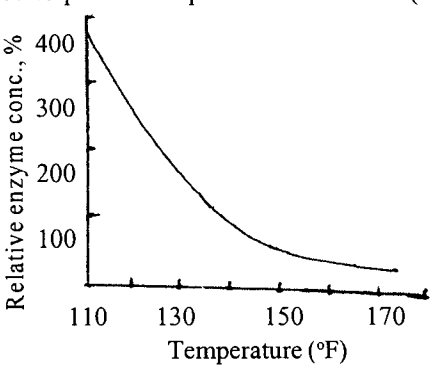


Figure 3-4. Effect of temperature on enzyme activity [8].

3.1). The pH of the desizing bath is maintained by adding acid or alkali. The effects of pH and temperature on enzyme activity are shown in Figs. 3-3 and 3-4 respectively. However storing the enzyme at a fixed temperature shows that the activity steadily decreases with time (Fig. 3-5). In general, changes in pH, tem-

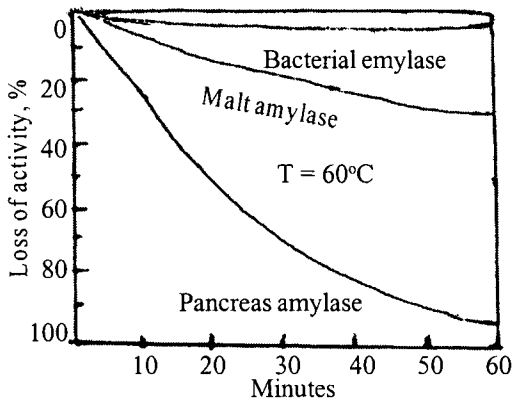


Figure 3-5. Decay of activity of various amylases [9] at 60°C.

perature and duration of storing alter both the activity and stability of enzymes very greatly.

Sometimes sodium or potassium chloride (0.18-1.0%) is added to the desizing bath for pancreative enzymes to get its full activity. For malt α-amylase calcium ion is effective and sequestering agent must be avoided in the desize bath. These salts are particularly used for desize mixture by affording heat protection to enzyme, increased stability of the enzyme and efficiency. On the other hand, heavy metal ions such as copper, iron etc. may combine with enzyme and inhibit its activity [8]. Sometimes hydrocarbon solvents such as xylene (50 ml/l) along with suitable emulsifier (4 g/l) are also added to facilitate removal of waxy components of the size.

Following the digestion period, a hot water wash, with or without subsequent alkaline scour, is required for complete removal for the size that has been solubilised by the enzymes.

3.2.4 Desizing with oxidising agents

Though the use of oxidants for desizing of cotton fabric is widely accepted but their large scale industrial application is yet to be exploited. The most important aspects of oxidising agents are that they can be applicable to wide range of fabrics, the size content of which is often not known. Table 3.2 summerises the necessary conditions for desizing starch in presence of some important oxidising agents.

TABLE 3.2.
Desizing Conditions with Oxidising Agents

Oxidising agent	Process	Additives (pad-bath)	pH	Time (min)	Temp. (°C)
Hydrogen peroxide	Pad-steam	1-2 vol. H_2O_2, 7-15 g/l NaOH.	8-9	1-5	90
Sodium bromite	Pad-batch (cold)	1-3 g/l active Br_2, 20-30 g/l Caustic soda, 5-10 g/l Wetting agent.	7.5-8.5	15	20-40
Persulphate	Pad-steam	3-6 g/l Na-persulphate 8-10 g/l Caustic soda, 5-10 g/l Wetting agent.	10-10.5	1-3	95-100
Persulphate + H_2O_2	Cold-batch	40 ml/l H_2O_2 (25%) 10 g/l Persulphate, 10 ml/l Water glass, 10 ml/l NaOH 5 g/l Stabiliser, 5 g/l Wetting agent.	10-10.5	6-20	20-40

The first oxidative desizing agent initially suggested is hydrogen peroxide [10]. For continuous desizing, first the cotton fabric is impregnated with a 0.8% solution of H_2O_2 at 90°C at near neutral pH; without intermediate rinsing, the fabric passes into the second bath which contains 0.5% caustic soda before final wash-off at minimum temperature of 70°C. Alternatively, the cloth may be desized by pad-steam system (Table 3.2) and longer steaming time will have some bleaching effect in addition to desizing.

Use of sodium hypochlorite, sodium chlorite and sodium bromite as desizing agents are reported [11]. Sodium chlorite, although an excellent bleaching agent, helps to 'fix' rather than remove size in single stage bleaching. Sodium bromite acts by the oxidation of starch in presence of cellulose. The sized cotton consumes bromite to a greater extent than that of unsized cotton [12]. Sodium bromite does not act as a bleaching agent. In continuous processes, bromite treatment can be carried out hot using a dwell time of 20 min. Hypochlorite and chlorite have the added advantage of some fabric whitening which gives a saving in the oxidant concentration in subsequent bleaching.

Alkaline peroxycompounds [13,14] have been found much more suitable for the effectiveness as desizing agent. Peroxymonosulphuric acid (H_2SO_5), sodium persulphate, peroxydisulphates [$Na_2S_2O_8$, $K_2S_2O_8$ and $(NH_4)_2S_2O_8$], acid hydrogen permonosulphates ($KHSO_5$ and NH_4HSO_5) and potassium peroxydiphosphate ($K_4P_2O_8$) have been shown to be effective for desizing [15-19]. Peroxymonosulphuric acid (2 g/l) is applied in a similar manner to that of mineral acid desizing. Persulphates are recommended for ambient temperature desizing containing 0.5% persulphate, 0.5% tetrasodium pyrophosphate and 0.5-3% caustic soda with 4-8 h treatment time. Perphosphate requires a higher temperature for activation than does persulphate, it is used more frequently in caustic saturator because of its stability at elevated temperatures. Perphosphate also exhibits a synergistic effect on the caustic treatment of the fabric as evidenced by the lower solvent extractibilities and the cleaner bottom. The inorganic persalts viz. sodium perborate ($NaBO_3$. $4H_2O$) and sodium carbonate hydrogen peroxide ($2Na_2CO_3$. $3H_2O_2$) have been shown to be effective in foam desizing and bleaching of yarn and dyed fabric.

The main limitations of oxidative desizing agents are increased pollution load, fibre damage and inability to recover and re-use water soluble sizes. Oxidative desizing agents require precise control on process parameters. Metals catalyse the action of oxidising agents and the desizing liquor should not be in contact with any metal fittings.

3.3 Desizing of Synthetic Fibre Fabrics and Their Blends with Cellulose

The most common sizing agents used for nylon are based upon PVA, gelatin, casein or variety of vegetable and mineral oils. Desizing of regenerated celluloses depends on nature of size that must be removed. Desizing is difficult as rayon swells in water to a great extent. This leads to poor penetration of enzyme.

When water soluble PVA is used as sizing agent in weaving, no desizing of synthetic fibre fabrics is necessary. Light scouring with non-ionic surfactant (3-5 g/l) at 95-100°C for 20-30 min is enough to remove the sizing material. However, high molecular weight PVA above 1,00,000 are found to be quite difficult to remove from the fabric during desizing and results in uneven desizing.

Polyester sizing agents are not removed by simple washing treatment. Suitable detergents for removing polyester size are the efficient anionic or non-ionic types

or blends containing both types. The grey fabric is treated with a solution containing non-ionic surfactant, 2-3 g/l; sodium hydroxide or soda-ash, 1-2 g/l at 80-95°C for 20-30 min. Alternatively, treatment with sodium tripolyphosphate (1-2g/l) in presence of soda-ash or sodium hydroxide (1-2 g/l) and non-ionic surfactant (2-3 g/l) at 80-90°C for 20-30 min can be used. It is recommended to use soft water during washing as metal ions may interfere with removal of size. Alternatively, suitable sequestering agents are added.

Polyacrylic is a water soluble salt of acrylic acid and are soluble in mildly acidic or alkaline solutions.

The desizing procedure of polyester/cotton blended fibre fabrics depends on the nature of the size to be removed. Acrylic copolymer is removed by simply mild alkaline scour, PVA and CMC are removed by hot water wash, a mixtrure of starch and emulsifying wax is removed by means of enzymatic desizing followed by alkaline scour. Acrylic copolymers are commonly added to starch sizes. Depending on their sodium carboxylate content they give a pH of about 9.95 and will tend to inactivate enzyme. In such cases fabric may be pre-acidified or acetic acid may be added to the desizing bath (pH $\simeq$ 8). Gelatin and dextrin are readily soluble in hot water. If casein or some other protein based products are used in substantial proportion along with starch, a proteolytic enzyme should be used in addition to starch liquifying enzymes in the same bath. PVA is difficult to be removed from blended fabrics which have been heat treated at temperatures above 135°C or when scouring temperature is below 75°C [20]. A desizing process using neutral hydrogen peroxide in presence of metal catalysts results in easier removal of PVA [21]. The desizing of diacetate/viscose fibres blended dress goods is carried out depending on the nature of size to be removed. Starch sizes are removed by treatment with malt extract or enzyme, to which has been added 1g/l of synthetic detergent, batching overnight, and then scouring at 70°C for 30-60 min containing a liquor of 1-1.5 g/l detergent and 2ml/l ammonia (sp. gr. 0.880). Large scale trails in which sizing and desizing carried out in solvents have also been described [22].

Recently a cold desizing process using sodium sulphide in a weakly alkaline solution is reported [23]. The rate of desizing is increased 5-fold compared with alkali alone. A mechanism involving a catalytic effect of the sodium sulphide in the hydrolysis of glucoside bonds in the polysaccharide is proposed.

3.4 Desizing Machineries

The desizing processes are very much dictated by economics in terms of the chemical or enzyme consumption, the equipment available and the end use requirements. With the introduction of J-Boxes and other continuous preparatory methods and equipment, desizing is gradually loosing its identity as a seperate process. Now-a-days desizing and scouring can be carried out in one operation and thus a substantial amount of time and energy can be saved. This has become possible mainly because of many mild oxidising agents can be added to conventional liquor to promote desizing, while the scouring is in progress. Simultaneous desizing and scouring can also be carried out in kiers by a judicious choice of chemicals. Desizing in the batch process can be carried out in a jig or winch or in a kier prior to boil-off. For small lots, for example of the order of 1000 m or less desizing can be carried out in jigs or rope washing machines. Comprehensive development of microprossor technology enables jiggers (Fig. 3-6) to be connected to a personal computer. Ev-

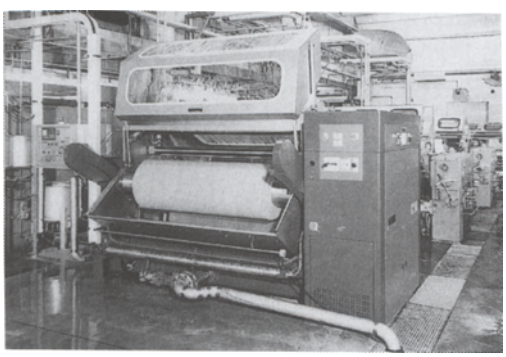


Figure 3-6. Universal Jigger for pre-treatment processes (Courtesy of Benninger AG, Uzwil).

ery stage of the process can be graphically displayed on the personal computer. The modern machine is supplied with batching up facilities, automatic selvedge shifting, automatic tension regulation and gentle handling of elasticised or ultra-delicate fabrics. The entire production data, from loading the fabric, desizing, washing and unloading etc. can be printed out. If enzyme treatment is carried out in winch or similar dyeing machine (Fig. 3-7) in form of rope, desizing may be carried out at 60-70°C for 30 min with reduced amount of enzyme. The modern

rope washing machines can be used for processing with any kind of fabric with reduced water consumption, chemicals and electrical energy. The fabric is pro-

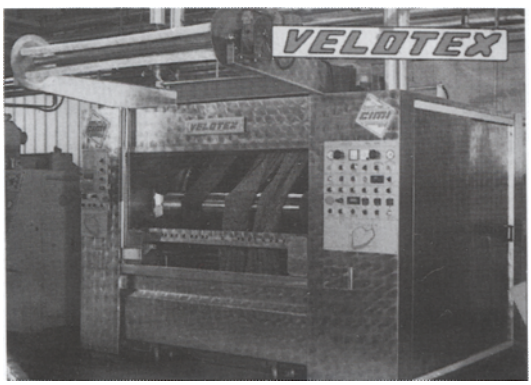


Figure 3-7. Machine for desizing and washing in the rope form [Courtesy Cimi S.R.L, (Biella), Italy].

pelled by a winch in conjunction with good milling effect. The fabric capacity of the machine is about 350 kg with maximum speed of about 600 m/min.

In the batch process (Fig. 3-8) long digestion time in the range of 6-16 h are

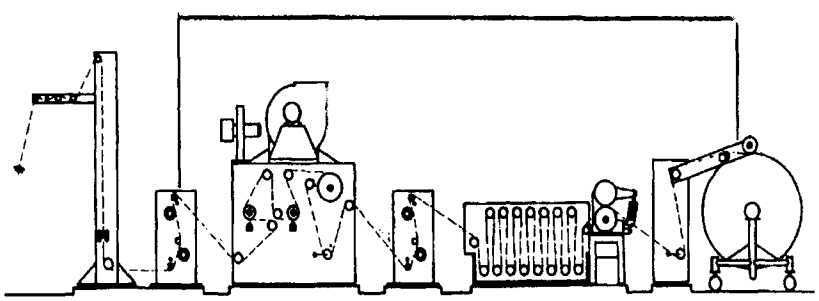


Figure 3-8. Schematic diagram of pad-batch system showing singer, desize saturator and padder. (Courtesy of Julien S.A, Belgium).

given because the material is unheated. After impregnation with the solution containing desizing agent, non-poisoning wetting agent and salt, the fabric in open width form is batched and covered with polythene sheet to prevent fabric being dried unevenly [24]. The saturator also works as a quench box in which all sparks are extinguished immediately after singeing the cloth.

In the semi-continuous process of desizing, the use of pad-roll installation is quite popular. Bacterial enzymes are widely used in pad-roll method [25] (Fig. 3-9). The cloth, in open width form is quickly pre-heated in a steam chamber or by infrared radiation immediately after impregnation with desizing agent containing other ingredients. The padded goods after steaming are batched in roll

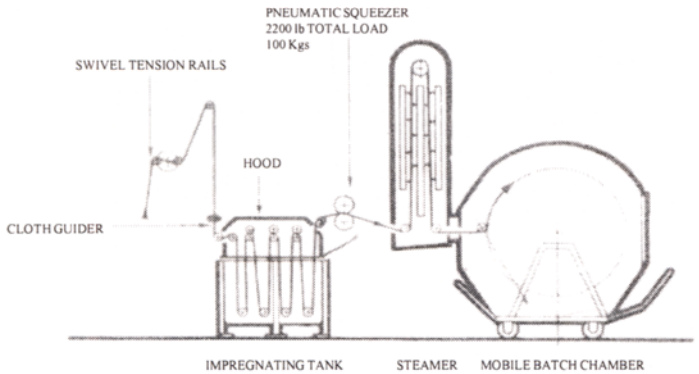


Figure 3-9. Pad-roll desizing unit (Courtesy of Farmer Norton).

form in moveable carraiges and let lie for 8-12 h. Whilst in storage the material is rotated gently to prevent uneven desizing due to drainage and steam can be fed into the chamber slowly to maintain the required temperature.

When a continuous process is used, the padded fabrics are steamed for 20-60 sec at temperatures of 95-100°C using saturated steam (Fig. 3-10). A short open

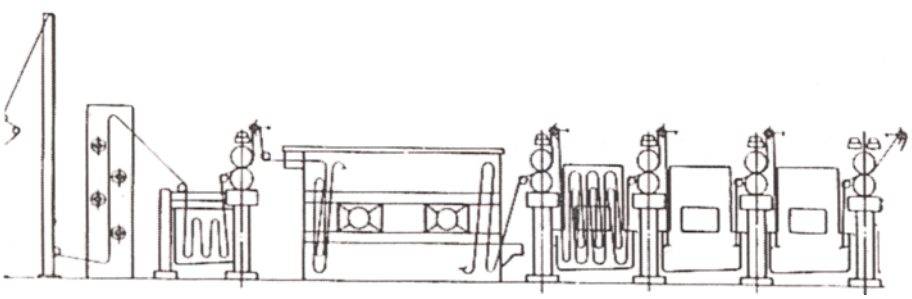


Figure 3-10. Schematic diagram of open width continuous desizing showing singer, saturator, padder steamer and enclosed washer (Courtesy of Morrison Machine Co.).

width steamer (Fig. 3-11) may be operated at temperatures of 95 to 100°C using

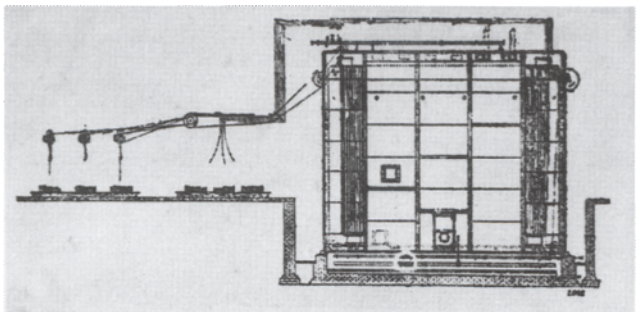


Figure 3-11. Continuous automatic steaming chamber.

saturated steam for 20-60 seconds. The bottom of the steaming chamber is provided with steam radiating pipes to obtain the necessary conditions of temperature and humidity. Alkaline peroxide is greatly used in continuous pad-steam processes [26] in which desizing, scouring and bleaching can be combined. When enzymes are applied to starch the enzyme sensitivity to heat is remarkably improved if the enzyme can be applied first and then steamed. After desizing is completed the fabric is washed in an open width washer (Fig. 3.12) to remove the short chain

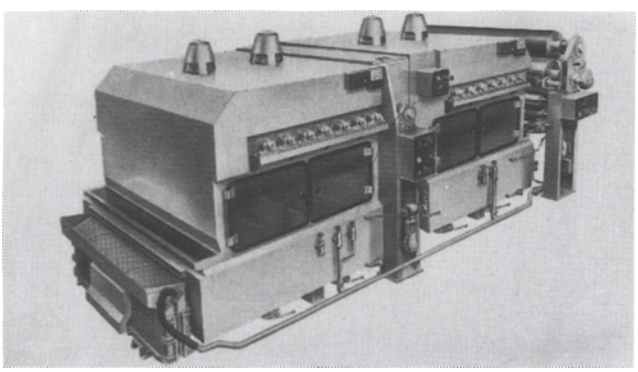


Figure 3-12. Open width washer (Courtesy of Farmer Norton).

sugars because these are water soluble. The washer is specifically designed to meet the current demand for greater energy saving and is totally enclosed and insulated. If J-Box (Fig. 3-13) is used for desizing of cotton fabric in continuous operation, a temperature range of 60-90°C for 15-20 min will suffice. The use of high pressure

continuous treatment machines such as Vaporloc and Benninger machines have necessitated the development of special amylase enzymes which are active at high

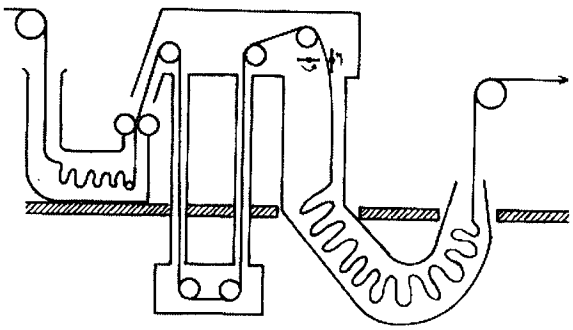
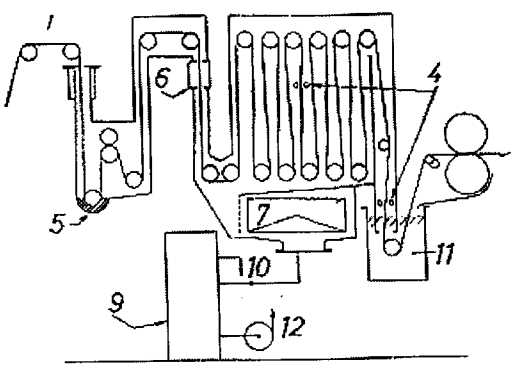


Figure 3-13. Continuous desizing in J-Box.

temperature of 100-110°C. Using these enzymes, high speed continuous desizing operations followed by continuous high pressure scouring and bleaching are being carried out.

Bacterial enzymes are used in the very elegant Markal method [27] (Fig. 3-14).



1 Application unit
2 Transfer duct
3 Solvent recovery/chemical reaction vessel
4 Steam jets
5 Chemical addition
6 Seal unit
7 Condenser
8 To water wash tanks
9 Water separator and hold tank
10 Water to drain
11 Water seal
12 Recovered solvent to storage

Figure 3-14. Continuous solvent desizing process
(Courtesy of ICI Mond Division, England).

The ICI Markal process is used for desizing and scouring by using suspension of enzyme in trichloroethylene and surfactant solution. The fabric is padded through the solvent formulation, steamed to remove the solvent and to activate the enzyme. A wash-off with water completes the process. The Markal processes are suitable for polyester/cotton, polyester/rayon and other blends as well as for cotton.

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Chapter 4

SCOURING

4.1 Introduction

The loom state cotton fabric contains about 8-12% natural impurities of total weight of the fibre. These impurities mainly consists of waxes, proteins, pectic substances and mineral matters. In addition to this, the mechanically held impurities called 'motes' are present containing seed-coat fragments, aborted seeds and leaves etc. that clinge to the fibre. Apart from these, the loom-state fabric is also contaminated with adventiteous oils such as machine oils, tars, greases etc.

Scouring is a purifying treatment of textiles. The objective of scouring is to reduce the amount of impurities sufficiently to obtain level and reproducible results in dyeing and finishing operations. Scouring agents can be generally classified into different groups (Fig. 4-1). The appropriate type of scouring agent gener-

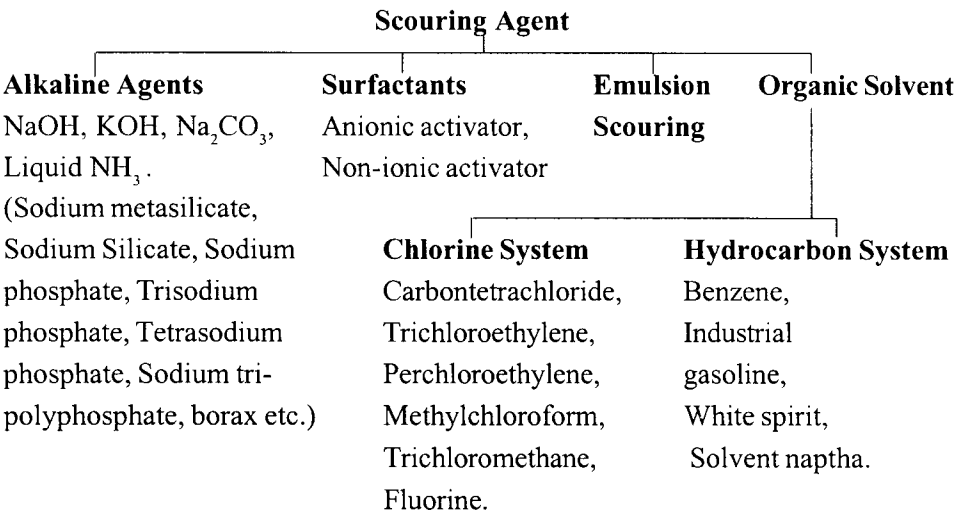


Figure 4-1. Classification of textile scouring agent.

ally depends on the kind of fibre ; fabric type i.e. woven or knitted, thick or thin ; texturised or non-texturised and the extent of impurities present in the fibre. The selection of alkali is most important as free alkali can have a deleterious effect on certain fibres. For example, wool and silk are dissolved by alkali, whereas acetate and triacetate are converted back to their original cellulose form. Cotton fibre ab-

sorbs alkali. Alkali neutralises the carboxyl group in cellulose and in pectin. The hydroxyl groups on the glucose units in cellulose are also weakly acidic. Owing to this preferential sorption, the concentration of alkali in the fibre is increased and thus attacks the impurities more intensively.

4.2 Mechanism of Removal of Impurities

The action of alkaline scouring agent is to saponify any residual oils, to neutralise carboxylic acids, to solubilise any sizing materials and to cause dispersion of naturally occuring impurities in natural fibres. Table 4.1 summerises the removal process involved during scouring.

TABLE 4.1.

Techniques for Removing Natural Impurities of Cotton During Scouring [1]

Impurities	Method of removal
Fats and waxes	Levels are reduced to acceptable limits by the action of alkali and surface active products, in extreme cases the use of solvent and surfactant mixtures may be necessary.
Pectins and related substances	Solubilised by the action of alkali, usually caustic soda, which also acts as a swelling agent to facilitate removal.
Minerals and heavy metals	(a) By producing more soluble salts e.g. acid demineralisation (b) By use of sequestering agents.
Amino acids or proteins	Solubilised by producing corresponding sodium salt.
Lubricants/Knitting oils	Modern mineral oil formulation usually contain their own self-emulsification system.

Natural fats, oils and lubricants (tallow) are mostly esters usually in the form of triglycerides. Being triglycerides, the lubricants can be almost hydrolysed by lipases, yielding glycerol, fatty acids and mono-and diglycerides as the reaction product. Glycerol is completely water soluble, fatty acid is removed during scouring and mono and diglycerides are known to be efficient surfactants or emulsifiers. Thus, a lipase treatment improve not only desizing but also the scouring processes. The esters react with sodium hydroxide to form soap and glycerine. The soap thus

form can serve as an effective detergent and promote scouring. The unsaponifiable oils are emulsified by the soaps formed during hydrolysis of the saponifiable matter and are easily removed.

Wax is difficult to remove. If wax is not removed, non-uniform absorption of dyes and finishing agents will take place. In fact it is the distribution of residual wax after scouring that determines the water absorbancy.

Pectic acid is insoluble in water but soluble in alkaline solution. Proteins are situated in the central cavity of the fibre and are therefore relatively inaccessible to chemical attack. The proteins and nitrogeneous materials are hydrolysed by alkali into soluble amino acids or ammonia.

The alkali earth elements represents a major variable in cotton fibre (Table 4.2) and mainly comes from cotton seed husks. Further the use of hard water can precipitate alkali earth metal phosphates on the fibre instead of eliminating them [2]. The reason for reddish shade after bleaching with peroxide is the high content of manganese, $Mn^{2+} \rightarrow$ colourless but $Mn^{7+} \rightarrow$ violet. The contents of Fe, Mn, Ca and Mg varies depending upon the origin of cotton (Table 4.2). With the demineralisation

TABLE 4.2.
Metal Content in Cotton Fibre

Country of origin	Content in p.p.m. (mg/Kg)			
	Iron	Manganese	Calcium	Magnesium
Brazil	100-250	10-30	1500-2500	800-1500
Russia	50-150	3-7	800-1500	500-1000
USA	30-50	< 1	500-800	300-600
Peru	10-30	< 1	500-800	300-600

treatment the mineral content of cellulosic substrates can be reduced substantially and thereby diminishing the negative influence of earth alkali and heavy metal ions in subsequent process operation. Complexion of earth alkali salts (Ca and Mg) is possible in the acid medium and heavy metals (Fe and Mn) is possible in alkaline medium. The advantages and benefits of the demineralisation are : better levelness and more brilliance in the dyeing process, lower peroxide consumption, reduction in the ash content, increase in degree of whiteness, regular decomposition of peroxide, no catalytic damage of the fibres (holes) and possibility of replacement of

hypochlorite bleach. Generally good pre-treated materials should have 100-300 p.p.m. of Ca and Mg and 4-8 p.p.m. iron.

Sodium hydroxide reacts with 'motes' (cellulose of low crystallinity). Motes are swollen in alkali to form sodium cellulosates which tend to become water soluble. If any 'motes' still remain in the fibre after scouring, subesequent bleaching operation destroys them completely.

4.3 Scouring of Cotton in Alkaline Agents

The complex nature of natural impurities present in the cotton substrate and its effect by treatment with alkaline solution is already highlighted. The various types of alkalies and other additives used for scouring of cotton are given below.

4.3.1 The lime-soda boil

In this process the fabric is boiled with milk of lime which convert the fatty acid into insoluble lime soaps. The lime soap is then converted into free acids on acidification and calcium is washed away as calcium chloride. The deposited free acid is then converted to soluble soaps on subsequent boiling with sodium carbonate. This method is tedius and not economical as two boils are required to remove the natural impurities.

4.3.2 The caustic soda boil

In this process cotton fabric is boiled with a solution of 10 to 20 g/l (3 to 6% o.w.f.) caustic soda in a kier with a liquor ratio of 3 : 1. In continuous scouring about 30 g/l of caustic soda is added in the pad-bath with a liquor pick-up of about 100%. In batch process the piece goods are treated in 4-6% sodium hydroxide for 8 h at 130°C (30 lb/in^2). Loose cotton for bandage and sanitary cotton, where absorbancy is the prime importance, are boiled at 80 lb/in^2. In continuous processes, it is possible to decrease the time of post impregnation steaming to about 2 min at a temperature of 130-135°C with sodium hydroxide solution of 40-60 g/l. The rate of saponification of waxes increases considerably as the temperature (pressure) of boiling increases. Generally, the rate of chemical reaction is doubled with each 10°C rise in temperature and saponification of oil is increased sixteen times from 60 to 100°C [3]. However, with increase in temperature oxycellulose formation is also increased. Cotton is not degraded by boiling with sodium hydroxide solution up to a concentration of 20 g/l in the absence of air.

4.3.3 The soda-ash boil

The type of alkali used for scouring of cotton depends on the quality of goods. For example, if coloured yarns present in the fabric, sodium carbonate is ideally suited because of its low pH. Cotton yarns to be dyed in dark shade should be scoured with 1-2% sodium carbonate solution for 30 min in presence of wetting agent.

4.3.4 The mixture of caustic-soda and soda-ash boil

A combination of 2 parts of caustic soda and 1 part of sodium carbonate is often used in single stage boiling. Soda-ash softens the water while interacting with Ca and Mg salts (if such are present) ; it creates an active reaction of the medium which is most favourable for the formation of stable emulsions and suspensions ; increases fibre swelling, thus contributing to the release of impurities from the fibre ; neutralises fatty acids contained in the fabric by soap formation ; obviates soap hydrolysis in the presence of wool ; reduces the adherence of detergents to wool in the alkaline medium conditions.

4.3.5 The soap/detergent – soda-ash boil

This combination is comparably milder combination than that of caustic soda and hence ideally suitable for more delicate cloths and colour woven goods compensating for the slower action of the milder alkali by the addition of a detergent. Anionic products like sodium alkyl sulphates and alkyl aromatic sulphonates and non-ionics like polyethoxylated compounds are used as detergent. Sometimes mixtures of anionic and non-ionic products are used. It is possible to obtain a synergistic effect between a detergent and alkali, so that the two agents when combined increase their total activities rather than inhibit each other. Fig. 4-2 shows the syn-

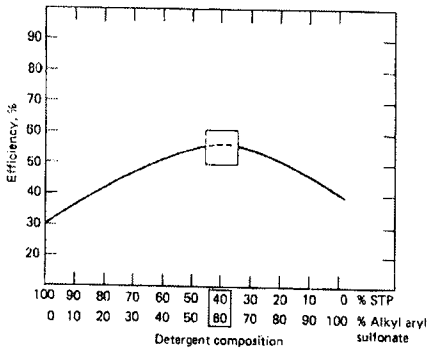


Figure 4-2. Effect of sodium tripolyphosphate (STP) on detergency [4].

ergistic effect when phosphates are combined with alkyl aryl sulphonates and are used as scouring agents in processing water. After scouring, washing is carried out by hot progressive rinsing while gradually decreasing the temperature in order to avoid break down of the emulsion and precipitation of the impurities onto the cotton. Washing is completed by treating the fabric in an acid solution to neutralise any alkali retained by the fabric.

4.3.6. Sequestering agents

Sequestering agents or chelating agents are negatively charged and are capable of forming strong ring structures (Fig. 4-3) with the metal ions present in hard

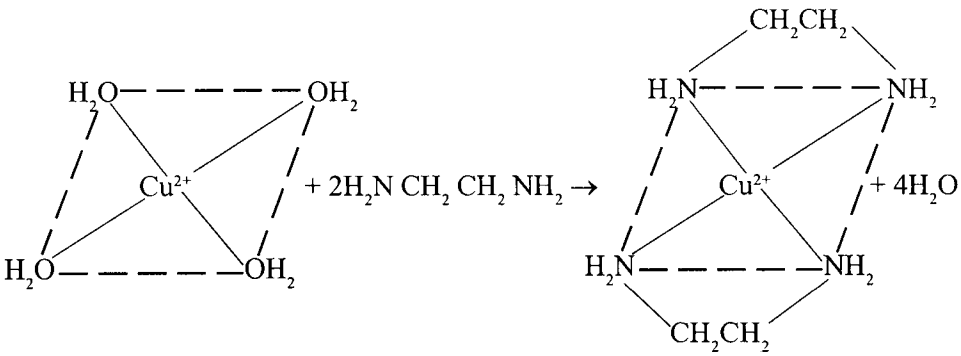


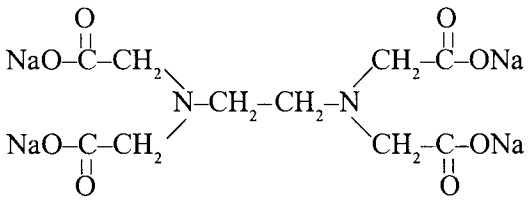
Figure 4-3. A typical chelate structure (Courtesy of Dow Chemical Co.).

water and in pectins of cotton. The positively charged metal ions, particularly Fe^{3+} and Ca^{2+} are readily available for reaction with any negatively charged anion such as OH^- or CO_3^{-2} and insolubilise soap in the fibre which may disturb subsequent operation. This problem is much more acute when scouring is carried out in continuous process involving padding bath where liquor ratio is much lower than the batch process [5]. Thus, the functions of the chelating agents in the soap and detergent formulations are for the prevention of –

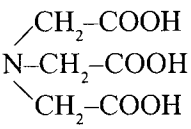
i) film and scum formation,
ii) precipitation of hard water,
iii) calcium and magnesium inhibition of foaming properties,
iv) clogging of liquid dispersions,
v) haze turbidity in liquid solutions, and
vi) rancidity and oxidation that cause discolouration of formulation.

Sequestering power is influenced by pH of the scouring bath. At a given pH,

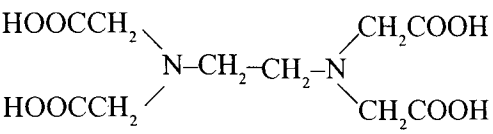
different amount of chelating agents are required to chelate a given amount of metal. Organic sequestering agents that find commercial uses (Fig. 4-4) are stable



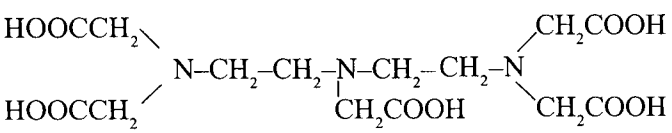
Ethylenediamine tetraacetic Acid (EDTA)



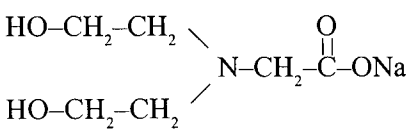
Nitrilotriacetic Acid and Salts (NTA)



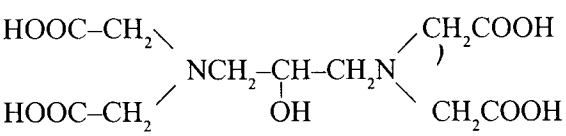
N-(2-Hydroxyethyl) ethylenediamine tetraacetic Acid (HEDTA)



Diethyltriamine Pentaacetic Acid and Salts (DTPA)



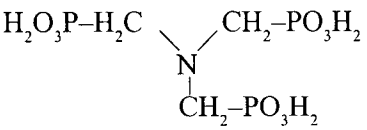
N, N-Di (2-Hydroxyethyl) Glycine (DHEG)



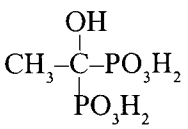
Diaminopropanol triacetic Acid (DPTA)

Figure 4-4. Aminocarboxylates and hydroxy carboxylates as organic sequestering agents.

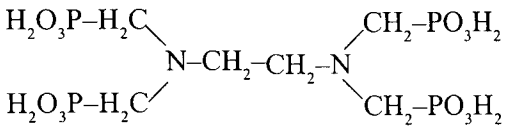
to hot alkaline scouring solutions. There are some organophosphonates (Fig. 4-5)



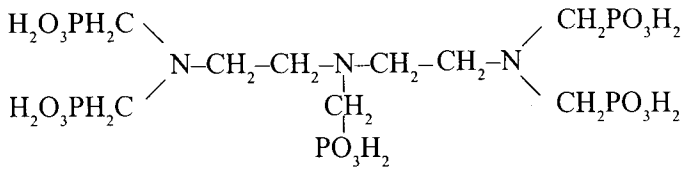
Aminotri-(methylene phosphonic acid) ATMP



1-Hydroxyethyledene-1, 1-diphosphonic acid (HEDP)



Ethylenediamine tetra-(methylene phosphonic acid) (EDTMP)



Diethylene triaminopenta-(methylene phosphonic acid) (DTMP)

Figure 4-5. Constitution of organophosphonate seqnestering agents [6].

which, however, act as a sequestering agent and at the same time contribute to detergency, dispersing properties and prevent soil redeposition on textile goods. However, the products are not stable in alkali solution at high temperature. At higher temperatures they are hydrolysed to orthophosphate which has no dispersing as well as sequestering properties.

4.3.7 Builders

Builders are generally added to the kier boiling bath to increase the activity of soap or detergents. Builders are generally salts such as borates, silicates, phosphates, sodium chloride, sodium sulphate etc. Sodium metasilicate ($Na_2SiO_3.5H_2O$) also acts as a detergent and buffer and assists other chemicals to penetrate into the lignin mass of cellulose materials. In general, the function of the builders is to drive the soap from water phase to fabric/water interface and consequently increase the concentration of soap on the fabric. It is inexpensive, but its addition in the scouring bath increase the ash content of cotton.

4.3.8. Fibre protecting reducing agents

Sodium hydroxide solution during kier boiling of cotton at high temperature can form oxycellulose in presence of oxygen. Generally, oxygen is removed from the kier before scouring starts, but even a small quantity of air entrapped in the fabric layers may cause problems and tendering of cloth takes place. Thus, a small quantity of mild reducing agent such as sodium bisulphite or even hydrosulphite is added to the kier liquor to prevent oxidation of cellulose during scouring operation.

4.3.9 Mild oxidising agents

Sometimes, woven fabric contains a vat or azoic dyed coloured yarn to have a stripe effect. When such fabrics are scoured in a pressure kier under alkaline condition, there is always a risk of staining the adjacent white ground by bleeding of dyes from the coloured thread. Azoic dyes may be mechanically transferred while the vat dyes may be reduced to its soluble leuco state in presence of alkali and impurities removed from the cloth. For such types of fabrics mild oxidising agents like Ludigol, Resist Salt L etc. may be added to the scouring bath to resist the reducing properties of dyes. Chemically, these products are sodium salt of nitrobenzene sulphonic acid. Alternatively, such fabrics containing coloured threads can be scoured in open kier, on winch machine, jigger or continuous machine with boiling soda-ash liquor (2.5% o.w.f.) instead of caustic soda to reduce the mark-off to a minimum.

4.3.10 Water insoluble solvents

For the purpose of accelerating the scouring process, wetting agents are sometimes used in conjunction with high boiling solvents (cyclohexanol, methylcyclohexanol, tetrahydronaphthalene, decahydronaphthalene etc.). The function of the solvent is to dissolve more insoluble fats and waxes and that of the detergent to emulsify the solvent and waxes.

4.4 Surfactants

A surfactant may be defined as a substance which, when applied in low concentration, markedly reduces the surface tension of a solvent. A good surfactant, for example, will reduce the surface tension of water from 72 dynes/cm to 30 dynes/cm at a concentration of less than 0.1%. The concentration at which no further reduction in surface tension occurs is known as 'critical micelle concentration'. Generally, surface tension between textile fibres, particularly synthetic fibres and

water is high, and hence wetting of the fibre surface does not take place thoroughly and quickly. Surfactants reduce the interfacial tension and thereby bring about quick wetting of the fibre surface. Surfactants are widely used in scouring of synthetic fibres which do not contain naturally occuring impurities like cotton. Surfactants are also used in wool scouring and also assist in the milling and development of woollen fabric.

A high quality synthetic detergent provides a good balance with wetting, cleaning, emulsifying, dispersing and foaming properties, thus providing it a good cleaning ability. Chemically, the surfactants are long chain organic compounds containing both a hydrophobic and a hydrophilic component. The hydrophobic character in the surfactant molecule is associated with the hydrocarbon chain, usually quite long in its length. Although lowering of surface tension is an essential requirement of a good surfactant, the compound should have proper hydrophobic lyophilic balance (HLB) to have balanced water solubility and water insolubility. Surfactants may be classified into four groups, viz. anionic, cationic, non-ionic and amphoteric surfactants. However, the non-ionic and anionic detergents and blends, solvent assisted detergent blends, soaps and pH buffered 'built products' are mainly used for scouring in textile industry.

4.4.1 Anionic surfactants

Anionic surfactants are those which bear a negative charge and migrate toward the anode or positive charge in solution. This class of salt like compounds include the soaps and many of the popular synthetics (Fig. 4-6). When fats are hydrolysed

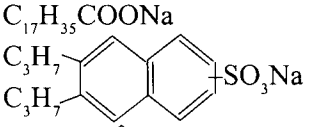
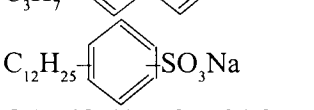
Anionic detergent	Chemical structure
Sodium stearate (soap)	$C_{17}H_{35}COONa$
Dipropyle naphthelene sulphonates	
Alkyl benzene sulphonates	
Alkyl sulphates	$CH_3–(CH_2)_{16}–CH_2OSO_3Na$
Alkane sulphonates	$C_{17}H_{33}COOCHCH_2SO_3Na$
	Igepon A
	$C_{17}H_{33}CO–N(CH_3)–C_2H_4SO_3Na$
	Igepon T
Phosphate esters	$R–O–(C_2H_4O)_x–PO_3Na_2$
	R = Octyl or nonyl phenol or fatty alcohol

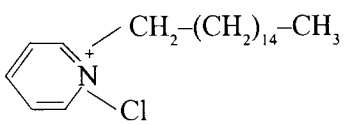
Figure 4-6. Typical examples of anionic detergents.

in presence of alkali fatty acid is formed which on neutralisation with caustic soda form a sodium salt of fatty acid, known as soap. The most important factor which determines the properties of soap is the number of carbon atoms in the aliphatic soap. Soap with high molecular weight (C_{12} to C_{18}) is only suitable for use when scouring can be carried out at or near the boiling point of the solution. The instability of soap in acid solutions is the main drawback. Synthetic detergents are surfactants developed to overcome the drawbacks of soaps. They are salts of strong acids and when pure they are practically neutral. In contrast to soap they are less liable to hard water precipitation and are readily rinsable.

In the late 1920's long chain fatty alcohols were sulphonated and sold as neutralised sodium salts. In 1930's long chain alkyl aryl sulphonates with benzene as aromatic neucleas and alkyl portion made from kerosine portion appeared on the market in U.S.A. Both the alcohol sulphates and trialkylaryl sulphonates were sold as such as cleaning materials but did not make much headway on the total market. In 1940's, dodecyl benzene, formed by the reaction of propylene tetramer with benzene, was available in plenty and dodecyl benzene sulphonate dominated the synthetic detergent market. Late in 1950's, higher molecular weight materials with an average of 13 carbon atoms instead of 12 as in dodecylbenzene was found to have better detergency. In the early 60's, it was found that the branched chain structure of dodecylbenzene sulphonates are not biodegradable and thus linear alkyl benzene sulphonate has replaced propylene tetramer. Anionic surfactants with phosphate esters are finding more and more uses in industry and are obtained by treating non-ionic surfactants with phosphorous pentoxide.

4.4.2 Cationic surfactants

Chemically they are just opposite to the anionic surfactant and hence are unsuitable for use as detergents or wetting agents. The hydrophobic part of the molecule of the cationic surfactant is the organic ammonium or pyridinium compound containing one or more hydrophobic residues as shown below :



Cetyl pyridinium chloride

Cationic surfactants are rarely used in preparation unless applied as a lubricant

or antistat at the end of the scour cycle on goods that are to be dyed but not bleached. A small quantity of cationic surfactant is also recommended as an aid in weight reduction in caustic treatment of polyester. Cationic surfactants are mainly used as softeners, levelling agents, retardants in dyeing, water repellents, bacteria growth inhibitors and emulsifiers.

4.4.3 Non-ionic surfactants

Non-ionics are second major surfactant class used in preparation and are manufactured in different forms. Non-ionic surfactants do not contain an ionisable group and have no electrical charge (Table 4.2). The most important non-ionic detergents

TABLE 4.2

Non-ionic Surfactants that Bear an Electrically Neutral Charge

EO-PO Ethers	Sorbitan ester-EO
EO-PO Esters	Sorbitol esters
Fatty esters	Sorbitol ester-EO
Amphoteric (at isoelectric point)	EO fatty acid
Thioethers	PO fatty acid
Sorbitan esters	Fatty alkanol amides

are those obtained by condensation of ethylene oxide or propylene oxide. Ethylene oxide can be reacted with fatty acids, alcohols and alkyl phenol, fatty amide etc. to give polyoxyethylene compound of ether, ester and amide known as ethylene oxide condensation product (Fig. 4-7). The non-ionics are rendered water soluble by

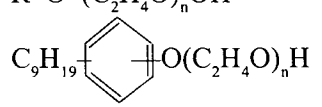
Non-ionic detergent	Chemical structure
Ethoxylated primary alcohol	$R–O–(C_2H_4O)_nOH$
Ethoxylated nonyl phenol	
Ethoxylated thio-ethers	$CH_3–S–C_2H_4–(C_2H_4O)_nH$
Ethoxylated fatty acids	$R–\overset{\overset{O}{\|}}{C}–(C_2H_4O)_n–OH$
Ethoxylated fatty amide	$R–CON(\overset{\overset{H}{\|}}{\ })–(C_2H_4O)_nH$

Figure 4-7. Some typical examples of non-ionics.

the solvation of oxygen in the ether and the solubility is proportional to the number of such oxygen atoms in the molecule. A primary hydrate is formed in which further water molecules participate, resulting in the formation of voluminous hydrate sheath with 20 to 30 water molecules to each oxygen atom. Some typical examples of non-ionic surfactants are given in Fig. 4-7.

Non-ionics are characterised by its cloud point. It is the temperature at which 1.0% solution of non-ionic surfactants, become cloudy or insoluble. The larger the number of ethylene oxide molecules in the product, higher is the cloud point. The exception to this rule is a non-ionic that is co-reacted or capped, with propylene oxide. Another method of overcoming the problem of cloud point is to blend the non-ionic with an anionic such as a soap, a sulphonate or a phosphate. The cloud point of non-ionic surfactant solution can be depressed by the addition of an electrolyte like common salt, Glauber's salt etc.

Non-ionic surfactants are free from precipitation and redeposition onto the fabric and can be safely used which also permit the caustic to act as a lime-soap detergent. Its advantages are excellent compatibility with all classes of surfactants, good wetters and rewetters, good emulsifiers, excellent oil solubility and good components of oil emulsifier.

4.4.4 Amphoteric surfactants

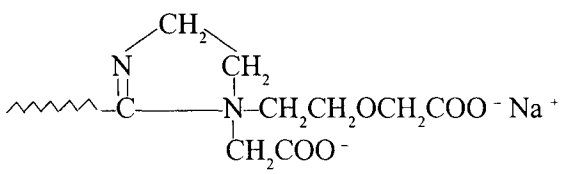
Amphoteric surfactants may be cationic, anionic or non-ionic depending upon the pH of the aqueous solution (Table 4.3). A typical amphoteric surfactant can be

TABLE 4.3.

Effect of pH on Ionic Nature of Amphoteric

Structure	pH	Ionic charge
$\overset{(-)}{Cl}\ R\ \overset{(+)}{NH_2}\ CH_2\ CH_2\ COOH$	Acidic	Cationic
$R\ \overset{(+)}{NH_2}\ CH_2\ CH_2\ \overset{(-)}{COO}$	Isoelectric range	Non-ionic
$R\ NH\ CH_2\ CH_2\ \overset{(-)}{COO}\ \overset{(+)}{Na}$	Alkaline	Anionic

represented by the following formula :



Amphoteric surfactants offer an excellent degree of lubrication, corrosion inhibitor, and wetting action and provide a protective colloid for silk and wool processing. The major uses of amphoterics are in the scouring and dyeing of protein fibres to prevent chafing, crack marks and crow's feet. Amphoterics are comparatively expensive and some of them are not heat stable and hence cannot be used at elevated temperature.

4.4.5 Blends of surfactants

Blended surfactants are commonly used in preparation auxiliaries as they are found to be more efficient than the single component. When natural waxes, and sizes are to be removed from cotton, anionics-or non-ionics built with anionics – appear to be the better choice. Anionics, whether sulphate or phosphate derived, when neutralized with amines or alkanolamines become solvent and oil soluble and may be used in conjunction with low-mole ethoxylates. A blend of propylene oxide-capped non-ionics or thioether ethoxylates, coupled with low-mole phosphate ester of dinonyl phenol ethoxylates that has been neutralised with alkanolamine, is commonly used to emulsify a high boiling mineral spirit type solvent. This combination product provides good detergency and satisfactorily accomplishes the removal of processing oils, greases and sizes. A simple blend of short-chain ethoxylates and long-chain ethoxylates of same hydrophobe that provides a balanced HLB can sometimes be the best choice. On many occasions, it is necessary to incorporate a solvent processing aids and a complex mixture of ethylene oxide and fatty acid derivatives produced with inorganic compounds to provide optimum processing efficiency.

4.4.6 Surfactant as wetting agent

Generally interfacial tension between the textile fibre and the liquor is high, and hence wetting of the fibre surface does not take place quickly. This is particularly true in the case of grey cotton fabric and hydrophobic fibres. One of the main function of the surfactants is to reduce the surface tension and thereby bring about wetting of the surface.

Water has an uncommonly high surface tension of 72 dynes/cm. The most important feature about high surface tension of water is its structure. A lone oxygen atom in the water molecules contains a pair of electrons, which is balanced by a correspondingly large positive charge in the hydrogen atoms. This structure gives

water a great dipole moment, and also the molecules 'stick' to one another when water is in its liquid phase. It is a mixture of clusters of tetrahydrally linked water molecules and a single molecule, with single molecule occupying spaces between the clusters. The water molecules in the clusters and molecular aggregates are held together by strong bonds. The energy of a hydrogen bond is even greater than that of any other molecular interaction. All these factors either alone or together make the wetting of textiles difficult.

It is possible to bring down the surface tension of water from 72 dynes/cm to 28 dynes/cm by dissolving soap in water. When a surfactant (soap) is dissolved in water the hydrocarbon chain (hydrophobic part tail, ▭) tries to get away from the

$$CH_3(CH_2)_{16}COONa \rightarrow CH_3(CH_2)_{16}COO^- + Na^+$$

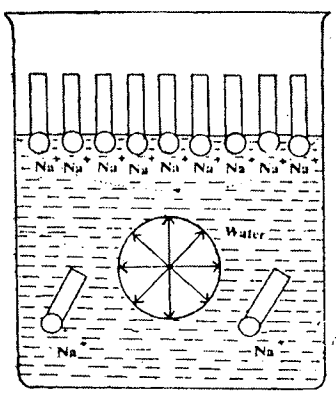


Figure 4-8. Surface activity and orientation of soap molecules.

water medium due to its hydrophobicity (Fig. 4-8) and concentrate at the surface. The hydrophilic grouping (carboxyl head, O) just dip in the water at the surface and the sodium cation is in the vicinity of negatively charged carboxyl head. Thus this compound, sodium stearate (soap), distort the structure of water and decrease the free energy of the system.

However, there is another means of minimising free energy of these systems. The distortion of the solvent structure can also take place by aggregation of the surfactant molecules into clusters (micelles) with their hydrophobic groupings directed toward the interior of the cluster and their hydrophilic groups directed towards the solvent. Micellisation is therefore a mechanism alternative to adsorption at the interfaces for removing lyophobic groups from the contact with water, thereby reducing the free energy of the system.

The wetting agent not only facilitates the wetting of the fibre by water but also results in the displacement of air from the micropores of cotton by the water. Thus the wetting of a surface involves the reduction of interfacial tension, so that liquid spreads as a continuous film instead of remaining as drops (Fig. 4-9). When the

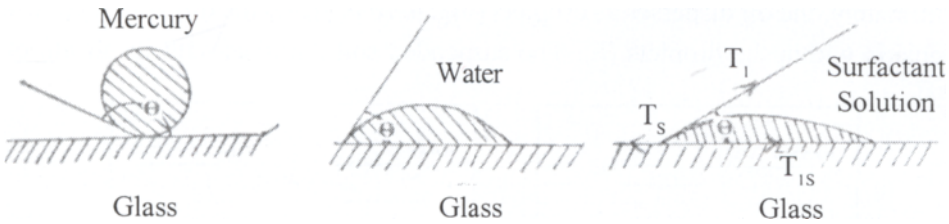


Figure 4-9. Angle of contact, θ.

interfacial tension is large, the angle of contact is also large. Surfactants can reduce the angle of contact, since they facilitate wetting (spreading) of the liquid on the surface. The relationship between the various forces can be written as :

$$\cos\theta = \frac{T_S - T_{1S}}{T_1}$$

For perfect wetting of the fibre, θ must be zero, so that,

$$\frac{T_S - T_{1S}}{T_1} = Cos\,0^\circ = 1$$

or, $T_S - T_{1S} = T_1$

This means that if θ is less than 90°, the oil will tend to spread over the fibre and adhere to it. But if θ is greater than 90°, the oil will tend to form globules which are easily detatched from the fibre. The effect of adding surfactant to water is that the surfactant molecules will congregate at the oil/fibre (T_S) and even more at oil/water (T_{1S}) interfaces, thus reducing the values of Cos θ.

4.4.7 Surfactant as detergent (scouring agent)

The function of the detergent is to remove the dirt and dust particles and other constituents of the size such as china clay from the cotton fabric. The detergent keeps the soils in dispersed or suspended form in scouring solution and prevents redeposition on the fabric. Fig. 4-10 illustrates the sequence of events of soil removal. Adventitious dirt adhere to the fabric because the oil acts as an adhesive towards it. The fabric/soil/water interfaces not soluble in water is shown in

Fig. 4-10 (A). When detergent is added [Fig. 4-10 (B)], the soil hydrophobe either dissolves into the soil or orient along the fibre surface. The largest concentration of detergent is present along the edge of the soil. Because of the hydrophile, the edges tend to associate with water and thus the removal of soil from the fabric starts. Ultimately, the oil disperses as droplets [Fig. 4-10 (C)] and the dirt is held in suspension within the droplets [8]. The suspended soil particles with its sheath of

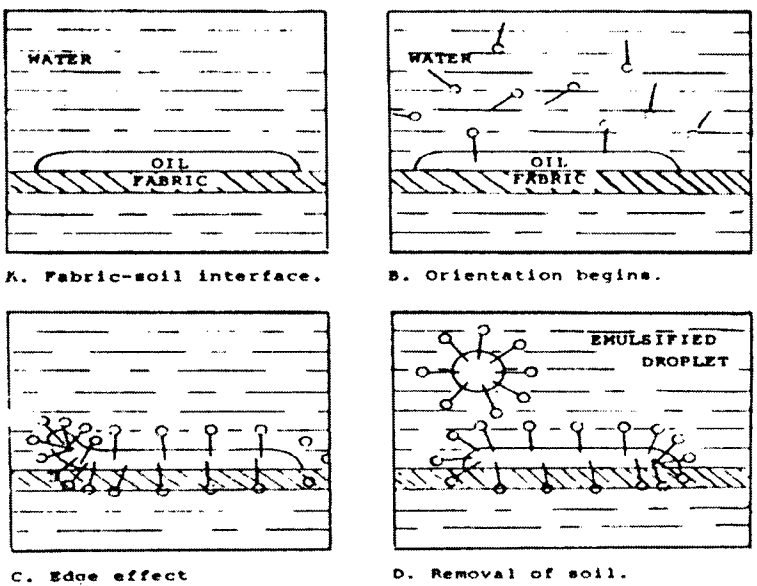
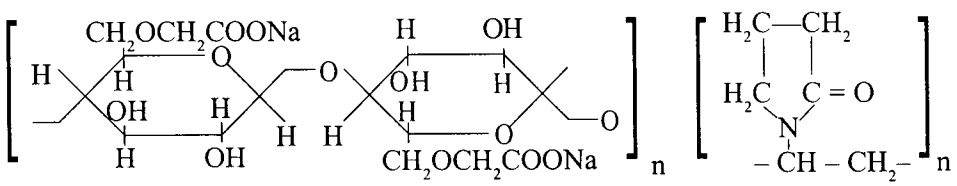


Figure 4-10. Schemetic diagram of events causing detergency [7].

oriented soap molecules assumes a net negative charge similar to the globular micelle of soap. Cotton fibres also take up a negative charge when immersed in water. The electrostatic repulsions between the particles and the fibre play a major role in preventing redeposition. The addition of carboxymethyl cellulose (CMC) and/or polyvinyl pyrolidone (PVP) (Fig. 4-11) can act as anti-redeposition agents.



CMC PVP

Figure 4-11. Chemical structure of CMC and PVP.

CMC is used primarily in surfactants and PVP is used as bath additive. Further, CMC also forms a protective colloid with the soil and thus prevents soil redeposition on the cloth. The emulsion of oil and dirt should be stable, otherwise there will be redeposition. Ordinary soap and detergent is a good emulsifying agent.

The most important consideration in scouring is the critical micelle concentration (CMC) of the surfactant. A reservoir is established at the CMC and several factors become evident (Fig. 4-12). The detergency is at its maximum while the

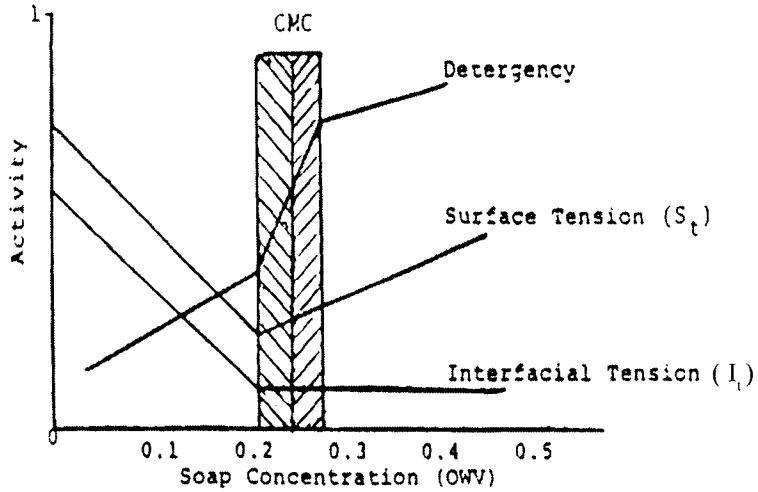


Figure 4-12. Relationship between detergency, surface tension, interfacial tension and CMC [9].

surface tension and interfacial tension are at their minimum. The CMC is different for different molecular structure of surfactants, and it varies with temperature, agglomeration number and average number of molecules per micelle.

4.4.8 Emulsion scouring

The knitting yarn in cotton weft knitted fabrics contains lubricants which replace the size on woven fabrics. Lubricants are widely used in worsted and woollen sectors of the wool industry, primarily to aid processes such as carding, combing and spinning. At the final stages of manufacturing of synthetic fibres, they are subjected to oiling to improve their physical and mechanical properties and to finishing with anti-static agents to reduce their ability to be electrified [10,11]. Stabilised bulked-polyester yarns for weft knitting are heavily oiled.

The term 'yarn lubricants' (or coning oil) is defined as all lubricants applied by textile mill or processors subsequent to application of spin finish. Increasingly sophisticated spin finishes are used and long group of compounds are known to serve as fibre lubricants, mineral oils being used since long. Straight chain esters such as methyl, ethyl or butyl of fatty acids with functional groups C_6 to C_{18} are the largest groups having excellent lubricity. Polyglycols or their fatty acid esters and fatty glycerides, more complex chemicals such as esters of dibasic acids, pentacrythritol, neopentylene glycol, and polycerols as well as aryl, alkyl, alkyl aryl phosphates, silicones, silicate esters, fluroesters and polyphenyl ethers have been used for greater stability. Lubricants have been modified by ester interchange, ethoylation or acetylation in order to influence the degree of lubricity and other properties. The main lubricants, however, used are saponifiable, water emulsifiable (ester based), water dispersible and water soluble (surfactant based). Out of these ester based and water soluble types are more popular because of their technical performance and ease of removal. Table 4.8 shows a range of typical application levels used for the main

TABLE 4.8.
Main Types of Lubricants Used on the Woollen System [12]

Yarn end use	Lubricant	Apply (o.w.f.)
Fabrics	Saponifiable	
	Emulsifiable	5 - 7%
Hosiery	Emulsifiable	4 - 11 %
Carpets	Emulsifiable	
	Dispersible	1 - 5 %
	Water soluble	

types of lubricants on the woollen system. Most oils have lower refrective indices than drawn polyester fibres, so that the presence of oil on the surface of the fibre reduces the scattering of incident light; impair level dyeing properties and the fastness to washing and rubbing; and modify the structure of polyester fibres on storage and thermal treatment. A proper selection of lubricants is necessary so that scouring must be thorough.

Non-scourable oils are difficult to remove from cotton giving rise to unlevel dyeings [13]. The oil, grease and tar stains are generally removed by spotting on

stained portion with stain remover comprising emulsified solvents in the liquid form. The stains are spotted with stain remover and rubbed and left for short time and then washed. The process may be repeated to remove stains completely. The treated areas however should not dry before they are washed as otherwise ring marks are likely to be formed. Emulsified solvents (Table 4.9) are used in the

TABLE 4.9.
Type of Emulsified Solvents

Type	Surfactants (emulsifier)	Solvents
Anionics	Sulphated oil, alkyl aryl sulphonates.	Carbon tetrachloride, and trichloroethylene.
Non-ionics	Ethylene oxide condensate with alkyl phenols, fatty alcohols and fatty acids.	Perchloroethylene, isopropylalcohol, oxycyclohexane, chlorobenzene, benzyl alcohol.

formulation of stain removers. They are usually organic solvents containing emulsifier dissolved in them and hence become self-emulsifiable. The solvent must be capable of dissolving the hydrocarbon impurity and the detergent must be capable of emulsifying both the hydrocarbon and the solvent. Solvents blended with surfactants are claimed to have superior environmental behaviour along with excellent grease removal [14].

Other alternative methods are that the powerful stain removers may be applied from the bath along with wetting agents cum detergents at high temperature and solvent scour. One such formulation which has been widely used for polyester/ cotton blended fabrics for removing unsaponifiable waxes from cotton portion apart from lubricants and conning oils from the yarn is given in Table 4.10. The left over

TABLE 4.10.
Emulsion Scouring Recipe

Ingredients	Proportion by weight
Essential Oil	40-50 parts
Perchloroethylene	20-10 parts
Emulsifier (e.g. nonyl phenol, HLB = 13-15)	40 parts
	Total 100 parts

solution as well as the wash water are removed. Rust stains are best removed by oxalic acid up to 10 g/l at about 60-70°C followed by washing.

The mechanism by which emulsion scouring occurs is attributed to the hydrophobic portion of the micelle being saturated with the solvent. The micelle, when loaded with solvent, is more effective in solubilising oily impurities from the fabric than is the detergent alone, provided both solvent and emulsifier are properly selected and used. The critical feature of such a solvent is its KB Value, which is a measure of its solvency for a particular oily soil.

4.5 Solvent Scouring

Solvent scouring appears to be alternative to aqueous scouring and particularly suitable for polyester and woollen goods. This process not only permits scouring, but also simultaneous scouring and desizing or even partial bleaching in one step [15,16]. Solvent scouring is also useful for the removal of lubricating oils from knitted polyester, oligomer from polyester and bulking of knitted goods. Wool felts less in solvent media and is particularly useful in wool milling and application of shrink-resist resins to wool [17]. Solvent processing has been established due to reduced water pollution, reduced energy cost and consumption apart from effective removal of impurities. Solvent preparation gives excellent results in terms of uniformity, reproducibility and high absorbancy [18].

Basically solvent scouring is a refinement of dry-cleaning and is carried out either batchwise or continuously (Chapter 5). Solvents intended for use in textile processing should ideally be inexpensive, readily obtainable, non-toxic, non-flammable, stable to repeated recovery, inert to textiles and non-corrosive. The most suitable solvents for textile processing are the chlorinated hydrocarbons, e.g. tetrachloroethylene (perchloroethylene), trichloroethylene and 1,1,1- trichloroethane. Perchloroethylene is widely used in drum machine [19]. Trichloroethylene is best avoided because of its stripping action of dyed polyester materials if the temperature should rise above 30°C. One important factor for solvent processing is the stability of solvents to recovery by distillation or by adsorption process. The recovery of stabiliser in the solvents is also equally important. The stabilisers recommended for different solvents are shown in Table 4.11. In certain processes 'booster solvents' are added to perchloroethylene. They are generally dipolar aprotic solvents [27.28]. Soil removal in chlorinated hydrocarbons can be improved by the addition of solvent detergents, e.g. monoethanolamine, alkylbenzene sulphonate,

TABLE 4.11
Solvents and Stabilisers for Textile Scouring

Solvent	Stabilisers	Ref.
Trichloroethylene	Substituted diamines	20
	or	
Perchloroethylene	Crotonaldehydedialkyl hydrazones.	21
1, 1, 1 – trichloroethane	Mixtures of acetonitrile and nitromethane	22
	or	
	Dimethoxyethane and 1, 4 – dioxan.	23
Helogenated hydrocarbons (general)	Triethyleorthoformate,	24
	Phosphoric acid,	25
	Benzotriazoic.	26

alkyl poly (glycol ether) and alkyl pyridine chloride [29]. Such products are usually mixtures, e.g. dodecylbenzene sulphonate (13%), nonyl phenol along with 5 ethylene oxide units (5%), isopropylalcohol (5%), water (7%) and chlorinated hydrocarbon (70%). Chlorinated hydrocarbons containing such products are capable of dissolving water and hence enhances detergency.

The main difficulties of solvent scouring are the need for systems to recover the solvent from fabrics after processing. Apart from this, solvent can remove binders from bowl fillings and adhesives from laminated bowl covers and rapidly attacks conventional rubber coverings with expensive effect. At high temperatures adsorption of solvent into the fibre web increases and the degreasing action in subsequent steaming operation can have embarassing side effects. However, the growing problems associated with the increasing demand for raw water in some countries and disposal of effluent in general have given an impetus to the solvent scouring system.

4.6 Scouring of Raw Wool

Raw wool is difficult to spin because of the natural grease/wax (yolk), large perspiration salts termed suint, acquired impurities like vegetable matters, dirt, proteinaceous contaminant layers (PCL) and wool burrs which contain hemi-cellulose

and lignin. Finer varieties of wool may contain fats and suint as much as 50% of the weight of raw wool. The optimal residual wax content after scouring should be of the order of 0.5 to 0.75% only because amounts in excess of this are liable to cause trouble in carding, doffing and in subsequent dyeing processes. On the contrary, too low a wax content impairs the handle of wool as well as spinning properties. To achieve satisfactory residual grease content on wool various scouring procedures have been used [30].

4.6.1 Emulsion scouring

Scouring of raw wool is carried out in tanks filled with detergents or oleate soap (2-4%) and sodium carbonate (2%) at 50-55°C for 10 to 15 min. The pH of the liquor is about 10. In practice the raw wool is propelled gently through the scouring tank, then squeezed between rollers and then passed through another or more tanks in this way, until eventually it is rinsed in clean water. Such a multi-stage scouring environment is needed to remove dirt from the wool.

The levels of wool wax and dirt (ash) remaining after conventional scouring are considerably higher on the top than base (Table 4.12). The hard to remove wool wax is principally oxidised wool whose emulsion stability is considerably higher

TABLE 4.12.
Levels of Residual Contaminants on Portion of a Wool Fibre

Portion of fibre	Wool wax	Ash
Base	0.46	0.42
Top	1.18	4.73

and in multistage scouring system more effective contact time is available for solubilisation rather than rolling-up mechanism [31, 32]. Thus, in the final stage of scouring in presence of detergent, the hard to remove wool wax is solubilised by the detergent to form a fairly dispersed micelles, whereas the strongly adhering dirt (inorganic or organic) is displaced by the adsorption on non-ionic detergent at the fibre/solution interface [33]. In the surfactant solution there are four stages in the removal mechanism [34] :

i) an initial swelling of the proteinaceous contaminants ;
ii) formation of grease globules within or on, the swollen PCL ;
iii) removal of the swollen PCL with attached globules; and
iv) breaking up of the swollen PCL/grease complex into spherical or irregularly shaped particles in solution.

4.6.2 Suint scouring

In this process the dusted raw wool is steeped in water at 16°C and then the liquor is withdrawn and clarified by sedimentation or centrifuging [35]. The pH of the suint liquor is between 5.5 to 8.8. For removal of wax the suint liquor should be heated at 60°C, when wax is emulsified. The material is in then rinsed, washed with soap and finally rinsed in the subsequent bowl.

4.6.3 Solvent extraction scouring

About 90% of the wool wax can be removed by this system. The recommended solvents are benzene, carbontetrachloride, solvent naptha, white spirit, trichloroethane etc. In one method solvent is applied under high pressure jet on the material placed on a permeable conveyer and dislodges much of the dirt and suint apart from removal of wax from the fibre [36]. The solvent content on the treated wool is reduced to about 45% by passing through the rollers and is further reduced to about 10% by centrifuging. Finally, the residual solvent is removed from the fibre by blowing hot air [37].

4.6.4 Refrigeration process

In this method raw wool is first exposed to low temperature environment of about –30°C which freezes the wax and vegetable matter and thus becomes hard and brittle. In the second stage these impurities are removed from the fibre by some mechanical means [38].

4.7 Scouring of Wool Yarn and Fabric

The scouring of loose wool is a common practice, although further scouring of wool yarn or piece is often carried out to remove the added impurities i.e. combing and spinning oil. However, before scouring treatments of wool yarns and fabrics, particularly all worsteds and wool/cotton union are given other pre-treatment processes like crabbing and potting.

4.7.1 Setting and scouring of wool yarn

Certain yarns such as those from cross-bred wools are wet set before scouring to prevent cockling occuring in the pieces. Setting of yarn is carried out by stretching the hanks in a suitable frame and the stretched hanks are immersed in boiling water for 30 min. The hanks are allowed to cool under tension before removing from the frame.

Woollen yarns are normally spun with a saponifiable oil, such as oleine based

lubricants (70% FFA /30% mineral oil). Scouring can be carried out by saponification system using soda-ash only and forming the necessary soap by reaction with the oleic acid content of the lubricant. Soap will exert a strong emulsifying action to remove grease and dirt from wool yarn. Worsted yarns are generally spun with up to 3% of emulsifiable oil (blends of mineral oil and emulsifiers). This is removed by soap added to the scouring bath together with alkali as a soap builder or by alkaline solutions of synthetic detergents. Surfactant types of lubricants are mainly used on worsted and semiworsted systems, and the low levels applied are often removed in the dyebath. Polyglycol type of lubricants used for carpet yarn spinning can be readily removed using non-ionic detergents in neutral conditions.

4.7.2 Crabbing (setting) of woollen fabrics

Crabbing is merely a relaxation process conducted under controlled conditions before scouring to prevent distortion during subsequent processing. Relaxation removes the latent strain introduced into the yarn before being woven. In the batch process the cloth is passed open width under guide rollers through boiling water in the first trough and is then tightly wound on the lower roller of the two large rollers in such a way that half of the rotating roller of cloth is immersed in the hot water. This treatment takes about 5 minutes. The process is repeated by passing the cloth to the second unit. In this way the outer layer of the cloth in the first treatment becomes the inner layer during the second and thus uniform treatment is possible.

4.7.3 Potting of woollen fabric

Crabbing is frequently followed by steaming or blowing with steam and the wool fabrics are given surface stability without losing their shaping capacity in the making up process. The bonds that stabilise wool fibres in a particular configuration are disulphide cross-links, hydrogen bonds, electrostatic bonding between anionic and cationic side chains and hydrophobic side chains in the protein molecules (Table 4.13). In the setting process, the stresses are relaxed within the fibre by mobilizing one or more various cross-linking bonds and thereby allowing them to rearrange into new, unstressed position. The action of steam on strained wool fibre is two-fold [40]. The first stage consists of breaking the existing bonds :

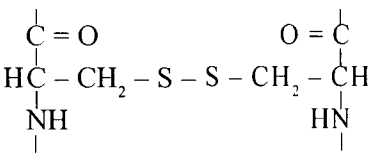
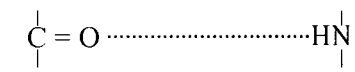
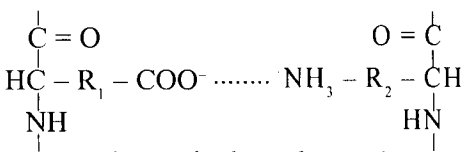
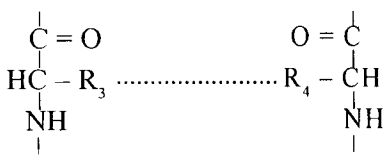
$$R\text{–}S\text{–}S\text{–}R + H_2O \rightarrow R\text{–}SH + R\text{–}S\text{–}OH$$

The second stage consists of a formation of new bonds :

$$R\text{–}S\text{–}OH + R\text{–}NH_2 \rightarrow R\text{–}S\text{–}NH\text{–}R + H_2O$$

TABLE 4.13.

The Cross-links in Wool and Reagents Capable of Mobilizing Each Type and Bringing About Stress-relaxation or Setting [39].

Cross-link	Mobilizing agents
Disulphide links 	Thioglycolic acid, reducing agents, alkalies, steam at high pressure or steam at atmospheric pressure for long periods of time.
Hydrogen bonds 	Water, steam or hydrogen bond breaking agents such as urea and DMF.
Electrostatic bonds  R_1 & R_2 = hydrocarbon units	Water or steam.
Hydrophobic bonds  R_3 & R_4 = hydrocarbon side chains	Organic solvents e.g., alcohols, DMF etc.

The redistribution of H-bonds is an accepted theory. Temperature, pressure, moisture and time are the parameters which introduce physical and chemical processes in kier decatizing. The optimum pH for crabbing has been shown to be around 6 [41].

The so-called ''disulphide exchange'' reaction is also accepted today. Wool is constructed of a matrix and microfibrils. The crystalline substance of the microfibrils is embedded in the matrix, the amorphous substance. The two morphological components, differ distinctly in sulphur content. During the kier decatizing, it is assumed that this disulphide exchange, the splitting of disulphide bridges, takes place

first in the matrix by means of water as a kind of preliminary stage. The so-called microfibril component is plastically deformable, i.e. these microfibrils are particularly stabilized by hydrogen bridges. Steam can actually only now attack these hydrogen bridges, which were previously masked by a complicated system of disulphide bridges. The important step therefore is that the microfibrils are deformed : then by cooling, oxidation and the blowing through of air, this set microfibril condition is re-locked by the reorganised disulphide bridges in the matrix. Fig. 4-13 shows how after the disulphide interchange an initially tense molecular structure goes into relaxed (stabilised) state in a new, geometric structure.

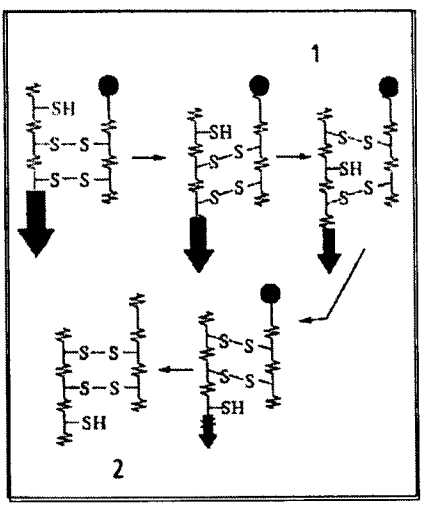


Figure 4-13. Exchange of sulphide and relaxation of the tensions [42]
1, internal exchange at the progressive relaxation of the tension and
2, final stage without tension.

In actual practice the fabric is wound on a perforated roller or cylinder covered with cotton cloth to prevent the perforation marking. Between each layer of wool fabric there is a similar thickness of interleaving fabric. The steam is blown through the inside of the metal roller under pressure of 40-50 lb for 10 to 15 min whilst the cylinder rotates. Then the absorbed steam is removed from the cloth by blowing compressed air through the fabric in much the same way as the steam was blown through it. The air also produces some cooling on the fabric. The cloth is then wound on a second steaming cylinder so that outer layer of the cloth forms the inner layer of the roll and is steamed as before. The cloth is then cooled or passed

through cold water in open width or squeezed. Potting also gives soft handle and bright finish. The main disadvantage is that steaming at high temperatures tends to yellow the wool.

4.7.4 Scouring of wool fabric

Woollen fabrics are still mostly lubricated with olein-based products or mineral wool oils. Worsted may be lubricated as in former times, with natural oils of vegetable or animal origin, or with polyalkylene glycol based lubricants with or without mineral oil additions. Woollen fabrics are generally scoured using scouring liquors similar to those used in yarn scouring. Use of soap and soda is mainly used as scouring agent. This system has certain advantages in promoting bulking and good handling.

4.8 Carbonising of Wool

Carbonising is done to remove the cellulosic impurities from wool by treatment with acid or acid producing salts. Carbonising may be carried out in loose wool or on piece goods after scouring. However, it is common practice to carbonise worsted piece goods as well as woollens.

The conventional carbonising process comprises five main stages : scouring, acidizing, drying and baking, burr crushing and dedusting and neutralising [43-46]. Wool piece goods are treated with sulphuric acid (6-8^0 Tw) containing acid stable wetting agent and hydroextracted. The treated wool substance is dried at low temperature (60-70^{0}C) very quickly to minimise degradation by sulphuric acid of intermediate critical concentration [47]. The dried wool is then heated at 110^{0}C for a short time. The goods are then neutralised immediately or run dry through a dolly or milling machine to remove the charred vegetable matter and then neutralised. Neutralisation of wool fabric can also be carried out in open-width scouring machine. Neutralisation with ammonia or ammonia/ammonium acetate mixtures removes acid from the fabric far more rapidly than either sodium carbonate and sodium acetate.

In a rapid carbonising process [48] wool is treated in up to 8% (w/v) sulphuric acid solution for 30 sec and time delay of about 10-15 min is introduced before drying. The locally damaged areas can greatly weaken the fibre if surface acid is not evenly distributed [49] during drying. However, in the rapid carbonising method with a delay of 10-15 min, the distribution of sulphuric acid between surface acid

and total acid inside the wool changes [50]. Free surface acid penetrate into the wool fibres and bonds to wool. Thus the amount of concentrated acid formed during drying and baking is minimised and as a consequence, less chemical attack occurs to wool in rapid carbonising.

Magnesium chloride, aluminium chloride (8-10^0 Tw) or gaseous hydrochloric acid may also be used for carbonising of wool. Rags are carbonised to remove cotton stitchings prior to use in shaddy by the 'dry carbonising' process by exposing to hydrochloric acid gas in an enclosed chamber. Metal acid salts liberate hydrochloric acid at high temperature and attack the cellulose in wool. But owing to their high cost and higher temperatures required which cause injury to dry wool, are rarely used.

The wool burrs contain hemi-cellulose and lignin apart from cellulose. The lignin is not effected by carbonising process on acid hydrolysis, but can be split oxidatively. Salt of persulphuric acid accelerates degradation of wool burrs which enable shortening the time of reaction [51].

Natural soiling of wool and vegetable matter and skin flakes, can also be enzymatically modified [52]. The replacement of carbonisation by the use of enzymes, such as cellulases, ligninases, hydrolases, lyases, oxidoredulases etc. are reported [53]. The main advantages of enzymatic carbonising are reduced wool fibre damage, effluent load and energy consumption.

Carbonised wool are more porous than scoured wool and hence the dye uptake is higher. Uneven dyeing may result due to faulty carbonising [54].

4.9 Degumming of Silk

Degumming or boiling-off is the process employed to remove the silk gum (sericin) enveloping the two raw silk threads (fibrion) (Fig. 4-14). During the

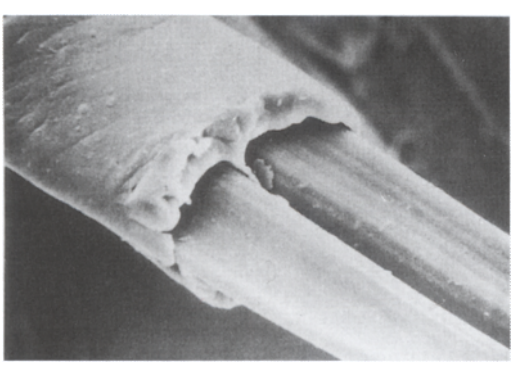


Figure 4-14. The microphotograph of raw silk [55].

spinoning process of silk by silkworms the two filaments are made into one by means of proteinious gummy substance called sericin. The gum content of silk varies according to quality and origin. Bombyx mori or Mulbery silks have about 20-30% gum and Tussah 5-15%. The gum is not completely removed in every case. The extent of degumming gives rise to different varieties of silk [56]. 'Ecru silk' (crude, bast silk) is rarely degummed, quite hard and without lustre. The degumming loss is maximum 4%, since mostly only grease, wax and resin substances are removed. This type of silk is mainly used as warp threads. 'Half-boiled silk' (souple, soft, matt silk) is partially degummed. The degumming loss is approximately 6-12%. In order to make the gum on the fibre to soften and remain in that condition, a treatment of 3-4% of tartar ematic is advisable. 'Cuite silk' (lustre silk) with nearly 18-30% gum loss can be classified as a completely degummed variety with a soft handle and high lustre.

Apart from sericin, other impurities present in silk are lubricants and softeners added during throwing or in preparation for weaving or knitting, dirt and oils picked up incidentally during processing and undesirable natural colours. The component of fats and oils is around 0.5-1% and that of natural pigments 1.0-1.4%. During the degumming process, soil, stain, oil and fats sticking to the material will also be removed. Thus degumming is synonymous with the scouring process normally used for the purification of cotton and wool.

Silk warp is not subjected to sizing before weaving like cotton. However, grey silk fabric and its blended fabrics are subjected to singeing prior to degumming. Degumming can be carried out by physical or chemical means on silk in the form of hank and also on fabrics which are subsequently taken for dyeing. The choice of degumming conditions depends on the type of silk product (yarn, twist, fabrics of different densities). Wild silk fabric is more difficult to degum than Mulbery silk. Tussah silk contains higher quantities of calcium salt. Loss in weight of silk by degumming process is also accompanied by a loss in strength of approximately 20%. The loss of weight and volume can be completely or partially compensated by the subsequent weighting process.

Degumming is effected by careful treatment of silk with high pressure water, acids, alkalies, soaps and synthetic detergents. Chemical dissolution of sericin is obtained partly by hydrolysis and partly by dispersion, independent of the method used. Soap works mainly by dispersion whilst alkalies have a strong hydrolytic effect [57].

4.9.1 Degumming of silk in water [58]

Cultivated varieties of silk can be degummed by extraction with water at 120°C for about 2 h and repeating the process three to four times. In this case degradation of silk is minimum, but use of pressure equipment is essential. However, some modification of the protein molecule does take place.

4.9.2 Degumming of silk with alkali [59] **and acid** [60]

Silk degumming in aqueous solutions of acids and alkalies is greatly influenced by pH and temperature. An alkaline reaction at a pH > 9 and acid reaction at pH < 2.5 ensure a rapid elimination of sericin completely after 30 min of treatment. The temperature should not exceed 95°C to avoid weakening of the fibre. The degree of hydrolysis of fibrion also depends on pH of the bath.

4.9.3 Degumming of silk with soap [61]

Degumming is effected by careful boiling-off in soap baths which should be slightly alkaline. The fibre is treated with soap solution to give a pH around 10.0 at 90-95°C for 1.5-2 h. In order to avoid lien soap deposits and resulting stains, the water should be properly softened. Sequestering agent may be added in the bath to correct the hardness of water. In case of white and delicate varieties a two bath method may be employed. The second degumming bath will consist of 50% quantity of soap taken for the first degumming bath and the duration of treatment may be divided equally between 40-45 min for each bath.

Neutral soap like Merseille soap or olive oil soap have no degumming property as the free alkali present in them are very negligible. However, Merseille soap (8 g/l) can be used in presence of non-ionic tenside (fatty alcohol polyglycol ether) (1-3 g/l), polyphosphate (1-3 g/l) (for softening the water) and soda (1 g/l) at 95°C for 1-2 h with a material to liquor ratio of 1:30. Here also a two bath method can be resorted to. Non-ionic tenside accelerates the degumming process and facilitates rinsing out the soap. Tussah silk is usually prewetted with boiling water before degumming and then degummed in strong alkaline bath [62].

4.9.4 Degumming of silk with synthetic detergents

Degumming with synthetic detergent is increasingly replacing soap. The main drawbacks are soap is expensive, great quantity of soap is required and longer treatment time. A large number of synthetic detergents are available in the market and their selection is very important particularly on the requirement of soft feel as

that achieved with soap. Non-ionic product like nonyl phenol ethoxylated compound in the pH range of 11.2-11.5 for a treatment time of 40 min at 95°C is found to remove the gum and maintain the strength of the yarn.

4.9.5 Enzymatic degumming of silk

Enzyme which can hydrolyse the sericin is classified as proteolytic enzymes [63-65]. The proteolytic enzymes cleave the peptide/amide linkages and convert them into amino acid. Mainly there are three types of proteolytic enzymes such as zinc protease (e.g. carboxy peptidase A), serine protease (Chymotrypsin, Trypsin, Thrombin) and thiol protease (acts as cystine residue in the protein). The function of proteolytic enzymes in their degree of degumming depends on the pH of the bath and the optimum activity is found to be different at different pH for different enzymes.

Usually enzymatic desizing of silk is a two stage process. In pre-degumming stage, the cloth is treated with a solution containing soda-ash (1 g/l) at 95°C for 20 min at a liquor ratio of 30. In the second stage, further degumming is carried out by treatment in a solution containing protein enzyme (0.06-0.1 g/l), non-ionic detergent (1 g/l) for 30 min at 55 to 60°C. It is usually impossible to achieve full degumming of silk by enzymes. A short-time treatment in a third bath containing soda-ash or soap may be given for the removal of the remaining sericin.

4.9.6 Foam degumming

The degumming of silk can also be carried out by foam method. The silk skiens are subjected to the action of foam from a boiling soap bath. Skiens are actually hung above the soap solution and the foam action has a tendency to dissolve and eliminate sericin. This method, however, is not popularly adopted.

4.9.7 Partial degumming of silk

Before partial degumming the silk is degreased in moderately warm (30-40°C) and slightly alkaline soap baths. The actual degumming is then taken place in a bath containing acid salts or acids. The sericin is not released as much in an acid medium as it is in a neutral or alkaline bath, thus only partial degumming results. Acid degumming has also a positive effect on the strength and handle. The actual degumming bath can have various compositions :

- Sulphuric acid and magnesium sulphate,
- Sulphuric acid and soap,
- Sulphuric acid and tartar,
- 4% strength soap solution,
- $NaHSO_3$ solution.

Depending on the nature of silk, it is treated for 1-3 h at boiling temperature. The weight loss with half boiled silk lies in the range of 6-12% on the original raw weight.

4.9.8 Washing of degummed silk

After boiling-off, the silk is thoroughly washed with lot of water at 50-60°C containing 1ml/l ammonia for 15-20 min. This is then followed by 1 to 2 cold rinsing baths. Half-boiled silk should not be subjected to hot soap baths and alkaline liquors over 30°C because this would act on the silk gum still present.

Following washing and drying silk is given further mechanical treatment in the form of stretching, beating or glossing. Scroop is imparted to the silk fabric by treatment with 2-5 g/l of 30% acetic acid at room temperature for 15-30 min. When silk is delivered in dyed condition, scrooping is done after dyeing.

Both degumming and partial degumming are only suitable for reeled silk (greige). These finishing processes are insignificant where schappe and bourette silks are concerned, since these are freed from their gum in the early stages of preparation before spinning [66].

4.10 Degumming of Remie

Degumming of remie is a long and complex procedure. Different degumming technologies [67-72] use different auxiliaries. Besides boiling-off, other treatments such as scuthing, washing in acid solution and water etc. directly effect the sheen and gum content of the mass of cleaned fibre.

In chemical degumming of remie, hot caustic soda solution of about 10% (o.w.f.) is used to dissolve pectic substances. Apart from this, sodium phosphate, sodium pyrophosphate, sodium metasilicate, sodium sulphite can also be used for degumming of remie.

Sodium pyrophosphate is better than sodium phosphate in washing and total cleaning [73]. Although sodium pyrophosphate is very permeable, diffusible and can scour as well in presence of metal ions, it is expensive. Sodium metasilicate shows good washing, total cleaning and emulsifying properties and it is inexpensive. Sodium sulphite, not only has a bleaching function, but also protects the physical properties of the fibres. The degumming efficiencies of these three auxiliaries was studied by using quadratic orthogonal rotation experimental design [74]. The concentration of auxiliaries and time of second boiling-off are the most important

factors in degumming. Sodium pyrophosphate can be replaced and replenished by sodium metasilicate over a definite range, so also decrease the manufacturing cost. The optimum conditions of sodium sulphite degumming are 1% and second boiling-off time, 3-3.5 h, the concentrations of sodium metasilicate and pyrophosphate are 2.5-3% and 0.7-1.0% respectively.

4.11 Scouring of Linen

The scouring of linen is associated with number of problems such as weight loss, release of cations from salts into solution and loss in strength. If the released cation is iron, this can lead to cationic tendering during bleaching. This problem can be minimised by adding suitable chelating agents in the scouring bath and thus sequesters any cations released from the proteins.

Traditionally, long slow processes are carried out to obtain correct balance between the required properties of whiteness, absorbancy etc. in one hand and chemical damage on the other. The traditional process usually consists of chlorination, extraction of the chlorinated lignin by scouring in soda-ash and then bleaching preferably with alternate chlorite and peroxide stages or even hypochlorite bleach. Process details of conventional method are shown in Table 4.14. Lime boil is

TABLE 4.14
Conventional Process Details for the Scouring of Flax

Kier boil	Lime	10-12% (o.w.f.), 8 h at 60°C
Cistern sour		
Kier boil	Soda-ash	12.5 g/l, 18 h at 60°C
Cistern chemic	Available Cl_2	1.7 g/l, 2 h at pH 4.3
Kier boil	Soda-ash	6.5 g/l, 18 h at 60°C
Chemic bleach	Available Cl_2	0.6 g/l, cold pad-batch over-night
	Soda-ash	2.0 g/l

followed by hydrochloric acid sour, alkaline (soda-ash) boils, acid chemic (hypochlorite at pH 4 to 5), a further alkaline boil with soda-ash which removes the chlorinated sprit (remnants of the woody core of the flax stem), and finally a hypochlorite bleach (pH 9-10). This complicated process sequence has been streamlined over the years. The lime boil has been replaced by a caustic-soda-ash boil.

4.12 Scouring of Jute

Although jute is a natural fibre like cotton, it differs in chemical composition. Unlike cotton jute contains a high percentage of non-cellulosic matter (about 40%) and the pre-treatment processes of jute are somewhat different from that of cotton. Scouring of jute with caustic soda under pressure cannot be carried out like cotton because of removal of hemi-cellulose which results in high losses of tensile strength (10-15%) and weight (6-8%).

Apart from natural impurities, jute yarns or fabrics contain mineral oil/jute batching oil (JBO), which is added to facilitate spinning of jute fibre. The JBO has a delustering effect and also contributes additional yellowing on exposure to light.

Despite golden brown colour of jute and presence of mineral oils it is directly taken for bleaching after a hot and cold rinse or an acid steeping or a neutral/mild scouring. Treatment with dilute solution of sodium hydroxide and soap at elevated temperature results in softer feel and pliability which may be attributed to the action of alkalinity in the soap and deposition of fatty materials on the fibre surface. An effective method of removal of JBO or mineral oil together with adhering/ extreneous dirts/impurities is to treat the grey material with an emulsified solvent for 15-20 min at 70-80°C, to which soda-ash may optionally be added. The advantage of the process is that the strength of jute is not affected much.

4.13 Scouring of Synthetic-polymer Fibres

Synthetic fibres generally do not contain naturally occuring impurities like natural fibres i.e. cotton and wool. However, spin finishes, processing and coning oils and antistatic agents are added to improve the physical and mechanical properties during spinning, weaving and knitting . Other impurities are dirt and sighting colours (to distinguish one kind of fibre from the other). The objective of scouring synthetic fibre fabrics is to remove the dirt, size, processing lubricants and sighting colours, achievement of relaxation in the case of texturised and knitted fabrics and production of special effects.

4.13.1 Scouring of polyester

Loose stock, slubbing and some types of polyester yarns may be simply rinsed with water or even be placed directly in the dyebath. The scouring of polyester fabric mainly depends on the type of sizing agents used on the yarn. Flat polyester-filament fabrics are commonly scoured to remove sizes and lubricants, after spotting (if necessary) to assist the removal of loom stains. The preferable condition for scouring of polyester in alkaline reagents (caustic soda, soda-ash, ammonium hydroxide) is about 2 g/l with a treatment time of 30-60 min at a temperature of 75-80°C. Alternatively, scouring can be carried out with anion active detergents in an amount 1-2 g/l at 80-95°C for 20-30 min.

Special precaution is necessary when polyester is scoured with strong alkali at higher temperatures and care has to be taken not to hydrolyse the fibre. Fig. 4-15 shows the reduction in weight of polyester on treatment with caustic soda at 100°C.

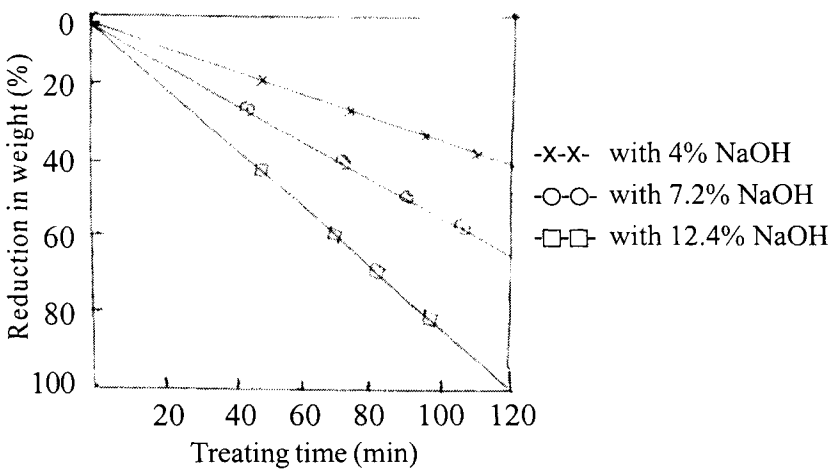


Figure 4-15. Loss in weight of polyester on treatment with caustic soda at 100°C.

4.13.2 Scouring of nylon

Nylons are scoured before dyeing to remove the added impurities and sighting colours. Synthetic detergents along with mild alkali are generally suitable for scouring nylons. Generally, non-ionic detergents are used in scouring of nylons as the anionic preparations are absorbed by the same sites of the fibre similar to that of anionic dyes and consequently reduce the exhaustion of the dyebath. Recipes for the scouring of nylon by batch and continuous processes are given in Table 4.15. Soft water should be used in the scouring bath to minimise the retention of heavy metals by the free carboxyl end groups of nylons. Emulsified organic solvent will

TABLE 4.15
Recipes for the Scouring of Nylons

Scouring chemical	Batch process	Continuous process
Non-ionic detergent (g/l)	2-3	2-3
Anionic detergent (g/l)	1-2	1-2
Soda-ash (g/l)	1-3	–
Sodium pyrophosphate (g/l)	–	3-6
Temperature (°C)	70	90
Time (min)	20-30	10-20

be of assistance if oil stain is also be removed from the fibre. The temperature of scouring depends on whether the material has been heat-set or not. For unset fabric the preferable temperature range is 70-80°C and for the set fabric it is 95-100°C. Unset fabrics have creasing problem if scouring is carried out in rope form above 60°C. After scouring the fabric is washed first at room temperature and then raised to the required temperature. An acidic wash-off is necessary when cationic finish is to be removed from the fabric.

4.13.3 Scouring of polyacrylonitrile fibres

Scouring is particularly necessary for yarns which are to be dyed in pale and medium shades as grey patches may appear due to soiling and lubricant present in the fibre.

Before scouring high bulk acrylic yarns on cones are relaxed in saturated steam at about 100°C for 20 min or in hot water. The hanks may be relaxed during dyeing also. Fabrics may be given dry heat treatment to impart some stability against creasing and to relax the material.

Alkaline solutions or soaps are not used for scouring of polyacrylonitrile fibres as they discolour the fibre. Scouring is carried out in a solution containing 1-2 g/l non-ionic detergent and 1 g/l trisodium phosphate at boil for 30 min. Anionic detergent should be avoided. 1 ml/l solvent-based detergent may be added in the bath for removal of oil and grease from the fibre. After scouring the bath is cooled to 60°C and rinsed at this temperature thoroughly to remove detergents as its presence affect the handle of the fibre.

Generally, scouring of modacrylic fibres is not always necessary. However, scouring and desizing may be carried out in a similar manner to that regular acrylic

fibres with non-ionic detergents at 50-60°C for 30 min under either weakly acid (acetic acid) or alkaline (trisodium phosphate) conditions followed by thorough rinsing.

4.13.4 Scouring of acetate fibres

The scouring of acetate fibres can be carried out in a solution containing 3 g/l soap and 1 g/l of a 25% solution of ammonia for 30-35 min at 70°C. Diacetate can be saponified under certain conditions of alkaline scouring and therefore careful control is necessary to avoid surface modification. Delustering of normally bright acetate fibres can be combined with scouring. Triacetate is not delustered by boiling or soap solutions. For triacetate higher temperature of wet treatment can be given than for diacetate.

4.13.5 Scouring of regenerated cellulose

Viscose and cuprammonium rayons do not contain natural impurities and scouring is done only to remove added impurities. Rayon can be cleaned by treatment at a temperature of 80-90°C with soap solution (0.3 - 0.5%) to which mild alkali like soda-ash or trisodium phosphate may be added. Rayon fabrics may be desized, scoured and bleached by treatment with a solution containing hydrogen peroxide (0.67 vol), caustic soda (5 g/l), together with sodium silicate (5 g/l) and wetting agent (1.5 g/l) by pad-steam method. The treated fabric is steamed for 2 min. After boiling-off, the fabric is washed with warm and cold water. The strength of hydrated cellulose is considerably reduced in wet condition and hence scouring should be carried out in a tensionless condition.

4.13.6 Scouring of texturised fabric

The filament yarn has an established superiority over spun yarns due to its high strength and lustre. However, fabrics made from filament yarn do not possess a soft feel and appear to be papery. To remove this drawback and to achieve suppleness in the fabric, the filament yarn is given what is called a ''Crimping''. The process of making crimp yarn is known as 'texturising''. Texturising is possible for synthetic fibre because of its thermoplastic nature. Texturising improves the elasticity, bulkiness, resiliency, crease resistance etc. of the fabric. False twist processes are widely used for the production of bulked polyester and nylon yarns for a variety of end uses in the woven and knitted goods, including socks, gloves, knitted underwear, mufflers, sweaters, bathing suits and many other products.

The textured woven and knitted goods possess latent heat of torque which is already set during texturising process. The warp yarn is applied with a large amount of sizing and oiling agent and thus the grey fabric loses its crimp by mechanical tension, becoming in a flat state. Therefore, it is necessary to restore the crimp of the yarn by relaxing treatment in water under tensionless condition. Relaxing can be carried out by water, steam and dry heat and it can be seen (Fig. 4-16) that hot

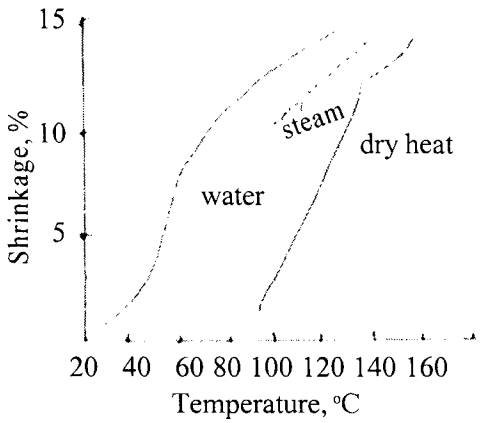


Figure 4-16. Effect of heating medium on relaxation of textured fabric.

water is better than steam or hot air for obtaining the fabric relaxation to develop stretch. The resultant shrinkage is about 15-20%.

The textured fabrics are relaxed in water at 80-95°C in the absence of tension for 20-30 min. For high twist yarn and fabric a longer time is required. A gradual elevation of temperature is more favourable to relaxation. A high temperature relaxing without tension may cause wrinkling, so that a little tension of the order of 1-2 mg/d is favourable. The force existing between yarns and in the textured woven fabric restrain the relaxation so that it is necessary to reduce the restrain by some mechanical impact in the form of bending, pressing, vibrating and rubbing action that can be utilised by making use of various machines.

Spin finishes of textured polyester yarns and knitted fabric normally contain oiling agent of self-emulsified type, and can therefore be readily removed by rinsing at 50-60°C without any addition of detergent. Spin finishes that do not contain emulsifying agent are removed by washing with 1-2 g/l a combination of non-ionic and anionic detergent at 60-70°C. The temperature of the bath should not be raised more than 2°C/min to avoid production creases.

In most cases scouring is carried out in conjunction with the relaxing process on a tensionless machine. In paddle scouring, circular knitted nylon fabrics or garments are loosely packed into polyester mesh bags and scoured/relaxed in overhead or side-paddle machines using 1 g/l non-ionic or anionic detergent, 0.5 g/l sodium hexametaphosphate and 1 g/l solvent scouring agent at 60°C for 30 min. The liquor is cooled, fabric in rinsed, hydroextracted and dried without tension at 60-80°C.

The goods may be solvent scoured in rotary drum machine, restricting the load to 50% of the machine maximum capacity and the centrifuging time to 1 min to avoid the formation of pressure creases. Warp knitted fabrics are, in general, more stable to tension than weft knitted fabrics.

4.14 Scouring of Blended Fibre Fabrics

The wide range of natural and man-made fibres provides many combinations to create new effects with desirable properties. Strength, wearibility and crease recovery are the main properties responsible for synthetic fibres becoming established for blends with cotton, viscose and wool. The acrylics are also in much demand for such blends, while polyamide fibres and triacetates are of secondary importance.

4.14.1 Scouring of polyester/cotton blends

Scouring is mainly designed to remove the natural oils and waxes from the cotton portion and the finish oils which manufacturer add to polyester fibres when extruded. Blends of polyester/cotton can be scoured with alkaline scouring agents as per conditions shown in Table 4.16. Trisodium phosphate can also be used as an

TABLE 4.16

Alkaline Scouring Conditions for Polyester/Cotton Blends

Equipment	Scouring agent and conditions
Jigger	Caustic soda (3%) at 70°C for 90 min or at 100°C for 15 min.
Jigger	Soda-ash (5-10 g/l) and detergent (2-5 g/l) at boil, or NaOH (2-5 g/l) and detergent (2-5 g/l) at 75°C.
Winch	NaOH (1-2 g/l) or Na_2CO_3 (2-5 g/l) at 75°C.
Pad-steam	Soda-ash (5-10 g/l) and detergent (2-5 g/l), 100% pick-up, steaming at 100°C for 30-60 min.

alkali. The use of emulsifiable solvent scouring agents are useful. Combined scouring and bleaching process using alkaline hydrogen peroxide is also preferred for the reason of economy. Fabrics containing polyester fibre should not be kier-boiled. In such blends, milder conditions of alkalinity and temperature are used to avoid detrimental effects on the polyester portion.

4.14.2 Scouring of polyester/wool blends

Polyester/wool blends are very popular, the most common blend ratios are 55:45 and 70:30 polyester : wool. Polyester rich blends are normally constructed from a texturised polyester fibre warp and 55:45 polyester : wool weft yarns. The 20:80 polyester/wool is woven from 55:45 warp and a pure weft yarn. Worsted polyester/wool blend yarns may contain 2.5 – 3% solvent extractable oil, compared with 3.5 – 5% for similar all wool yarns. The oils have much greater affinity for polyester fibre than wool and after normal piece scouring, the blends contain residual oil content of 0.6 – 1.2% compared with 0.3% for wool. Oxidation of combing oil is influenced by exposure to light which should be avoided before scouring. Addition of surfactant to combing oil improves the scourability of the blend fabric [75].

The object of scouring polyester/wool blended fabric is not only to remove spin finishes, lubricating oils, sizes and contamination of all types, it also helps in fabric relaxation and parting the necessary compactness. Blended fabrics may also be pressed and flattened by any of the usual methods employed with all–wool cloth before scouring.

Scouring can be carried out either in rope form in Dolly washing machine for wool rich blends or open width form for polyester rich blends. The spin finishes are removed by 0.5-1% non-ionic alkyl phenol polyglycol ether type of detergent and 0.25-0.5 ml/l NH_3 (25%) or 0.2-0.4 g/l soda-ash at pH 8 to 9 for 20-30 min at 40-50°C. Synthetic detergent solution at pH 5 to 6 can be used to minimise degradation. The presence of man-made fibre in a blend with wool (greater than 20%) may inhibit milling. In general, the greater the percentage of wool in the cloth the greater is the shrinkage. The fabric is finally washed-off at 35-40°C for 45 min, and then cooled gradually. A typical procedure for a soft finish for polyester/wool knitted goods is to scour in tubular form (face inside) at 30-35°C for 25 min in 4° Tw Na_2CO_3 (1.9% solution) and 4% soap (o.w.f.). After washing-off in water at 35°C for 15 min, the fabric is dried on either tubular drier or stenter, is cropped

closely on the face side, open steamed for full relaxation and finally decatised.

In case of solvent scouring it is claimed that trichloroethylene at the boil provides a satisfactory method in a continuous open width plant of special design.

4.14.3 Scouring of polyester/acrylic blends

Scouring of polyester/acrylic fibre blended fabrics can be carried out in either a weakly acid or alkaline bath using a combination of 0.5-1 g/l non-ionic and anionic detergents. The pH of the bath is adjusted to 5-6 with acetic acid or 8-7 with ammonia or soda-ash and the treatment is done for 20-30 min at 60°C (for acidic pH) and 40-50°C (for alkaline pH). The amount of detergent used depend on the degree of soiling. After washing, rinsing proceeds until the cloth is free of alkali. It is an advantage to sour the last rinsing with a little acetic acid.

4.14.4 Scouring of acrylic/wool blends

Wool/acrylic fibre blend yarns are prepared on the woollen or worsted systems of spinning. Generally, fatty acid type of lubricants applied in woollen processing should be avoided to prevent discolouration of the acrylic fibres. High bulk acrylic fibres are also used in the wool industry. Blend yarns containing unrelaxed high-bulk acrylic fibre should be completely relaxed before being dyed, either by steaming in an autoclave at 107°C for 10 min after preliminary evacution of the steamer, or by immersion in boiling water for 5 min.

For worsted yarns, scouring can be conducted at a maximum temperature of 60°C for 30 min with 1 g/l non-ionic detergent and 0.5 ml/l acetic acid (80%). Woollen spun yarns lubricated with oleine are scoured at 30°C with soap or synthetic detergent and sodium carbonate. The addition of solvent is sometimes advantageous for the removal of oils. Tape scouring machines are generally used for the scouring of hanks.

Acrylic/wool blended fibre fabrics may be prepared according to established practice for wool, except that precautions are taken to allow for the thermoplastic properties for the acrylic fibres. Relaxation is done to remove the inherent strain. Worsted fabrics are crabbed and then scoured in either a Dolly at temperature not exceeding 40°C or in winch.

4.14.5 Scouring of acrylic/cellulosics blends

Blended yarns of acrylic/cellulosic fibres are prepared on the woollen system. Yarns prepared in the cotton system of spinning may be scoured at 60°C (30°C for

unrelaxed bulked yarns) for 30 min in a liquor containing 1 g/l non-ionic detergent and 0.5 ml/l acetic acid (80%). Fabrics should be desized and scoured to remove sizes, spinning assistants and other impurities. Scouring can be carried out with 1 g/l non-ionic detergent, 1 g/l trisodium phosphate at 60°C for 30 min followed by rinsing well with sufficient water.

4.14.6 Scouring of acetate/wool blends

Diacetate and triacetate are both used in blends with wool. Scouring and milling can be conducted with the minimum quantity of alkali at temperatures not exceeding 50°C and care should be taken to avoid excessive mechanical friction on the fabric. Fabrics made from triacetate/wool blends should be given a crabbing treatment before dyeing.

4.14.7 Scouring of blends containing viscose

Standard viscose and polynosic rayons are blended with cotton for improved physico-chemical properties of the blended fabric. The increase in tensile strength brought about by blending wool with viscose is well-known. Fabrics containing around 65% triacetate with viscose may be given durable pleats. Bulked or textured nylon is sometimes used with viscose rayon for fabrics. Table 4.17 shows

TABLE 4.17
Scouring Conditions for Blends Containing Viscose

Blend	Treatment conditions
Viscose/Cotton	0.1% soap ; 0.1% NaOH ; 1 h at boil.
Viscose/Wool	3% non-ionic detergent ; 1 ml/l NH_3 (0.88 sp. gr.); 15-20 min at 40-45°C.
Viscose/Acetate	0.2% soap, 0.2% ammonium hydroxide (sp. gr. 0.88) ; 30 min at 90°C. Temperature should not exceed for bright acetate.
Viscose/Acrylic	0.25% synthetic detergent ; 0.5% sodium acetate or acetic acid, adjusted to pH 5.5-6 ; 30 min at 90°C.
Viscose/Nylon	2-5% (o.w.f.) soap or synthetic detergent ; 2-5% trisodium phosphate ; 30 min at 40-70°C.
Viscose/Regenerated protein	Solution is same as for viscose/acrylic blend ; 30 min at 50°C.

some representative scouring treatments that are suitable for specific blends containing viscose fibres but in practice the precise conditions vary also with the procedure and machineries used.

4.14.8 Scouring of polyester/silk blends

Blends of natural silk and polyester fibres (35:65) are sometimes used for dress goods, blouse fabrics and men's fashion wear. Sizing agents and soils are removed by washing with a minimum tension in open soaper containing 1 g/l non-ionic detergent and 1 ml/l NH_3 (25%) at 50°C.

4.14.9 Scouring of blends containing casein fibres

Casein/cellulosic fibre blended fabric is first desized under mildly acidic conditions at 60-70°C for 30-60 min and then scouring is carried out in a fresh bath at pH 6 with 3-4 g/l non-ionic detergent at 50-60°C for 30 min, and rinsed well, first in warm and then in cold water.

Blends containing casein/wool can be scoured with 1 g/l non-ionic detergent, 1 g/l sodium hydrosulphite and 1 ml/l NH_3 (sp. gr. 0.88) for 30 min at 50°C. The grey fabric is scoured in the Dolly or winch with minimum mechanical action. Strong alkalies and prolonged wet processing temperatures above 80°C are not advisable. Apart from certain limitations in scouring, most other woollen and worsted preparation and finishing operations can be carried out without major changes, they include carbonising, crabbing, blowing, decatising and pressing.

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Chapter 5

SCOURING MACHINERIES

5.1 Introduction

Scouring can be carried out in batch, semicontinuous and continuous processes. The machinisation of the post-kier scouring stages had been progressively developed from the early 1930^{s}. The non-continuous process consists essentially of circulating hot alkali liquor through the cloth in a vessel called kier. The continuous scouring and bleaching in the J-Box has been established after 1960. The continuous process is based on the impregnation of the fabric in an alkali solution followed by steam ageing stage, the fabric being either in rope form or open width form. Kiers have given way to J-Boxes and J-Boxes are discarded in favour of open width scouring which requires only 2-15 min having very high production. In comparison kiers take 6-12 h depending upon the amount of impurities.

5.2 Batch Type Scouring Machines (Rope Form)

5.2.1 Low pressure kier

Various designs of kiers are available [1,2]. Low pressure or open kiers are generally made with a hinged lid, and the scouring liquors are circulated by injector system or by the provision of an external multitubular heater and pump (Fig. 5-1).

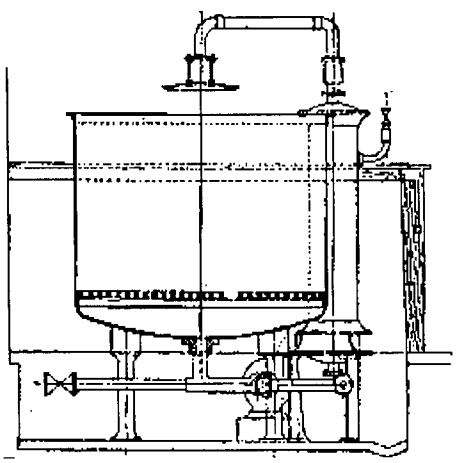


Figure 5-1. A typical low pressure kier.

The steam injector located at the centre of the kier permits the heating of the bath

and the liquor is circulated from bottom to top before spraying it on the fibre. Open kiers are mainly used for linen, yarn and cloths made of loosely woven goods and knitted materials etc. which will not stand high pressure boiling in alkaline solutions. This type of kiers are also preferred for coloured woven goods which operates at atmospheric pressure below 100°C. The main disadvantage of this type of machine is the dilution of the bath by condensed steam on account of direct steam heating system.

5.2.2 High pressure kier

The prototype of modern high pressure keir (Fig. 5-2) with multitubular heater is often referred to as Walsh's kier and considered to be the best. A 2 tons capacity

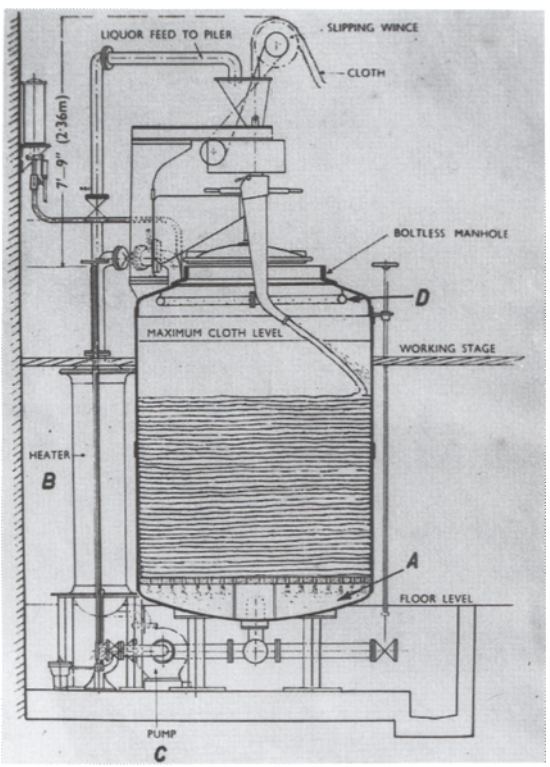


Figure 5-2. High pressure vertical kier with multitubular heater.

kier is most common which is about 9' high and 6.5' in diameter and mounted on R.C.C. columns. The kier is generally made for a maximum likely working pres-

sure 40 lb/in^2 (2.812 kg/cm^2) at 141°C and is composed of mild steel plates with countersunk rivet heads inside to give a smooth surface. The kier is provided with various mountings and accessories such as pressure gauge, safety valve, blow off valve for air and steam, steam trap, liquor level indicator, drain cock etc.

The goods in rope form are piled either mannually or by mechanical plaiting on the perforated false bottom. The cloth can be saturated with alkaline solutions containing caustic soda (2 to 3%), sodium silicate (0.75 to 1%), sodium carbonate (0.5 to 1%) and wetting agent (0.1%) during piling. Sufficient scouring liquor is then admitted to the kier from below to sweep out entrapped air from the goods to avoid the formation of oxycellulose. The lid is then closed but the air valve is kept open. Steam is turned on and liquor is circulated by centrifugal pump (C) coupled to an electric motor. High pressure kier operates at about 130°C (2.109 kg/cm^2) for about 8 to 10 h with a liquor ratio between 5:1 to 6:1. After scouring the drain cock is opened at reduced pressure (5 to 6 lb/in^2) and equivalent amount of hot water is admitted from the top. After circulating cold water the goods are removed and washed in a rope washing machine. The liquor is withdrawn from the bottom of the kier (A) and forced through the heater (B) and spread over the top of the load by the distributor (D).

Fabrics which are to be sold in white state are given two boils and the fabric intended for printing, single boil is sufficient. Recently, the kier has been so modified as to reduce the time for pressure kiering or even peroxide bleaching. This is achieved by using saturators, autopilers and resorting to steaming as in the case of J-Box range.

5.2.3 Jafferson-Walker's kier

Kier of this type (Fig. 5-3) is also a vertical kier but utilises a vacuum system for

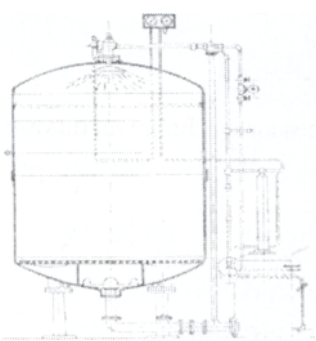


Figure 5-3. The Jefferson - Walker kier.

circulation of the kier liquor. In this system, there is a small subsidiary receiver kier between the actual kier and supply pipe. About one-fifth of the liquor in the kier is withdrawn into the receiver kier and this creates a partial vacuum, drawing fabric together. The kier liquor is periodically withdrawn, heated and then returned to the kier. The entire liquor is circulated every 10-12 min.

5.2.4 Gebauer kier

The unit (Fig. 5-4) consists of two concentric vessels one inside the other with a

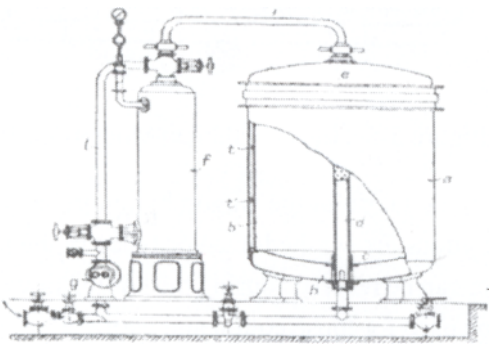


Figure 5-4. The Gebauer's kier.

perforated inner jacket. The heated scouring liquor is injected at the top between the two concentric walls. In this system the flow of liquor is radial instead of vertical circulation and thus the cloth more or less floats. The pressure difference between top and bottom is eliminated.

5.3 Batch Type Scouring Machine (Open Width Form)

Heavy fabrics like drills, corded fabrics and other weaves show rope marks and creases if they are scoured in rope form. Such fabrics are scoured in open width form.

5.3.1 Mather and Platt's horizontal kier

Mather and Platt horizontal kier (Fig. 5-5) consists of a horizontal shell with usual mountings and accessories. Four wagons are supplied with the machine, two are filled with fabric outside the kier whilst the other two are in process in the kier. The goods saturated with scouring solution are run on the iron rails secured to the kier bottom and then the front door is closed and fastened. The hot alkaline liquor is then circulated for 6-8 h under required pressure and temperature depending on the type of goods. The bath is heated by an external multitubular heater and the

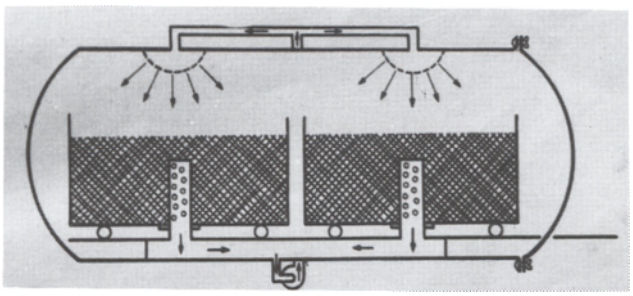


Figure 5-5. Horizontal kier (Mother & Platt).

liquor is sprayed on the fabric in the wagon by umbrella spraying device. After boiling is over the goods are washed once or twice in the kier. The direction of circulation of liquor can be reversed during the boiling or washing processes. The machine can also be used for loose cotton and yarn.

5.3.2 Jackson kier

Fabrics are secured in open width form in the Jackson kier as shown in Figs. 5-6(a) and 5-6(b). It consists of a horizontal shell and a carraige which sup-

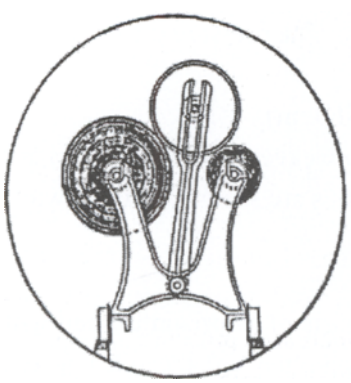


Figure 5-6(a). Jackson kier.

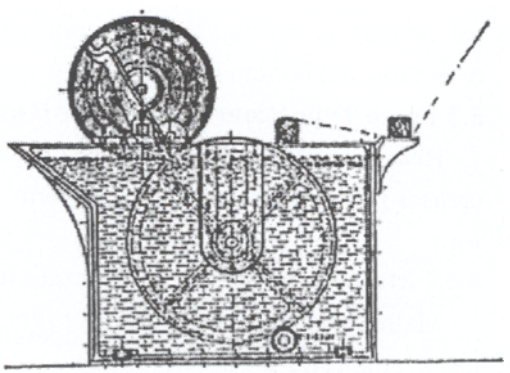


Figure 5-6(b). Impregnating device.

ports three rollers. The two outer batch rollers rotate in the fixed bearings at either end of the carraige. The roller or drum is large, hollow and perforated and is carried

on oscillating arms pivoted at either end of the base of the carraige. The fabric is saturated with scouring liquor outside in an iron tank [Fig. 5-6(b)]. The batch roller is then placed on the carraige and pushed into the kier on guide rails and then door is closed. The fabric is wound from one roller to the other during the scouring process. Hot scouring liquor is circulated by the centrifugal pump and is continuously sprayed over the fabric as it passes from one roller to the other. Scouring is done under a pressure of about 30lb/in^2.

5.3.3 Jig process

Fabrics can be desized and scoured in open width form using a jigger, which is one of the oldest and most universal machine in textile finishing. A centrally controlled fully automated jigger (Fig. 5-7) to secure improved processing quality with

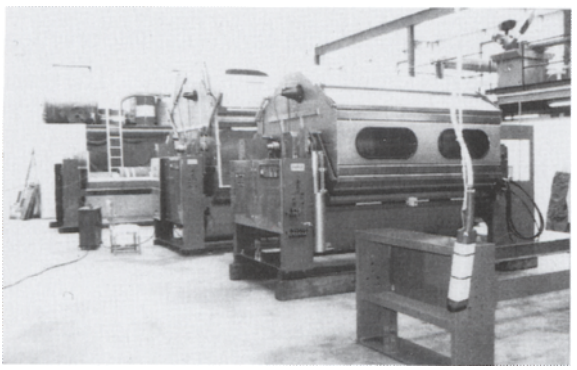


Figure 5-7. New generation of jiggers (Courtesy of Asyst S.L., Sabadell).

reduced operator involvement is shown. Generally, the goods are batched onto rolls and given 6 to 15 ends on the jig through the scouring solution at boiling temperature. After scouring the goods are rinsed several ends on jig. In this process there is danger of oxycellulose formation by hot alkaline solution in presence of air. Closed jiggers are used for operation under increased pressure.

At the end of eighties jiggers were already controlled by microprocessor system and today microprocessor technology enables all jiggers to be connected to a personal computer. All process data, from loading the fabric, scouring, washing and unloading, is stored and can be requested any time for subsequent processing. In addition to the possibility of major automation, the machine can be supplied with

batching-up facilities and such other options as automatic selvedge shifting, and a system of automatic tension regulation with floating roller in the vat designed for precise and gentle handling of elasticised or ultra-delicate fabrics.

5.4 Semi-continuous Scouring Machines

5.4.1 Pad-roll system

In this process goods are padded through the scouring solution and then batched open width onto rolls which rotate slowly for several hours ranging from 6 to 24 h depending upon the type of cloth. The goods are then washed and rinsed in open width washers.

5.4.2 Pad-steam-roll system

After impregnation with scouring liquor, the fabric is quickly pre-heated in a steam chamber or by an infra-red radiation. When it has reached a high enough temperature, the fabric is introduced into a transportable reaction chamber heated by steam injection, where it is stored in a rotating roller. The reaction time is of the order of 1-1.5 h at 100°C.

5.4.3 Pad-roll on perforated cylinder [3]

In this method the fabric after padding with scouring solution is wound on to a perforated roller. The loaded fabric is then rotated in a treatment chamber provided with a liquid reception vat and a circulation pump, The liquor is circulated from inside to outside of the loaded beam by a centrifugal pump. The main advantage of this type of machine is that the scouring, bleaching and washing operations can be carried out on the same fabric roll.

5.5 Continuous Scouring Machines

5.5.1 Saturator – J-Box-rope washer

In continuous machines, scouring can be carried out through a series of J-Boxes or range type operations for progressive desizing and scouring. The desized and washed cloth is first saturated with scouring solution at about 70-80°C in a saturator. After padding the saturated cloth, it enters into Du Pont type J-Box (Fig. 5-7) where it remains for 40-60 min in plaited form at a temperature of about 100°C. The cloth before entering J-Box is rapidly pre-heated by means of steam in a U-shaped heating tube. In case of Becco system (Fig. 5-8) there is no pre-heater and the cloth is directly heated in the J-Box which is used as a steamer. The internal surface of the entire J-Box is very smooth to avoid any friction on the moving

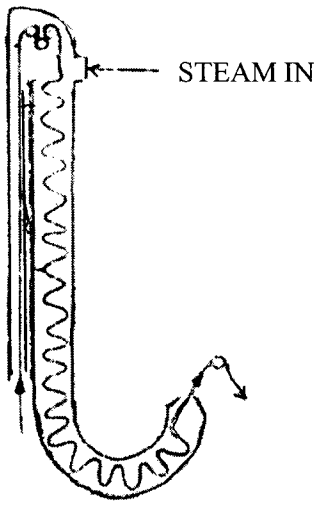


Figure 5-7. Closed-top J-Box system (Du-Pont type).

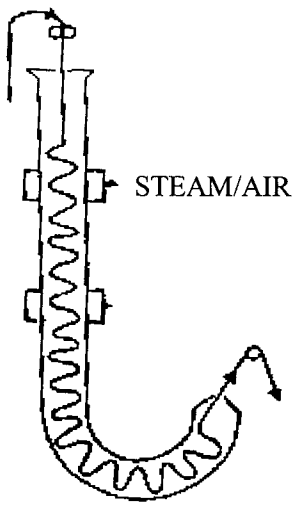


Figure 5-8. Open-top J-Box system (Becco type)

cloth. In stead of rope form a multi-stage J-Box in open width form can also be used with a dwell time of 8-10 min in J-Box. The scoured fabric is washed outside heaving a counter current arrangement at temperature of about 70-80°C.

5.5.2 Open width roller steamer

The fabric in open width form is padded (Fig. 5-9) through the scouring solu-

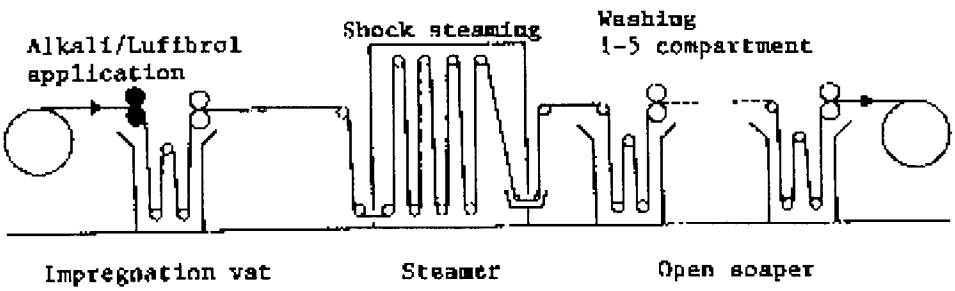


Figure 5-9. Continuous scouring of Polyester/Cotton blends [4].

tion to at least 100% pick-up at 60°C with a running speed of 60 m/min and then passed through a shock steamer. The residence time in this steamer may range from 30 sec to 5 min. The usual time is 1 to 2 min exposure to wet steam at 100 to

110°C. The amount of fabric inside the steamer is about 60-100 yds with a production rate of about 60 m/min. The fabric is then washed in open soaper at 70-80°C with counter current flow arrangement.

5.5.3 Batch or rebatching system [5]

In this system (Fig. 5-10) there are two winding systems, one above the another.

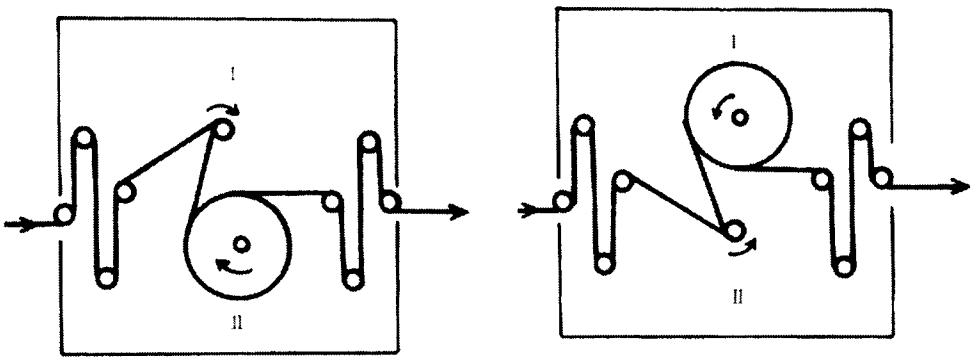


Figure 5-10. Continuous rebatching system.

The cloth is batched into two sup
layer comes from the other layer after partial ageing and the second layer comes from the impregnation device. As soon as the batch is complete on the first winder, the direction of rotation is reversed and the second layer, which comes first from the impregnation squeezer, is led to the second winder below the entering cloth, while the other layer, which has been completely aged, leaves the reaction chamber. For reaction period of about 1-2 h, the system allows fabric treatment with a production speed around 120 m/min. The main disadvantages of this system are : (i) it is suitable only for treatment of fabrics with same width and (ii) moire effect (water marks) cannot be avoided.

5.5.4 Vaporloc system

The cloth in open width form is first saturated with sodium hydroxide solution (5-9%) along with wetting agent at 70°C, padded and then entered into vaporloc reaction chamber which operates at 30 lb/in^2 (2 atm.) at a temperature of 134°C with a reaction time of 90-120 sec (Fig. 5-11). The fabric is deposited on roller-bed system and thus allows the fabric to be in a relaxed state inside the pressure chamber [6, 7]. The fabric passes in between the low friction teflon material and the centre beam special seals enables the generation of necessary pressure inside the

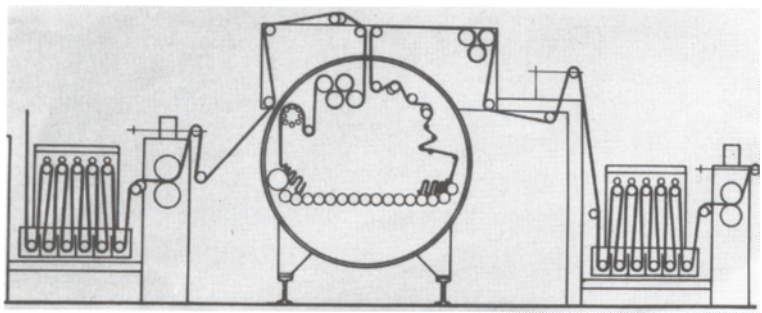


Figure 5-11. Mather & Platt continuous open-width pressure reaction chamber [8].

steamer. The cloth content inside the steamer is about 200 meters. The production speed is of the order of 120 m/min. The goods after scouring are washed off first with hot water and then with cold water.

5.5.5 High pressure Klienewefer roller steamer

Continuous processing pressure steamer of Klienewefer (Fig. 5-12) utilises roller

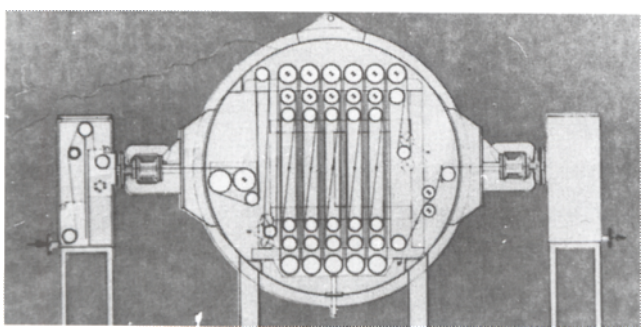


Figure 5-12. High pressure roller steamer (Courtesy of Klienewefers GmbH.).

steamer which operates at 3 atm. pressure in dwell time to 30-180 sec for a sodium hydroxide impregnation concentration equal to 60-100 g/l at 130-140°C. The production speed is of the order of 30-60 m/min depending on the capacity of the vessel. Hydraulic sealing heads are subjected to a pressure inside the vessel where the cloth is guided on rollers. The sealing heads permit continuous cloth feeding and delivery [9].

5.5.6 Conveyer storage steamer system

Another way of storing impregnated fabric consists of the use of a continuous pile storage steamer where the cloth is plaited down onto conveyer belts for necessary time [10]. In this system the accumulation of goods is such that the risks of creasing are not suppressed.

5.5.7 Roller bed steamer with pre-swelling zone

In this system the fabric in open width form is first impregnated with a scouring solution and then guided to rollers for a time sufficient for swelling (Fig. 5-13).

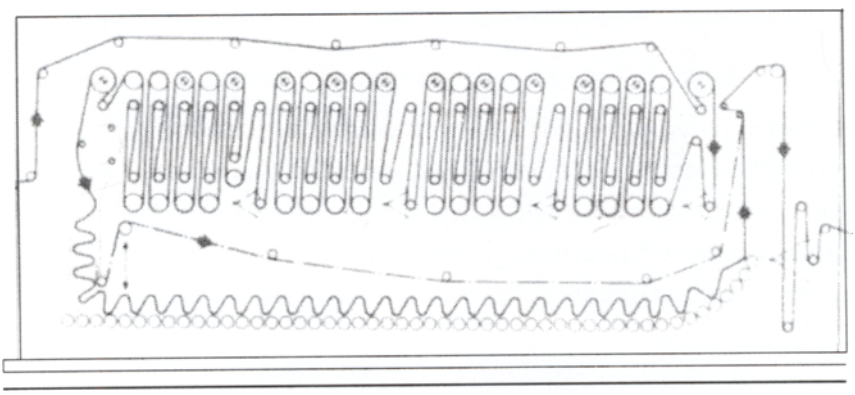


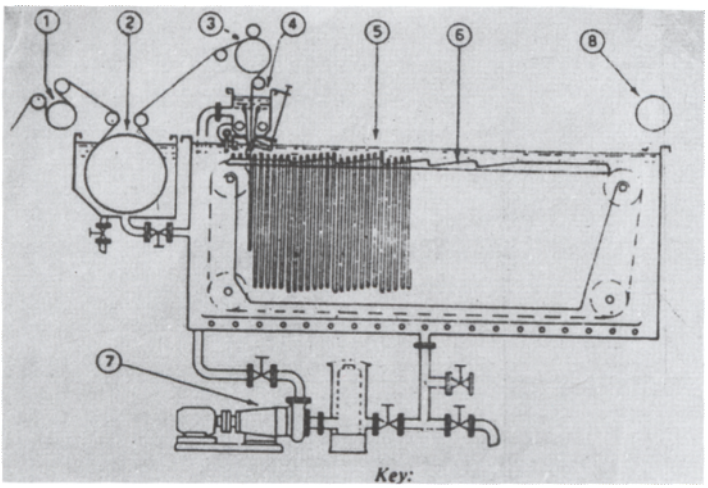
Figure 5-13. Roller bed steamer (Courtesy of Klienewefers GmbH).

The fabric is pre-swollen in the tight-strand roller section before being plaited down onto the roller bed for the required time. The roller bed conveyer can be replaced by a conveyer belt. This kind of installation permits 6-20 min dwell time at 100°C for NaOH concentration around 3-6% with a production speed of about 100 m/min. Vacuum impregnation of the fabric with the scouring solution before steaming is sometimes recommended for rapid wetting of the goods [11].

5.5.8 Continuous relaxing/scouring machine

Rotary washers (see chapter 7) have been used as an open width treating apparatus of batch type ; this has a large effect, but has such demerits as fear of relaxation specks (spot mark) and flaw (defect, spot etc.) and inefficiency. Hence continuous relaxer has been developed. The absence of tension is favourable for relaxing and each machine manufacturer has given vibration to the fabric in his own way. Mechanical impacts in the form of bending, pressing, vibrating and rubbing action are utilised for better effect during relaxing process.

In the Mezzara relaxing machine (Fig. 5-14) the fabric suspended in loops from



1. Draw rollers for controlling feed
2. Pre-wetting bath with driven roller
3. Draw rollers
4. Trough with V-slot
5. Main tank
6. Saw-tooth rails
7. Cerntrifugal pump with filter

Figure 5-14. Mezzera (Italy) open-width relaxing/scouring unit.

a series of parallel rods move forward very slowly along the length of the machine. These rods are mounted in tracks on either side of the machine tank. They are located just below the surface of the liquor. The rods rise up a saw tooth ramp and then drop, say about 5 cm, thus giving an opportunity for the fabric in contact with the rod to be slightly displaced. The fabric is carefully guided into the centre of the machine and fed over a full width reel, into a V-shaped trough, with an open bottom. The trough is kept half filled with water which pulls the fabric off the reel and carries it down into the bath to form a loop, generally about 80 cm long. The maximum speed of operation is dictated by the speed of the water pouring out of the bottom of the V-trough. The bottom of the trough slowly moves forward with the advance of the rod, being loaded, and then about every 5 to 6 sec rotates back to start loading the next rod. After carrying the fabric through the machine the rods move down to the bottom of the bath and return to the feed end. The fabric being immersed in the liquor in loop form for about 20 min has a good chance to relax. The fabric is then drawn off by roller and sprayed with warm water and then cold water before being plaited down, outside the machine.

5.5.9 Solvent scouring machines

Scouring of knitted goods, wool and blended woven fabrics in discontinuous rotary-drum washing machines has been established in many countries for a number of years. Equipment for continuous preparation and dyeing from non-aqueous solvent have been developed by several companies (Table 5.1).

TABLE 5.1
Continuous Solvent Scouring Machines

Company	Unit
Bohler and Weber [12-14]	C 1600 / C 1800
ICI [15]	Markal
Bruckner [16, 17]	Solvanit
Dow [18]	Dow Scouring System
Rimmer [19]	Vibro Scour
Riggs and Lomband [20]	Scour-kleen
Neil & Spencer [21]	Libatex

In ICI's Markal process (Fig. 5-15) the dry cloth first passes through trichloroet-

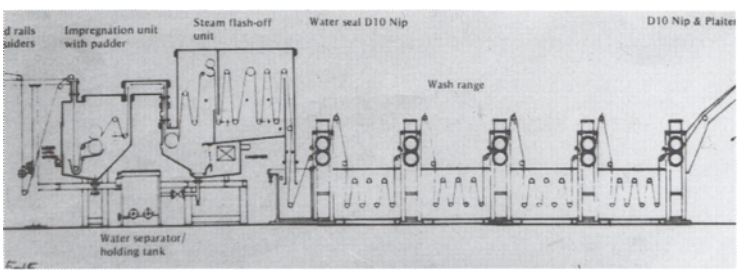


Figure 5-15. Commercial Markal (I C I) machine and combined washer.

hylene (TCE) in the dewaxing vessel which is divided into number of seperate compartments. From the last compartment the cloth passes through a solvent seal and heavy mangle where much extrained solvent is removed from the cloth. The cloth then passes through a chamber into which steam is injected. Thus rapid evaporation of solvent in the cloth and the mixture of steam and TCE vapour is condensed and returned to the solvent seal where the solvent and water are seperated. In alternative method, the solvent is removed from the cloth by the use of an enclosed hot water (95°C) bath instead of steam chamber [22]. After passing through

the water wash tank, the cloth leaves the scouring machine saturated with water. The Markal II process consists of effecting simultaneous scouring and desizing by using suspension of enzyme in TCE and surfactant solution. The treated sample is then passed through steaming chamber for 10-20 sec where the solvent is flashed-off. The fabric is then given normal wash to remove the size [23, 24]. Markal III process combines bleaching with scouring and desizing by using emulsion of aqueous hydrogen peroxide in the TCE-surfactant solution, again followed by steaming and washing-off.

Another continuous solvent scouring machine for knitted and woven fabrics is shown in Fig. 5-16. The Bruckner Solvanit continuous process is used for simultaneous scouring, cleaning and for shrinking. The cloth is transported by a patented

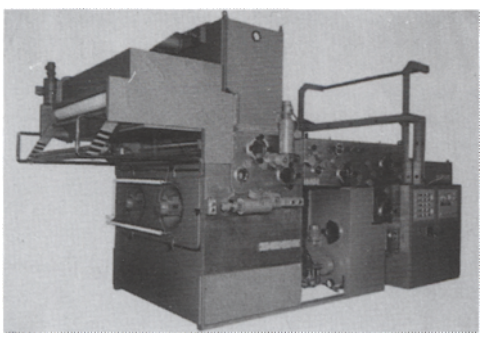


Figure 5-16. Continuous solvent scouring and finishing machine (Courtesy of Sperotto Rimar, Italy).

paddle wheel which ensures thorough removal of contaminants by countercurrent flow of fresh perchloroethylene. Relaxation and bulking of knitted goods occur during solvent flash-off.

5.6 Wool Scouring Machines

Scouring machines of wool depend on the kind of wool to be scoured i.e. raw wool, hank form or woven fabrics. Scouring of wool can be carried out in batch or continuous process, aqueous or solvent media and rope or open width form.

5.6.1 Raw wool scouring machines

In the conventional scouring machine (Fig. 5-17), raw wool is propelled through a tank filled with warm water containing detergent, raked through the bowl, conveyed by means of a transfer mechanism to squeezing rollers and then carried into another similar tank. The bowls have false bottoms consisting of perforated plates

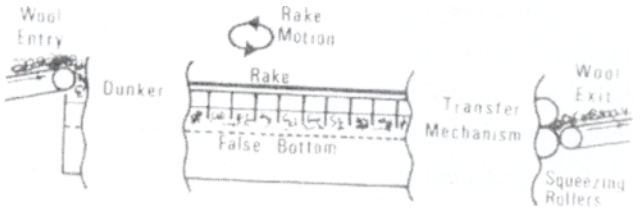


Figure 5-17. Scouring of raw wool in traditional scrouring machines.

which allow removal of dirt from the wool to fall through the perforations while preventing the fibre from passing. The wool may pass through four or more tanks in this way, until eventually it is rinsed in clean water.

The raw wool is also scoured by some unconventional machines [25]. In the Fleissner machine loose wool is conveyed through the bowl by a series of suction drums (Fig. 5-18). The flow of liquor through the wool and into the three suction

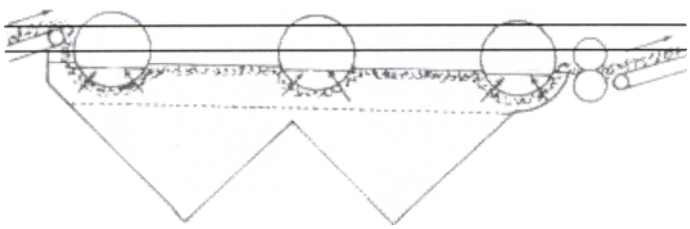


Figure 5-18. The Fleissner scouring bowl.

drums is done by pumps through the perforated surface of the drum from outside to inside. In this type, the efficiency of removing impurities is comparatively lesser due to the gentle scouring action and are also comparatively costlier than the conventional machine.

In the jet scouring machines (Fig. 5-19) the wool travels on a conveyer belt or a

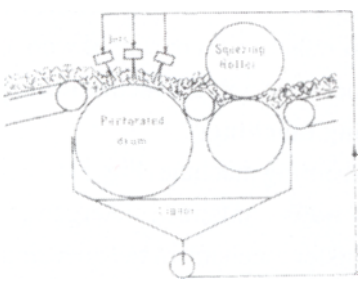


Figure 5-19. Jet scouring bowl [26, 27].

perforated drum and the scouring liquor is sprayed on the fibre through low pressure jets. Less felting takes place due to low velocity of jet and gentle movement of wool.

In the CISRO Lo-flo system [28], first one or two bowls of conventional machine are replaced and wash plate bowls (Fig. 5-20) are used instead. The wool is

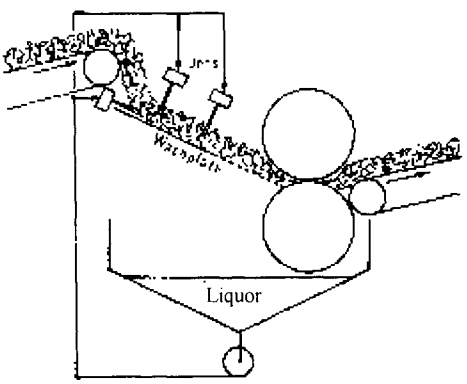


Figure 5-20. Washplate bowls used in Lo-flo process.

washed down a perforated plate into the squeezing roller by jets or sprays of scouring liquor. Liquors from Lo-flo unit and the conventional bowls are both recycled through interconnected loops incorporating heavy solids settling and centrifugal operation. This has the shortest possible bowl and has poor scouring efficiency. The process is mainly used to recover grease and for pollution control.

5.6.2 Wool hank scouring machine

Woollen and worsted yarns, unless dry spun contain significant amount of lubricating oil and are usually scoured in hank form in a continuous scouring machine. The hanks are transported through the scouring sets either by tape (Fig. 5-21) system or by battrices (Fig. 5-22). Usually, the sets have four bowls : two scour bowls, one rinse bowl and a final bowl where acidification and moth proofing is carried out. There is a pair of squeeze roller between each bowl. The top roller is usually lapped with wool or cotton sliver and the bottom roller is made of metal. Pressure is applied to have an expression of about 60%. The characteristic features of the two types of machines are summerised in Table 5.2. It is normal to scour only 1-2

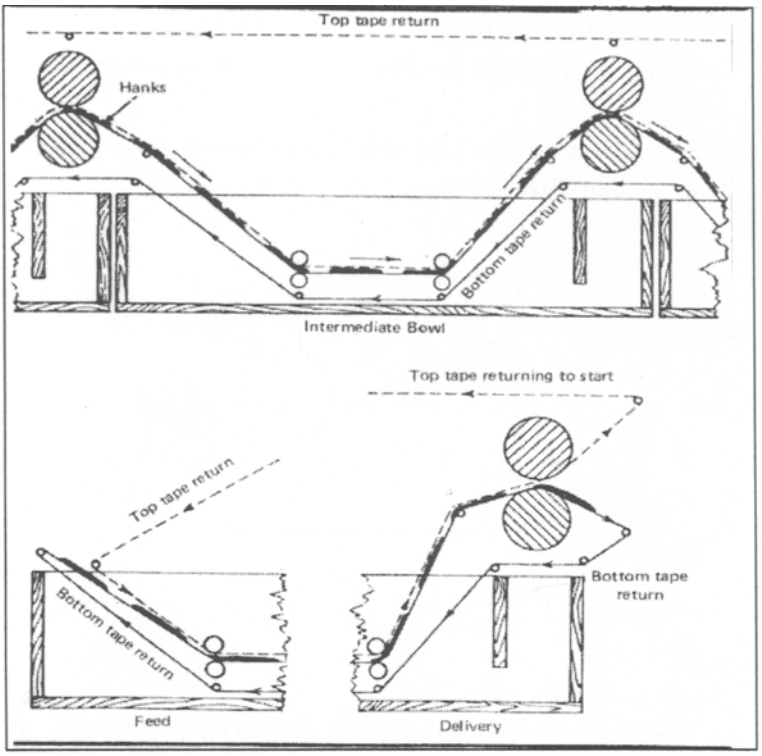


Figure 5-21. Principle of a tape scouring machine.

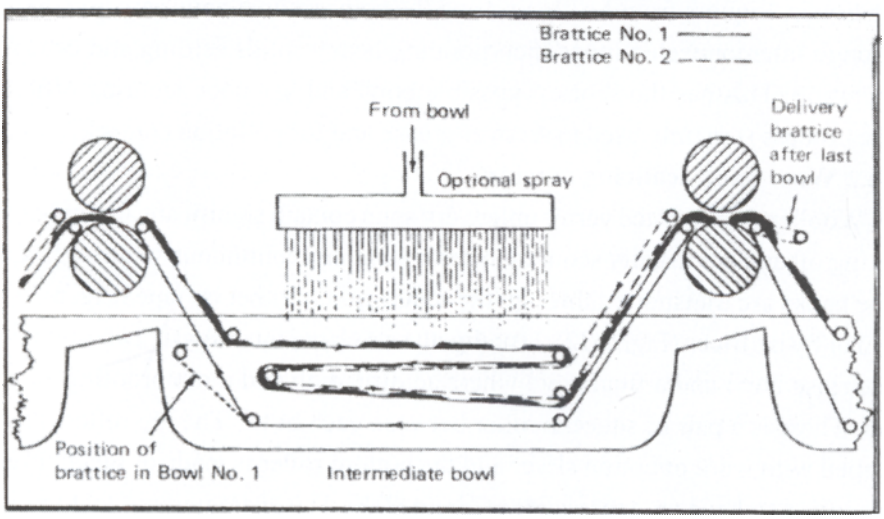


Figure 5-22. Principle of a battrice scouring machine.

TABLE 5.2
Characteristic Features of Yarn Scouring Machines [29]

	Battrice	Tape
Length of bowls (m)	2.5-4	1.5-3.5
Width of bowls (cm)	80-135	70-120
Depth of bowls (cm)	55-85	55-85
Capacity (l)	1600-2500	500-2200
Running speed (m/min)	4.5	9.0

tons of yarn in such types of machines. Due to lower running speed, battrice machines give lower immersion times compared to 6 to 12 sec given by tape machines. The bowls are usually heated by direct steam through perforated pipes or controlled steam valves.

Woollen yarns can also be scoured in packages such as in the form of cones or cheeses. Small batches may be scoured in Klauder-Weldon machine or on a Dolly washing machine.

5.6.3 Wool fabric scouring machine

Batchwise rope scouring in the Dolly [30] using soap and soda is widely practised. The Dolly consists of a wooden vessel across and over the winch vat is mounted a pair of heavy wooden squeezing rollers. Modern machines are developed (Fig. 5-23), in which the operations of washing/fulling or of high speed washing can be carried out without the need for additional machinery. Combined scouring and milling save time, man-power, water and energy. The cloth is run through the scouring liquor and the scouring is continued till the fabric is cleaned. In one system jets of scouring liquor are forced into and through the fabric ropes as they pass through a jet box immediately in front of the nip rollers. By means of two transporting and squeezing rollers (7), the fabric is compressed into the fulling tank (9), and a star cylinder (10), operating at variable speed, enables the desired packing density in the fulling tank to be achieved with the greatest accuracy and reproducibility. The setting of the pressure at the fulling flap (11) leads to a more uniform fulling effect. The material is conveyed out of the fulling tank via the cylinder (10) and after passing over another star cylinder (13), returns to the fulling liquor. In the case of high-speed washing, or after fulling, the cylinder (13) opens-out the fabric

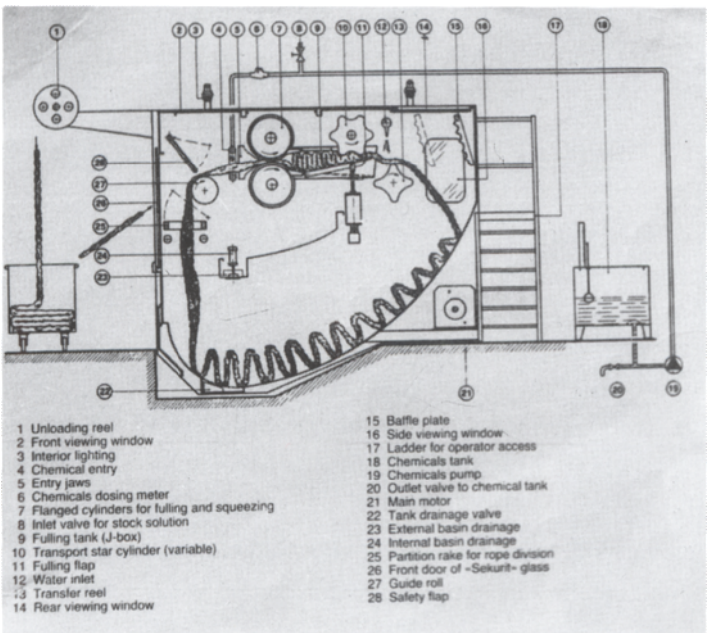


Figure 5-23. Diagram of a soft and rapid scouring and milling machine (Courtesy of CIMI Cerreto Castello, Italy).

and throws it against the baffle plate (15). The high-speed washing machine is available with 2 and 4 fulling tanks (J-Boxes), with the possibility of one or two entries per tank. The fulling tank capacity may be 50-400 kg for the machine with two tanks and 50-600 kg fabric for the machine with four tanks. The working speed can be infinitely varied between 60-400 m/min in addition to the choice of 5 preselectable speeds, which may be changed as necessary. There are some machines which can load up to 12 ropes of light fabrics. The well-known bag stitchings for all fabrics are not necessary anymore and it is guaranteed the absence of the traditional problems of creases, abrasions, tears and holes also on blends particularly sensitive to these defects. The cloth after scouring is washed-off in luke warm water.

5.6.4 Carbonising range for woollen fabrics

The carbonising process usually comprises : acidifying – drying – carbonisation – scouring. The process is same for loose stock and piece goods. The carbonising machine (Fig. 5-24) comprises : entry frame, acid bath, J-Box reaction, perforated

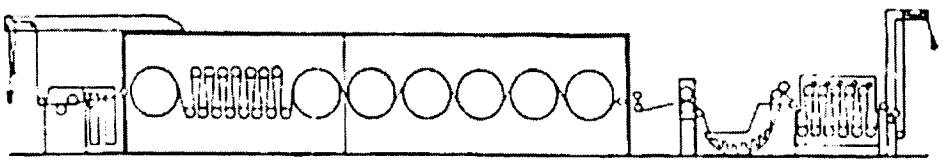


Figure 5-24. Carbonising range for woollen fabric
(Courtesy of Fleissner GmbH & Co. Germany).

drum dryer with carbonising section, beating and brushing unit and plaiting or batching unit. Depending on the further process sequence, a neutralising phase (Fig. 5-25) can follow.

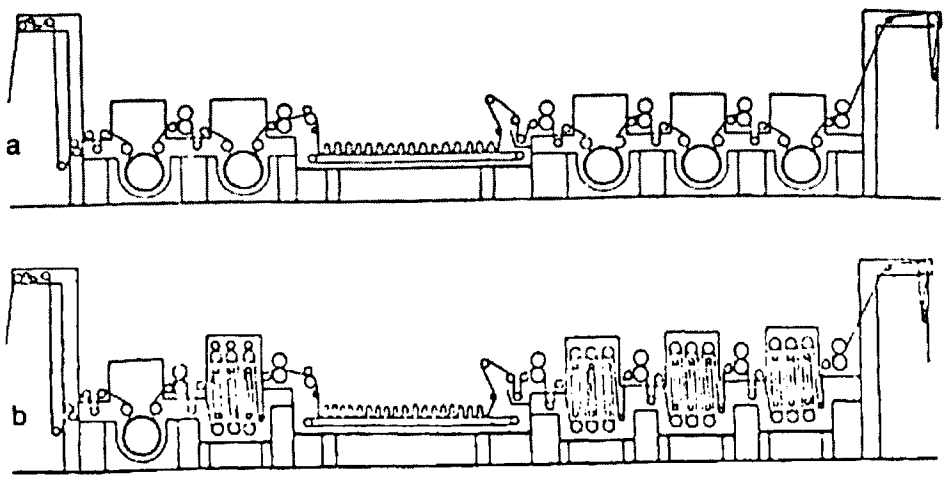


Figure 5-25. (a) Machine concept as perforated drum washing range,
(b) Roller vat range for more closely woven cloth qualities.

The acid bath is designed as a roller vat with single fabric thread-in. Rubber covered rollers press on the upper guide rollers in order to promote evacuation of the air and soaking of the fabric. Without being subjected to excessive squeezing, the fabric is deposited in J-Box reaction vessel holding about 100 m of fabric. Here the cloth, which is saturated with the liquor, has ample opportunity to absorb the acid. Following an adequate reaction period, the fabric is drawn out of the J-Box via a high expression nip. The expressed liquor is conducted back to the impregnating bath. There is also a liquor return flow connection leading from the reaction vessel. The impregnating bath is provided with a liquor circulation facility which ensure uniform concentration in the bath. The used liquor is replenished by a level controller. An automatic titration station constantly monitors the acid.

The fabric is then dried at 80°C in perforated drum dryers where the drying air is drawn through the fabric which ensures a fast, gentle and uniform drying action. Finally, the dry fabric is heated up to 120-130°C on a perforated drum in the carbonising section, and this temperature is maintained constant in the hotflue chamber, which holds approximately 30 m of cloth. The drying chamber is seperated from the carbonising section by a partition. Following carbonisation the fabric is guided through a beating and brushing unit where the combusted cellulose impurities are removed and exhausted.

A carbonising range for wool fabrics which probably applies hydrochloric acid from perchloroethylene has been developed (Fig. 5-26).

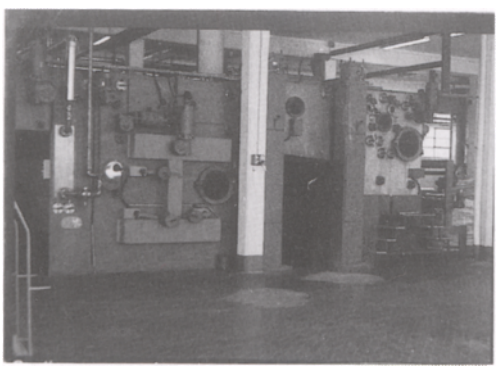


Figure 5-26. Continuous range for solvent carbonising of woollen fabrics (Courtesy of Sperotto Rimar, Italy).

5.6.5 Crabbing and decatising machines

Crabbing and decatising represent important processes in the finishing of wool goods providing wool fabrics with a top-line shrink-free finish. The continuous finishing line for worsteds are shearing – pressing – humidifying – decatising and for woollen fabrics are shearing – pressing – shrinking – humidifying – decatising.

A continuous crabbing by overheated water without rubber belt (Fig. 5-27) gives permanent effect with brighter appearance. The notable improvement of the fabric quality is due to the calendering effect in water at 110°C. There is no need for use of expensive rubber belts. Fig. 5-28 shows a continuous multiset crabbing machine.

The kier decatising (Fig. 5-29) of wool fabrics is also a process for permanently setting wool fabrics. In this way wool fabrics are given surface stability without

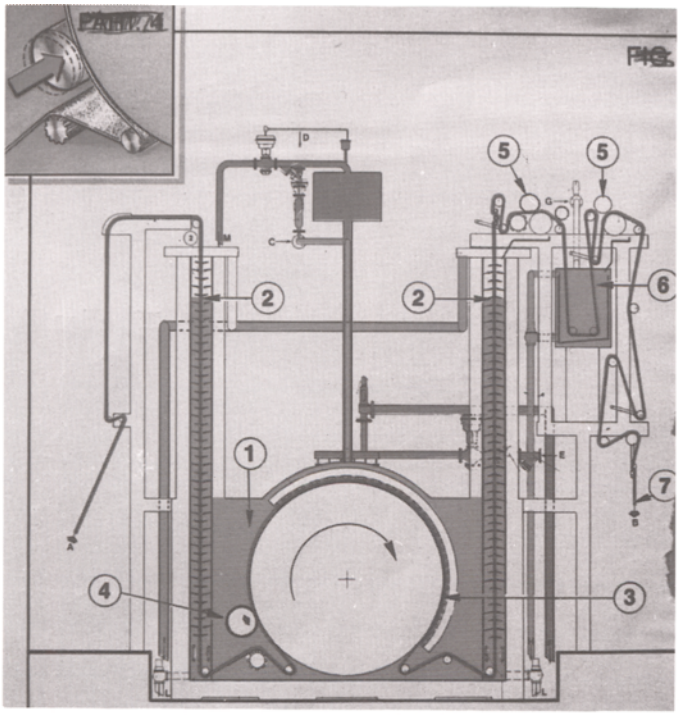


Figure 5-27. Schematic representation of Conticrabbing
(Courtesy of MAT diA. Bertoldi S.p.A.).
1. Water-tight main compartment 2. Barometric columns 3. Main drum 4. Presssing roller 5. Pair of pressing roller 6. Cooling tank 7. Device to arrange fabrics in laps.

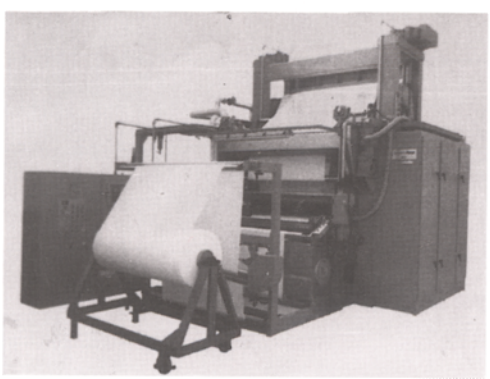


Figure 5-28. Continuous crabbing machine (Courtesy of Sperotto Rimar, Italy).

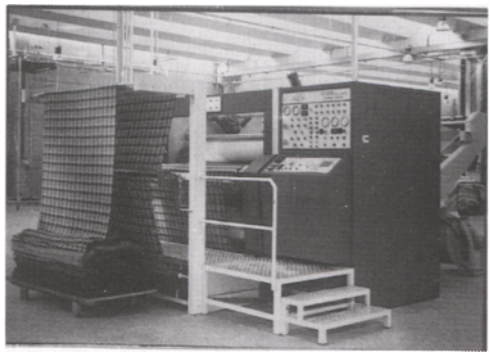


Figure 5-29. Kier decatising machine (Courtesy of Sperotto Rimar, Italy).

loosing their shaping capacity in the making up process. Temperature, pressure, moisture and time are the parameters which introduce physical and chemical processes in kier decatising. One of the disadvantage of kier decatising is its batch type method of operation. Chemical decatising of wool fabrics has long been a subject of discussion in basic research centres. The ''Menschema process'' (Kettling + Braun, Hemmer) is a low add-on applicator in combination with a Contripress® and a decatising machine. Menschner and Triatex presented it only in the form of a ''mural relief''. The new MR process (Menschner – Rotta chemical decatising) is shown in Fig. 5-30. The operational sequences of the MR process are wet finish-

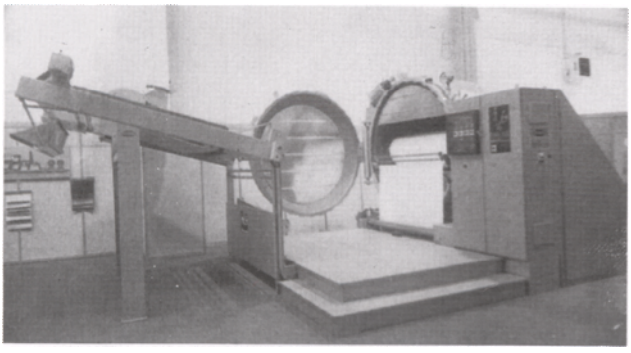


Figure 5-30. Universal permanent decatising machine
(Courtesy of Menschner – Kettling & Braun, FR of Germany).

ing, padding, depending on the effect (Rotta), drying, redamping (Weko), contripress (Menschner) and continuous decatising. Before the wool fabric is treated on the Contripress® the stabilising agents or similar products are applied in exactly the right amount by the low add-on route and then can react completely under the impermeable Contripress belt in the temperature and pressure zone. The effective range of application is freely variable. Other chemicals that set wool in the dry and wet states can also be applied. Besides greatly simplifying the finishing sequence, the process cuts costs and saves floor space.

The evaluation of the decatising effect is commonly based on subjective estimates. The handle, the glaze, the brightness of the colours, the bulkiness or hardness of the fabric are obtained from the decatising machines, the flow diagrams of which are shown in Figs. 5.31, 5.32 and 5.33. Therefore, it is required from the decatising machines that may have a wide and effective versatility.

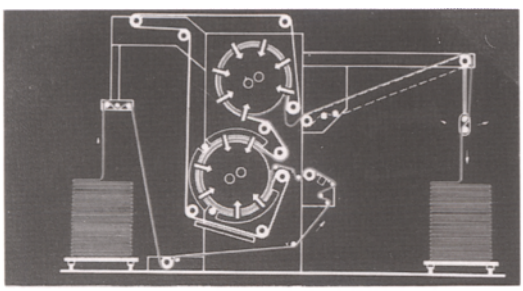


Figure 5-31. Finish decatising machine
(Courtesy of Drabert Shöne, Kettling & Braun, Germany).

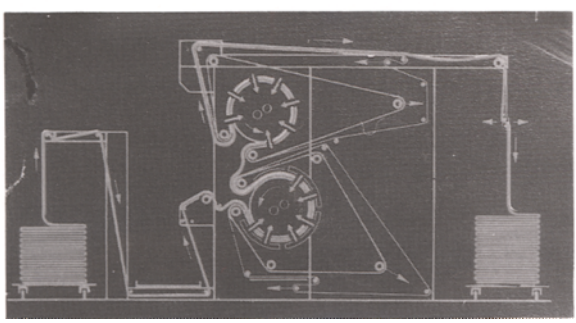


Figure 5-32. Lustre decatising machine
(Courtesy of Drabert Shöne, Germany).

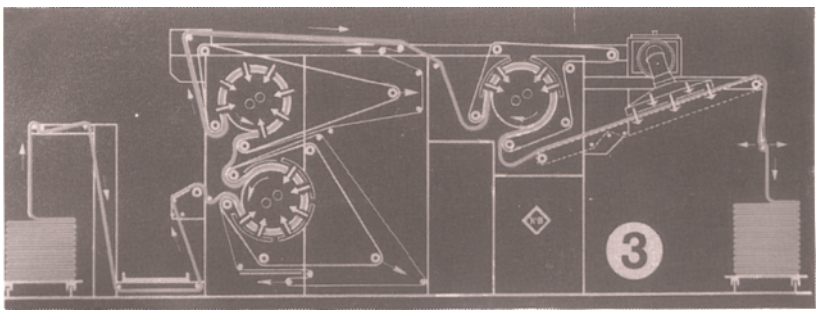


Figure 5-33. Permanent continuous decatising machine (Courtesy of Drabert Shöne, Germany).

5.7 Silk Degumming Machines

Proper selection of equipment for degumming of silk is essential to prevent chafed surface, chafe marks, uneven degumming and chemical damage. However, the selection of equipment depends on the type of the article to be processed.

5.7.1 Yarn degumming machines

Silk yarn is normally degummed in the hank form. In the pack (beck), the hanks are normally hung on polished wood or metal rods which are submerged in the bath and turned by hand. Alternatively, hank and spray dyeing machines can also be used for degumming of silk in yarn form. In the foam boiling process foam produced by soap bath comes in contact with silk and thus causes degumming.

5.7.2 Piece goods degumming machines

Degumming of piece goods can be done on beck or pack system and the star machines (Fig. 5-34) are particularly suitable for delicate articles. In the beck system with strings the pieces are hung on bamboo or smooth metal rods so that the goods remain submerged in the degumming bath. The main disadvantage of this system is chafe marks (blanched places) or irregularities in the form of spots. In the well known star machines the goods may be hung from above only in the case of vertical simple star or the goods may be attached from below on hooks as well as hanging from above in the case of vertical double star or may be horizontally double star system. During degumming shrinkage takes place and hence the star machines are so designed that the hanks can be moved along the arms of the star, thus allowing for shrinkage.

In the continuous degumming machines (Fig. 5-35) the goods are hung in loops

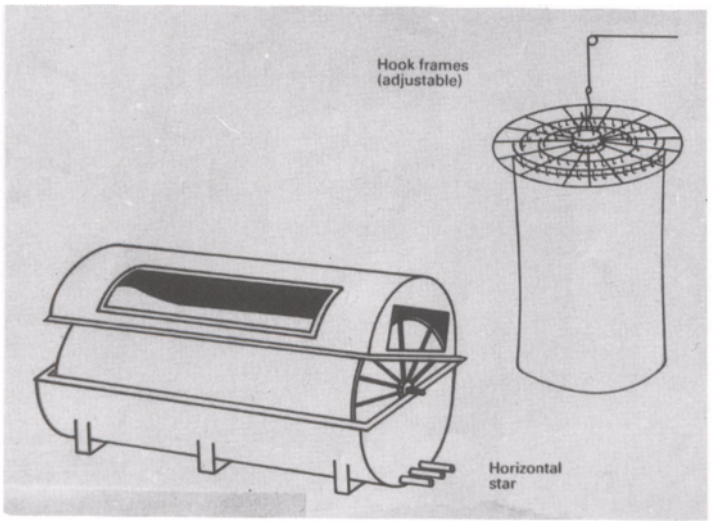


Figure 5-34. Star machines [31].

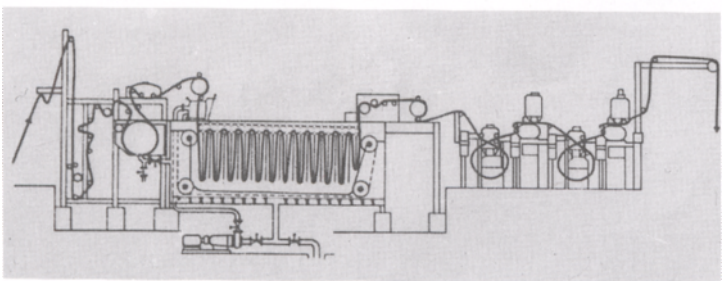


Figure 5-35. Continuous boiling off machine from Mezzera.

on rods which remain fully submerged in the bath and move continuously forward.

Articles with tight, smooth weaves may be degummed on the jig. Winches and jets are not generally recommended for complete degumming, but overflow machines can be used for knitted goods.

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Chapter 6

BLEACHING OF TEXTILES

6.1 Introduction

The natural fibre and fabrics even after scouring still contain naturally occuring colouring matter. This yellowish and brown discolouration may be related to flavone pigments of the cotton flower. The climate, soil, drought and frost can also cause various degrees of yellowness. Tips of leaves or stalks coming in contact with the moist ball after opening will cause dark spots and discolouration. Discolouration may also come from dirt, dust, insects or from harvesting or processing equipment in the form of oils and greases. The object of bleaching is to produce white fabrics by destroying the colouring matter with the help of bleaching agents with minimum degradation of the fibre. The bleaching agents either oxidise or reduce the colouring matter which is washed out and whiteness thus obtained is of permanent nature. Chemical bleaching of textile fibres is further aided by addition of optical brighteners.

The primitive method of cloth bleaching, namely harsh scouring and exposure to the sun was also a chemical process in which light served as an oxidation catalyst. However, the processes are time consumable, labour intensive, highly variable in quality of goods produced, and tied up large amount of capital. The first major break with traditional methods of bleaching came in 1756. Nine major breakthroughs in the field of bleaching flax and cotton are shown in Table 6.1. During

TABLE 6.1
Nine Major Break-throughs in Bleaching Cellulosics

Approximate Date of Significant Usuge	
Sulphuric acid Scour	1756
Chlorine Bleach	1790
Le Blanc Process for Soda Ash	1791
High Pressure Kier	1815
Rope Washer	1830
Enzyme Desizing	1900
Peroxide Bleaching	1925
Continuous Peroxide Bleaching	1939
Fluorescent Brighteners	1950

the later stage of twenteeth century the time required for bleaching dropped steadily from months to days to hours. Now-a-days, manpower required for average plant is declined considerably and the cost of bleached finished product is also reduced. This technical break-through will continue in the future also and will reduce the cost of bleaching further.

A general classification of bleaching agents is shown in Fig. 6-1. In 1790 Bertholet

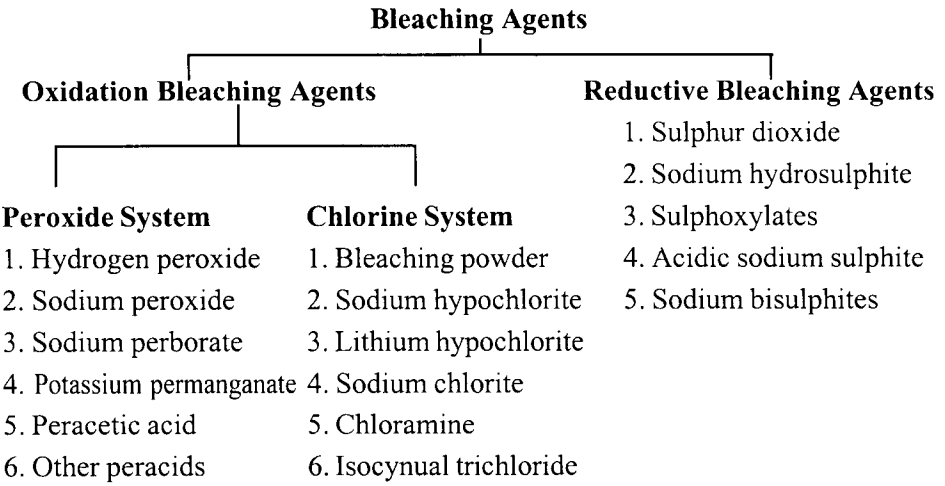


Figure 6-1. Classification of bleaching agents.

developed bleaching process using water solutions of chlorine. Tennant in 1978 developed solid bleaching powder. Chlorine based materials such as sodium hypochlorite, calcium hypochlorite and sodium chlorite, predominated until the late 1920s when peroxide came into wider use with the cheaper electrolytic synthesis of hydrogen peroxide. By 1940, about 65% and to-day about 90% of all cotton is bleached with hydrogen peroxide.

6.2 Bleaching with Hypochlorites

Hypochlorites as bleaching agents are still popular despite the anti-chlorine lobby and environmental pressures. Some of these salts which are used for the bleaching of textiles are briefly described.

6.2.1 Calcium hypochlorite (Bleaching powder)

A solution of bleaching powder contains calcium hypochlorite [$Ca(OCl)_2.4H_2O$], calcium chloride [$CaCl_2$, $Ca(OH)_2.H_2O$], lime hypochlorous acid formed by the

hydrolysis of hypochlorite, possibly free chlorine and other soluble impurities like calcium chlorate, calcium permanganate etc. Calcium hypochlorite is generally prepared from bleaching powder or from liquid chlorine and slaked lime suspension. It is also possible to make solutions of hypochlorite by passing chlorine into milk of lime. Solid bleaching powder may be obtained by passing chlorine over hydrated lime [1]. In this process care must be taken not to increase the temperature above 55°C, since at higher temperatures, chlorate and chloride are formed.

Bleaching powder is partially soluble in water. A smooth paste with water is first prepared and then diluted with water. This is then allowed to stand until whole of the suspended matter has settled to bottom. The clear supernatent liquid is then drained-off for use which is about 12°Tw and contains about 3.9% available chlorine. This is then diluted to the required strength.

Calcium hypochlorite undergoes rapid exothermic decomposition on heating above 175°C. Bleaching powder solution reacts with acids with the evoluation of chlorine.

$$Ca(OCl)_2 + HCl = CaCl_2 + 2HOCl$$
$$Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HOCl$$
$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$
$$2HOCl + 2HCl = 2H_2O + 2Cl_2$$

Certain metals or their oxides bring about catalytic decomposition of bleaching powder. Similar reaction can also occur with other metals such as iron or copper.

$$Ca(OCl)_2 + 4CoO = 2CoO_3 + CaCl_2$$
$$2CoO_3 = 4CoO + O_2$$

The oxidising action of calcium hypochlorite is due to hypochlorous acid. The conditions (pH) which favour the formation of hypochlorous acid increase the oxidising power of bleaching powder. Freshly prepared calcium hypochlorite solution has a pH of about 11.05 which on standing or agitation reduces the alkalinity by precipitating insoluble carbonate and thus increasing the concentration of hypochlorous acid. This acidic hypochlorous acid is more powerful bleaching agent than the alkaline hypochlorite and are not safe as this causes degradation of the cellulosic material due to the formation of oxycellulose.

6.2.2 Sodium hypochlorite

Sodium hypochlorite is a sodium salt of hypochlorous acid (HOCl). Sodium hypochlorite can be prepared by passing chlorine gas into a tank containing pre-

pared solution of caustic soda, sodium carbonate or mixture of the two (about 4% by weight) at about 27°C.

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O + 25\ Cal$$

$$6NaOH + 3Cl_2 = NaCl + NaClO_3 + 3H_2O$$

Another way of preparing sodium hypochlorite solution is by the electrolysis of a solution of sodium chloride. In this method sodium hydroxide is formed at the cathode and chlorine at the anode on passing electric current through this solution. The sodium ion reacts with water to form sodium hydroxide and the liberated chlorine reacts with sodium hydroxide forming sodium hypochlorite.

$$Na + e \rightarrow Na$$

$$2Na + 2H_2O \rightarrow 2NaOH + H_2O$$

$$2Cl \rightarrow Cl_2 + 2e$$

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

Sodium hypochlorite solution is strongly alkaline (pH $\simeq$ 11.55) and the free caustic present in the solution acts as a stabiliser. Soda-ash scavanges free hydrochloric acid forming a non-volatile salt and maintain its alkalinity. Stability of sodium hypochlorite solution is also improved by storing it in a dark room below 30°C and free from contaminations of any heavy metal salts. The decomposition of sodium hypochlorite can be represented by the following reactions :

$$2NaOCl \rightarrow NaCl + NaClO_2$$

or $$2NaOCl \rightarrow 2NaCl + O_2 \uparrow$$

or $$3NaOCl \rightarrow 2NaCl + NaClO_3$$

The bleaching mechanism of sodium hypochlorite consists of the following reaction [2] :

$$NaOCl \rightarrow NaCl + (O)$$

The above reaction is accompanied by severance of glucose linkage in cotton, resulting in loss of tensile strength.

6.2.3 Lithium hypochlorite and chlorinated trisodium phosphate

Lithium hypochlorite can be obtained by mixing strong solutions of sodium hypochlorite with lithium chloride. This results in partial precipitation of sodium chloride. The product obtained by evaporation of supernatent solution typically contains 30% lithium hypochlorite (LiOCl), 34% sodium chloride and other salts. Chlorinated trisodium phosphate is a hydrated complex having chemical formula ($Na_3 PO_4 . H_2O$) NaOCl and contains approximately 4% available chlorine. Gener-

ally, they are mainly used as laundry detergents, because sodium and lithium do not precipitate anionic surfactants as the calcium salts.

6.2.4 Factors effecting in hypochlorite bleaching operations

Cotton can be bleached with hypochlorite solution at room temperature containing 1-3 g available chlorine per litre at pH range of 9.5 to 11. The pH is maintained by adding 5 g/l sodium carbonate in the bleach bath. After bleaching the cloth is treated with dilute hydrochloric acid to neutralise any alkali (souring) present in the cloth. An antichlor treatment with sodium thiosulphate or bisulphite is also recommended to remove any residual chlorine from the cloth. Finally, the cloth is washed with water to rinse out acid from the cloth.

$$2NaOCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HOCl$$

$$2HOCl \rightarrow 2HCl + 2O$$

$$HOCl + HCl \rightleftharpoons Cl_2 + 2H_2O$$

6.2.4.1 Effect of pH

Hypochlorite ionises differently under different pH conditions and active component can be effective in three different states (Fig. 6-2). In the region of pH 7,

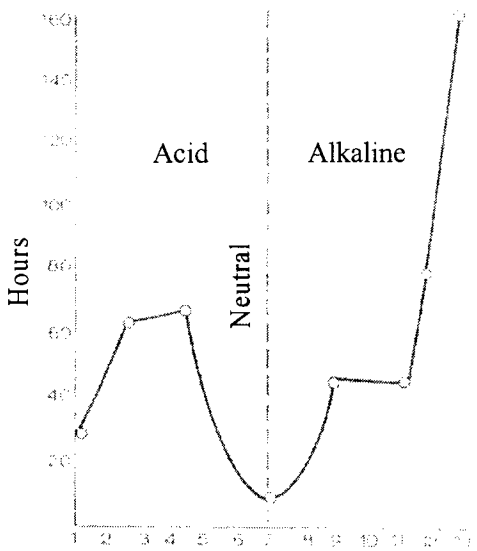


Figure 6-2. Rate of oxidation of cellulose in terms of the consumption of half the total available chlorine.

when hypochlorous acid and hypochlorite ion are present approximate the same

concentrations, the rate of attack on cellulose is greatly enhanced. In the case of bleaching powder the pH has fallen to within the danger zone after 15 min and after 1h when sodium hypochlorite is used. As the pH falls below 5, the liberation of chlorine begins to take place and pH below 1.5, the whole of hypochlorous acid is converted into chlorine. In the pH range 9 to 11, a plateu occurs at which little change occurs and is the normal use range for bleaching with hypochlorite solution. The active species [4] appear to be OCl^- ion, or a complex of HOCl and OCl^-. The pH (8.5-11.0) is stabilised by the addition of buffers (5 g/l Na_2CO_3).

$$HOCl \rightleftharpoons H^+ + OCl^-$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$$

6.2.4.2 Effect of temperature

Generally bleaching of cotton is carried out with 1.5 g/l of hypochlorite solution at about 40°C for 1 h. Higher temperature increases the rate of bleaching but at the same time degradation of cotton is also increased. Hypochlorite solutions by themselves are quite stable at the boil at pH values 11 or higher, but decomposes at lower pH values [5]. During the decomposition of hypochlorite solutions, chlorate formation predominates in the absence of cotton, while in the presence of cotton, it is practically absent under alkaline condition [6]. Hypochlorite solutions if buffered to pH 11, the rate of bleaching is increased by a factor of 2.3 times for every 10°C rise in temperature. It is thus, possible to bleach at 60°C in 7 min, but is difficult to control the degradation of cotton in such short period of bleaching.

6.2.4.3 Effect of concentration

The commercial solution of sodium hypochlorite contains 14-15% available chlorine, compared to 35-36% in bleaching powder. The concentration of hypochlorite in the bleaching bath generally varies from 1 to 3 g/l available chlorine. The optimum bleaching conditions, however, depend on the degree of discolouration of the cloth and thus the temperature and time of reaction should be adjusted according to the requirement. The concentration of hypochlorite solution is normally estimated by means of standard thiosulphate or arsenite titration.

6.2.4.4 Effect of electrolyte

The addition of salt in the hypochlorite bleaching bath increases the activity in the initial period due to the production of nascent chlorine. The addition of chloride moves the equilibrium to the left-hand side, but after, say 15 min, when the

new equilibrium is reached, the sudden stimulated effect is ceased and bleaching resumes its normal course and hence action of salt is only temporary and confined to the first stage of bleaching.

$$2Ca(OH)_2 + 2Cl_2 \rightleftharpoons Ca(OCl)_2 + CaCl_2 + 2H_2O$$

$$HOCl + NaCl = 2Cl + NaOH$$

6.2.5 Accelerated hypochlorite bleaching

The aim of accelerated bleaching is to adopt a continuous bleaching by reducing the bleaching time and chlorine consumption with the help of more reactive bleach liquor. However, the accelerated bleaching may lead to degradation and yellowing of the cotton fabric.

6.2.5.1 Accelerated bleaching in the danger zone

Bleaching with hypochlorite solution containing 1 g/l of available chlorine with the addition of 5 g/l sodium carbonate at pH close to 7 can be done in just 10 min. The system is more reactive in the danger zone and thus bleaching can be done in a shorter time.

6.2.5.2 Accelerated bleaching in conjunction with H_2O_2

Hypochlorite bleaching can be accelerated by the addition of hydrogen peroxide, ammonia, chloramine etc. [7, 8]. Hydrogen peroxide reacts with hypochlorite forming hydroxyl and $HO_2^{\bullet}$ radicals. The hydroxyl radical may react as before or

$$H_2O_2 + \bar{C}l\,O \rightarrow H\,O_2^{\bullet} + \bar{C}l^{\bullet} + OH$$

$$HO_2^{\bullet} + \dot{O}\,H \rightarrow H_2O + O_2$$

terminate by reaction with $HO_2^{\bullet}$. In actual practice fabric is first treated with cold alkaline hypochorite solution as a pre-bleaching agent and then an after bleach is carried out (without rinsing) in conjunction with hydrogen peroxide or sodium chlorite [9]. The cold hypochlorite treatment can be carried out in a J-Box type cold reaction chamber of 7 min reaction time. The cloth then passes in another hot reaction J-Box in open width form and plaited into a bigger pile without any serious risk of creasing and possible crease marking. The advantages of this process are that the total reaction time of the bleaching process can be reduced, H_2O_2 acts as an antichlor and fabrics containing cotton/rayon mixture as well as colour-woven goods can be bleached due to milder conditions employed in the hypochlorite stage.

6.2.5.3 Accelerated bleaching at elevated temperature

Another possible way to reduce the bleaching time is to work at elevated tem-

perature [5, 10]. Rapid bleaching may be done at 60-80°C containing 0.9-1.6% of active chlorine (o.w.f.) in the pH range of 8.6 to 12.8.

6.2.5.4 Accelerated bleaching in presence of additives

Sometimes bromides or related compounds are added to the hypochlorite liquor to accelerate the bleaching action. It is likely that sodium hypobromite is formed which is a stronger oxidising agent than hypochlorite.

Methods of bleaching at high temperature and pH close to 7 in presence of sulfamic acid in hypochlorite bleaching of cotton has been suggested [11]. It has a stabilising effect, slowing the rate of decomposition of hypochlorite and reducing the damage to the fibre, without having any adverse effect on the final whiteness.

6.2.5.5 Accelerated bleaching by steaming

An accelerated method for bleaching polyester/cotton blended fabric is described [12]. The process consists of steaming at 100 ±15°C for 60 min followed by washing and padding through a solution containing 10-12 g/l active chlorine at 25°C. The fabric is then aged in a series of chambers for 60 min and then led through an acidifying bath with 2-2.5 g/l sulphuric acid at 20°C. The accelerated effect is achieved by changing the order of the operations.

6.2.6 Advantages of sodium hypochlorite bleaching over bleaching powder

Sodium hypochlorite has practically replaced bleaching powder due to its various advantages although solutions of hypochlorite are more expensive than calcium hypochlorite.

(i) Bleaching powder is a mixture of calcium hypochlorite with lime. Thus, calcium carbonate settles on the fibre during bleaching process. On the contrary, sodium hypochlorite is free from any such danger of specks of lime being deposited on the cloth.

(ii) Bleaching powder is partially soluble in water and exists in a solid form. However, sodium hypochlorite, being a sodium salt of hypochlorous acid, does not require any dissolving arrangement and are ready for immediate use. Hypochlorites are easy to handle.

(iii) Chlorinated lime requires higher alkalinity than that of sodium hypochlorite solutions for active bleaching conditions.

(iv) Sodium hypochlorite solutions have less tendency for the pH value to fall during bleaching. Caustic soda is liberated by the hydrolysis of sodium

hypochlorite form sodium carbonate under the action of carbon dioxide from atmosphere. Sodium carbonate thus formed can be easily washed away with water and reduces acid requirement for souring. In such case, sulphuric acid may be used as souring agent in place of the more costly hydrochloric acid.

(v) Sodium hypochlorite can penetrate into the fabric more thoroughly than in the case of bleaching powder and therefore shorter time of bleaching is possible in the case of sodium hypochlorite.

6.2.7 Disadvantages of sodium hypochlorite

(i) Sodium hypochlorite does not produce completely satisfactory whites inspite of many advantages.

(ii) Bleaching with sodium hypochlorite produces slight damage to cellulosic fibres.

(iii) Sodium hypochlorite cannot be used for the bleaching of synthetic fibres as it produces greater damage to such fibres.

(iv) Bleaching with sodium hypochlorite solution requires corrosion resistant equipment.

(v) Sodium hypochlorite produces unpleasent odours in working environment.

(vi) Sodium hypochlorite solution is harmful to skin in concentrated form.

(vii) It produces harsh handle on fabric. Furthermore, it cannot be used on natural animal fibres.

(viii) Stabilisation of sodium hypochlorite is difficult to achieve where pH varies.

(ix) The formation of highly toxic chlorinated organic biproducts (AOX) during the bleaching process has limited its use because these compounds are a potential hazard to the drinking water resources when discharged [13, 14].

6.3 Bleaching with Peroxide

Hydrogen peroxide was discovered in 1818 and its use in bleaching textiles was first suggested in 1866. However, its high cost limited its use in cotton bleaching until 1935. The problem was partially solved by the process using barium peroxide and phosphoric acid. In 1926 hydrogen peroxide was manufactured by an electrolytic process based on the decomposition of persulphuric acid (H_2SO_5) [15].

Sulphuric acid is first ionised into hydrogen and bisulphate ions which is discharged on the anode and then form persulphuric acid, which on vacuum distillation reacts with water to form hydrogen peroxide. Hydrogen peroxide can also be obtained by dissolving sodium peroxide in water. Instead of dissolving the peroxide and then neutralising the liberated alkali, the peroxide can slowly be stirred into slight excess of sulphuric acid. The reaction is carefully controlled as a large amount of heat is evolved. For every 100 lb of H_2O_2 (40% by volume) 95 lb of Na_2O_2 is to be used.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$2HSO_2^- - 2e \rightarrow 2HSO_4$$
$$2HSO_4 \rightarrow H_2S_2O_8$$
$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$$
$$Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$$
$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

Pure hydrogen peroxide is fairly stable in presence of sulphuric acid and phosphoric acid if stored away from sunlight in a perfectly smooth bottle. In alkaline medium it is less stable and even traces of alkali (NaOH, Na_2CO_3) decompose aqueous solution of hydrogen peroxide. The addition of alcohol, glycerine or berbituric acid also stabilise hydrogen peroxide. Hydrogen peroxide also decomposes in the presence of finely divided heavy metals such as copper, iron, manganese, nickel, chromium etc. or their oxides with liberation of oxygen.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The volume strength of hydrogen peroxide is expressed as the volume of liberated oxygen at N.T.P. on heating one volume of hydrogen peroxide sample. Hydrogen peroxide is generally made of 10, 12, 20, 100 and 130 volume strength. A 10 volume peroxide solution is one which will liberate 10 times its own volume of oxygen. The percentage concentration is expressed as the quantity of pure hydrogen peroxide in 100 parts of sample and is expressed as x%, y% etc. The commercial supply of hydrogen peroxide are generally 35% and 50%. A 10 volume hydrogen peroxide contains 3% hydrogen peroxide and thus, 1% H_2O_2 = 3.3 volume concentration. The strength of the available oxygen can be estimated by titrating the peroxide using standardised potassium permanganate ($KMnO_4$) until or faint permanent pink colour appears. However, iodine method is preferred to permanganate method.

6.3.1 Mechanism of peroxide bleaching

Though hydrogen peroxide is stable in acidic medium, but bleaching occurs by the addition of alkali or by increased temperature. Hydrogen peroxide liberates perhydroxyl ion (HO_2^-) in aqueous medium and chemically behaves like a weak dibasic acid. The perhydroxyl is highly unstable and in the presence of oxidisable substance (coloured impurities in cotton), it is decomposed and thus bleaching action takes place. Sodium hydroxide activates hydrogen peroxide because H^+ ion is neutralised by alkali which is favourable for liberation of HO_2^-.

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$

$$H_2O_2 \rightarrow H^+ + HO_2^- \xrightarrow{OH^-} HO_2^- + H_2O$$

However, at higher pH (above 10.8) the liberation of HO_2^- ion is so rapid that it becomes unstable with the formation of oxygen gas which has no bleaching property. If the rate of decomposition is very high, the unutilised HO_2^- may damage the fibre. A safe and optimum pH for cotton bleaching lies between 10.5 to 10.8 where the rate of evolution of perhydroxyl ion is equal to the rate of consumption (for bleaching). At higher pH, hydrogen peroxide is not stable and hence a stabiliser is frequently added in the bleaching bath.

6.3.2 Stabilisers for peroxide bleaching

The process of regulation or control of perhydroxyl ion to prevent rapid decomposition of bleach and to minimise fibre degradation is described as stabilisation. Stabilisers for peroxide normally function by controlling the formation of free radicals. These are complex blends of a selection of materials serving a number of functions. They could include any of the following :

- Alkali, e.g. caustic soda/carbonate/silicate.
- Dispersant, e.g. acrylates/phosphonates.
- Sequestrants, e.g. EDTA/DTPA/heptonates/gluconates.
- Inorganics, e.g. magnesium salts.
- Colloid stabilisers, e.g. acrylic polymers.

The selection of alkali to be used in peroxide bleaching is dependent on the fibres or blends being bleached. Sodium hydroxide, sodium carbonate are generally used on cellulosic fibres whilst ammonia and various phosphates are used when bleaching protein fibres. Of the various phosphates only tetrasodium pyrophosphate, $Na_4P_2O_7$ and hexametaphosphates are of interest as stabilisers in alkaline bleach bath.

Sodium silicate is the most conventional, easily available and widely used stabiliser. Sodium silicate [16] is mildly alkaline in nature and the commercial grade consists of polysilic acid and having a Na_2O : SiO_2 ratio 1 : 3.3. The most preferred ratio for bleaching is 1 : 1, however, the final ratio will depend on the bleach bath and alkali used. Sodium silicate forms a complex compound with perhydroxyl ions which are liberated slowly at higher temperature during bleaching process. Metallic silicates are also oxidation and thermal resistant, offer a buffering effect, are colloidal in nature and are not greatly effected by the presence of ionic iron. Sodium silicate, however, has a greater stabilising action in the presence of calcium and magnesium salts so that water with hardness between 2° and 5° is recommended or, if water of zero hardness be used, 0.06 g/l magnesium sulphate may be added. The effect of magnesium ions in the form of $MgSO_4.7H_2O$ for stabilising peroxide bleaching bath is recommended [17]. Colloidal magnesium silicates and hydrated silicas must be kept in colloidal form during their formation and during bleaching. Since this is seldom fulfilled completely under plant conditions, some deposition of silicate onto fibre produces harsh feel and silicate scale on J-Box surface which abrades the goods producing defects. It is advisable to rinse very thoroughly after bleaching to avoid harshness on the fabric. Alternative way to avoid precipitation, an additional alkali may be added to bring the ratio of Na_2O : SiO_2 to within the region of 2.25 : 2.75. Calcium phosphate, produced by the addition of disodium phosphate brought to pH about 9.6 with caustic and buffered with borax, substitutes satisfactorily for silicate and no scale is formed.

Sequestering agents for heavy metals should theoretically make the best stabilisers. In effect, stabilisation may be effected by elimination of heavy metal ions that are responsible for free radical formation. This appears to be an anticatalytic reaction. Many types of sequestering agents are used in textile processing. The main types are :

- polyphosphonates,
- polyhydroxy-carboxylic acids,
- aminopolycarboxylic acids,
- phosphonic acids,
- polyacrylic acids.

Organic stabilisers are often commercially blended products which may or may

not contain magnesium salts, the three main types being the aminopolycarboxylate, protein degradation products and selected surfactants. The preferred sequestering agents in terms of both sequesteribility and stability to oxidation are diethylene triamine pentaacetic acid (DTPA), either as sodium or magnesium salt, and its hydroxy derivatives. Aminopolycarboxylic acids used in the form of their magnesium and calcium salts have the advantage over conventional amino polycarboxylic acids in that they are not reduced to amino oxides at high temperature and thus do not loose their sequestering power. Polycarboxylic acids act mainly as dispersing ion-exchangers. Phosphonates have limited application and since recently, due to their eutrification nature, are not preferred. Phosphonates are active as complex formers with good dispersing properties.

In recent years acrylates have been used in preference to phosphonates and whilst heptonates and gluconates have replaced EDTA and DTPA. Acrylic acid copolymers are normally not biodegradable. A method has been patented to introduce sugar molecules directly in the polymer chain of polycarboxylic acid [18]. The sugar molecule in the tautomeric endiol form has C=C double bond which is necessary for copolymerisation with acrylic acid. Sugar polyacrylates, however, due to the hydroxyl groups of sugar, have a binding capacity for ferric ion. Other biodegradable compounds (stabilisers) are prepared by graft copolymerisation of available unsaturated monomers such as maleic acid, vinyl acetate, methallyl sulphonates, methoxy PEG, methacrylate and saccharose and have a molecular weight range of 3-20 thousand. They can be used in the form of free acid or their salts. The binding power of calcium and magnesium salt is 3-5 times that of homopolyacrylates, particularly for hydroxides of iron, calcium and magnesium at room temperature as well as at boil. They have high dispersing power for iron oxides, of the level of phosphonates.

6.3.3 Parameters in peroxide bleaching operations

It is very difficult to specify strict guidelines for optimum bleaching conditions for hydrogen peroxide as the operation is normally affected by the nature and quality of the goods to be bleached, the amount of bleaching required and on the equipment available. However, the following general variables are considered to be important :

6.3.3.1 Effect of pH

The stability of hydrogen peroxide depends on pH. At pH 1 to 3 it is stable ; but

at highly alkaline pH 11.5 to 13 it has least stability. The bleaching takes place around 10.5 due to accumulation of perhydroxyl ions in the bleaching bath. At neutral or weak alkaline media, hydrogen peroxide does not produce any whitening effect and may cause degradation of cellulose.

6.3.3.2 Effect of temperature

In practice cotton bleaching with hydrogen peroxide is carried out at 90-100°C, but the temperature may be increased to 120°C in the case of pressurised equipment with a corresponding reduction in process time. The rate of bleaching increases with the increase in temperature, but at the same time solution becomes unstable and degradation of cotton increases. Below 80°C, the evolution of perhydroxyl ion is very slow so also the rate of bleaching.

6.3.3.3 Effect of concentration of liquor

The optimum concentration of hydrogen peroxide depends on number of factors namely liquor ratio, temperature and class of fibre. In the batch process using kiers about 2-4% (o.w.f.) hydrogen peroxide is sufficient for cotton fabrics with a liquor ratio of 10:1 to 20:1. In the continuous process, the cotton fabrics are saturated with bleach bath containing 1-2% (o.w.f.) hydrogen peroxide. Very high concentration may damage the fibre.

6.3.3.4 Effect of time

The time required to bleach with hydrogen peroxide depends on temperature, class of fibre and equipment used for bleaching. In general, the time of bleaching is inversely proportional to the temperature of the bleaching bath. Cotton may be bleached in open kiers by circulating heated hydrogen peroxide solution (88-95°C) for 6 to 10 hours.

6.4 Bleaching of Wool with Hydrogen Peroxide

The natural colour of animal fibre is closely related to the character of environment in which the animal lives [19]. Wool lots completely free of dark fibres do not exist [20]. In animal (and human) hair two kinds of pigments occur, namely eumelanin (responsible for black, dark brown and grey colours and commonly referred to as melanin) and pheomelanin (present in yellow, reddish-brown and red hair). Both are thought to be formed by different mechanisms and chemically differed [21]. Eumelanin is formed by enzymatic (tyrosinase) oxidation of tyrosine and polymerisation of several oxidation product [22]. Pheomelanin occurs in form of discrete grannules. Melanin grannules can occur in the cortex or in the cuticle.

Scoured wool varies in shade from the light cream of wools considered to have good colour to discoloured, urine-stained wools and the near black of heavily pigmented wool. Bleaching is common with all these wools which has been well reviewed [23-25]. The main problem is that the whiteness of wool attained during bleaching is not permanent. Wool tends to yellow over a period of atmospheric exposure of approximately six months. Blueing or optical whiteners may be added either to bleach liquor or to final rinse bath. The main bleaching agents for wool are oxidising and reducing agents. Amongst the oxidising agents hydrogen peroxide is most commonly used because sodium hypochlorite gives a deep rust colour and sodium chlorite develops pink colouration on wool. Traditionally wool is bleached by oxidative processes either in the presence of alkaline stabiliser or under acidic condition of hydrogen peroxide [27, 28].

6.4.1 Bleaching of wool in alkaline hydrogen peroxide solution

In the alkaline condition, wool is treated at pH 8-10 with a 1.5-3 vol. solution of hydrogen peroxide containing 2-3 g/l stabiliser, which may be sodium silicate or sodium pyrophosphate. A mixture of sodium pyrophosphate and ammonium oxalate is also useful for use as a stabiliser in bleaching of wool with hydrogen peroxide [28]. Bleaching may be carried out at 50°C for 3 to 5 h and then rinsed, treated with dilute acetic acid and rinsed again. The level of whiteness can be controlled by concentration of hydrogen peroxide, length of treatment time, pH and temperature of treatment bath.

6.4.2 Bleaching of wool in acidic hydrogen peroxide solution

In the acid process wool is treated with a solution of hydrogen peroxide containing formic acid (2.5 g/l) at pH around 4 to 4.5 at room temperature. The treated wool is then squeezed to remove excess liquor and passed into a drier where bleaching takes place. Ageing is preferable because the colour of the wool continues to improve for 24-48 h after drying. Citric acid activates peroxide bleaching of wool between 80 and 60°C [29]. Activated hydrogen peroxide bleaching of wool with reduced bleaching time and damage is reported by treatment in a bath consisting a mixture of organic salts that form carboxylic acids [30, 31]. Further, bleaching with alkaline and acidic hydrogen peroxide at 60°C can be improved by adding 100 to 200 g/l of urea [32]. The precautions during bleaching are exactly the same as those needed in the bleaching of cotton with hydrogen peroxide. The advantages of

acid process are lower chemical degradation of wool, rinsing after bleaching is not required and no tendency for bleeding of coloured threadings.

6.4.3 Alkaline peroxide bleaching followed by hydrosulphite treatment of wool

Where an excellent stable bleach is required, especially if it is to be followed by the application of a fluorescent brighteners, then an alkaline peroxide bleach followed by stabilised hydrosulphite treatment is necessary. Bleaching is carried out for 3-5 h at 50°C with alkaline hydrogen peroxide followed by a second treatment with 2 g/l of hydrosulphite solution to raise the whiteness further.

6.4.4 Mordanting and peroxide bleaching of wool

The best chance for an efficient bleaching of highly pigmented wool with minimum fibre damage is provided by the use of metal catalysts in a mordanting step preceeding peroxide bleaching.

Mordanting is done in presence of hypophosphorous acid and it is an excellent stabiliser for iron (II) ions under mordanting conditions (Table 6.2). More impor-

TABLE 6.2
Mordanting and Rinsing Conditions for Pigmented Wool [33]

	Mordanting	Rinsing
Iron (II) sulphate heptahydrate	10 g/l	–
Hypophosphorous acid (50%) (reducing agent)	3-4 g/l	–
Formic acid	To pH 3 to 3.5	–
Temperature (°C)	80	80
Time (min)	60	20

tantly, cystine suffers hardly any attack from hypophosphorous acid under conditions that favour disulphide scission induced by sulphur containing reducing agents [34-36]. It is possible to avoid the use of formaldehyde in pigment bleaching when a mild reducing agent such as hypophosphorous acid is present. However, with hydrosulphite, ferrous sulphate and ammonium sulphate mordanting, addition of 4% of 40% formaldehyde as a cross-linking agent to prevent fibre degradation is suggested [37, 38]. Rinsing following the mordanting step proved to be critical with regard to selectivity and consequently to fibre damage. A normal cold rinse would remove virtually no iron from the fibre.

In the second stage, bleaching is carried out in alkaline condition of hydrogen peroxide. Iron that settles on the surface and inside the fibre acts as a catalyser and brings about enhanced bleaching action by extremely reactive radicals ($HO\cdot$ and $HO_2\cdot$) that are produced from oxidising agent. The bleaching conditions are summerised in Table 6.3. Tetrasodium pyrophosphate (diphosphate) (10 g/l) is a

TABLE 6.3
Bleaching Conditions for Wool Pigmented in the Bulk

Fibre type	H_2O_2 (35%) (ml/l)	pH (adjusted with amm. hydroxide)	Temp. (°C)	Time (min)
Karakul Wool, Cashmere, Alpaca, Camel, Yak.	25-45	8-8.5	50-60	45-180
Rabbit, Chicken feather.	20-40	8-8.5	50-60	45-120
Goat, Human hair.	30-50	8.5	60-70	60-180

good stabilising agent in peroxide bath having liquor ratio of 15:1. After bleaching the wool is thoroughly rinsed with water. The retention of non-selective ferrous ions on wool following rinsing and subsequent bleaching with hydrogen peroxide leads to an undesirable light brown discolouration from ferric species. Selectively bleached fibre may be given a second step reductive or oxidative bleaching to yield whiter material for customer requirement.

6.4.5 Sequential oxidative and reductive bleaching of wool

There are two approaches for sequential oxidative/reductive bleaching of wool in a single bath. In the first approach, following the oxidative bleaching of wool using hydrogen peroxide, the peroxide bath is converted to reductive bath by addition of thiourea and bleaching continues without the need for a fresh bath for the reductive steps. In the second approach after bleaching of wool with oxidative hydrogen peroxide (alkaline or acidic), the remaining active hydrogen peroxide is decomposed by the use of an organic catalyst, and finally a reductive bleaching agent is added to the bath with necessary pH adjustment.

Regarding the first approach vast amount of information is available on thiourea [39-43] and the reaction mechanism can be represented as :

$$\underset{\text{thiourea}}{H_2N-C(=NH)-SH} + 2H_2O_2 \xrightarrow{pH\ 4.5\sim5.5} \underset{\text{thioureadioxide}}{H_2N-C(=NH)-SO_2H} + 2H_2O$$

$$H_2N - C(=NH) - SO_2H + 2OH^- \xrightarrow{pH\ 7-8} H_2N - C(=NH) - OH + SO_2^-$$

urea sulphinate ion

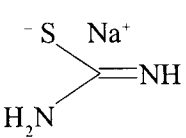
SO_2^- + [chromophore] → SO_4^{2-} + [reduced chromophore]

The reaction route and the final products of the reaction of thiourea with hydrogen peroxide are very much dependent on the molar ratio of reactants and the pH of the reaction. Thiourea dioxide is produced in situ and reductive bleaching occurs. The bleaching conditions developed are, alkaline hydrogen peroxide bleaching at 60°C for 60 min followed by an addition of thiourea, pH adjustment, and subsequent reductive bleaching at 60°C for 25 min followed by washing and rinsing. There are number of patents on these new bleaching process [44, 45].

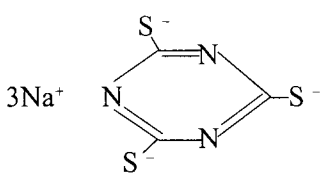
In the second approach, the addition of thiourea directly to hydrogen peroxide bath is avoided because it wastes considerable reductive agent due to large excess of hydrogen peroxide usually left in the bleach bath. To avoid this problem, organic catalysts that decompose hydrogen peroxide are added and finally thiourea dioxide or methane sulphinate is added directly to the bath with necessary pH adjustment. There are many inorganic catalysts that readily decompose hydrogen peroxide, but some (Fe^{3+}, Fe^{2+}, Cu^{2+}, Mn^{2+}) tend to cause excessive damage as well as discolouration of wool. Co^{2+} is the only metal cation reported to cause no damage or discolouration [46].

Despite the advantages of using thiourea to induce in situ reductive bleaching, some potential users of single bath processes hesitate to use it due to the toxic nature of thiourea. Furthermore, thiourea though easily handled and thoroughly consumed, is classified as carcinogen unlike its oxidised counterpart, thiourea dioxide (formamidinesulphinic acid).

Trithiocyanuric acid (TTCA; s-triazine-2, 4, 6-trithiol) is a cyclic analog of thio-



Thiourea



Sodium salt trithiocyanuric acid (Na_3TTCA)

urea. Na_3TTCA is not classified as a carcinogen and thiourea may be replaced by it. Na_3TTCA is most effective at 90% of the stoichiometric weight to peroxide, as

opposed to 70% for thiourea. The Na_3TTCA is more sensitive to the pH of the rinse bath than the thiourea process and is more expensive than thiourea. Nevertheless, the attractiveness of using Na_3TTCA is the avoidance of a potential carcinogen and achievement of exceptional whiteness over conventional peroxide bleaching [47, 48].

6.4.6 Bleaching of wool with emulsion of hydrogen peroxide

Wool has been successfully bleached with a stable emulsion of hydrogen peroxide [49] or permonosulphuric acid [50] in perchloroethylene. By this means it appears to be possible to obtain the same degree of whiteness as that attainable in a standard aqueous bleach, but more rapidly and with the use of less peroxide. No stabilising or activating agents are needed, but the bleaching of wool in perchloroethylene seems to be more deleterious to mechanical properties of bleached wool than equivalent aqueous procedure.

6.5 Bleaching of Silk with Hydrogen Peroxide

The natural colour of silk thread differs depending upon the type of silkworm and its feeding habit. Although the bulk of the natural dyestuff such as chlorophil, xanthophil and carotin are to be found in the silk gum, the degummed mulbery silk also has strong yellowish inherent colour. Since some of the sericin is tenaciously held by fibrion, complete elimination of colour by degumming is not achieved. Thus, the fabrics manufactured from yellow raw silk retain a yellowish tint after boiling-off. This natural yellowish tint on silk is desired by some fashion designers as a 'soft white' or natural shade. The desired degree of whiteness can be relatively easily achieved with Bombyx mori silk on bleaching. With tussah silk the yellowish colouring of the fibrion is considerably more intensive. One reason for this is that with the tussah silk the sericin also penetrates the actual silk fibre, so that the natural dyestuffs lend the tussah fibrion a typical brownish yellow to greenish yellow colour. The natural colouring matter is the tannin of the oak tree leaves on which tussah silkworm is fed. The bleaching process for tussah silk to get white fabric is thus usually very difficult, which makes such silks unsuitable for white fabrics or for certain pastel tones. The silk may be bleached by oxidative as well as reduction methods. If a very high degree of whiteness is required, a combination of both methods in the form of double bleach is applied.

The best method of bleaching silk is the use of hydrogen peroxide in a seperate

bath. The perhydroxyl ion or even atomic oxygen is responsible for the oxidation effect on the organic colouring matter present in silk and thus for bleaching effect. The recipes for bleaching two varieties of silk with hydrogen peroxide are given in Table 6.4. The material after degumming is entered into the prepared bleaching

TABLE 6.4
Recipe for Bleaching Silk with Hydrogen Peroxide

Chemicals	Mulbery silk	Wild silk (tussah, muga, eri)
Hydrogen peroxide (35% by wt.)	15-20 ml/l	20-30 ml/l
Stabiliser	2 g/l	4 g/l
M : L ratio	1 : 20	1 : 30
Temperature (°C)	75-80	80-90
Time (h)	1-2	3-4

bath at 40°C. With these fibres, which are sensitive to alkali, the alkali necessary for activation of hydrogen peroxide must be added to the bleaching bath should be ammonia or tetrasodium pyrophosphate. The pH value of the bleaching liquors should lie between pH 8.5-9. Stabilisers are added to the bath to achieve a slow seperation of the oxygen needed for the bleaching effect. Water glass, which is often used as a stabiliser, should not be used for bleaching silk, because owing to the precipitation of silicic acid the silk can get a hard, brittle handle [51]. In this case, tetrasodium pyrophosphate and fatty protein condensates are the ideal choice. The mixtures of sodium silicate and trisodium phosphate or organophosphates exert a great stabilising effect on peroxide and help to control bleaching action. Generally, one should consider whether instead of the seemingly contradictory method of using activators on the one hand and stabilisers on the other hand, it would be better to have exact metering of the hydrogen peroxide solution. The dispensing systems that most dyehouses are now using make this feasible. Hard water with metallic salts or impurities is avoided as the metals act as catalyst and weaken the silk. It is advisable to use stainless steel or aluminium vessel and rods. Bleaching above the specified temperatures lower the tensile strength of silk and becomes yellow. The bath is gradually raised to required temperature in 1 h and bleaching is done at this temperature for specified time. Whereas bleaching of mulbery silk is

complete after about 2 hours, the time required for bleaching tussah silk can be a lot longer depending on the origin and inherent colour. The silk after bleaching is thoroughly rinsed first with warm water and then with cold water, hydroextracted and dried. Standing baths of peroxide can be used by replenishing the bath with 1/3rd the quantity of hydrogen peroxide and 1/4th the quantity of stabiliser originally taken for bleaching.

Silk goods to be sold as white require a treatment with 0.08 to 0.5% optical whitening agent along with 0.5% glauber's salt at 45°C for 20 min at pH 4 to 5 with the addition of acetic acid. Ultramarine Blue is also recommended in the optical brightening bath to obtain a bluish tinge to the white silk goods.

6.6 Bleaching of Synthetic Fibres with Hydrogen Peroxide

6.6.1 Bleaching of regenerated cellulose

Filament viscose rayon may not require bleaching since this is normally carried out during manufacture. However, viscose in staple form requires bleaching as it may not necessarily include a bleaching treatment during its manufacture. The same reagents as those used for bleaching linen and cotton fabrics are useful for these fibres. For very good whiteness, rayon may be bleached on a jigger with alkaline hypochlorite or combined scour and bleach using hydrogen peroxide (up to 1 vol. strength) containing sodium silicate and alkaline detergents at a temperature of about 70°C. The presence of heavy metals (from Xanthate hydrolysis stage) makes the use of peroxide a hazardous process. It is also possible to use peracetic acid with viscose rayon.

6.6.2 Bleaching of acetate fibres

The whiteness of the fabric made of acetate may be improved by treatment with hydrogen peroxide (30%), 1-3 g/l in presence of sodium silicate, 0.3 g/l. During this treatment the alkalinity of the bath and the required temperature should be carefully maintained. The pH of the bleach bath should not be greater than 9 and treatment for 1 h at 45°C gives combined scour and bleaching with the addition of non-ionic detergent.

6.6.3 Bleaching of acrylic fibres

Certain acrylic fibres should not be chlorite bleached because of their tendency to yellow/or loose stability to light. Many fluorescent brighteners added to the chlorite bath are also not stable and such materials may exhibit an accelerated fade when

exposed to sunlight in wet alkaline condition. Such fibres can be bleached with hydrogen peroxide or hydrosulphites. However, the need for bleaching varies with different acrylic fibres. Acrilan 16 is sufficiently white for most purposes, but Acrilan 1656 has a more yellowish brown natural colour. Orlon 42 has a colour which is intermediate between natural and bleached cotton.

6.7 Advantages and Disadvantages of Peroxide over Hypochlorite Bleaching

Advantages :

(i) Peroxide is an universal bleaching agent and can be employed for wool, silk as well as cotton. It is specially suited to the bleaching of union fabrics containing both cotton and wool or silk.

(ii) Hydrogen peroxide is a milder reagent than hypochlorite and the degrading effect of peroxide bleaching on cellulose is less influenced than is the case with hypochlorite.

(iii) Peroxide is capable of continuing the scouring action simultaneously with the bleaching action, thus a single stage combined scour and bleach or a continuous method is possible using hydrogen peroxide.

(iv) Peroxide bleaching is in general less liable to have adverse effect on dyed threads. The white effect is good and permanent and there is less risk of yellowing at a later stage.

(v) Thorough rinsing followed by scouring or antichlor treatment is required with hypochlorite bleaching, whereas with peroxide a comparatively short rinsing suffices.

(vi) With hydrogen peroxide, there is no danger of equipment corrosion, no unpleasent odours and no limitations as to processing techniques.

(vii) Increasing strict control over the discharge of AOX from chlorine bleaching liquors has led to a greater advantage of peroxide processes for bleaching cellulosic fibres [52-54].

Disadvantages :

(i) Bleaching with peroxide is costlier than that of hypochlorite or bleaching powder.

(ii) Hydrogen peroxide bleaching requires stabilisation usually with silicates which brings the risk of forming resist stains in subsequent dyeing, and causes a build-up of hard crystalline deposits on plant and machinery causing abrasion damage to the fabric during passage.

(iii) 'Catalytic damage' occurs during hydrogen peroxide bleaching of cotton fabrics and results in small spots of unevenly dyed fabric or even, in severe cases, the formation of small holes.

(iv) There is limitation in white obtained on acrylic fibres. It also causes deleterious effect on skin when used in a concentrated form.

6.8 Bleaching with Sodium Chlorite

Commercial manufacture of sodium chlorite under the trade name of 'textone' began in 1930s and by 1939 it was being promoted for continuous bleaching of cellulosic textiles for which purpose US manufacturers, Mathieson Alkali Co. designed a large conveyer system. Sodium chlorite ($NaClO_2$) in its white crystalline form is highly hygroscopic in nature. Solid sodium chlorite is stable at room temperature for a longer time when it is mixed with small quantity of alkali (Na_2CO_3). Now-a-days chlorile bleaching is increasingly being used for polyester, because the chemistry is better understood [55].

6.8.1 Mechanism of chlorite bleaching

Sodium chlorite on decomposition produces a strong oxidising gas known as chlorine dioxide. The lower the pH values and higher the temperature (above 70°C) of bleach bath, the greater is the speed of decomposition [56]. The rate of chlorine dioxide formation is proportional to the concentration of sodium chlorite in the solution. Chlorous acid ($HClO_2$) that is formed is unstable and decomposes to chlorine dioxide (ClO_2) which is the acitve species so far as bleaching is concerned. Maximum chlorine dioxide is formed between pH 2.5 and 3.0. In the absence of metal ions and textiles, the rate of formation of chlorine dioxide approximately doubles for each 0.4-pH drop, in the 3.0-5.0 range, at 85°C. Addition of an acid such as formic, acetic or phosphoric acid is recommended so that pH lies between 3 to 5. If the pH drops below 3.0, cotton fibre is severely damaged because weak acid ($HClO_2$) and strong acids (HCl and $HClO_3$) are formed which hydrolyse the cellulose. On the other hand, the loss of oxygen evolution from hot chlorite solution when cotton is added also suggests that chlorite ion rather than chlorous acid is responsible for bleaching [57].

$$2NaClO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HClO_2$$

$$HClO_2 \rightarrow ClO_2 + H^+$$

$$HClO_2 \rightarrow HCl + 2O$$

Aqueous sodium chlorite solutions, which are stable under alkaline conditions are to be activated by acidification. Activation with strong acid produces a toxic corrosive chlorine dioxide gas. It is thus necessary to control its rate of evolution. Technical developments have been linked mainly to control the chlorine dioxide evolution [58-60]. In practice this is generally achieved by controlling the temperature and pH by addition of buffers in the bleach bath. This can be avoided by addition of weak acid (which forms a buffer with the alkali in the chlorite) or a mixture of weak acid and its salt wtih a strong base [61]. Some auxiliary products function by giving a slow development of acidity on heating or long stroage at ambient temperatures. Special brands of sodium chlorite are available which contain acid generating materials and thus attain the required pH, without further addition on reacting at bleaching temperature. Activation with persulphates above pH 7 [62], aldehyde at pH 3-7 [63], bromides [64], salts with cobalt , nickel and manganese at pH 5-8.5 [65], sulphur, selenium or finely divided carbon [66] and chlorinated hydrocarbon [67] have been proposed and also acitvation by organic acid esters such as ethyl lactate (1-3 g/l) with addition of sodium nitrate (1-3 g/l) to inhibit corrosion [68] is possible. Sodium hydrogen orthophosphate (NaH_2PO_4), sodium formate which produce acid when the liquor is heated are also suggested as buffers. Organic esters such as diethyl tartarate which hydrolyses to give tartaric acid, or sodium chloroacetate which liberates hydrochloric acid and glycollic acids during steaming, have also been suggested as buffers [55]. Other alternatives are the use of either special auxiliary products which limit chlorine dioxide evolution, for example, foam formation on the bleach liquor surface or other chemicals capable of trapping chlorine dioxide chemically.

6.8.2 Bleaching of cotton with sodium chlorite

Cotton can be effectively bleached with sodium chlorite (1-2%) at a pH 4.0 ± 2 containing sodium dihydrogen phosphate (0.2-0.5%), stable foaming and wetting agent (0.1-0.25%), nitrogenous chlorine absorber and formic acid to maintain the pH. The temperature of the bleach bath is raised to 82-90°C and maintained at this temperature for 1-3 h depending upon the machines (batchwise) employed for bleaching. Chemicals should be added in the following order : water, previously dissolved sodium nitrate, buffer salts or other chlorite stabiliser, surfactants, sodium chlorite (pre-dissolved, if solid product) and lastly the diluted acid. The addi-

tion of acidic materials to concentrated sodium chlorite solutions must be avoided. Sodium nitrate is used as a corrosion inhibitor. It is not essential to use acid chlorite solutions in the semi-continuous processes (pad-roll or pad-stack) where effective liquor ratio is low and neutral chlorite solutions (10 g/l) are recommended. When long batching time are used, soda-ash (1 g/l) is added to maintain stability of the bath.

Cotton goods that have been prepared in kiers are advantageously bleached by an alkaline sodium chlorite activated by hypochlorite. In this method, cotton goods

$$2NaClO_2 + NaOCl + H_2O \rightarrow 2ClO_2 + NaOH + NaCl$$

passes through a saturator containing (1-3 g/l available chlorine) mixture of sodium chlorite and sodium hypochlorite and a buffer mixture of bicarbonate of soda and soda-ash. An available chlorine pick-up of 0.3% (o.w.f.) is typical. In actual practice, the hypochlorite : sodium chlorite ratio can vary between 3 : 2 and 3 : 1, on an available chlorine basis. The acceptable pH varies from 8.8 to 9.7 maintained by buffer. After leaving the saturator, the goods remains in J-Boxes or bins for the time necessary for bleaching, usually 1-2 hours. At the end of the bleaching cycle the goods are washed, antichlored, and washed again.

The third method of activating sodium chlorite involves the reaction of sodium chlorite with chlorine. The reaction goes to completion very rapidly. However, this

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

method has not yet found an application in the industry.

6.8.3 Bleaching of polyester with sodium chlorite

Synthetic polyester fibres are normally supplied in an off-white state. Sometimes high degree of whiteness is required for white goods. The polyester is generally bleached with sodium chlorite in a bath containing sodium chlorite (50%), 3-5 g/l, formic acid to get pH 3.0 for 1-2 h at a temperature of 95°C. A small quantity of wetting agent can be added in the bleaching bath. Bleaching is followed by anti-chlorination with thiosulphate (2-3 g/l) at 60°C for 20 min. Finally, warm (60°C) and cold rinses are given for 10 minutes.

6.8.4 Bleaching of nylon with sodium chlorite

Nylon is also supplied in quite white state. Bleaching of nylon is normally carried out where the nylon has been discoloured by heat-setting treatment. The problem of discolouration is comparatively less in the case of nylon 6 than that of nylon

6,6 due to the lower temperature required in the spinning process and lower softening point of nylon 6,6.

Neither sodium hypochlorite nor hydrogen peroxide is recommended for bleaching of nylon. When hypochlorite is used, there is a tendency for chlorine to combine with secondary amino groups, causing decrease in tensile strength. Nylon can be bleached in a bath containing sodium chlorite (80%), 1-2 g/l, sodium nitrate, 1-3 g/l, formic acid (85%), 2 ml/l for 1 h at 80-85°C. Acetic acid is preferred to formic acid for adjusting the pH (3.5 to 4) because it has a buffering action on sodium chlorite solution in the required region. A small amount of acid stable detergent (0.2 g/l) may be added to the bleach bath to have a combined effect of scouring and bleaching as well as reduction in the loss of chlorine dioxide to the atmosphere due to the formation of surface froth. An activator for bleaching with sodium chlorite is also recommended so that bleaching can be carried out in near neutral pH. Acid donors organic esters e.g. ethyl lactate are readily hydrolysed in bleach bath and split into alcohol and organic acid. As the hydrolysis progresses

$$R\text{-}COOR' + H_2O \rightarrow RCOOH + R'OH$$

the organic acid which is slowly liberated regulates the the decomposition of chlorite. The pH of the bath. is maintained within 6.6 to 6.0 during the period of bleaching. The amount of ethyl lactate added to the bath depends on the liquor ratio. For short liquor ratio 2-3 ml/l and for long liquor 1 ml /l of ethyl lactate is sufficient. Sometimes ammonium chloride is also used as an activator for bleaching with chlorite. Bleaching of differential dyeing nylon is not normally recommended since this tends to limit the contrast effects during subsequent dyeing. However, when bleaching is essential a mild chlorite bleach [69] can be employed.

6.8.5 Bleaching of acetate fibres with sodium chlorite

It is more safe to carry out bleaching of acetate fibres with sodium chlorite than with hydrogen peroxide. Bleaching can be carried out with sodium chlorite (0.5-2 g/l) in presence of mono substituted ammonium phosphate (0.5-2 g/l) and non-ionic detergent at 70-80°C for 60-100 min.

6.8.6 Bleaching of polyacrylonitrile with sodium chlorite

Fabrics made from polyacrylonitrile in grey condition have a yellowish or cream tint. Polymer textile finishing agents containing polyacrylonitrile and nitrile groups tend to yellow during fibre processing and requires bleaching [70].

6.8.7 Bleaching of polyvinylalcohol with sodium chlorite

After boiling with 1-2 g/l of non-ionic or anionic detergent for 45-60 min at 85-90°C, the fabrics requrie bleaching if they are delivered undyed. The bleaching can be carried out with a solution containing sodium chlorite, 0.4-0.7% (o.w.f.), pH 3-4, at 70-80°C for 30-45 min.

6.8.8 Problem of corrosion and its prevention in chlorite bleaching

Most of the materials used in the construction for bleaching equipment, are corroded due to free chlorine dioxide gas evolved during bleaching process. Various approaches have been suggested to minimise the evolution of chlorine dioxide gas and corrosion problem.

(i) Stainless steel containing 2.5% molybdenum makes the bleaching equipment quite resistant to chlorine dioxide. Titanium also does not corrode in presence of chlorite [71], but its use is limited due to its high cost. Vessels lined with titanium, glass or ceramics can be used. Fibre-glass J-Boxes are sufficiently smooth, resist reactions with chlorite. Cross-linked polyester and resins [72] used in surface coatings are sufficiently resistant to chlorine dioxide.

(ii) Corrosion can be suppressed virtually completely by adding selected assistants which tend to harness the free evolution of chlorine dioxide [73]. These assistants are those products which contain nitrogen and have the ability to scavange chlorine and its products. These assistants range from products such as ammonium dihydrogen phosphate, sodium and ammonium nitrate (NH_4NO_3), nitric acid to nitrogenous resins such as melamine, urea and others.

(iii) The problems of corrosion hazard, fuming and formation of chlorate are all minimised without loss of bleaching efficiency by raising the pH from 3 to 5 by means of magnesium dihydrogen phosphate activator [74].

(iv) It is claimed [75] that the salts of mono –, di – or triethanolamine will maintain a pH of 7.0-8.5 at 20-50°C and yet bring about quantitative decomposition of chlorites at temperatures above 70°C.

(v) To eliminate the corrosion of the exposed parts by chlorine dioxide vapour, the machine should be designed in such a manner that condensation is prevented [76] or by means of gas washeries which are installed within the ventilation duct with water or an alkaline hydrogen peroxide solution [77].

(vi) Corrosion can be well controlled by the use of ammonium salts, which

reacts with commercial alkaline chlorite in the following manner,

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$$

The ammonium salts appear to act by neutralising chlorite solutions. Moreover, they appear to improve bleaching at 100°C.

(vii) The suppression of chlorine dioxide by addition of hydrogen peroxide has been suggested [78], but, although this is effective at pH 4.0-7.0, there is some deterioration in bleaching efficiency.

(viii) Sometimes surfactants which are stable in acid chlorite bath of producing minute foam cells are added. The foam bubble can trap the gas formed before it is emitted to the atmosphere.

(ix) It has been stated that corrosion difficulty may be partly circumvented by pad application of cold chlorite solution followed by steaming.

(x) Use of a discontinuous process i.e. closed jigger, the closed package bleaching methods have also been successfully employed to minimise the problem.

6.8.9 Merits and demerits of chlorite bleaching

Sodium chlorite as a bleaching agent has got the following technical merits :

(i) Sodium chlorite is a versatile bleaching agent. It can be used for cotton and synthetic fibres and their mixtures. Man-made fibres which are sensitive to alkali can be safely bleached with sodium chlorite.

(ii) Sodium chlorite bleaching will give permanent white coupled with excellent mote removal on cotton which has not been kier boiled. There is little or no tendency to degrade cellulose.

(iii) The vigorous alkaline treatments employed in kier boiling are not necessary in using sodium chlorite for bleaching. Cotton waxes are very easily freed from bleached cloth by hot-alkaline after-treatment.

(iv) Under the acid conditions of chlorite bleaching, hardness of water has little harmful effect and therefore low ash content is obtained on bleached cotton.

(v) Sodium chlorite is rather insensitive to the presence of metal ions as iron with peroxide.

(vi) Sodium chlorite is ideally suitable for bleaching of cotton/polyester blended fabrics since both fibre components respond to acidic chlorite bleaching. However, hydrogen peroxide is also found equally satisfactory for this fibre blend.

The chlorite bleaching process suffers from certain drawbacks as follows :

(i) Sodium chlorite is more expensive than hydrogen peroxide. It is not useful for the bleaching of silk and wool, since it gives pink colouration which, however, can be removed with treatment of soidum bisulphite solution.

(ii) Even at pH 4-5 certain amount of chlorine dioxide is evolved, and the bleaching action is extremely corrosive to metals including stainless steel. Neutral and alkaline pH may tender the cotton.

(iii) Chlorine dioxide is a very toxic gas because it can decompose into both hydrochloric acid and chlorine gases. The gas mixture is a skin irritant, attacks mucous membranes and can cause fatal pulmonary edema. The TLV of this compound is 0.1 p.p.m. and shows the necessity for adequate care and ventilation during usuage.

(iv) Explosions are fostered when gaseous chlorine dioxide and $HClO_2$ is exposed to uv light.

6.9 Bleaching with Peracetic Acid

Peracetic acid is an equilibrium solution consisiting of hydrogen peroxide, acetic acid and peracetic acid. It can be used for bleaching of nylon, viscose rayon, cellulose acetate and even cotton [79, 80]. Peracetic acid is commercially available for textile bleaching in 5, 15 and 40% solutions as what is known as ''equilibrium peracid''. Peracetic acid can be prepared by the interaction of concentrated hydrogen peroxide and acetic acid in the presence of strong mineral acid such as sulphuric acid [81, 82]. Alternatively, it can be prepared by mixing hydrogen peroxide with acetic anhydride at room temperature in presence of suitable catalyst like caustic soda or EDTA [83]. The optimum reaction takes place with 1 part of hydrogen peroxide and 6 parts of acetic anhydride after about 4 h at room temperature to give a yield of about 80%. The excess acetic anhydride may, however, cause an undesirable side reaction to yield highly explosive diacetyl peroxide.

$$H_2O_2 + CH_3COOH \xrightarrow{H^+} \underset{\text{peracetic acid}}{CH_3.CO.O.OH} + H_2O$$

$$\begin{array}{l} CH_3{-}C{=}O \\ \qquad | \\ \qquad O + H_2O_2 \overset{\text{Cat.}}{\underset{\text{NaOH}}{\rightleftharpoons}} CH_3CO.O.OH + CH_3COOH \\ \qquad | \\ CH_3{-}C{=}O \end{array}$$

acetic anhydride

The physical and chemical properties of peracetic acid is summerised in Table 6.5. The concentrated solution of peracetic acid is volatile and has a pungent smell

TABLE 6.5
Properties of Peracetic Acid

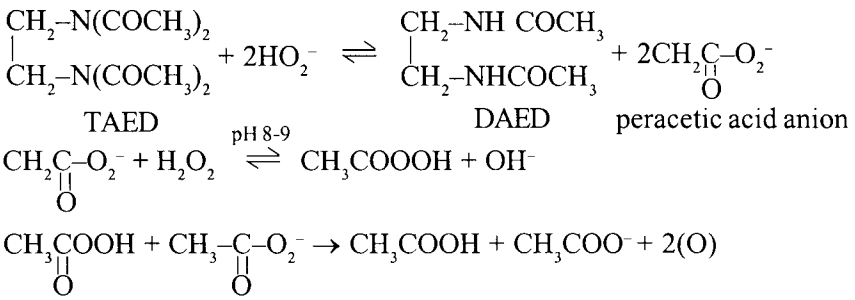
Properties	Concentration of peracetic acid	
	5%	15%
Physical properties		
Appearance	–	colourless liquid
odour	–	pungent
pH	2.0	2.0
Density (g/mL, 20°C)	1.120	1.480
Chemical properties		
H_2O_2	27.0	22.0
Acetic acid	6.3	16.6

and strongly irritates the mucous membrane. The stability of peracetic acid is not quite high as that of stabilised hydrogen peroxide. Free radicals may be produced in the presence of ions such as copper, iron etc.

Peracetic acid has proven to be effective bleaching agent in the household detergents and also found wide application in the laundry industry. To reduce the danger in the on-site production of peracetic acid from acetic anhydride/hydrogen peroxide, activators can be used in household detergents to generate peracetic acid in situ. The commonly used activators are sodium perborate and acetylated 0 or N-compounds such as tetraacetylethylenediamine (TAED) [84, 85]. The perborate activators are assumed to act via the stages of peracetic acids [86]. Perborate hydrolyses in aqueous solution and hydrogen peroxide is produced. Reactive peroxide anion is produced from hydrogen peroxide under weakly alkaline medium and

$$Na_4(H_4B_2O_8) + 4H_2O \rightarrow 2Na_2[B(OH)_4] + 2H_2O_2$$
$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$
$$X\text{-}Ac + HO_2^- \rightarrow X^- + AcOOH$$

then the activator reacts [87]. The chemistry of TAED/H_2O_2 bleaching is based on the following mechanism :



The peroxide anion reacts with TAED to form DAED (diacetylethylenediamine) and peracetic acid anions. At pH 8-9 the peracetic acid anion is in equilibrium with the free peracetic acid. This equilibrium peracetic acid oxidises its own per anion to form active oxygen, which acts as a bleaching agent [88].

6.9.1 Bleaching of cotton with peracetic acid

Though the use of peracetic acid has been suggested for bleaching of cotton but has never reached the commercial success like hypochlorite, chlorite and peroxide [89]. The mechanism of reaction is somewhat similar to that of hydrogen peroxide.

$$CH_3COOOH \rightarrow CH_3COOH + (O)$$

Recently, peracetic acid is used as a replacement of hypochlorite in multi-stage bleaching process of cotton and linen [90, 91]. Peracetic acid is most effective as a bleaching agent of cotton in the pH range of 6 to 7. The preferable bleaching temperature range is between 50-80°C and bleaching time of 20- 60 min depending on the temperature. The degree of brightness increases proportionately with the concentration of bleaching agent. To avoid the damage of cloth, a sequestering agent may be added to remove to those catalytically active ions such as Cu, Fe etc. which can be absorbed by fibre.

Bleaching of 100% cotton in rope form in a J-Box with peracetic acid (1.5-2.5 g/l) at room temperature, followed by an alkaline hydrogen peroxide treatment at 90°C yield a good whiteness.

Linen can be successfully bleached using a process consisting of scouring, alkaline hydrogen peroxide bleach and a peracetic acid bleaching stage.

6.9.2 Bleaching of nylon with peracetic acid

Peracetic acid is particularly suitable for bleaching of nylon because this can be applied in a liquor which pH is virtually neutral and hence there is no danger of loss of strength of nylon fibre. The bath is set with pre-dissolved chemicals containing

sequestering agent(0.75%), sodium bicarbonate (0.75%), caustic soda (flake) (2.00%) and peracetic acid (5.0%) on the weight of the fabric. Seperate container is used for peracetic acid and concentrated alkali is not mixed. Bleaching may be carried out at a pH between 6.0 and 7.5 for about an hour at 80°C. After bleaching the material is rinsed thoroughly in cold water. The bleaching equipment should not contain copper, brass or iron and preferably it should be made of ceramic or stainless steel.

6.9.3 Bleaching of cellulose acetate with peracetic acid

Peracetic acid is very suitable for bleaching of cellulose acetate fibres. The liquor should be made-up in the following manner :

Peracetic acid (36 - 40%)	0.3 kg
Sodium hexametaphosphate	0.05 kg
Wetting agent	0.1 kg
Water	99 litres

The solution is adjusted to pH 5-6 by the addition of well diluted sodium hydroxide and bleaching is carried out in 1 h at 66°C. It is desirable that pH should be checked at intervals. The bleached goods is then rinsed in hot and then in cold water.

6.9.4 Bleaching of acrylics with peracetic acid

The bleaching bath is set with predissolved (all o.w.f.) sodium hydroxide (50%), 1%, sodium bicarbonate, 1%, sequestering agent, 1% , and prediluted peracetic acid, 5% in the given order. The goods are run cold for 10-15 min and then the bath is heated slowly to 75°C and bleaching is continued at this temperature for 20 min. The bath is then cooled, dropped and the goods are rinsed well. For white goods, an optical brightener may be added.

6.9.5 Merits and demerits of bleaching with peracetic acid

The advantages of peracetic acid as a bleaching agent are :

(i) Peracetic acid is environmentally safe since it decomposes to acetic acid and oxygen and do not form any toxic product [81].

(ii) Peracetic acid as an industrial chemical is easily available and can be safely introduced to an existing process design [82].

(iii) Peracetic acid is very suitable for bleaching of nylon and it can be used successfully for the bleaching of cotton dyed with indanthrene colours.

(iv) Peracetic acid bleached goods show comparable or even higher brightness with less fibre damage.

(v) In the household powder detergent, peracetic acid is generated in situ from activators.

The disadvantages of peracetic acid as a bleaching agent are :

(i) Concentrated solution of peracetic acid (35-40%) is dangerously explosive and cannot be handled. The concentrated solution has a pungent odour, is caustic and burns the skin. It needs to be carried in specially protected tanker wagons when transported by rail.

(ii) It is expensive for bleaching of cotton and rayon and is used only as a last resort.

(iii) The stability of peracetic acid is not quite high as that of stabilised hydrogen peroxide. Free radicals may be produced in the presence of Cu and Fe ions.

6.10 Reductive Bleaching of Wool

Reductive bleaching treatments are normally employed for the bleaching of wool, silk and nylon fibres. Now-a-days, the main form of reductive bleaching employs hydrosulphite compounds. The treatments using sulphur dioxide or sodium bisulphite are now only of historical value as the process has many practical disadvantages. Sodium hydrosulphite may be used alone, provided the temperature of the bleach bath is kept low to prevent rapid decomposition. However, a stabilised form of sodium hydrosulphite is more commonly used, in which the inclusion of sodium pyrophosphate (or other non-phosphate buffers) controls the pH close to neutral to inhibit the too rapid decomposition of the hydrosulphite. By the use of such stabilised hydrosulphite compound a much higher temperature can be employed. Thioureadioxide is sometimes employed as a reducing agent for the bleaching of wool [93-95]. The decomposition rate of thioureadioxide increases with increasing pH and temperature and decreases with increasing concentration [96].

6.10.1 Bleaching of wool with sulphur dioxide (stoving process)

In this method moist woollen yarn in the hank form is exposed to the action of sulphur dioxide produced by burning sulphur (3 to 6% o.w.f.) placed in an iron or earthenware pot inside the chamber. Sulphur is converted to sulphur dioxide and

sulphurous acid gas in the presence of moisture. Sulphurous acid is a strong reducing agent which reduces the organic colouring matter into colourless substances. The material is exposed to sulphur dioxide for 6 to 8 h or over-night and then rinsed for 15 min in H_2O_2 (0.1%) solution at 35°C which oxidises retained sulphur dioxide (present as sulphurous acid) to sulphuric acid and finally neutralised with dilute sulphuric acid and blued. Piece goods in moist condition can also be stoved in a similar manner by passing them into the stove through a narrow slit in the stove and suspending on wooden rollers arranged in two tires.

The disadvantages of this method are :

(i) Bleaching effect is not permanent, the natural colour of wool returns gradually.

(ii) The sulphurous acid gas may be formed by the reaction of SO_2 and water, which can cause permanent damage to eyes and respiratory system.

(iii) Even after thorough washing wool retains sulphur dioxide and hence treatment with oxidising agent like NaOCl or H_2O_2 is necessary.

(iv) The process requires longer time for bleaching.

(v) If wool is too dry, the bleaching effect is poor.

6.10.2 Bleaching of wool with sodium bisulphite

In the sodium bisulphite method [97], wool is impregnated with a solution containing 2°Tw sodium bisulphite and 1°Tw H_2SO_4 for 2 h. Alternatively, wool can be treated with a solution of sodium bisulphite (2°Tw) for 6 to 10 h, squeezed, and is then followed by second impregnation in H_2SO_4 (1°Tw) and washed thoroughly.

6.10.3 Bleaching of wool with sodium hydrosulphite

Reductive bleaching with non-stabilised sodium hydrosulphite [98], sodium hydrosulphite-based sulphoxylate formaldehyde [99] and sodium and zinc hydroxymethanesulphinate [100] have been shown to provide wool excellent whiteness, with a lower cystine content than in the case of bleaching wool with other reducing agents. The result obtained is permanent, in contrast to the unstable peroxide white.

The goods are treated with a solution containing sodium hydrosulphite (4-8 g/l) or stabilised sodium hydrosulphite (5-10 g/l) and pyrophosphate or buffer (3-4 g/l) at 50-55°C for 1-2 h. Sodium hydrosulphite in aqueous solution is converted into sodium bisulphite when applied at 50°C at pH around 7.0. After bleaching the

goods are rinsed in warm water and then in cold. The presence of sodium laurylsulphate (SLS) in the bleaching bath improves the whiteness and mechanical properties of the bleached goods without affecting the cystine content [101]. The protection is the outcome of sulphitolysis inhibition derived from the ionic or non-ionic interaction of SLS in the positive sites of keratine ($-NH_3^+$) or in the paraffinic side chains of same amino acid residues. The interaction or combination of SLS with protein increases its net negative charge and hinders the access of the reducing agent to the disulphide linkage [102]. Iron and copper in the hydrosulphite bleach bath can cause a greyish discolouration due to the formation of their respective sulphides which are difficult to remove during washing.

6.10.4 Bleaching of wool with thio-urea dioxide

The optimum bleaching value of wool can be achieved at thio-urea dioxide 1.5 g/l, time 30 min and temperature 80°C. The cost of bleaching with thio-urea dioxide is claimed to be three times lesser than that of bleaching carried out with sodium hydrosulphite. Also, its lack of mutagen activity and its low COD and BOD values recommended it as a non-toxic product giving a low concentration of effluents.

6.10.5 Photobleaching of wool

The novel method of bleaching wool by exposure to intense light are attractive because of the dry and pollution-free nature of the process. Photobleaching can be rapid and the resulting colour and brightness are similar to those of peroxide bleached wool [103]. Though photochemical bleaching is industrially possible, but not economically attractive yet. Wool can be photochemically bleached [104] by exposure to u.v. light below 360 nm. When wool is treated with a zinc complex of thioglycollic acid to minimise yellowing and then exposed to sunlight, undergoes photochemical bleaching which effectively destroys the impurities caused by photo-degradation.

6.11 Bleaching of Silk with Reducing Agents

Silk fibrion is highly sensitive to oxidising agents like hypochlorite and chlorite solutions. Oxidation and substitution in the benzene ring of tyrosine is responsible for degradation of silk with the formation of chloro-amino acids, ketonic acids and chloramine in several stages [105].

Reduction bleaching of silk is generally carried out with sodium hydrosulphite or appropriate stabilised commercial products on this basis. The silk fibrion is

resistant to the reducing agents. Since the bleaching effect is poorer than with peroxide bleach, the term ''half bleach'' is sometimes used. A brief resume of the

TABLE 6.6
Bleaching of Silk with Reducing Agents

Reducing agent	Condition
Sulphur dioxide or Sulphurous acid.	4 to 6 h at an atmosphere of SO_2, yellowish tint obtained.
Sodium hydrosulphite. $Na_2S_2O_4 + 4H_2O_2 \rightarrow 2NaHSO_4 + 3H_2$	4 to 6h at temperature around 50°C, pH 7, concentration around 45 g/l.
Stabilised hydrosulphite.	30 to 90 min at temperature of 60-90°C, pH 5 to 7, concentration around 10 g/l.
Sodium sulphoxylates. $NaHSO_2.CH_2O + H_2O \rightarrow NaHSO_3 + H_2$	Concentration 4 to 6 g/l, temperature 60-95°C, pH 4 to 5.5, time 20-30 min.

bleaching operations is highlighted in Table 6.6.

Sometimes silk is still bleached with sulphur dioxide in gas form. To do this the damped fabric is subjected to the sulphur dioxide gas for several hours in an enclosed chamber. Through the formation of sulphur dioxide some natural dyestuffs are reductively destroyed, whereas others are only converted to water soluble leuco compounds, which then have to be washed out, so as not to risk reoxidation and thus yellowing during storage. The frequently noticed unpleasant odour of the remaining sulphur dioxide on the fabric can be eliminated by a rinsing process with hydrogen peroxide of 35% strength (1 mg/l).

If a very high degree of whiteness is required, a double bleach process is recommended. Here bleaching is carried out on two seperate stages, first the silk is treated with 3 to 5 g/l stabilised sodium hydrosulphite at 60°C for 1 h, followed by oxidative bleaching using H_2O_2, 10-20 ml/l (35% strength), 2-3% sodium silicate, the pH of the bath being maintained at 8.5-9.0 at 90°C for 1 h. With this process, as a rule, an excellent full white is achieved, which will endure storage and is lightproof. Certain tussah silks cannot, however, be bleached to a full white, even applying this process [106].

6.12 Reductive Bleaching of Nylon

Reductive bleaching of nylon is normally employed under acidic conditions.

Virtually no fibre degradation occurs and the resistance of the fibre to photo-degradation is not impaired. The liquor is set with 2-4% (o.w.f.) stabilised hydrosulphite, 2% (o.w.f.) sequestering agent, 0.2-1% (o.w.f.) selected fluorescent brightener and acetic acid to pH 4.5. The goods are entered into the bath and the temperature is raised slowly (1°C/min) to 85-100°C. Treatment is continued until the desired colour is achieved. The goods are then cooled and rinsed thoroughly.

6.13 Peroxygen Bleaching Compunds

There are several peroxygen derivatives that occasionally find use in textile industry. These are potassium peroxymonosulphate (monopersulphate), potassium perphosphate and urea peroxide. These compounds are rarely used by themselves, but are used primarily as bleach boosters. They are all powders and are usually compounded where a strong colourless oxidising agent is indicated. The mechanism of potassium peroxydisulphateperoxide is represented by the following reactions ;

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}\bullet$$

$$SO_4^{-}\bullet + H_2O \rightarrow H^+ + SO_4^{2-} + OH\bullet$$

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$$

$$HO_2\bullet + S_2O_8^{2-} \rightarrow O_2 + HSO_4^{-} + SO_4^{-}\bullet$$

$$HO_2\bullet + H_2O_2 \rightarrow O_2 + H_2O + OH\bullet$$

to give a net reaction

$$S_2O_8^{2-} + H_2O_2 \rightarrow O_2 + HSO_4^{-}$$

Above pH 5.0, the addition steps are written :

$$HO_2\bullet \rightleftharpoons O_2^{-} + H^+$$

$$O_2^{-} + S_2O_8 \rightarrow O_2 + SO_4^{2-} + SO_4^{-}$$

$$O_2^{-} + H_2O_2 \rightarrow O_2 + OH^{-} + OH\bullet$$

Under the name of ''Oxone'' Du Pont has put on the market a bleaching agent for polyamide fibres. Its active bleaching component is potassium persulphate ($KHSO_5$, pH of a 1.0% solution is 2 to 3). Oxone is used for the bleaching of nylon, together with NaCl and a mixed buffer K_2CO_3 and $NaH_2PO_4.2H_2O$ at pH between 7.5 and 8.0 at 80°C. This bleaching auxiliary is used more for domestic bleaching than for bleaching finish works.

6.14 Bleaching of Jute

The art of bleaching jute has received fresh attention as diversified jute products like decoratives, soft luggage, and upholstry material are in great demand now-a-days. Raw Indian jute is brown in colour and requires bleaching. Scoruing of jute

fabric before bleaching has no beneficial effect, rather it deteriorates whiteness index. The grey jute fabric attains reddish tone after scouring in alkali. However, scouring of jute fabric before sodium chlorite bleaching enhances the whiteness index. A damage to the jute fibre occurs at concentrations of caustic soda higher than 9.0% [107]. Bleaching renders jute near white resulting in better lustre and appeal to the fabric. Bleaching of jute is also required for good colouration background.

Bleaching of jute can be affected by all bleaching agents, but bleaching powder and hydrogen peroxide [108,109] find commercial application. Owing to the presence of non-cellulosic constituents, particularly lignin, the actions of conventional bleaching agents such as H_2O_2, $NaClO_2$, peracetic acid and NaOCl are somewhat different as compared to their action on cotton [110,111]. The bleaching effect of H_2O_2 and peracetic acid on lignin is almost nil. The use of sodium hydrosulphite, sodium bisulphite, sodium borohydride have also been recommended for bleaching of jute [112]. Jute bleached with reducing agents is not all stable and develops reddish or brown tinge on storage.

6.14.1 Bleaching of jute with sodium hypochlorite

Jute piece goods are bleached in open width e.g. on jigs and jute carpet yarn is bleached in hank form or in the form of cross-wound cheeses in an open machine. Jute can be bleached with alkaline hypochlorite using 5-7 g/l available chlorine. Afterwards the goods are usually given an antichlor with sodium bisulphite, but it is not soured because of the difficulty of removing the traces of acid. However, the sodium hypochlorite bleaching produces poor whiteness which is not acceptable for subsequent dyeing and printing.

6.14.2 Bleaching of jute with hydrogen peroxide

Hydrogen peroxide bleaching process is most suitable for bleaching jute fabrics and the bleached goods are suitable for making diversified jute products.

Bleaching exclusively with hydrogen peroxide in the presence of silicate generally necessitates high peroxide consumption level and rigorous conditions and hence substantial fibre damage can result. Bleaching of grey jute can be carried out with H_2O_2 (2 vol.), sodium silicate (10 g/l), sodium hydroxide (1 g/l), trisodium phosphate (5 g/l), pH around 11 at 80°C for about 1 h. After bleaching the fabric is thoroughly washed, neutralised with 2 ml/l acetic acid and then usual washing and drying is carried out. Alkaline hydrogen peroxide gives a good white colour and less marked yellowing than that of hypochlorite bleach. The losses in strength and weight due to

bleaching treatment are also less in case of peroxide bleaching process, compared to hypochlorite bleach.

Process involving only use of H_2O_2 is not very suitable as above certain percentage of H_2O_2 (6% of 50% H_2O_2) concentration, there is no appreciable increase in brightness value. Modified bleaching recipes for jute are now being reported [113, 114]. Jute with high lignin content compared with other cellulosic fibres, can be bleached in a sequential process using sodium chlorite or hypochlorite followed by hydrogen peroxide-sodium silicate bleach to produce the best fibre whiteness without appreciable strength loss. Lignin present in jute is chlorinated to convert into chlorolignin which are further extracted during alkaline extraction. This is then followed by peroxide bleaching. The whiteness can further be raised by the application of a suitable fluorescent brightening agent to the bleach bath or seperately.

6.14.3 Bleaching of jute with sodium chlorite

Scouring and bleaching of jute with sodium chlorite with an acceptable whiteness can be achieved, but the process is a time consuming two step process. Moreover, sodium chlorite is metal corrosive and health hazardous.

A single stage process containing 5% sodium chlorite solution at 65-70°C with a liquor ratio of 10:1 can produce pale yellow colour, with moderately good wet strength, but the fabric is turned yellow on exposure to light [115]. In another attempt, treatment of jute with 3 g/l sodium chlorite at boil for 90 min at pH 4 and then followed by treatment with H_2O_2 (0.5 vol.) solution buffered to pH 10 at 80°C for 30 min, gives a product with comparatively improved whiteness and resistance to yellowing on exosure to light [116]. A direct bleaching process [117] by the use of a solution containing sodium chlorite, hydrogen peroxide as a stabiliser for the chlorite, and buffer salts such as mono-and di-sodium phosphate (50-250% based on chlorite content) at pH 4.5-7 is also reported. The fabrics are wrung out to remove excess liquid, are heated by means of a superheated steam and are kept at a temperature of 90°C for 3 h. The whiteness of the fibre is uniform and of a high standard. A minimum change in the DP occurs when the jute is bleached with 0.7% sodium chlorite at pH 4 and 65-70°C for 80 min. The rate of bleaching can be increased by increasing the temperature [118].

6.14.4 Bleaching of jute with peracetic acid

The use of peracetic acid as a bleaching agent for jute fabrics is reported [119]. The optimum bleaching results are obtained at 70°C around pH 6.5. The mild acidic condition is most suitable because of the fact that neither hydrocellulose nor

oxycellulose is produced at this pH. Peracetic acid bleaching is more effective in reducing losses in weight and tensile strength than hydrogen peroxide bleaching. The improvement in handles/feel and low ash content of peracetic acid bleached jute fabrics is attributed to silicate free bleaching. Jute can also be effectively bleached with peracetic acid in the presence of selected buffering and stabilising agents [120]. A superior bleaching effect can be achieved by using tetrasodium pyrophosphate (TSPP) as a stabiliser under mildly alkaline conditions (pH 8.0-8.5) and excellent fibre brightness can occur at temperatures as low as 40-60°C. This process offers a more energy efficient option for bleaching 100% jute fabric. This process can also be extended to bleaching of jute/cotton blends.

6.14.5 Drawbacks in bleaching of jute

There are some serious drawbacks with reference to the bleaching of jute. They are :

(i) Jute fabric bleached with alkaline hypochlorites or hydrogen peroxide undergoes marked losses in weight and strength and also shows decrease in width. These are mainly attributed to the action of bleaching agent or alkali or alkaline reagents on the non-cellulosic constituents of jute i.e., hemi-cellulose and lignin [121, 122].

(ii) The heavy deposits of calcium or magnesium silicate on the surface of the fabric, resulting from peroxide bleaching with silicate, produce harsh feel and present difficulties in subsequent processing.

(iii) The main drawback of hypochlorite or peroxide bleached jute is photoyellowing. The reason for yellowing is environmental effects like heat, air, uv radiation in sunlight etc. On exposure to light, the shade of bleached jute turns to brownish yellow, which ruins the decorative look. This yellow-brown colour can be removed by second bleaching treatment, but it appears on further exposure to light. The on-set of yellowing varies considerably with the bleaching agent used.

6.14.6 Causes of yellowing and improvement of photostability of bleached jute

Jute has three main components α-cellulose (60%), hemi-cellulose (24%) and lignin (13%). The first two components do not absorb uv-radiation present in the sun-light (300-400 nm), lignin however does. The reaction is believed to be oxidative in nature and heat and oxygen in the air cause photo-sensitization of lignin. This discolouration is also associated with loss of strength. The degradation of lignin

may be associated with the production of simpler aromatic compounds having two phenolic functional groups, or a phenolic and an aldehyde functional group attached to the nucleus. The compounds then appear to undergo condensation reactions involving a free radical mechanism. In this process, chromophore groups are formed with quinone-methide types of structures, and these are responsible for yellowing.

The improvement of photostability of jute fabric itself is an important matter to be given priority. Various processes have been developed in which bleached jute does not revert to its natural colour on exposure to light. The blocking of reactive phenolic groups by etherification or esterification is expected to arrest the yellowing process. The presence of some chromophore in dyes can cause absorption of near uv-radiation of sunlight and prevent discolouration. Bleached jute goods treated with copper-potassium dichromate (0.25% o.w.f.) improve photostability over conventional bleached fabric [123].

Bleaching of jute with H_2O_2 followed by treatment with an aqueous solution of potassium permanganate (8-12% o.w.f.) and a mineral acid, H_2SO_4 (8-12% o.w.f.) is recommended [124]. Subsequently, the reduced permanganate is cleared by rinsing the fabric in an aqueous solution of sodium bisulphite or sodium sulphoxylate formaldehyde at pH 3.0-3.5. Another process [125] consists in bleaching of jute fabric at a pH below 3.0 and a temperature in the range 15-43°C in an aqueous solution of potassium permanganate and phosphoric acid in amounts such that the ratio of potassium permanganate to phosphoric acid ranges between 1 : 0.7 and 1 : 1.1. The bleached fabric is then scavanged with an aqueous solution of an organic reducing agent, such as sodium bisulphite, at a pH below 4.0. The fabric is then scoured with hot water or steam.

A continuous or semi-continuous process for bleaching of jute fabric with chlorinated derivatives of cyanuric acid is developed [126]. The process comprises a preliminary treatment with boiling water, followed by impregnation of the materials with 0.4-0.6% aqueous alkaline solution, and then subjection of the material to steam treatment. Thereafter, the material is treated at 20-50°C with a mixture of trichlorocyanuric acid and cyanuric acid (with available chlorine content 7-15 g/l), containing sodium carbonate or bicarbonate. The pH of the solution is finally adjusted to 4-5 with acetic acid or phosphoric acid. The treated material is then bleached with H_2O_2. The time of treatment is usually 40-60 min, but can be extended to 2 h in the case of a heavy fabric with high lignin content.

A two step process [127] based on the preferential removal of lignin from the surface of jute fibres has been developed. In the first step the fabric is treated with either moist chlorine gas and aqueous chlorine solution or with an aqueous solution of hypochlorous acid at pH 6 and containing available chlorine equivalent to 5-10% (o.w.f.). In the second step, the treated fabric is extracted with an aqueous solution of at least one compound selected from : sodium hydroxide, phosphates, and sulphites ; an equivalent to 5-10% (o.w.f.). Finally, the fabric is washed, and is bleached by the conventional H_2O_2 and/or hypochlorite method.

Biological bleaching techniques using direct growth of lignin degrading fungi [128-130] or pre-treatment with hemi-cellulase enzymes [131] have been reported in the delignification of kraft pulp. A brief pre-treatment of lignocellulose jute with mixed enzyme preparation containing cellulase and xylanase enhances the brightness of fibres after bleaching with alkaline hydrogen peroxide [132].

Surface fuzziness and yellowing on exposure to light can be overcome and the cloth may be made more dyeable with improved light-fastness by judicious use of sodium hydroxide on the bleached fabric or enzymatic treatment of the grey state material. The effects of progressive delignification and various bleaching processes on jute fibres show that surface features progressively changes with gradual removal of lignin and lead to the ''cottonization'' of jute fibre at 93% delignification [133, 134].

6.15 Bleaching of Linen

The morphology of linen and the nature and amount of impurities is related to the scouring and bleaching method. The recipes for scouring and bleaching linen by conventional process are already discussed in Chapter 4. There is an interaction between scouring and bleaching that can cause a wide spectrum of cottonization effect. Green scutched flax generally bleached more easily than retted flax, but the bleaching of green flax, even after boiling with alkali, gives a higher loss in weight than of retted flax. The loss in weight is generally 18% by the older method of bleaching. This is due to the removal of hemi-celluloses, which are low molecular weight polysaccharides and polyuronides. These are sensitive to alkaline treatments and are present in linen fibre to the extent of about 18%. The optimum results are generally obtained with a mixture of (3:1) soda-ash and causitc soda followed by chlorite and peroxide bleaching sequence [135-138]. The lignin content of flax is

much lower than that of jute. The lignin is difficult to remove in the wet processing of flax, and incomplete removal is responsible for yellowing of the fibre after bleaching.

Bleaching of linen can be carried out by either sodium hypochlorite or sodium chlorite. Linen can be bleached white from the grey state without any prior boiling treatment by using higher concentration of sodium chlorite (20-30 g/l at 80°C and pH 3.5-4), the impurities in grey flax activate sodium chlorite. However, bleaching by chlorine containing compounds gives organohelogen compounds AOX. This is caused by reaction with chlorine containing bleaching agents with lignin [139]. This problem is eliminated by replacing it with another bleaching agent that also lignify fully.

A technique for removal of flax rust (Melampsoza lini) from flax fabrics is established [140] by using bleaching mixture ($NaOCl - H_2O_2$). The fabric made from rusted flax yarns is treated with an aqueous solution of NaOCl (2.5 g/l of active chlorine) at pH 9 and ambient temperature. This is followed by treatment with 30% H_2O_2 (3.5 g/l) at pH 9 and at a temperature of 85-95°C. For good white, optical brightening agent may be finally applied. The exhaustion of the oxidant is slow and the degree of whiteness can be improved, if the moderate scouring is done before bleaching [141]. The main disadvantage by using sodium chlorite or peroxide bleaching of linen is that of presence of ''sprit' (remmnants of woody core of flax stem). The dyeing properties of sprit may differ from those of the linen fibre. The only effective way to remove it is by treatment with hypochlorite.

Peracetic acid/peroxide combinations can replace hypochlorite/peroxide and similar whiteness can be obtained as the chlorine route [142]. The results are summerised in Table 6.7. Peroxide itself is a good delignification agent, and in

TABLE 6.7
Reflectance Value of Bleached Linen

State	Reflectance (%)
Grey linen	20
Ash scoured	30
Peroxide bleached	65
Peracetic acid process	77
Hypo/peroxide bleach	67

fact, better than peracetic acid [143]. It is likely that peracetic acid will be able to replace these agents both as bleaching and delignification agents. The water insoluble products of peracetic acid on lignin is almost nil. On chemical analysis of the water insoluble product after treatment for 1 h, the proportion of functional groups are also reduced by different degrees (Table 6.8). The high chlorine content in lignin treated with hypochlorite indicates that in this chlorination is more vigorous, whereas with sodium chlorite oxidation processes are dominant and the chlorination reaction is almost absent.

TABLE 6.8
The Effect of Oxidising Agent in the Functional Groups of Lignin Extracted from Flax [144]

Functional group	Percentage of functional groups in Original lignin	Lignin treated with Hypochlorite	H_2O_2	PAA	$NaClO_2$
Methoxyl	4.47	2.23	1.55	2.91	1.62
Hydroxyl	6.50	0.83	4.15	3.76	2.41
Carboxyl	1.23	0.23	0.34	1.03	0.76
Aldehyde	6.50	7.50	4.30	5.80	4.55
Elemental Analysis	%	%	%	%	%
Carbon	58.39	39.86	51.03	51.23	49.27
Hydrogen	6.40	5.96	7.45	7.48	7.68
Chlorine	–	12.90	–	–	0.30

6.16 Bleaching of Blended Fibre Fabrics

In tropical countries like India synthetic fibres blended with cellulosic fibres fabrics are very popular due to their excellent combination of aesthetic properties and easy care properties. Thus, bleaching of blended fibre fabrics before further processing is an important step. Many of the preparatory processes used for natural and synthetic fibres have little or no application in preparation of blended fibre fabircs.

6.16.1 Bleaching polyester/cotton blends

Polyester fibre in blends with cellulosic fibres in the ratios of 65/35 and 50/50 are common construction. When cellulose portion is rayon, the blends rarely require

bleaching, but when cotton is present bleaching is usually necessary. Bleaching treatments of such blends are normally required to remove the natural colours of cotton, sighting colours and if the polyester portion is turned yellow at the time of heat-setting operation. Chlorine bleaching, peroxide bleaching and chlorite bleaching are employed widely. If the polyester portion requires bleaching, then chlorite bleaching is used, as this bleaching agent bleaches both polyester and cellulose. If the polyester portion does not need bleaching, then a peroxide bleaching is more convenient. However, in case of hypochlorite bleaching, if chlorine remains in fibre degradation can occur. Peracetic acid bleaching causes no undue degradation of the fibre.

Chlorine bleaching can be done at 1-2°Tw bleaching powder solution for 2-3 h, which is followed by dechlorinating treatment. Sodium thiosulphate, acidic sodium sulphate, ammonia, H_2O_2 etc. can be used as dechlorinating agents.

Alkaline hydrogen peroxide bleaching is the most preferred system for polyester/cotton blends and bleaching can be carried out on various equipment using batchwise, semi-continuous and continuous method. Table 6.9 shows conditions for bleaching

TABLE 6.9
Bleaching of Polyester/Cotton at HT/HP Condition with H_2O_2

Chemical	Concentration
Hydrogen peroxide (35%)	30-40 ml/l
Sodium silicate (38°Be')	10-12 ml/l
Sodium hydroxide (solid)	2-4 g/l
Sodium tripolyphosphate	some quantity
Surfactant	some quantity
Temperature	130-140°C
Time	60-120 sec

with hydrogen peroxide in HT/HP equipment by batchwise system. However, the use of continuous open width bleaching with short reaction time has led to considerable and dramatic advances in the bleaching of polyester/cotton blended fabrics. It enables the complete pre-treatment to be accomplished in 12 min instead of 24 h required for pad-roll system. In this system the desized fabric after impregnation with a liquor containing H_2O_2 (above recipe) solution at 35°C is

steamed (heated to 95-96°C) and stored in the J-Box for 75 min. The fabric is then washed at 65°C and dried. Blended fabrics containing coloured threads can be bleached at 80°C instead of 95-96°C without danger of bleeding.

The most effective method of bleaching polyester/cotton is sodium chlorite, which may be followed by peroxide bleaching. Chlorite bleaches the husk, but does not destroy them completely. Polyester/cotton blends may be bleached with sodium chlorite in long liquors and also by pad-steam process [Table 6.10]. The

TABLE 6.10
Recipe for Bleaching Polyester/Cotton Blends with $NaClO_2$

Condition	Jig	Winch beck	Pad-steam (Dry-in-wet)
Liquor ratio	7:1-3:1	50:1-20:1	70% pick-up
$NaClO_2$ (80%), g/l	5-7	1-2	10-20
Stabiliser, (g/l)	2-4	0.5-1	–
Sodium nitrate, (g/l)	2-3	1-2	10-15
Formic acid to maintain pH to	3.5-4	3.5-4	5.5-6
Reaction temp., (°C)	80-90	80-90	85-90
Reaction time, (h)	1-3	1	2-4

amount of various chemicals required for bleaching depend on the liquor ratio. The fabric after bleaching is rinsed as hot as possible and an antichlorination treatment is given with sodium bisulphite. In another method, the cloth is steeped in the liquor at pH 3 to 3.5, squeezed at 100% pick-up, put in a reaction tower made of titan, passed through a heating duct so that the cloth temperature is raised to proper temperature, put in a staying chamber where the cloth is steamed and bleached.

Peracetic acid can also be used for bleaching polyester/cotton blended fabrics with a solution containing 4 g/l peracetic acid, 1 g/l tetrasodium pyrophosphate (stabiliser) and 1 g/l wetting agent with a liquor ratio of 5 : 1. Peracetic acid has a pH of about 1.5 and the bleaching bath solution is adjusted to pH 5.5 with the help of dilute alkali. The material is entered cold and run for 10 min. Then the temperature is raised to 65-70°C in 15 min and bleaching is continued at this temperature till the concentration of peracetic acid drops to 0.09 g/l. The fabric is then washed thoroughly

with hot and cold water. The bleaching can be performed in the kier or in the jigger.

A single stage combined scouring and bleaching of polyester/cotton blended fabric can also be done for economy. There are various approaches which include : alkali treatment with detergent and peroxide hot bleach ; alkali treatment with detergent and sodium chlorite bleach ; sodium chlorite and peroxide bleach ; and peroxide cold and peroxide hot bleach.

6.16.2 Bleaching of polyester/wool blends

The wool portion contained in the blend show reversion to a creamy colour and yellowing of the fabric. In general, blends containing wool and polyester fibres can be bleached with hydrogen peorxide either in acid or alkaline medium without risk of damage.

In acid medium, the fabric is treated with a solution containing 30-40 ml/l H_2O_2 (35%), 2-4 g/l organic stabiliser, 0.25 g/l wetting agent and 0.25 g/l detergent at pH 5.5-6 (acetic acid) for 40-60 min at 80°C or 2-2.5 h at 65°C. The treated fabrics are then given warm and cold rinse.

In alkaline medium, the bath comprises of H_2O_2 (35%), 30-40 ml/l ; sodium pyrophosphate, 2-4 g/l ; ammonia to maintain the pH between 8.5-9.0. The bath is set at 40°C and the goods are treated for 2-4 h, and rinsed well in warm and cold water.

As peroxide-bleached goods tend to show reversion to a creamy colour, it is usual to follow with a treatment in reducing agent to stabilise the bleach in a bath containing 3-4 g/l stabilised hydrosulphite and 1 g/l synthetic detergent at 50°C for 30-40 min, rinsed and dried.

Polyester/silk blends can be bleached by a similar manner to that of polyester/ wool blends.

6.16.3 Bleaching of nylon/cellulose blends

Blends of nylon and cellulosic fibres may be bleached with either H_2O_2 or $NaClO_2$, using batchwise or continuous method [145, 146].

H_2O_2 does not bleach nylon and normal methods of bleaching degrade nylon and cause yellowing. Blends containing 30% or less of nylon may be bleached by the continuous H_2O_2 method, and in such cases cotton will absorb the peroxide preferentially and so protect the nylon from damage. The use of protective agents which prevent undue damage to the nylon poriton of the blend is reported [147].

The goods are entered into a bath containing 2-3 volume H_2O_2, 1 g/l sodium hydroxide flake, 0.2 g/l peroxide stabiliser, 0.25 g/l sequestering agent and 0.002 to 0.05 g/l free radical suppressor at 40°C, the temperature is raised to 85°C and then the treatment continued for 1 h. The treated goods are then cooled and rinsed thoroughly. When appropriate, selected optical brighteners may be incorporated in the peroxide bleach bath.

Hypochlorite does not damage nylon but it has got no bleaching action on it. Sodium chlorite causes no degradation of either cellulosic or polyamide and is a better bleaching agent than peracetic acid for cotton. For batchwise bleaching the fabric is treated with a solution containing sodium chlorite (2-5 g/l) at pH 3 to 4 at 90°C for $1^1/_2$ to 2 h. This is followed by a treatment in a 2 g/l solution of sodium carbonate at 40-50°C and finally hot and cold rinses are given in water. Pad-roll and continuous processes are also used for bleaching polyamide /cellulose mixture.

6.16.4 Bleaching of nylon/wool blends

It is difficult to bleach this blends since the method normally used for nylon degrade wool. The usual method is either to bleach the wool portion with H_2O_2 at low temperature [148] or to carry out reduction bleaching process [149]. Alkaline H_2O_2 bleaching always damage the polyamide fibres to some extent. Normal alkaline H_2O_2 bleaching process may be used with safety on blends containing up to 25% polyamide, but an acid bleach must be used when proportion exceeds this figure. The fabric can be bleached with a solution containing 12-15 ml/l H_2O_2 (35%), 2 g/l tetrasodium pyrophosphate, 1 g/l EDTA (30%) and 0.25 g/l protective agent at 60-65°C for 45-60 min and then rinsed well in water.

6.16.5 Bleaching of acrylic/cellulosic blends

If the cellulosic portion is cotton, bleaching is invariably required for this fibre. If the acrylic portion does not require bleaching, then a peroxide treatment can be done at pH 9.5. The alkaline condition should not be high as otherwise it would cause degradation of the fibre. The fabric is treated with a solution containing 7.5-10.0 g/l H_2O_2 (35%), 3 g/l sodium silicate (79°Tw) and 1 g/l sodium carbonate at 90°C for 45-60 min. After bleaching the bath is cooled slowly to 50°C, rinsed and neutralised.

When acrylic fibre also requires bleaching, then mild chlorite treatment will act on both the fibres in the blend. The bath is prepared at 35°C with 1.5 g/l sodium

chlorite, 2 g/l oxalic acid, 1 g/l tetrasodium phosphate and 1 g/l corrosion inhibitor. The bleach bath should give a pH of about 3.5 to 4.0. The temperature of the bath is raised to 90°C over 30 min and processing continued for 30-45 min at this temperature. The bath is cooled slowly to 50°C and then rinsed thoroughly. An antichlor treatment is given in a bath containing sodium bisulphite (1.5 g/l) and tetrasodium phosphate (1.5 g/l) at 60°C for 20-30 min, cooled the bath and rinsed well. The temperature of drying should not exceed 80°C.

6.16.6 Bleaching of acrylic/wool blends

Hydrogen peroxide is not suitable for acrylic fibre at highly alkaline condition and moreover acrylic fibre turns yellowish on alkaline peroxide treatment. The discolouration can be improved by after-treatment with formic acid in presence of detergent. Acrylic/wool blends can also be bleached by a reduction bleach or by combination of peroxide and reduction bleaching process.

6.16.7 Bleaching of acetate/cellulosic blends

Diacetate/viscose blends have been used in dresswear, shirting and under-wear. These blends may be bleached with hydrogen peroxide or sodium hypochlorite, preferably the latter.

The goods may be treated with a solution containing 5 g/l H_2O_2 (100 vol.), 2 g/l sodium silicate and 1 g/l soap at 70-75°C for a minimum time of 30 min.

Bleaching can be done by treatment with a solution containing sodium hypochlorite (2-3 g/l available chlorine) adjusted to pH 10 at room temperature for 30 min, and then the fabric is given cold treatment with 1 ml/l HCl and thorough rinsing. Alternatively, an acid solution is prepared with 10 ml/l sodium hypochlorite (50°Tw) and 2 ml/l hydrochloric acid adjusted to pH 3. The treatment is carried out cold for 40 min, goods are well rinsed and then treated in a second bath with 3 g/l sodium bisulphite at 40°C for 20 min.

6.16.8 Bleaching of polyester/linen blends

Polyester/long-staple fibres are used in the linen industry, where yarns may be of either the ''stretch broken'' or ''unbroken'' type, but more commonly of the latter. The linen component of the blend may be of bleached or unbleached fibre and yarns spun from unbleached fibre may be bleached before weaving. Most fabrics in this blend are woven on sized (singles) warps. Unmodified warp sizes are removed by enzyme treatment and non-cellulosic matter is removed by an alkaline scour.

Goods made from bleached yarns or fibres require only a light scour with 2 g/l soda-ash along with 1 g/l detergent. Goods prepared from unbleached yarns or fibre are padded with dilute caustic soda solution at 70 to 80°C, batched on a roll and allowed to rotate at this temperature for 24 h. The goods are then rinsed, scoured and bleached with hydrogen peroxide or with sodium hypochlorite. Sodium chlorite is not normally used for bleaching this blend.

6.16.9 Bleaching of wool/viscose blends

Bleaching is usually carried out by immersion of the material in a liquor containing 1-2 vol. H_2O_2 and 5 g/l sodium silicate or sodium pyrophosphate at 30°C overnight or at 40-50°C for 4 h. The bath is adjusted to pH 8 and it is advisable to add 0.25-0.5 g/l of a suitable sequestering agent. For treatment by the shorter time, the concentration of H_2O_2 may be increased to 3 to 3.5 vols. The amount of H_2O_2, however, depends on the quality of wool or proportion of viscose in the blends.

6.16.10 Bleaching of viscose/cotton blends

Viscose/cotton blends can be bleached either by batch method on jig and winch or by a continuous process using J-Box [150]. Bleaching is done on a winch with sodium hypochlorite (2 g/l available chlorine) adjusted to pH 10-11 with sodium carbonate, for 1 h at 25°C, or alternatively, with 5 g/l sodium chlorite adjusted to pH 4 with acetic acid for 30 min at 80°C. Alternatively, the bleaching treatment may follow with alkaline hydrogen peroxide at 85°C.

In the continuous method the fabric is saturated with bleach liquor consisting of H_2O_2 and potassium persulphate, passed through a J-Box, followed by short boil-off, rinsing and drying over cans with a total processing time of 15 min. The temperature in the J-Box approximates 70°C and that of wash liquor 80°C.

6.17 Bleaching of Cotton Weft Knitted Fabrics

Knitted fabrics can be produced from a wide range of fibres and blends, either as flat fabric or garments. Garments, ranging from outerwear (including sport and leisure wear) to hosiery, are generally weft knitted. Warp knits usually require filament yarns which are 100% synthetic and do not normally require bleaching. The weft knitted fabrics produced from 100% cotton and synthetic fibre/cotton blends may be called jersey, rib or fleece depending on how the loop lie. While weft knitted fabrics are comfortable to wear, since they are light and pleasing to the

skin, they do have disadvantages in that they are easily deformed by mechanical stresses and wet creased than woven fabrics.

Since knitting yarns are unsized and usually combed to reduce seed and 'trash content', there is normally any need for treatment prior to bleaching. The knitting lubricants which replace the size on woven fabrics are usually self scouring, but sometimes from their very volume may create problems with foam and stains in wet processing or in the knitting machine which need to be treated with solvent containing auxiliaries.

The bleaching of knitted fabrics-like that of woven fabrics-should result in high whiteness, low chemical or abrasion damage, low crease formation and high absorbancy to water. Sodium hypochlorite is generally not suitable for bleaching of knitted fabrics on account of alkaline nature of the bleach process and recent restriction on adsorbable organo-helogen compound (AOX) generation. However, hypochlorite may be used at pH 11 and at temperature not exceeding 30-35°C in presence of effective wetting agent [151]. Then the fabric is given an antichlor treatment, the whole process taking 3-4 h.

The acidic nature of sodium chlorite bleaching process make it ideal for knitted fabrics, as the natural fats and waxes of the fibre were not scoured out, enhancing the soft, voluminous handle of the goods. Alternatively, a single-stage combined scouring and bleaching can be operated using a peroxide solution containing mild alkali, a detergent and sodium silicate as stabiliser. The alkalinity of peroxide bleaching conditions may scour out the natural fats and waxes from knitted fabrics and results in harsher handle and poorer sewability. A soft fabric can be produced by treating with softener after peroxide bleaching. The combined hypo/peroxide process generally provides the highest whiteness on knitted cotton fabrics. Cotton hosiery made from dark coloured mercerized yarn can be rapidly bleached by hypochlorite followed by peroxide without preliminary scour. Cotton in knitted fabrics is usually less seedy than for woven fabrics making one step scour/bleach with peroxide more readily applicable. Low tension machineries are generally suitable.

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Chapter 7

BLEACHING AND WASHING EQUIPMENT

7.1 Introduction

Textiles can be bleached and washed in loose form, yarn form and fabric (woven and knitted) form. Loose stock can be bleached by steeping method in a suitable vessel. Yarns and tops are bleached using skiens or package machines. Knit goods are commonly scoured and bleached in comparatively small batches in winch and jet machines [1, 2]. However, continuous bleaching ranges for cotton knit goods are available. Rotary machines can be used for bleaching of hosiery fabrics. Woven fabrics can be bleached in three different ways, such as batch process (kiers), semi-continuous process and continuous process. In the semi-continuous process, pad-batch and pad-roll systems and in continuous process, rope or open-width J-Boxes are popular. Over the past few years, there have been new open-width continuous machineries designed, developed and installed in the modern bleach house and have made efficient impression in the industry.

7.2 Batch Bleaching Process Machineries

In the earlier days bleaching of woven piece goods was usually carried out by piling the material into glazed brick or tile lined tanks containing hypochlorite solutions. The usual practice is to turn the load into an adjacent second tank, so that the end which entered first is also drawn out first. The bin or pits have false bottom which allows drainage of bleaching solution. The cloth is allowed to dwell there until the bleaching is complete.

Bleaching of cotton, linen, rayon, man-made fibres etc. in the form of woven or knitted fabrics, hanked yarns and loose stock with appropriate bleaching agents can be carried out in pack bleaching ranges (Fig. 7-1) or in kiers. The bleaching tanks can be fully enclosed or open type equipped with automatic temperature control and the entire process can be programmed control. The capacity of the machine may be 200-2000 kg goods. There is an arrangement of automatic plaiter to pile the fabric ropes (Fig. 7-2). This ensures even twistless piling of fabric ropes at all speeds, regardless of fabric weight. Rail is mounted to serve several tanks seperately. After the bleaching solution is added sufficient water is added to ensure that the load is completely immersed. The temperature is raised to the required tempera-

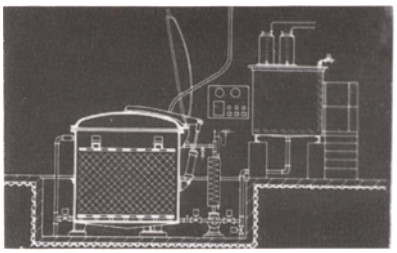


Figure 7-1. Pack bleaching ranges (Courtesy of Friedrichsfeld, Germany).

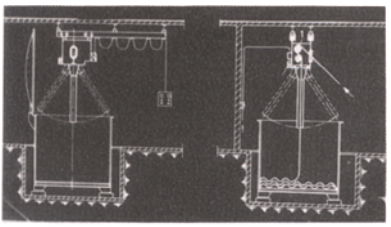


Figure 7-2. Automatic rope piler for circular tanks.

ture, the bleach liquor is sprayed from the top and the liquor percolates through the batch continuously. In the liquor circulating system only 2 h may be necessary, but longer time is required for open kier type of machineries. After bleaching, the goods may be washed in the same machine itself, preferably with warm water, then put through a rope washer.

Raw stocks and yarns in packages or in beams can be bleached only by the liquor circulating machines. Cotton yarn in the form of hank can be bleached as a rope of cloth using pressure kiers, washing machines and hypochlorite bleaching pits. But the modern tendency is to bleach in a more efficient manner in dyeing machines in the form of beams (Fig. 7-3) and packages (Fig. 7-4). This machine

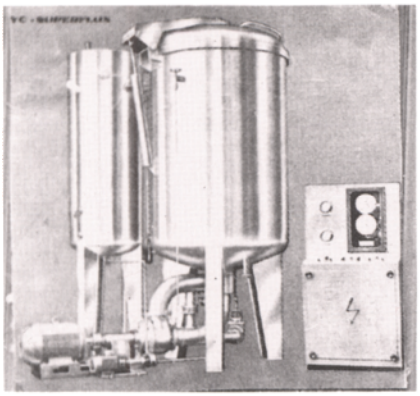


Figure 7-3. Universal HT dyeing and bleaching machine (Courtesy of Argelich, Teames & C.A., Spain).

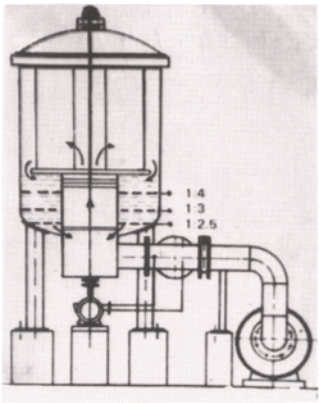


Figure 7-4. Rapid low liquor ratio package dyeing and bleaching machine [3].

(Fig. 7-3) is suitable for dyeing and bleaching of loose stock and yarn as well as of warp beams, tops and carded sliver. All known natural and synthetic fibres can be treated. The cylindrical, vertical autoclave is lifted with a central, conical support for the material carrier, as well as with a drain valve. The cover is lifted with a rapid lock. Counterweight springs assist easy opening and closing of the lid. The main line of development in package dyeing machines (Fig. 7-4) has been the ability to dye and bleach at high temperature and pressure with greatly improved liquor flow. The alkali scour and hypochlorite process is not particularly suitable for yarn in such forms. A single stage peroxide bleaching and for full white double peroxide bleach may be required.

In the past it has been and still is common practice to use mainly winches or jet machines for preparatory of both woven and knitted fabrics in tubular form. Starting with the winch beck, machineries for pre-treatment processes have passed through several stages of development (jig, beam, jet, overflow), some paralleled in washing machines. The current trends towards smaller series have led to a comeback of the conventional systems using jigger machines (Fig. 7-5) for textile processing.

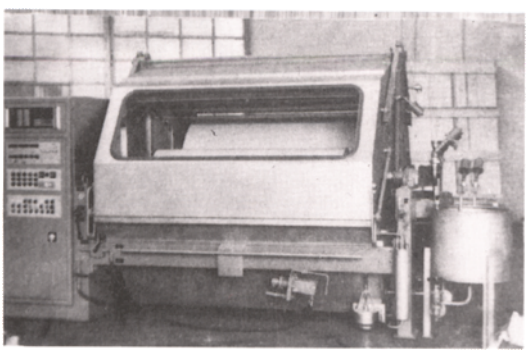


Figure 7-5. Automatic jigger offering maximum automation and enhanced quality (Courtesy of Mezzera-Kleinewefers S.p.A., Italy).

Now-a-days, old obsolete hydraulic jiggers are replaced by new models capable of working with constant fabric tension and adjustment ranging from 1 and 500 Nw/m with a maximum working speed up to 150 m/min. Where batched size is around 6000 m, jumbo jiggers and pressurised jumbo jiggers [Fig. 7-6(b)] can be used for bleaching in open-width form. In non-pressurised jumbo jiggers [Fig. 7-6(a)] prepa-

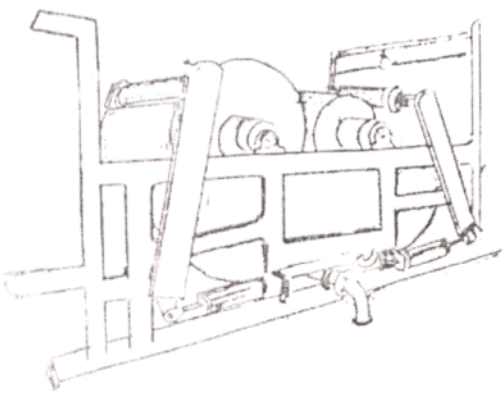


Figure 7-6(a). Open super Jumbo Jigger.

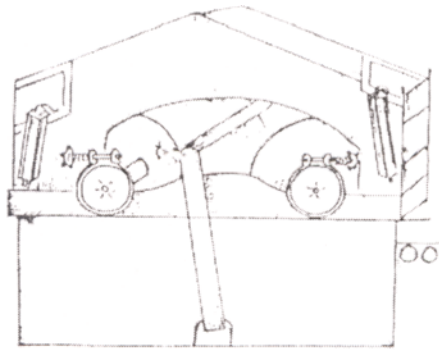


Figure 7-6(b). Pressurised Jigger.

ration of cotton fabric does not yield a satisfactory performance, though this is adequate for polyester/cotton blends.

Most knitted goods are batched process in winches which operate up to 140°C under pressure in an autoclave with usual fittings. The entire sequence of operations can be program controlled. In the modern winch machines (Fig. 7-7) the fabric runs through in 30 sec as against the 3-4 min otherwise required, and also penetration is excellent. The fabric is propelled by a winch in conjunction with bath circulation. Maximum liquor ratio is 10 : 1. Such batch processes are made continuous with the development of 'spiral' winches and 'spiral' jets [4-6]. Scouring and bleaching performance has been considerably improved with the novel rope washing machine (Fig 7-8), in which tubular fabric is moved through the machine

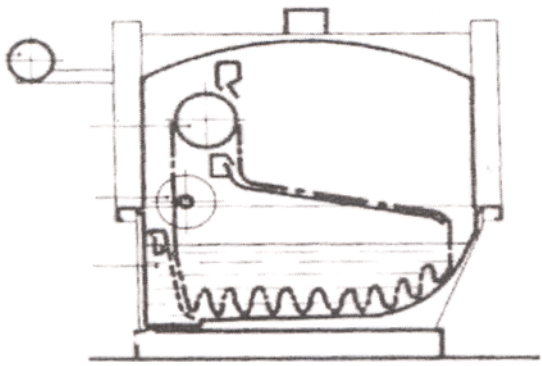


Figure 7-7. Winch machine.

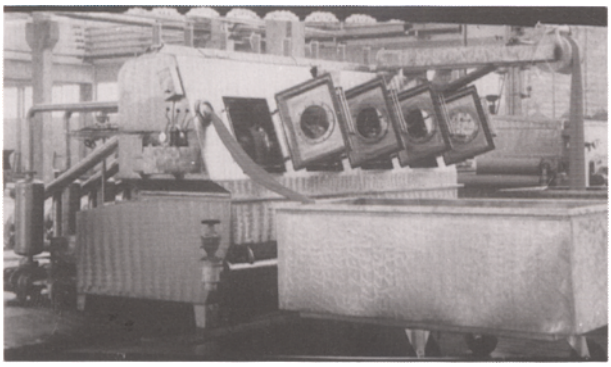
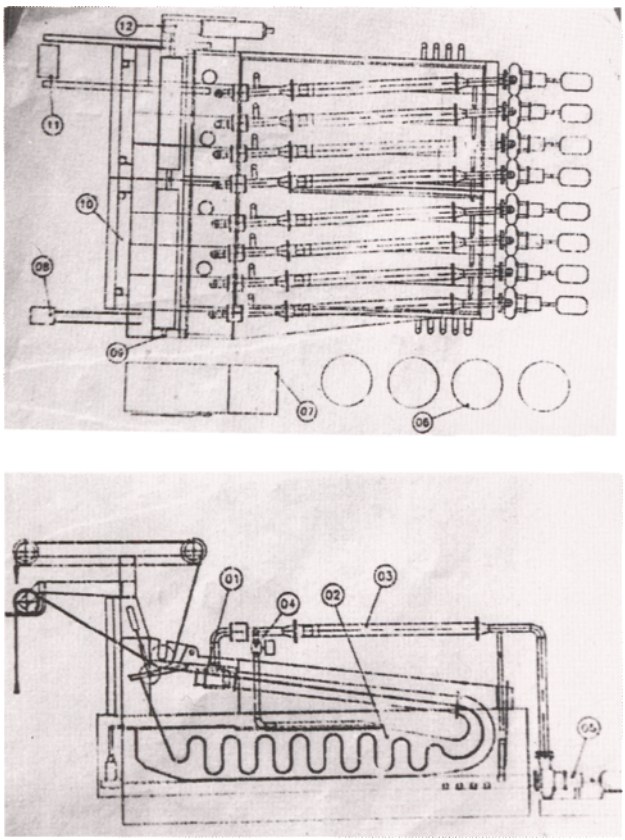


Figure 7-8. Novel counterflow rope treatment machine (Courtesy of MCS, S.p.A., Italy).

in a sprial fashion. The new ranges are primarily intended for prewashing, bleaching and afterwashing of knitted and woven fabrics in rope form. They can comprise 6 or 12 washing sections connected in series, a guide roller, a rotary pulsator fitted with several individual milling rollers, a heat recovery unit and a fabric feed and delivery system in a stainless steel housing. The washing sections each have an inlet and outlet and are interconnected by a flexible tube round the rotary pulsator. The fabric is drawn into the machine by means of a transport roller and fed to the individual washing sections. The latter are connected so that fresh water can be supplied to the entire machine on a counterflow principle. There is provision of metering the chemicals and the necessary textile chemicals can be added in controlled quantities and the correct processing temperature can be maintained for the individual washing sections. The process control technology stores all machine and process cycle data and makes overriding operating data logging units accessible via profibus.

Another one is spiral jet bleaching unit in which the woven and knitted fabrics can be pre-treated as shown in Fig. 7-9. In this machine, the fabric is moved in a spiral, in rope form, through the tube, using jets that lifted the fabric out of one compartment and deposited in the next [7-9].

A comparison of typical bleaching recipes of cotton fabric for batch bleaching in different equipment with hydrogen peroxide is summerised in Table 7.1. When making-up a bleaching bath, naturally the quality of cotton, degree of pre-treatment, liquor ratio, equipment used and temperature must all be taken into account.



1. Jet
2. Channel
3. Heat exchanger
4. By-pass
5. Circulation pump
6. Side tank
7. Control panel
8. Loading winch
9. Rolls
10. Doors
11. Unloading winch
12. Drive

Figure 7-9. Spiral jet bleaching unit (Courtesy of Küster KBR).

7.3 Semi-Continuous Bleaching Process Machineries

Both peroxide and sodium chlorite can be used for bleaching of cotton and polyester/cotton goods by semi-continuous open-width form. In the pad-batch (or pad-stack) process the padded goods are batched and then covered with plastic sheet to prevent evaporation of bleaching agent or gas and then allowed to lie for 24 h. In the pad-roll process (Fig. 7-10), the goods after padding with bleaching solution are then heated in a steam chest and rolled-up in a mobile batch chamber for 4-12 h. The chamber can be sealed so that no gas can evolve during bleaching.

TABLE 7.1
Comparison of Bleaching Recipes for Various Batch Processes

Form of material	Fibre, Stock	Yarn	Fabric	Fabric	Knitted fabric	Hosiery
Machine used	Circulating machine	Package m/c	Kier	Jig	Beck	Rotary
L:m	8:1	10:1	6:1	1:1	6.6:1	20:1
Amount of H_2O_2 (35%) (o.w.f.), %	3-4	5-10	0.5-1.5	1.17-2.34	3.5	1.4-2.2
On weight of solution (o.w.s.), %	0.37-0.5	0.5-1	0.8-0.25	-do-	0.53	0.7-1.1
Sodium silicate						
o.w.f., %	3.5	4.0	1-3	0.84-1.33	–	1.8
o.w.s., %	0.44	0.4	0.17-0.5	-do-	–	0.9
Sodium carbonate						
o.w.f., %	1.0	1.0	–	–	–	–
o.w.s., %	0.125	0.1	–	–	–	–
Trisodium phosphate (o.w.f.), %	–	–	0.25	–	–	–
Sodium hydroxide						
o.w.f., %	–	0.5	0.06	0.04	3.0	–
o.w.s., %	–	0.5	0.01	-do-	0.45	-

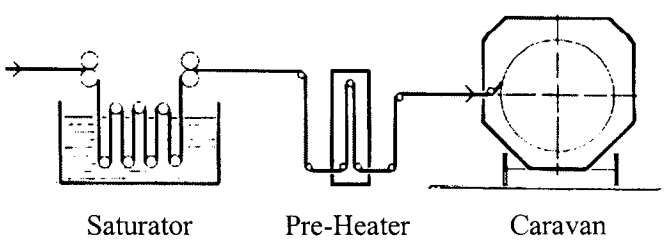


Figure 7-10. Pad-roll range.

Generally, the goods in open-width form are padded (100% expression) with either 4.3% H_2O_2 (35%) along with usual chemicals or with sodium chlorite (10 g/l) containing soda-ash (1 g/l) and wetting agent (3 g/l). It is not essential to use acid chlorite solutions in this process where effective liquor ratio is low and thus neutral

chlorite solutions are suitable. However, for a longer bleaching time, a small amount of soda-ash is useful to maintain the stability of the bath. The roll is rotated gently during its dwell period. The procedure is followed by a hot wash with 1% soda-ash in the case of H_2O_2 and antichlor treatment with bisulphite in the case of sodium chlorite and then soaping the goods in a bath at about 80°C. The pad-jig process is also used for the bleaching of textiles. These systems are simple to operate but have some disadvantages like impairment of the levelness of pre-treatment due to variation in dwell time and temperature from batch to batch. However, machineries with easy and automatic batching and unbatching systems are developed with special features for the various pre-treatment and bleaching plant.

7.4 Continuous Bleaching by J-Box Systems

The main purpose of the continuous bleaching system, whether in the rope form or in open-width form, is to reduce the time of bleaching and the cost of labour involved. Continuous bleaching in J-Box in rope form was started in the late in 1930s with the introduction of hydrogen peroxide [10, 11] and plant scale equipment had been built and a suitable procedure was developed [12]. In 1942, the unit used in the bleach range was called a J-Piler [13], but by 1952 the name had become J-Box and bleacher's dream of one-step process had finally come true [14].

The heart of the process is the J-Box storage unit and the shape is like the English letter 'J'. In rope bleaching the fabric is pulled together to form a somewhat circular mass, which is loose enough for penetration and resembles a large rope ; in open-width form the fabric is under tension and is flat and smooth. J-Boxes, whether open (Becco type) or closed (Du Pont type) can both be used for pre-treatment. In the Becco type (Fig. 7-11), the cloth is piled cold into the top and is heated as it passes down through the box by steam and passed through the perforated plates around the box, just below the top of the pile. Two heating positions are provided, the lower one for use when the box is being filled. In the Du Pont type of J-Box units (Fig. 7-12), the fabric passes through the long entering box which enables the fabric rope to reach the desired temperature (98°C) before piling down into the top of the J-Box itself. The internal surface of the entire J-Box is ground very smooth to avoid any friction on the moving cloth. The material of construction of J-Box should be high quality stainless steel for peroxide treatment, fibre glass reinforcement plastic for hypochlorite treatment, stainless steel with titanium component

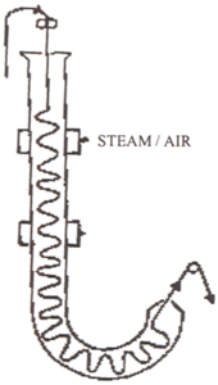


Figure 7-11. Opern-top J-Box system (Becco type).

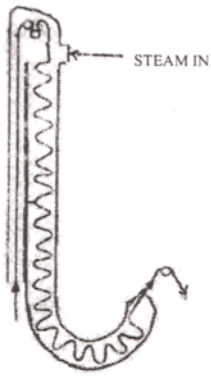


Figure 7-12. Closed-top J-Box system (Du-Pont type).

with sodium chlorite bleaching and special high molybdenum stainless steel for all treatments consisting of chlorite solutions. The J-Box may store up to 2500 yds of continuously moving goods.

Many modifications of the continuous bleaching sequences have been suggested [15]. Fig. 7-13 shows a typical three-stage (singe → desize → scour → bleach →

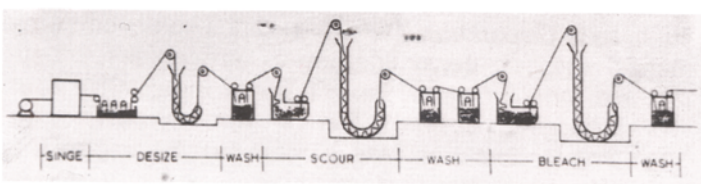


Figure 7-13. Operating sequence of a three-stage rope range.

wash) rope range sequence in a continuous J-Boxes bleaching plant. The energy conservation is a major factor in multi-stage processing and hence considerable importance has been given to the development of modified routes, first by combining scouring with desizing or bleaching. Fig. 7-14 shows the Du Pont two-stage (singe → desize → scour & bleach → wash) bleaching range. In this range the cloth in rope form is saturated with 2.5-4% caustic soda solution at 30°C and squeezed to 100% pick-up. The cloth is then rapidly heated to 100°C and piled in J-Box for about 1 h. The goods are then saturated with 0.5-1 volume peroxide solution of pH 10.6 to 10.8 in presence of sodium silicate (1-1.6%). The fabric after squeezing is

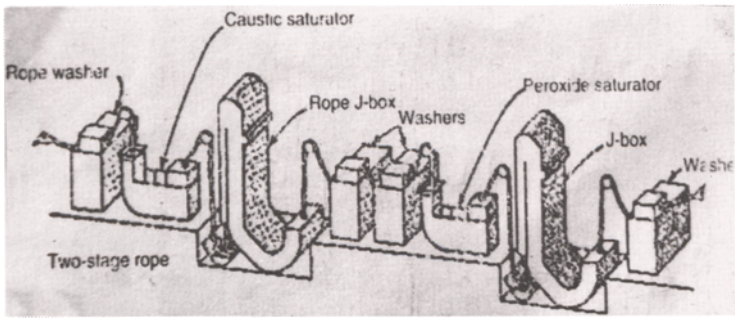


Figure 7-14. Du Pont continuous two-stage bleaching range [16].

once again heated to 100°C in the heater tube and stored for 1 h in J-Box. Goods containing dyed yarn are heated at slightly lower temperature. Finally, the goods are washed in a rope washer. Bleaching with hypochlorite can also be done using J-Box system with saturator. The fabric after saturation with hypochlorite solution containing 0.75 g/l non-ionic wetting agent and 0.25 g/l of 15% chemic at room temperature are piled into J-Box for 15-40 min at 60-100°C and then washed. The two-stage plant with a speed of about 100 yds/min requires treatment of about 2 h and also proper time and pH is required to be maintained to control the rate of reaction which may damage the cloth. Thus, in one-stage continuous rope bleaching ranges (Fig. 7-15), one more stage is eliminated and the goods are caustic treated

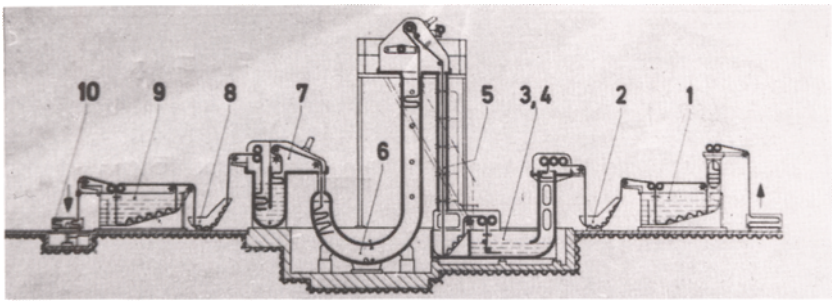


Figure 7-15. One-stage continuous rope bleaching range using J-Box (Courtesy of Friedrichsfeld GmbH, Germany).

and bleached in one bath. The sodium chlorite method is often the only feasible

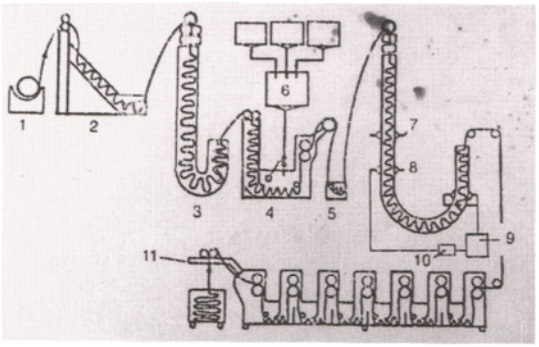
procedure for bleaching blends of cotton and synthetic fibres by one stage system. The wetting and rinsing unit (1) is made up of three compartments, each with its own squeezing unit. Before entering the next stage the goods are deposited on a chute (2) coated with PTFE in the impregnating machine (3), liquor uptake is kept constant at about 30% by means of squeeze rollers. The impregnating liquor is circulated and filtered continuously, and the concentration of chemicals is measured and topped up automatically (4). In the heating up and shrinkage unit (5) the goods are heated to 98°C by spraying with saturated steam and piled into the J-Box (6). After exiting from the J-Box, the goods are conveyed loosely and without creasing to a water and neutralising bath by a winch forming part of the washing and neutralising section (7). The rope is squeezed only when cooled and then deposited in another intermediate store (8). The following section of the range is used to apply fluorescent whitening agents and all compartments are fitted with their own squeeze units. On leaving the range, the rope is piled into a trolley (10) for loading into a centrifuge. The concentrations of bleaching bath are given in Table 7.2. If hydrogen peroxide is used as a bleaching agent, the fabric is saturated with a

TABLE 7.2
Recipe for One-Stage Bleaching with Sodium Chlorite

Additives	Cotton	Polynosic/Cotton	Polyester/Cotton
Sodium chlorite (80%), g/l	12-20	12-15	10-12
Bleaching auxiliary, g/l	5	5	5
pH (with formic acid)	3.8	3.8	4.0
J-Box dwell period, min	90-105	60	60

solution containing H_2O_2, wetting agent, sodium silicate, caustic soda, softeners and whitening agents. The process, operated by two men at up to 200 yds/min can turn out about 10,000 yds of fabric an hour.

In the case of knitted goods, peroxide bleaching on either FMC wet bottom J-Box (Fig. 7-16) or on the Gaston County DuBec system (Fig. 7-17) are suitable. Such ranges (Fig 7-16) consist of an unwind cradle , a sewing scray , a dry storage J-Box, holding about 900 kg of tubular fabric, a saturator, a bleach J-Box and a washer. The FMC system has a wet bottom created by having a 540 litre heel tank of liquor, which is made by dropping 270 litre of the saturator liquor to it, making



1. Cradle
2. Sewing scary
3. Dry J-Box
4. Saturator
5. Wet scray
6. Mix tank
7. Air/steam mixture
8. Wet J-Box
9. Heel tank
10. Pump
11. In-line washer

Figure 7-16. Wet bottom J-Box.

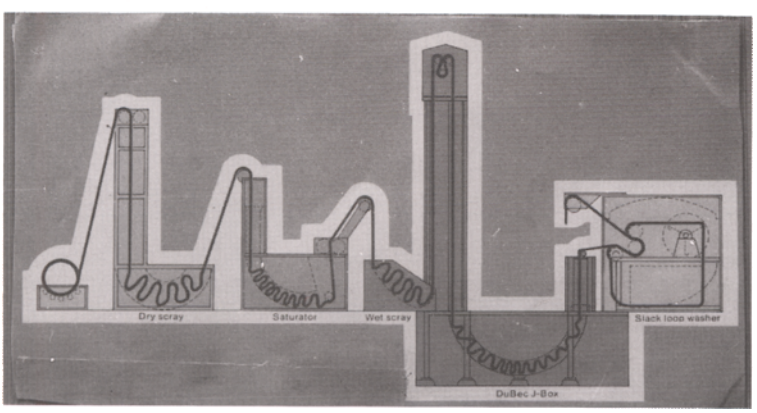


Figure 7-17. The Gaston County DuBec system.

up to 540 litre with water and circulating the liquor by means of pump inside the J-Box. In contrast, in the DuBec system (Fig. 7-17), the bleaching J-Box has a PTFE lining and the washer is a spiral rope washer. This dry storage J-Box is run 20% faster than the wet J-Box and any variation in load in the system is accomodated

with compensating or balanced scrays. The DuBec range combines the best features of two well-known processes : the Du Pont single stage method and the Becco Wet heel J-Box method. Capacity of the DuBec's J-Box is 3,000 pounds. Range speeds from 50 to 150 yds /min with a production averages of about 2000 lbs/h. The J-Box recipes for the two types are compared in Table 7.3. Kolmer describes

TABLE 7.3

J-Box Recipes (100% Pick-up , Steam 90 Minutes at 90°C)

Chemical	FMC	Du Pont
Wetting agent (g/l)	5	5
DTPA, 40% (g/l)	1	1
Sodium silicate, 79°Tw (g/l)	10-20	10-20
Sodium hydroxide, 100% (g/l)	7-10	4-7
H_2O_2, 35% (ml/l)	45	45

a development of the Galaxy which uses J-Boxes for storage and washes the fabric as a flattened ''open-width' tube. Each section of the washer (the Tubolavar) consists of a small J-Box in which the flattened tubes are spray washed. On emerging from the J-Box the tube is inflated, to alter the crease location, and nipped, before going into the next section.

The follwing are the advantages and disadvantages of continuous rope bleaching in J-Box :-

Advantages :

i) J-Box offers economy in space, time, water, steam, and chemicals.

ii) Material to liquor ratio is 1:1. Minimum electrical power is required with advantage of variable speed.

iii) Uniform and reproducible absorbancy with good whiteness of the goods is obtained.

iv) Minimum handling damage with less loss of tensile strength is observed.

v) Fabrics of different width, weight and densities can be run through the plant without alteration or adjustment, except for speed and dwell time at each stage of the process.

Disadvantages :

i) J-Box system is economical only if the production target is big enough to

feed the J-plant by about 2 lacs linear meter per day . However, smaller units have also been developed for handling 2 to 3 tons of cloth per day.

ii) Pin holes-catalytic action of iron coming from steam pipes is observed sometimes on the bleached fabric.

iii) Some silicates from the wet cloth containing bleaching solution may be deposited on the heated walls of the J-Box. The cloth sliding down the J-Box rubs against these silicate scales that lead to abrasion marks which shows up in subsequent dyeing.

iv) Due to great weight of the cloth, the lower portion of the fabric is subjected to great pressure, which may be up to 2 tons in larger J-Boxes. This may lead to severe rope marks in certain compact and heavier varieties of cloth. Continuous treatments in rope form are also likely to cause lengthwise crease marks.

7.5 Continuous Open-Width Bleaching Equipment

Some fabrics such as heavy drill, corded fabrics, satins and other sensitive weaves are liable to be damaged if they are bleached in rope form. Creaseless running and low cloth tension are also important factors for blends with synthetics. These necessitated the development of new types of open-width bleaching machineries for fabrics. Generally, a continuous open-width bleaching range consists of 2 to 3 units with maximum speed of 100 to150 m/min and reaction time of about 2-7 min per treatment unit. Different types of steamers can be combined in various ways to form a large number of different ranges, to cater for a broad spectrum of requirements in terms of productivity, fabric qualities and subsequent treatment [17,18]. It is difficult to explain various fabric paths in different types of steamers and steaming operations, however Table 7.4 mentions some of them.

For chemical pre-treatment of woven cotton and polyester/cotton blended fabrics Benninger has developed the ''Ben Bleach system'' for desizing, scouring and bleaching in one operation i.e, ''Ben-Injecta'' for desizing, ''Ben-Impacta'' for impregnation , ''Ben-steam'' for steaming and ''Ben-Extracta'' for washing. Following desizing in the ''Ben-Injecta/Ben-Extracta'' section, the fabric is saturated and loaded with bleaching solutions in the ''Ben-Impacta'' for high degree of penetration and high fabric -liquor interchange. Ben-Impacta (Fig. 7-18) is in its geometry like an upside down Injecta. The fabric passes through two long narrow slots , in

TABLE 7.4
Different Open-Width Continuous Bleaching Steamers [19]

Manufacturer	Name	Features
Artos	Continuous open-width steaming machines with ARTOX "Rapid Relax" U-box	(a) Capacity-400 kg/m of fabric width. (b) Running speed up to 100m/min.
Air Industry	Roll-a-Belt combination steamer	(a) Tight-strand section-30 m. (b) Conveyer capacity-100 kg of fabric per meter of width.
Brugmann Estafette	Conveyer steamer	Capacity-3000 m.
Benninger	Type DS combination steamer	(a) Tight-strand section 50,100 or 150 m. (b) Roller-bed-Minimum 7 min dwell at up to 150 m/min.
Goller	Conveyer steamer	(a) Capacity-300 to 400 m fabric per meter of conveyer. (b) A range of conveyer length is available.
Kleinewefer	Combi-steamer box	(a) Tight-strand section 40 or 80 m. (b) Roller-bed-400 to 600 kg of fabric per meter of fabric width. (c) Reaction time – 10 to 15 min.
Mather & Platt	Vaporloc Roller-bed pressure steamer	(a) Dwell time – 2 to 3 min at 100 m/min. (b) Pressure – up to 30 p.s.i. (c) Temperature – up to 134°C.

which the impregnating liquor circulates. Impregnation at 40°C is normal with perox-

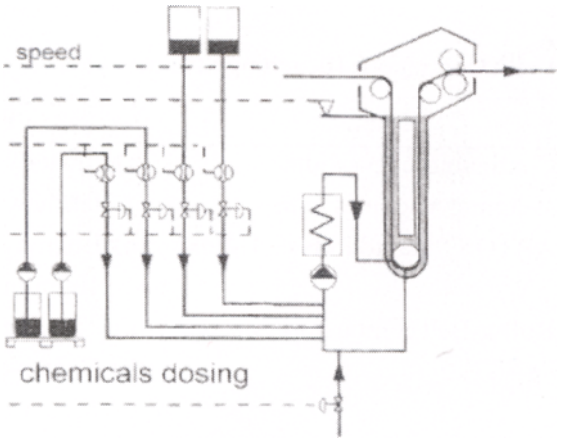


Figure 7-18. Impregnating unit (Ben-Impacta) for pre-treatment (Courtesy of Benninger AG).

ide, but with good stabiliser the temperature can be raised even up to 60°C. The advantages of this type of impregnating unit are : small liquor volume, intensive fabric-liquor interchange over a long reaction zone, variable liquor application, low consumption of chemicals, even saturation and loading, small space requirement, no streakiness or creases and self- regulation of liquor concentration. Monitering of the liquor concentration in the impregnation unit is nonessential, except at material changeover.

7.5.1 Steamers without plaited storage

Figures 7-19 to 7-23 show the various fabric paths in continuous open-width bleaching equipment with steamer systems based on positive fabric guidence without plaited storage. The main features of this system are : very much suitable for crease susceptible fabric, fair degree of whiteness, fabric with good absorbancy, less chances of fabric degradation and fair mote removal.

7.5.2 Conveyer steamer without pre-steeping zone

Conveyer steamer was first designed by Mathieson Alkali Corporation in USA [20]. Figs. 7-24 to 7-28 show the line diagrams of such conveyer steamer systems based on plaited fabric storage without pre-steeping zone. During the early 60s steamers were developed to treat the cloth in open-width form for very short steaming time (90-120 secs) at 120-130°C under pressure for continuous scouring

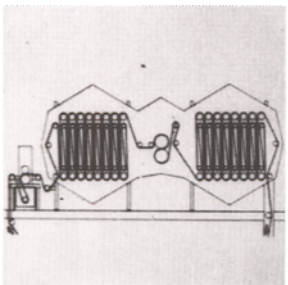


Fig. 7-19

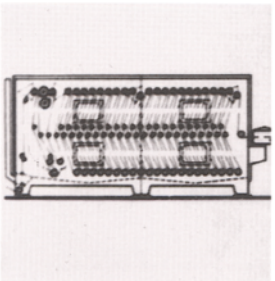


Fig. 7-20

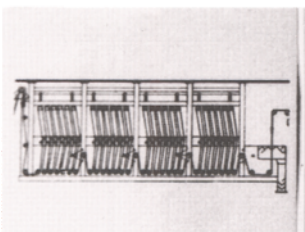


Fig. 7-21

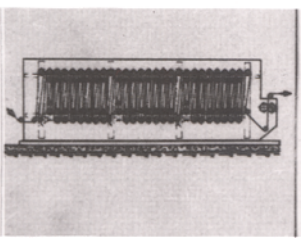


Fig. 7-22

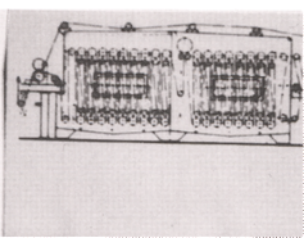


Fig. 7-23

Figures 7-19 to 7-23. Steamers without plaited storage. Figure 7-19. Babcock KG ; Figure 7-20. Benninger AG ; Figure 7-21. Klieinewefers GmbH ; Figure 7-22. E. Kusters ; Figure 7-23. Cmez S.p.A.

and peroxide bleaching [21]. The main difference between the Kleinewefers (Pressurlok) and Mather & Platt (Vaporloc) systems is the means of fabric transport. Klienewefers uses a tight-strand design while Mather & Platt uses a roller-bed system. The latter allow greater flexibility in running speed [22]. The rollers are positively driven which pushes the fabric forward. The time for storage varies from 7 to 15 min or more. The entire set of rollers is placed in a steaming chamber. The fabric content is about 6000 m at a production speed of about 100 m/min. The fabric is sensitive to creasing owing to the tightly compressed cloth piles within the steamer. Tight-strand steamers with a reaction time of 1 to 2 min and without any plaiting or batching avoid above difficulties. Howerer, these units are not suitable for fabric containing seed husks which are, even otherwise difficult to remove [23].

In the multilayer conveyer steamer (Fig. 7-29) the cloth is bleached by

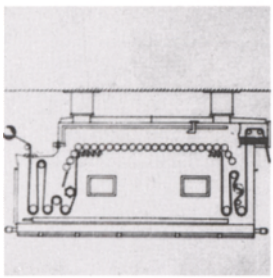


Fig. 7-24

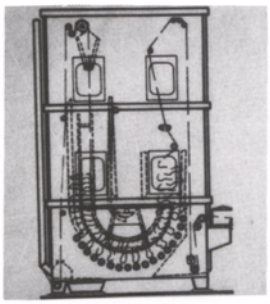


Fig. 7-25

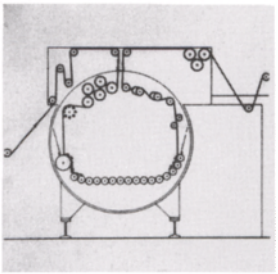


Fig. 7-26

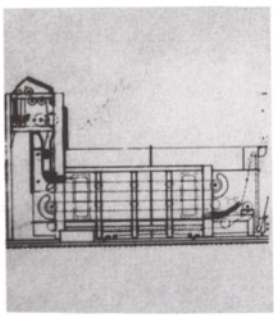


Fig. 7-27

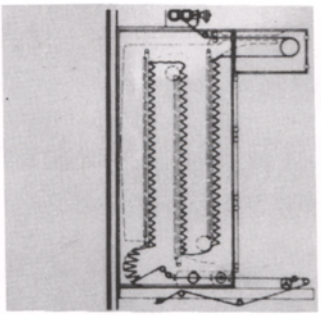


Fig. 7-28

Figures 7-24 to 7-28. Steamers with plaited fabric storage without pre-steeping zone. Figure 7-24. Babcock KG ; Figure 7-25. Sir James Farmer Norton ; Figure 7-26. Kleinewefers GmbH ; Figure 7-27. Mather & Platt Ltd ; Figure 7-28. K. Menzel.

impregnating with peroxide solution, and then drawn into a steamer where it is plaited on to a slowly moving conveyer by the action of steam jets. The time of steaming can be varied by altering the speed of the conveyer. Speeds of 60 to 100 yds/min are claimed. The fabric is then withdrawn from the conveyer at the exit end of the steamer and washed in an open soaping range.

7.5.3 Conveyer steamer with pre-steeping zone

The various fabric paths in continuous open-width bleaching equipment with a conveyer system based on plaited fabric storage with pre-steeping zone are outlined in Figs. 7-30 to 7-33. The salient features of this system are : not much suit-

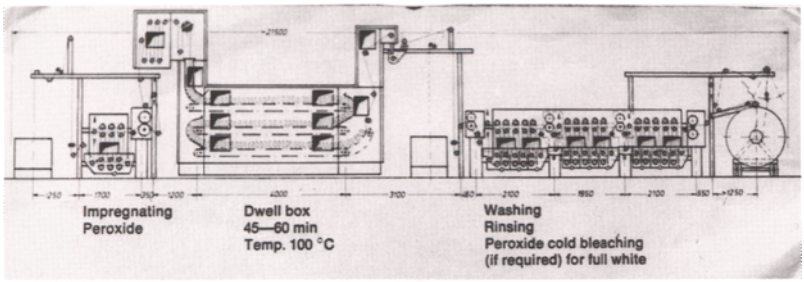


Figure 7-29. Continuous open width bleaching range (Courtesy of Maschinenfabrik Max Goller).

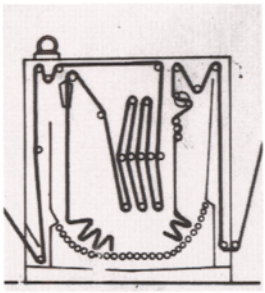


Fig. 7-30

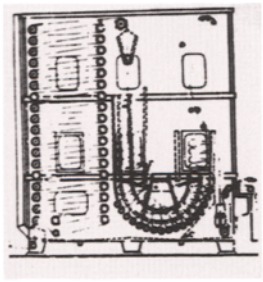


Fig. 7-31

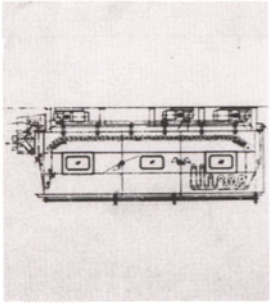


Fig. 7-32

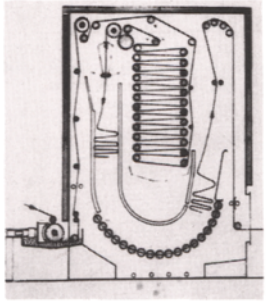


Fig. 7-33

Figures 7-30 to 7-33. Conveyer steamers with pre-steeping zone. Figure 7-30. Babcock KG ; Figure 7-31. Sir James Farmer Norton ; Figure 7-32. Kleinewefers GmbH ; Figure 7-33. Mather & Platt Ltd.

able for crease sensitive fabrics, fair degree of whiteness, better absorbancy, low DP values and fair seed husk removal. Such steamers also have tight-strand section of 40-80 m with a roller-bed of about 400-600 kg of fabric per meter of fabric width with a reaction time of 10 to 15 minutes.

7.5.4 Pressureless or combi-steamers

The combi-steamers are associated with horizontally laid out positively driven roller-bed and a heating-up and reaction zone which is judiciously combined. The tight-strand fabric transport has the object of ensuring uniform swelling of cellulosic fibres. Here the fabric is subjected to lengthwise tension and the rollers simultaneously exert an ironing effect which levels out internal tension within the fabric during the treatment. The plaiting down system on the conveyer belt or roller-bed offers flexibility as far as the reaction times are concerned, and allows production speeds up to 150 m/min. Some typical combination steamers are shown in Figs. 7-34 to 7-37. One-step continuous bleaching range with maximum impregna-

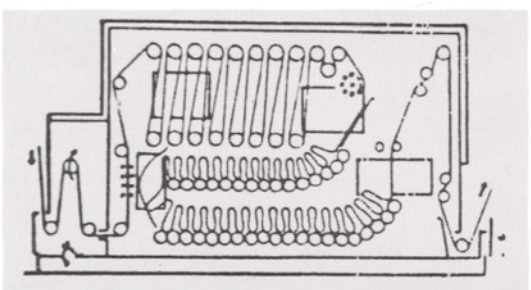


Figure 7-34. Benninger type DR combination steamer.

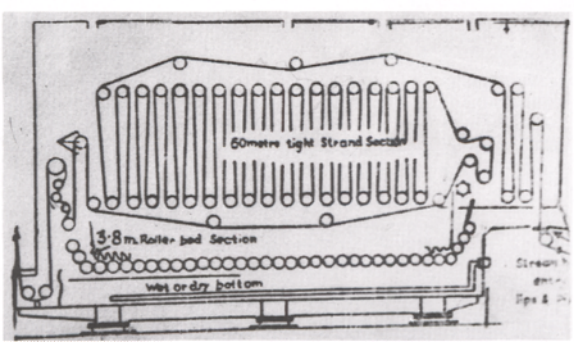


Figure 7-35. Farmer Norton combination steamer.

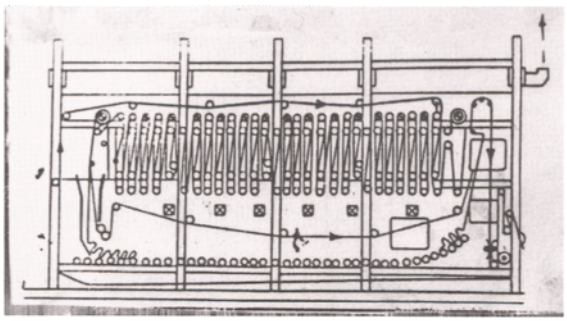


Figure 7-36. Kleinewefers combination steamer.

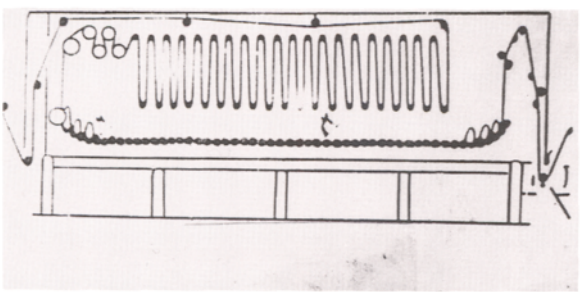


Figure 7-37. Mather & Platt combination steamer.

tion using combi-steamer is shown in Fig. 7-38. The first step of the unit for maxi-

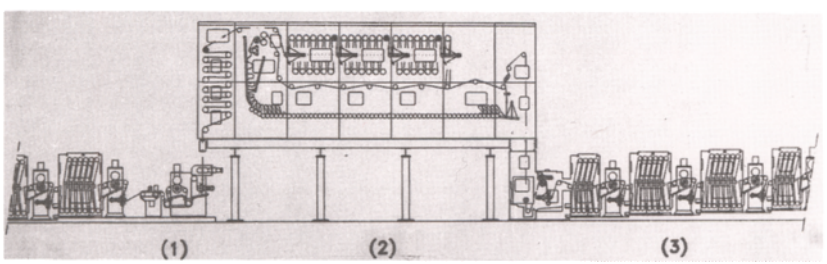


Figure 7-38. One-step continuous bleaching range using combi-steamer (Courtesy of Exclusivas TEPA S.A.).

mum impregnation (1) is a combination of spraying and vacuum extraction by

which the fabric attains a previous residual moisture of 35-55%. The fabric is then passed through Pad-Steam bleaching steamer, ''combi'' type (2) with upper fabric passage between rollers and lower roller-bed for long batching. The washing units (3) at the end of the steamer completes the range.

In all types of combi-steamers the fabric enters through an air-lock which is followed by heating-up zone at 100°C for about 15-20 min. From the extreme end of the steamer the fabric is carefully led out of the machine through the delivery air-lock. The tight-strand steamer section of the combi-steamer is assembled on a modular principle. Each module generally has a fabric content of 50 meters. The problem of crease marking is also eliminated in all types of fabrics.

7.5.5 Continuous submerged bleaching system

The continuous submerged bleaching process is also known under the designation PKS (peroxide continuous rapid bleach) process [24]. The horizontal storage chamber and the continuous PKS range are shown in Figs. 7-39 and 7-40 respec-

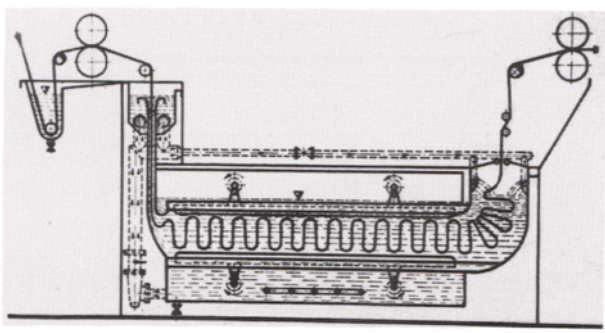


Figure 7-39. The horizontal PKS storage chamber.

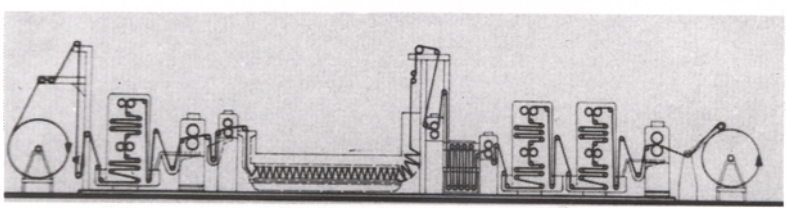


Figure 7-40. Continuous, submerged, open-width PKS range.

tively. Ahead of the store (Fig. 7-39) is an impregnating padder to apply various

liquors required. After padding, the fabric is run over a guide roller into the entry slot and passes through a hot aqueous bleach liquor which allows bleaching for 15-20 min at 95-98°C. The liquor which is continuously circulating and overflowing in the pre-chamber, sweeps the fabric gently and without tension into the horizontal storage chamber, which is closed at top and bottom by a special conveyer grid that is driven by means of cam-shaft. At each revolution of the shaft the fabric, which is plaited down in folds, advances a given distance. This conveyer grid is fitted above and below the storage chamber to enable all kinds of goods to be treated. Part of the circulated liquor is fed to the goods running out so as to prevent creases owing to over-rapid cooling in the plaited state. Because the dwell occurs under the bleach liquor surface, the process is also referred to as ''under liquor bleach''. Bayer followed their original reports with others [25-28]. A recipe for reservior is given in Table 7.5 and the economy of the process is reviewed [29].

TABLE 7.5
PKS Bleaching Recipes from Bayer and Menzel [30]

Chemical	Bayer	Menzel
Organic stabiliser (g/l)	6	5
Sodium silicate, 79°Tw (g/l)	7	6
Wetting agent (g/l)	–	1
Detergent (g/l)	2	1
Sodium hydroxide (solid, g/l)	4	4
H_2O_2, 35% (ml/l)	20	10-17
Minimum dwell time (min)	10-15	20-40
Temperature (°C)	95	85

The fabric leaves the store via a regulator and a pair of squeeze rollers, then runs to a wash unit and bleaching can be made into a continuous process (Fig. 7-40). The use of tower washing units, which work according to a pure counter current principle can save water during washing. Küsters [28] additionally recommended a steaming stage for the fabric emerging from the reservior, before washing and drying. In 1986, Heetjans [31] and Witte [32] announced the entry of Thies into the PKS market. It is claimed to produce 400-500 kg/h at a running speed of 40 m/min.

This machine is very good for the bleaching of all types of woven and knitted

fabrics of natural and synthetic fibres and their blends, as well as for the bleaching of coloured woven goods as very little tension is applied. Advantages claimed for this process are : minimum chemical damage, short bleaching time at an average liquor ratio of 15 : 1, low machinery costs and good shrinkage values. The main disadvantage is the bleaching chemical cost.

7.6 Washing Equipment

Washing is called for at all stages of textile processing, in pre-treatment, after dyeing and printing, after resin finishing etc. The aim is to remove impurities, size, softening agents, lye, degradation product, residues of auxiliaries, unfixed dye, thickening agents used in printing etc. All these substances must be water soluble or, with the aid of added chemicals, emulsifiable. Fig. 7-41 shows the situation

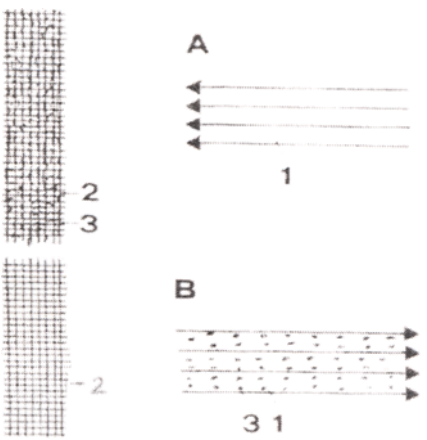


Figure 7-41. Situation before and after washing [32].
A – Actual state ; B – Desired state ;
1 – Liquor, 2 – Fabric, 3 – Extraneous matter.

before and after washing. In general the washing process can be divided into three phases : loosening of extraneous matter, transfer of extraneous matter and removal of extraneous matter. In the first phase the extraneous matter must swell and loosen as quickly as possible. In the second phase the matter is transported by diffusion to the layer of liquor flowing next to the surface of the textiles. In the third phase the extraneous matter is carried away by the flow of the washing liquor and the movement of the goods. In actual practice all the three phases are found to overlap. Washing is characterised by maximum efficiency combined with significant sav-

ings in water, electricity, heat and chemicals. The efficiency of washing action is promoted by mechanical movement, liquor flowing counter to the run of the goods, efficient drives and controls, suitable fabric guides etc. Taking all factors into consideration, the best average consumption for modern machines is of the order of about 4-6 kg water/kg goods.

The fabric can be washed in rope and open-width form. Pot eyes, made of porcelain or stainless steel, are used for drawing the fabric in the rope form from one step to the other. Open-width washing gives more uniform results than does the rope form. Furthermore, delicate fabric and texturised woven and knitted fabrics need a very soft treatment during scouring and washing. Both the form, that is the rope and open-width washing can be done in batchwise or continuous fashion. Manufacturers all over the world have marketed and established their rope and open-width washing machineries and it is difficult to describe all of them, however, a few of them designed on different principles are described.

7.6.1 Rope washing machines

The line diagram of tight rope washing machine is given in Fig. 7-42. The machine

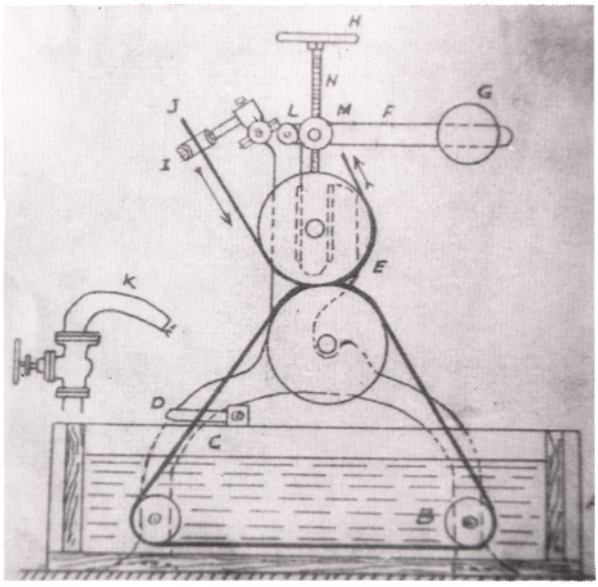


Figure 7-42. Tight rope washing machine.

consists of two cast iron side frames and a pair of heavy and wide squeezing bowls (E). The bowl is driven positively while the upper one rotates by frictional grippage. Two ropes of cloth are generally washed at a time. One rope (J) enters through a pot eye (I), passes into the nip of the squeezing bowls (E), enters the water in the trough (A), passes under the trough guide rollers (B) and between the pegs (D) and then passes into the nip again. Pressure is applied by simple lever (F) and weight (G). H is the handwheel, L is fulcrum, M is internally threaded block and N is threaded bar. The passage of both the ropes through the machine continues in a spiral fashion to the centre where both the ropes finally leave the machine. The tank usually receives fresh water (K). The out put of the machine is about 250 to 350 m/ min. Due to considerable tension on the fabric, this type of machine is utilised in the case of medium or heavy fabrics.

In the slack rope washing machine (Fig. 7-43), the fabric rope is allowed to drop

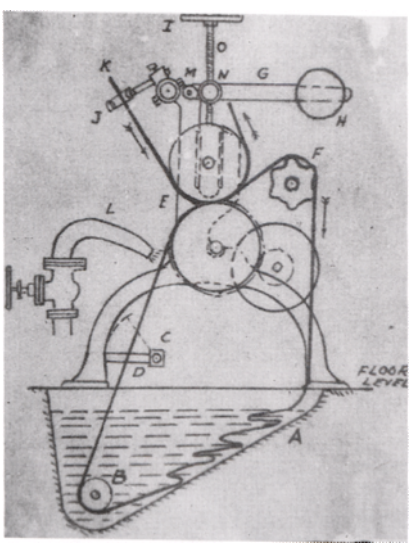


Figure 7-43. Slack rope washing machine.

down the machine tank and is maintained there for a certain amount of time in a relaxed form. The fabric rope (K) enters the pot eye (I), passes between the squeezing bowls (E), over the winch (F) and then into the deep trough (A) with a sloping base down which the cloth falls in a slack and slightly plaited state. The fabric then passes under a wooden guide roller (B), then upward between the pegs (D). A peg

rail (C) is fitted to prevent the entanglement of ropes and then passes through the nip again. Thus, the fabric takes a spiral path. The production is about 150 m/min with an water consumption of about 6 to 8 litres/kg of cloth.

Another type, namely square beater washing machine is used mainly for washing printed goods. The beater revolves in a direction opposite to that of the cloth so that it receives a flapping motion which beats out loose particles adhering to the fabric.

The high speed rope washing machine (Fig. 7-44) offers efficient processing

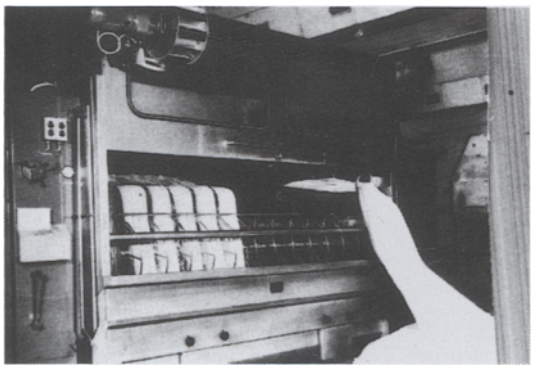


Figure 7-44. High speed rope washer (Courtesy of Hemmer, Germany).

without cumbersome threading up. In this type the liquor trough is divided into two or more parts or sections by means of clearly rounded removable partitions. The fabric is fed into the machine from a suitably positioned pot eye and first washed in one side of the partition and then on the other side and so on. The wash liquor is arranged to flow in a direction opposite to the fabric rope. The fabric rope passes alternatively under a stainless steel bottom roller and a loose stainless steel bobbins on the top shaft. At the end of the washing section, the fabric passes through pneumatically loaded squeeze device located at the top. The machine is totally enclosed and fitted with sliding glass panels. The fabric is guided through the machine in such a manner that lowest possible tension is exerted on the fabric. The high performance rope washing machines may be employed both as a single unit or in continuous operation with similar machine with a working speed of up to 200 to 250 m/min.

After rope washing, the fabric is passed through the rope squeezing machine

(Fig. 7-45) which allows the fabric to have reasonably consistant water content.

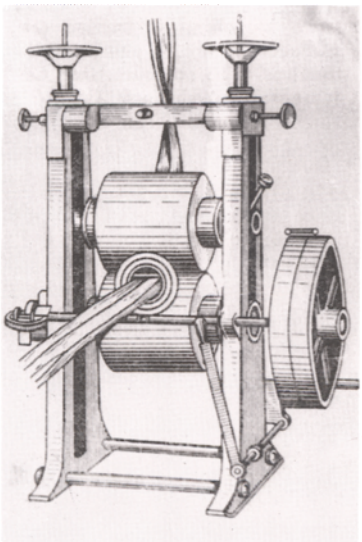


Figure 7-45. Rope squeezing machine.

The fabric is then piled uniformly in the storage pits or glazed tile lined piling pits. The bin pilers (Fig. 7-46) drop the fabric on pits. The pilers are mounted on rails

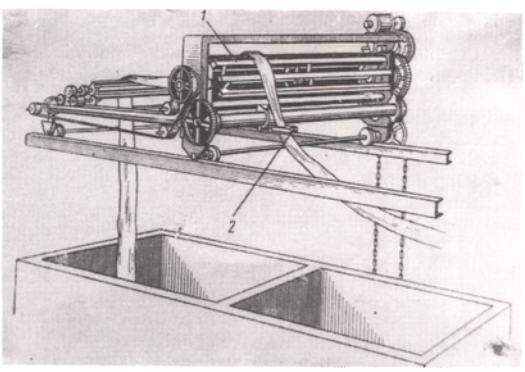


Figure 7-46. A carriage piler for fabrics.

which move forward or backward in one direction over the rope of pits. Then the fabric is opened out from rope to open width form with the help of an opener (Fig. 7-47) or scutcher (Fig. 7-48). Rope expanders or rope openers are usually fitted

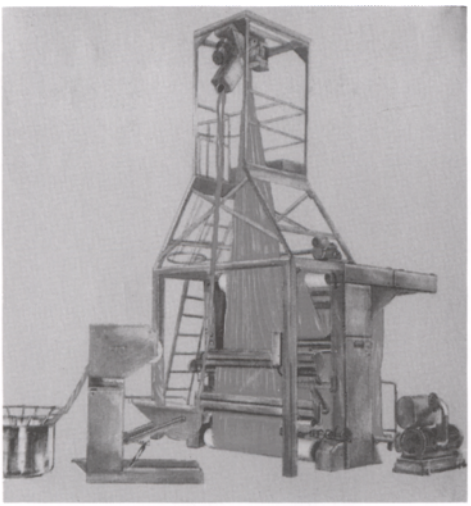


Figure 7-47. Rope opening line for woven and knitted goods (Courtesy of Bianco, Italy).

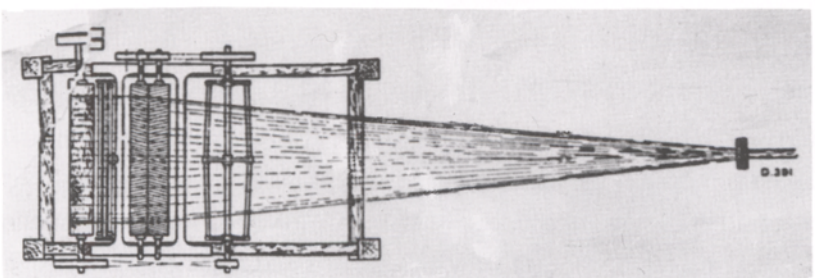


Figure 7-48. Diagram of scutcher for opening cloth from rope form.

behind the rope washing machines. In the case of rope openers without scutcher, the fabric ropes are opened with the aid of cloth guiders and sometimes additional scroll rollers are used. The scutcher usually consists of a revolving brass beater, two scroll rollers, a pivoted guiding device and draw rollers. The two scroll rollers are geared together by means of spur wheels and are driven in pairs in the counter direction to the cloth which passes between them. The beater is also driven in the opposite direction of the cloth. For both the systems, an adequate unhindered feeding distance of at least 6-8 m is necessary to ensure that the fabric rope can be sufficiently detwisted. Occasionally rope detwisters are fitted between the last rope guide ring or wheel and the rope opener. Scanners sense the direction of twist of the rope and

appropriate signal is given to the controll element. Sometimes ''Whittler'' rope openers are fitted with the scutcher and the particularly good opening effect is due to the fact that the fabric rope is subjected to a rhythmical undulating movement of the two, three, or four part scutcher, which causes the rope to loosen up and decrease, and existing twist is eliminated. The essence of the ''Whittler'' rope opener is, however, the regulator (Fig. 7-49), which keeps the open-width fabric on centre

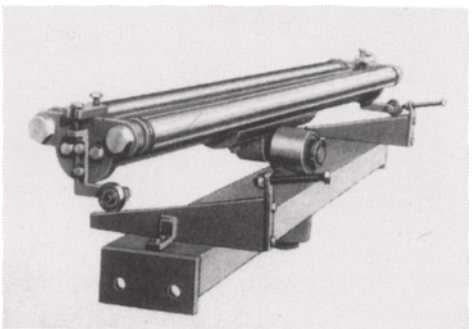


Figure 7-49. Whittler rope opener regulato.

and guides it to further processing operations. Machine speeds from 120-180 m/min can be achieved if the regulator can fulfil its task in every respect. With rope openers of other designs machine speeds of only 40-60 m/min can be attained.

After leaving the opener, the cloth is then passed through hot water in water

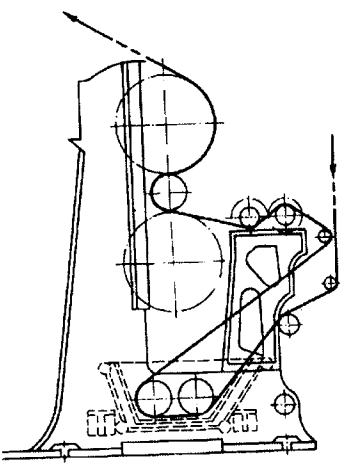


Figure 7-50. Water mangle.

mangle (Fig. 7-50). The water mangle removes last traces of dirt, excess water, rope marks and flattens the fabric. A water mangle has 3 to 6 bowls, but sometimes even 8. The mangle is equipped with an entry scaffold, an adjustable tensioner, two scroll rolls and automatic cloth guiders suitable for wet fabrics at the entry side and a piling winch at the delivery side. The cloth speed ranges from 100 to 200 m/min depending upon the type of the fabric. The water mangle can be synchronised with the dryer, which usually follows the water mangling process.

7.6.2 Open-width washing machines

Of the many open-width washing machine concepts, the three drum washing machines, namely perforated oscillating drums, perforated drums with oscillating central units (Rotowa), perforated rotating drums and spraying arrangements are very popular in the batch form. The more common type of open-width continuous washing machine is open soaper. Modification followed modification in which the manual operations are progressively mechanised, the aim being to co-ordinate the individual steps. Different effective and inexpensive systems for washing even very sensitive woven and knited goods are available.

In the suction drum washing machine (Fig. 7-51) the scouring liquor is drawn

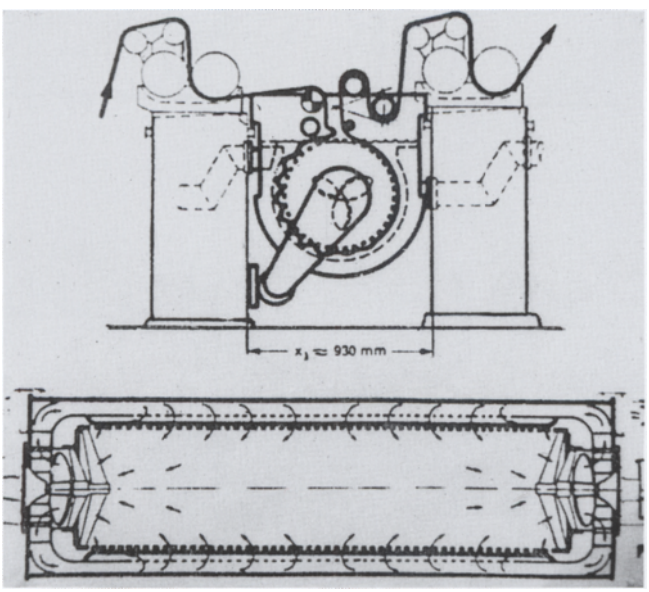


Figure 7-51. Suction drum washer (Courtesy of Artos, Germany).

through the perforations of the drums, and the fabric interstices, thus effectively removing the water soluble material. Suction drum washers usually have two or more bowls driven at some synchronous speed, the fabric covering about 80% of

Fig. 7-52.

Fig. 7-53.

Fig. 7-54.

Fig. 7-55.

Fig. 7-56.

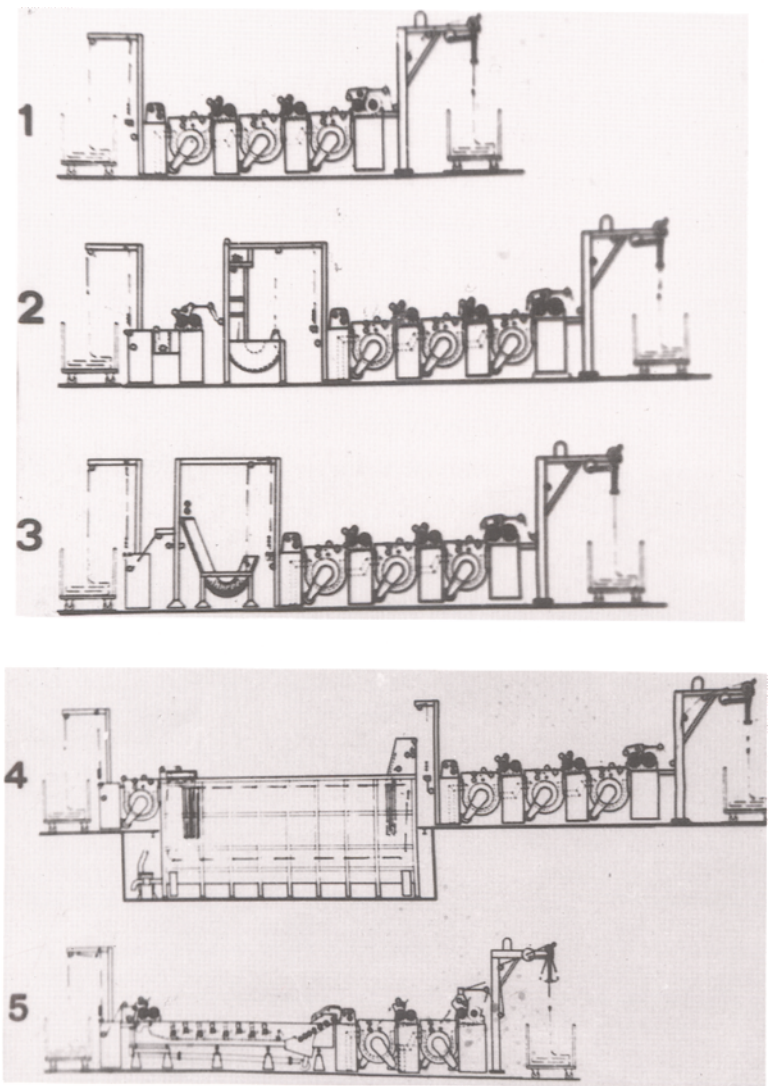


Figure 7-52 to 7-56. Typical installations of various suction drum washing ranges [32].

the circumference of the drums. Liquor is pumped out at the end of the drum (Fig. 7-51) and is recirculated through the washer. Edge uncurlers are fitted before the first drum on the machine. A simple nip may be fitted between the successive bowls. The function of the nip is mainly to advance the fabric into the unit rather than to remove the surplus liquor. The suction drum washing machine (Fig. 7-52) treats the goods under low tension with a good convective rinsing action. The same machine can be used in tendem with impregnation squeeze rollers (Fig. 7-53), with impregnation trough (Fig. 7-54), with festoon boiling off range followed by rinsing tanks (Fig. 7-55), and special washing and bulking machine followed by rinsing tanks (Fig. 7-56).

In the Rotowa washing machine (Fig. 7-57) the fabric is wound on to the perfo-

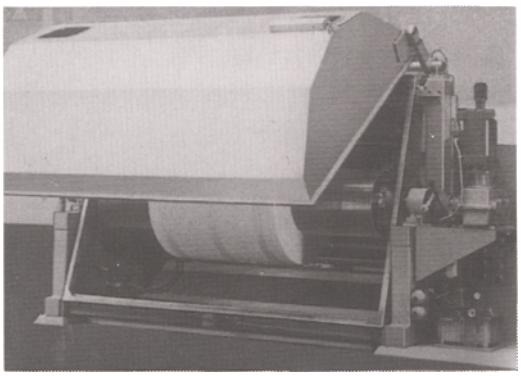
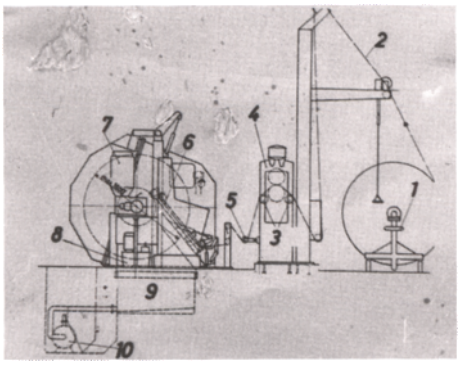


Figure 7-57. Rotowa washing machine (Courtesy of Heberlein & Co. AG).

rated beam on the batching trolly. The range (Fig. 7-58) comprises with perforated drum and liquor circulation, plus associated combined winding and washing drive. The fabric is washed by pumping liquor through the perforated drum. The liquid is forced from the centre to the outer layer of the fabric batch at right angles ensuring good washing effect. This process is intensified by the centrifugal action of the drum. Working speeds range from 20 to 140 m/min. The range is supplied in roller widths of 1400 to 3600 mm. The water consumption is 6-8 l/kg of dry goods. On completion of processing, the chamber is opened and the goods are reversed through the squeezer or feed rolls and either wound up onto a giant batch or plaited down.



1. Batching unit
2. Fabric
3. Expander rollers
4. Squeezer with d-c motor
5. Faller roller
6. Winding arm
7. d-c motor winding and washing drive
8. Hydraulic system
9. Liquor reserve
10. Circulation pump

Figure 7-58. Rotowa open width washing range (Courtesy of Heberlein & Co. AG).

The spray drum washing machine (Fig. 7-59) consists of stainless steel perforated drum which allows easy wash liquor through the perforations. The drum runs in ball bearings mounted outside the tank. The movement of the drum is brought about by the drag of the running fabric. The washing drum is set in a stainless steel tank, with provision to properly drain away the wash water. A set of nozzle batteries is placed round the circumference of the drum, with a view to spray water jets on the fabric. The jet washer (Fig. 7-60) consists of a trough and a cascade zone.

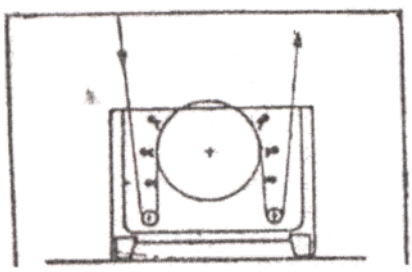


Figure 7-59. Wash tank with spray drum.

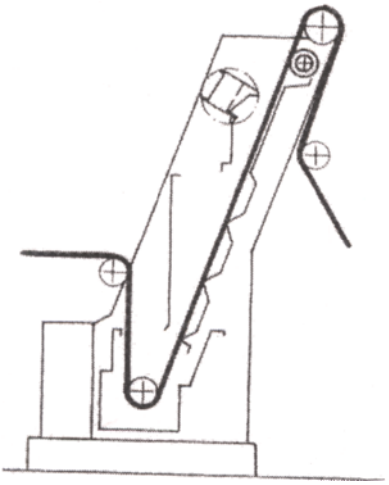


Figure 7-60. Jet washer (Courtesy of E. Küsters, Germany).

Above the cascade zone, there is a nozzle with a wide slot which forms a continu-

ous curtain of water across the full width of the goods. The trough is fitted with filter and liquor circulation pump. Water is pumped into the fabric at a high speed via the wide slot nozzle. The cascade zone, an inclined plane, ensures that the water from the wide slot nozzle has to flow through, and in countercurrent with, the pile. The fabric runs over the drum and is guided to be taken away from the drum over suitably positioned, ebonite covered, rollers running in ball bearings.

In some cases a longer washing time with spray is required and this can be achieved by using wash tank containing roller bed as shown in Fig. 7-61. The fab-

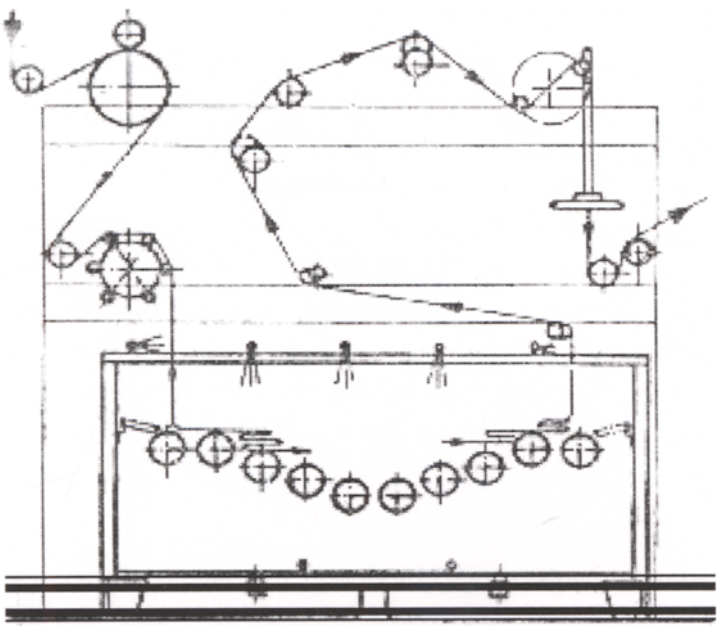


Figure 7-61. Spray washing and soak tank roller-conveyer.

ric transport is effected by means of a positively driven set of transport rollers. The first roller pushes the cloth, the second roller in turn transport the fabric to the third roller and so on. About 150 to 300 m of fabric is piled on the roller conveyer in order to allow complete relaxation of the fabric. A powerful spray through the jet is arranged for an efficient washing of the fabric, while the fabric is adequately soaked in the roller bed. The fabric is lifted and led further from the washing part over a set of guide rollers and a special rotary fabric guiding device.

The open soaper is the common type of continuous washing machine in open-

width form (Fig. 7-62). The machine consists of six or more compartments or

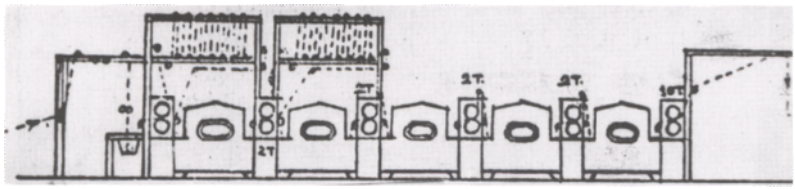


Figure 7-62. Continuous open-width washing range
(Courtesy of Farmer Norton, Type R-16).

tanks depending upon the processes to be carried out. It has a series of bottom and top rollers. The lower set is usually immersed in the washing liquor. The fabric passes over the adjustable tensioners and then over and under the guide rollers which guide the fabric in vertical folds through different liquors in the tank. The fabric is sprayed with water from the spurt pipes and squeezed between the bowls before entering the next tank. The speed range of this machine varies between 20-40 m/min depending on the number of tanks. The execution of the machine may be open at the top or closed depending upon the expected performance of the machine. In some machines the washing tanks are fitted with special beaters (Fig. 7-63) to have more efficient washing. The beater consists of copper gutters

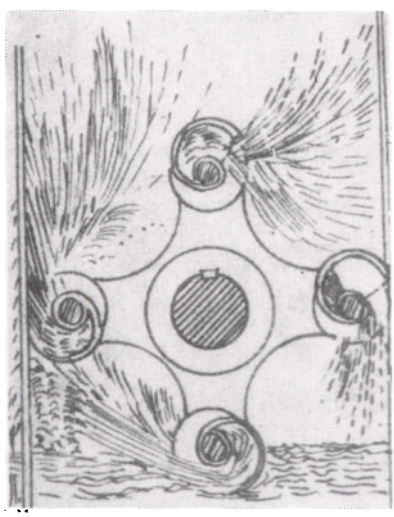


Figure 7-63. Beater with four swivelling gutters for washing tanks.

soldered on stiff steel rods, the ends of which are carried loose on spider wheels keyed on beater shaft. Two sets each of three beaters are inserted between the folds of the cloth and do not touch the fabric. The beater revolves at a great speed, so that gutters are caused by the centrifugal force to fly out. They are partially dipped into the water and give an elastic beating without rubbing. For soaping and washing of delicate goods with a minimum tension, Aquatex soaper (Fig. 7-64) with expres-

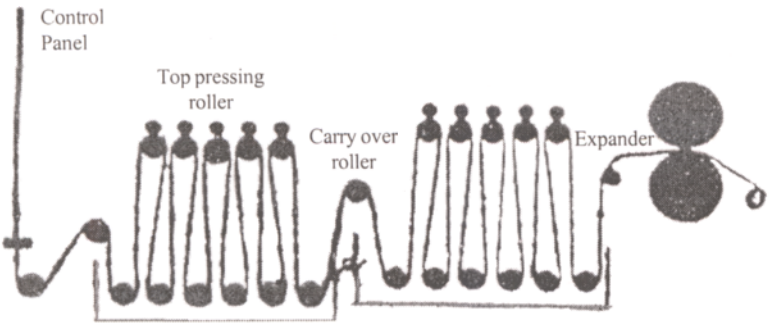


Figure 7-64.Aquatex units with expression nip.

sion nip is used. In this modified machine, every roller runs on ball bearings. The top rollers are driven by roller chains or V-belts in a bank of five or six, which make-up the compartment or unit. The bottom rollers are freely rotating in bearings which are sealed and self-lubricating. Both top and bottom rollers are 12 to 13 cm in diamerter. These arrangements keep the cloth under controlled tension throughout. Another modification is the open soaper with double fabric threading (Fig. 7-65) which gives increased production, economy of space and capability of

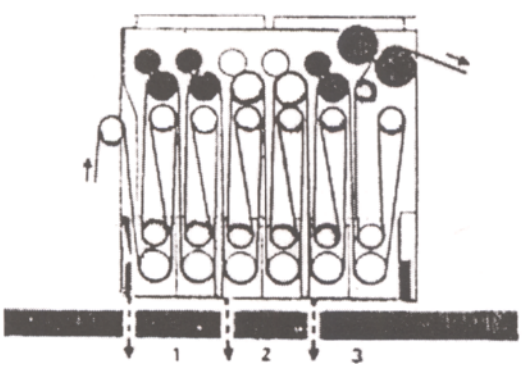


Figure 7-65. Benninger Becoflex washing compartment.

processing goods of any width. Creation of turbulance in the wash tank by arrang-

ing ingeneous fabric passage forward and reverse is an added advantage. Such unit is also used to remove alkali from the mercerized cloth. However, this arrangement is more complicated and costly. The need to improve the washing efficiency has further led to the adoption of counter-current flow, of the wash liquor, in the washing compartment (Fig. 7-66). Vertical metal plates seperate the liquor between the

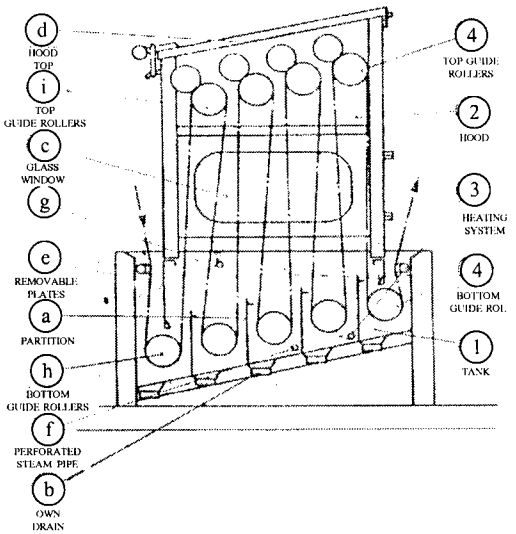


Figure 7-66. Counter-current open-width washing unit.

metal rollers. The liquor flows in the direction opposite to the fabric travel either by cascade arrangement of the sections or by arranging vertical positions in such a manner, that the liquor flows in a serpentine manner. Each seperate successive immersion of the fabric is in a cleaner liquor, whereas the liquor becomes increasingly contaminated as it approaches the discharge point, close to the fabric entrance. Similar arrangement is used for washing mercerized cloth in chain mercerizing machine.

Washing compartments with a horizontal fabric run have been purpose-built down to the very last detail. In horizontal fabric layer washing machine (Fig. 7-67), the fabric enters at the bottom and stepwise ascends to the top. The distance between the two vertical banks of rollers is about 70 cm. Washing is done by multiple counter-current principle. The fresh water enters at the top, and after being expressed at the top roller is collected in the tray and fed to lower ones, turn by turn. Intermediate squeezing of the fabric at the extreme positions increases the washing

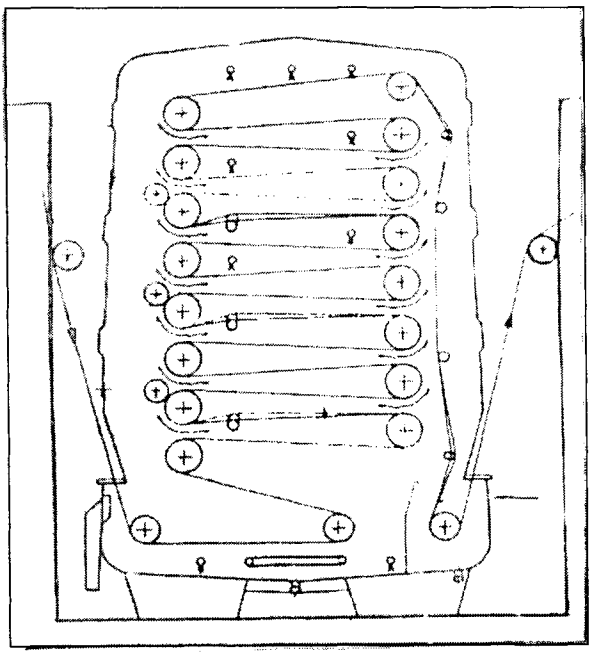


Figure 7-67. Horizontal washer.

efficiency. Each washing unit holds 24 m of cloth and fabric changes direction 12 times. The machine can be coupled together as duplex or triplex assembly. Water consumption is about 4 to 5 l/kg of fabric. The horizontal fabric run has fundamental advantages because of the automatic two-sided treatment, beneficial counter-current flow with liquor circulation, more efficient use of space, use of gravity, centrifugal force and guide roller washing action. Provided full use is made of the available height, horizontal fabric guidence enbles 2 washing compartments to be arranged one above the another. The top compartment can be run with fabric and liquor in counter-current, while in the bottom compartment the liquor is circulated. Using this arrangement, radial flow can be combined with the tangential flow along the fabric surface essential for washing, and diffusion can still take place.

The importance of squeeze rollers for liquor exchange on open-width washing ranges has been demonstrated by many machinery manufacturers. In one system the goods are squeezed off while hot to exploit the lower viscosity of water. Spray assembly to remove insoluble impurities from the fabric by sweeping away by kinetic energy is mentioned. High rates of hydroextraction are achieved by the

Roberto roller principle. "Bicoflex" roller produced by Kleinewefers-Jaeggli/of Germany is designed more for uniform expression : an air cushion inside the roller automatically adjusts the pressure to ensure an uniform squeezing effect, even with extremely narrow or thick goods. In the conventional sqeezing units pressure is applied pneumatically or hydraulically. However, in the "Aquapress" squeezing unit (Kusters) pressure is applied hydrostatically i.e. by means of a large diameter cylinder floating on the liquor. The nip is formed by this floating (stainless steel) roller and a driven counter-roller. It provides even line pressure over the full width of the nip. The roller surfaces are self-cleaning in this system.

The degree of expression largely determines the cost of drying afterwards. Fig. 7-68 shows a few conventional hydroextraction systems. The floating roller

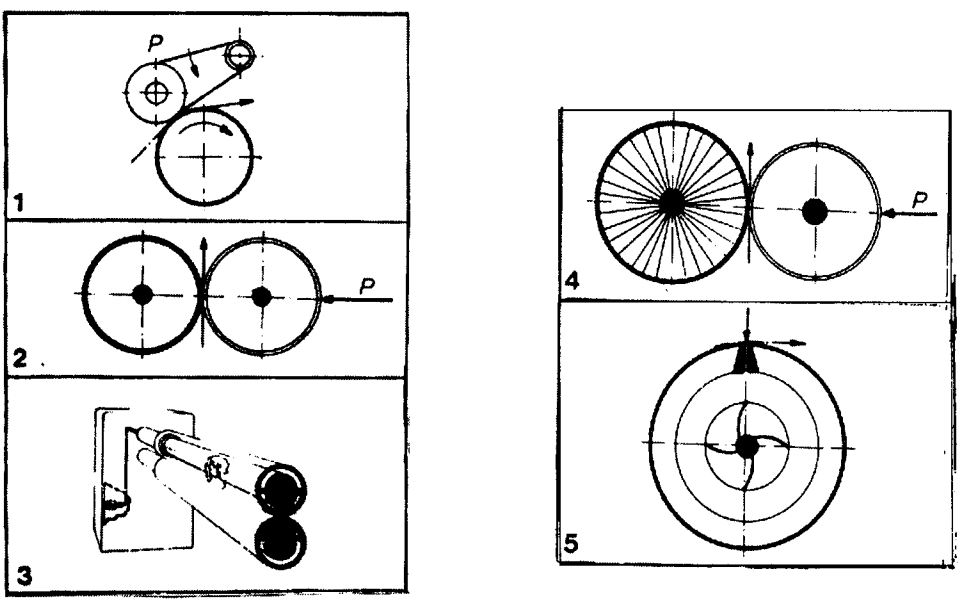


Figure 7-68. Different types of hydroextractor.
1. Feed roller, 2. Horizontal nip, 3. Floating roller,
4. Roberto squeeze roller, 5. Suction device, P Force.

arrangement has already become a tradition. Good results are achieved with suction or other squeezing systems. Suction systems are heavy consumers of energy. Chemical finishes have traditionally been applied to the fabrics using immersion (dip padding) or low wet pick-up techniques such as lick roll, porous bowls, vacuum

extraction or foam [33]. Alternative methods include coating and laminaiton technologies [34]. In the Nextec Application process [35] individual fibres within the fabric are encapsulated or wrapped with an ultra-thin film of polymer. A specially designed blades are used to shear thin polymer compositions into fabrics that are under tension. Pre-treatment of the fabric, and polymer selection are used to increase the polymer flow and prevent saturation of the fibres. On removal of the shear forces, the polymer return to a higher viscosity and then the polymer is cured. It is, thus, possible to provide breathable barrier film as low as 100 nanometers and up to several microns within the fabric, preventing liquid water from penetrating while allowing moisture vapour to pass through to close to the same rate as the original fabirc. This technique of fibre encapsulation process is already being applied on silicone-based polymers, polyurethanes, polyacrylics, specialty nylons, and other polymers and may open many opportunities for exploitation of chemical finishes for providing multi-functional finishes on cotton fabrics [34].

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Chapter 8

HEAT-SETTING

8.1 Introduction

Fabrics produced from synthetic fibres or from blends containing large proportion of such fibres are normally heat-set to stabilise them. Heat-setting is a heat treatment by which shape retention, crease resistance, resilience and elasticity are imparted to the fibres. It also brings changes in strength, stretchability, softness, dyeability and sometimes on the colour of the material. All these changes are connected with the structural and chemical modifications occuring in the fibre. An unset polyester filament yarn shrinks about 7% when allowed to relax in boiling water. This shrinkage is about 10% in the presence of carrier at boil. It is, therefore, necessary to confer on fabric some degree of dimensional stability in order that the yarns or fabrics retain their shape during subsequent processing, washing and ironing.

8.2 Thermal Behaviour of Synthetic Fibres

Synthetic fibres, mainly polyester and nylon, consist of long chain molecules and are held together by interchain bonds. Fig. 8-1 shows how the chains are ir-

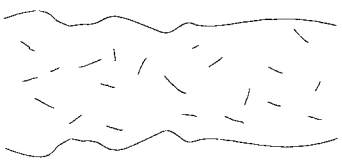


Figure 8-1. Probable disarray of polymer after spinning.

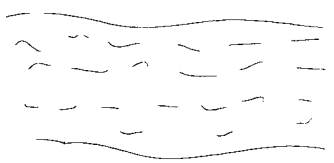


Figure 8-2. Parallel orientation of chain molecules in drawn fibre.

regularly distributed at random in single fibres immediately after spinning. The fibres are then stretched several times their original length to impart desirable properties to the fibre and this causes orientation of chain molecules parallel to the fibre axis (Fig. 8-2). The single chains are now held together by intermolecular forces, hydrogen bonding or by a combination of Van der Waals' forces and H-bonds. As a result of stretching the fibre molecules come closer to each other, resulting in closer alignment, increased density and thus increased H-bonding. The H-bonds are formed at random and there are strains between the chains. The single chains

are, however, not yet completely stretched out and are still kinked having a zigzag configuration. If energy in the form of heat is supplied, the chain molecules starts vibrating, some of these interchain bonds break and some parts of the molecular chains have a greater freedom and relax. The temperature at which there is certain increase in molecular vibration of polymer molecules depends on Tg of the particular fibre. The higher the temperature the more interchain bond breaks and greater the relaxation, but care has to be taken not to heat the fibre so as to damage it. The supply of energy is stopped as soon as the minimum potential energy is reached and the fibres are cooled as quickly as possible, one succeeds in ''freezing'' the H-bonds. The newly formed bonds are more difficult to break and the fibres are dimensionally stable and will not shrink at approximately 10^0C below the temperature of setting. At this juncture the process temperature commences to produce a new heat memory and Tg is changed. Thus the process of thermosetting in stenter can be broken down into four distinct phases :

i) The goods are run wet or dry into the machine and heated superficially to the heating temperature (heating phase).
ii) The heat penetrates the fibres untill all points, inside and out, are at the same temperature (penetration phase).
iii) Heating of the fabric to a temperature which is specific for each fibre, ensuring breakage of intermolecular bonds and equalising internal stresses (transition and stretch phase).
iv) Cooling the fibre resulting in the restoration of intermolecular bonds which are free from internal stresses (cooling phase).

8.3 Stages of Heat Setting

Heat-setting can be carried out at three different stages in a processing sequence i.e. in grey condition; after scouring; and after dyeing. The stage of heat-setting depends on extent of contaminations and types of fibres or yarns present in the fabric.

If heat-setting is carried out in the loom state, mineral oils and non-ionic emulsifiers can modify the fibre structure and rubbing and perspiration fastness may be reduced due to the solubility of disperse dye in the coning oil [1-4]. PVA size above 135°C looses its Tg which is followed by becoming crystallized and melts. The H-bonds, therefore, can no longer be broken with the result that PVA becomes difficult to remove from the fabric. However, grey heat-setting is useful in the

warp knitting industry for materials that can carry only small amount of lubricants and for goods that are to be scoured and dyed on beam machines. The other advantages of grey heat-setting are : yellow colour due to heat-setting can be removed by bleaching, fabric is less sensitive to crease formation during subsequent processing etc.

Heat-setting can be carried out after scouring if it is suspected that the goods will shrink or for the cloth in which 'stretch' or other properties are developed during a carefully controlled scouring process. However, this stage requires drying the cloth twice.

Heat-setting can be carried out after dyeing also. Post set fabrics show considerable resistance to stripping compared with the same dyeing on unset fabric. The disadvantages of post setting are : yellow colour developed cannot be removed any more by bleaching, handle of the cloth may get altered and there is a risk of colours or optical brighteners be faded somewhat.

8.4 Methods of Heat-Setting

8.4.1 Contact method

In this method the fabric is run in contact with a heated metal surface. Some machines are composed of metal rollers having gas fired cores and are filled with a liquid known as diatherm to uniformly distribute the heat. Sometimes enclosed rollers are heated with high temperature steam. This method is mainly used for heat-setting of polyester/cotton blended fibre fabrics. Though heat is used efficiently in this method, the width of the fabrics cannot be controlled while fabrics run flat against the roller surfaces, apart from variation in degree of setting caused by variation in tension.

8.4.2 Steam-setting method

Short staple polyester yarns including polyester/cotton blends are normally set by relaxation in saturated steam. The most effective means of stabilising these materials are to steam at 107°C on the ring spinners tube and soft dyeing packages under minimum tension. Steaming is carried out in an autoclave fitted with vacuum pump, e.g. two times 15 min at 125-135°C with intermediate evacution or alternatively, for 60 min with saturated steam. Sewing threads receive special setting treatments, designed to confer stability whilst preserving their high tensile properties. Polyester garments, garment lengths and hosiery are also stabilised by steaming in much the same way as for yarns.

Nylon can be set in saturated steam at temperatures above 100°C in an autoclave by batchwise process. Nylon yarn is wound on to a collapsible paper tube or cross-wound in cheese form to a spring core and is treated in steam for 30 min cycles, vacuum/steam 5 to 20lb/in²/vacuum and rewound on to the spring in the case of paper tube. For textured nylon yarn similar packages can be used but the package density is very much lower. Woven or warp knitted nylon fabrics are batched in open-width on to a perforated roller and setting cycle commences by a vacuum exhaustion down to a pressure of 28 inches of Hg. Saturated steam is then injected at the desired temperature and treatment continued for 10 min. This is followed by a further vacuum exhaustion and prolonged steaming cycle of 20 min at selected temperature. A final vacuum exhaustion completes the process. In the case of hose and half-hose, the goods are framed onto metal formers on which the goods are shrunk during steaming operation. Typical steam setting conditions are 115°C (10lb/in²) to 130°C (25 lb/in²) for nylon 6,6 and 108°C (5 lb/in²) to 121°C (15 lb/in²) for nylon 6. Steam setting increases the build up of acid dyes and unlevel dyeings will result if the temperature varies throughout the batch.

8.4.3 Hydro-setting method

The hydro-setting or aqueous heat-setting of polyester is done with hot water in a high temperature liquor circulating machine at about 130°C. A typical cycle may require 30 min. Water (or steam) promote swelling of fibre and may cause some hydrolysis in the ester groups in polyester chain. This causes partial destruction of intermolecular bonds and depolymerisation of fibre with a result in loss in tenacity. However, the hydrosetting temperature can be lowered by adding some selected organic or inorganic substances causing swelling of polyester, but such conditions have not yet found industrial application.

Nylon fabric can be hydro-set in hot water since the swelling action assists in weakening or breaking intermolecular bonds. The fabric in flat form is batched onto a perforated metal cylinder and immersed in hot or boiling water for a short period of time. Hydrosetting at boil is roughly equivalent to dry setting at 185°C. The texturised and tubular knitted fabrics are suitable as the fabric quality depends greatly on the methods of application. After setting in boiling water polyester is further shrunk by 11-12% on exposure to hot air at 200°C. Unlike polyester, nylon fabrics if set (relaxed) with boiling water shrinks only 3-4% on subsequent exposure to hot air at 200°C.

8.4.4 Heat-setting using tenter frame

Stenters are widely used for stretching, drying, heat-setting and finishing of fabrics (Fig. 8-3). Woven and knitted fabrics of polyester and nylon fibres and

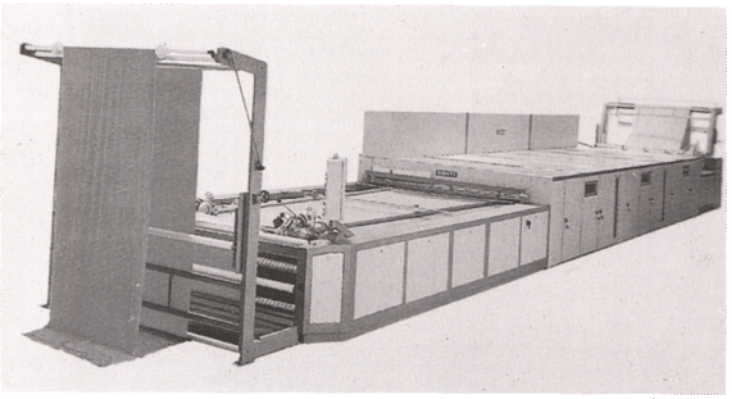


Figure 8-3. Stenter for drying, finishing and heat-setting knitted and woven fabrics (Courtesy of Monti s.p.A.).

their blends are normally heat-set on pin-stenter in hot air. An alternative to the pin stenter is the clip machine. The fabric is held into the chains either by pins mounted into a base plate or by clips in which the fabric edge is clamped between two smooth surfaces. Stenters that are used for setting only have a light pin chains whereas stenters used for both drying and setting (finishing) are provided with a heavy combined pin and clip chain. For knit goods vertically running pin stenter chains are particularly suitable. In order to be suitable for drying and setting purposes, the stenter rails are divided into three sections and can be moved laterally about the centre line. The entry section consists feeding in, with padding mangle, selvedge uncurler (for knitted goods), shrinkage apparatus (up to 30%), selvedge feeler for automatic correction of width and instrument panel with all switches. This section is usually about 5 m long for woven fabrics and 7 m for warp knits. The centre section is as long as oven, which may have from 3 to 8 heating chambers (sections), each about 3 m long. There should be at least two setting fields. The delivery section is about 4-5 m long to permit sufficient cooling to take place before the fabric is stripped off the pins by a roller and either rolled or plaited. On some machines an air blower is fitted after the heating sections to force cool air

onto the fabric. The stenter frame is usually 80-100 feet long and 70-100 inches wide. The speed ranges from 10-45 m/min with a maximum setting time in the setting zone 30 sec at temperature ranging from 175 to 250°C depending upon the thickness and type of the material.

The stenter chambers should be thoroughly insulated from all sides and rest freely on pedestals. The choice of heating system used-direct gas, indirect steam or oil heating or electrical heating-depends on the customer's requirements. Since air is the transport medium for heat, thus as the air velocity decreases, available energy in the form of heat also decreases. Different systems, namely Puffer, Krantz, Jet etc. are used for circulating air around the cloth. In conventional air flow systems, fresh air is fed seperately to each compartment in a stenter, and the exhaust is similarly extracted seperately from each compartment. The demand for multilayer stenter (Fig. 8-4) is increasing. By combining a multi-layer stenter with the con-

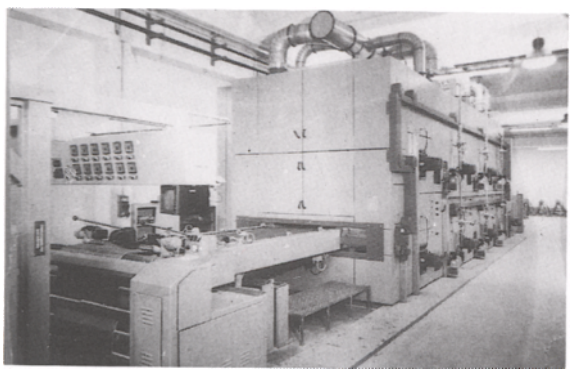


Figure 8-4. Multi-layer stentering machine (Courtesy of Bruckner GmbH).

ventional entry and exit of single-layer stenter it is possible to obtain operating flexibility. The main advantages are the avoidance of longitudinal distortions and the ease of operation and maintenance with this ground level arrangement. The multi-layer stenter is available in versions with 3 or 5 fabric passes (layers).

The shrinkage in length and width may be as much as 10% and this must be taken into consideration in determining the overfeed and the adjustment of the width. Most of the stenters make provision for overfeeds – 5% to + 40%. If the entry rollers feed the cloth at a slower speed, the cloth will be actually pulled by the

travelling chains, thus gaining in length, but may correspondingly lose the width. Thus, slightly under fabric can be reduced to the required width by having positive speed difference and slightly narrower fabric can be brought to its required width by lessening the speed difference and increasing the widthwise pulling action. The extent to which overfeeding can be effected depends on fabric texture, construction, weave, fibre component, closer or broad coarses and wales in knit goods. Polyester knit goods should not be stretched more than 5% wider than the desired end width. An overfeed of up to 20% (generally 6-10 %) is commonly used in knit goods or texturised fabrics in order to level out variations in tensions caused by knitting. For woven goods an overfeed of 5 to 7% is generally sufficient. The overfeed device mechanism varies from make to make of stenter. Some have electrical device (e.g. Artos) whereas others make use of mechanical device (e.g. Primatex). It is also possible to adjust differential overfeed for right and left selvedges to correct distortions.

Knitted fabric finishing still has considerable rationalisation, reserves to offer especially in the fields of process and recipe optimisation. The principal processing problems are inadequate elimination of wash shrinkage; the phenomena of skew and bow distortion; and the poor reproducibility and frequent impairment of the look of the fabric. It is essential to work at the lowest possible tension and with short, contact-guided fabric paths with vertical chain return. This maintains a smaller gap between the upper traction roller and pinning device than with horizontal chain return. The vertical transport chain, designed for speeds of up to 140 m/min, can continuously maintain the production speeds required in knitted fabric finishing. An easy running compensator, developed specially for knitted fabric finishing, allows for speed regulation with extremely low fabric tensions by comparison with conventional dancing roller combinations. From the traction roller, the knitted fabric is fed via a very short transport path to the overfeed unit with specially developed brush belts, which press the edges of the knitted fabric into the pin plates with uniform ''gather'', even at rates of 50%. When feeding dry fabric it is advisable to insert a steamer using saturated steam in the entry section for uniform homogeneous moisture distribution. Widthwise contraction of up to 50% can be smoothly extended without any fear of centre and selvedge breakage. Production speed can be considerably boosted by the use of infra-red radiators (dryer) before

drying. The Convey-Air nozzle system produces a special supporting effect and ensures absolutely uniform ''floating'' of the fabric, permitting permanent rapid relaxation of the fabric before the setting process proper. Methods of supporting knitted structures during stentering include the use of air cushions, endless belt or other supports [6-9]. Stenters considered to be particularly suitable for the processing of knitted fabrics have been described [10-13]. They include drum stenters [14] and stenters capable of processing fabric in either open-width or tubular form [15]. Heat-setting calenders may also be used for the treatment of tubular fabric [16].

Many important advances have been made in the design of control equipment for stenters include methods of measuring weight per unit area [17,18], moisture content [19] and fabric temperature [20]. The recommended method for checking the temperature is to secure thermoelements or thermopapers to piece goods passing through the stenter. Improvements have also been made in methods of feeding fabric to the stenter [21, 22].

8.4.5 Selective infra-red emitters method

Polyester can be heat-set by exposing the material under selected areas of magnetic spectrum of infra-red rays. The wavelength of the radiation source must be chosen with respect to the absorption band of the fibre i.e. a particular infra-red wavelength is chosen for a particular fibre. For example, in the case of polyester the selective infra-red radiation wavelength is the region of 1 to 4 μ. The radiations of wavelength of 1 to 2 μ passes freely through the polyester fabric and that of 3 to 3.5 μ are practically completely absorbed by polyester. Because of this absorption, it can be assumed that the energy is given up to the interior fibre structure, while emissions below this range are dissipated elsewhere. Such radiation sources and filters which closely approach the requirements, are now developed and are called ''selective emitters''. The absorbed energy is redistributed within the structure of the fibre, H-bonds and Van der Waals' forces binding the molecules together are disrupted and these disrupted molecules are at liberty to rearrange themeselves into positions of lowest energy (least stress).

Setting machines with infra-red selective emitters are designed in a manner which permits infra-red waves to be generated at temperatures in the $100 \pm 20^{o}C$ range. The machine allows continuous processing and consists of an entry stand, a setting chamber with vertical rows of infra-red burners, an adjacent cooling zone and a

delivery device. The distance of the burners from the fabric can be adjusted. One such machine is Polyfix machine (Timex, France) and can operate at speeds from 15 to 50 m/min and is available in different working widths. As a rule these machines do not control warp and filling tensions. However, these devices can be used within tenter housings and necessary controls can be done indicated under tenter frame.

8.5 Heat-setting Conditions for Different Kinds of Fibres

There are various kinds of synthetic fibres structurally with different melting points and with different heat-setting conditions. Even a slightest variations in heat-setting conditions, namely temperature, time and tension influence the setting effect, regardless of the system used.

8.5.1 Polyester fabrics

Polyester piece goods are pre-set with hot air on pin stenters for 20-40 sec at 180-210°C according to the type, density and weight of the material, with minimum tension on the goods to control the dry heat stability to less than the accepted 1% shrinkage [23]. Heavier fabrics like suitings require more time as fabric heating time is more. Plain fabrics, woven from unset yarns may be expected to shrink by approximately 5% in warp and weft during scouring process and their residual potential shrinkage range from 4.5% to about 11% over the temperature range of 150 to 220°C. Staple fibre fabrics shrink less than filament fabrics and stability adequate for apparel fabrics is conferred by setting at 170 to 180°C. Polyester fabrics are effectively dimensionally stable if it is set at a temperature of 30 to 40°C higher than the temperature to which the fibre is subjected to expose during subsequent processes.

8.5.2 Nylon fabrics

The setting conditions used for different nylon fabrics vary depending upon the melting point of nylons, heat-setting methods, rate of transfer of heat and the weight of the cloth being processed. For practical purposes, the conditions of hot air setting being used for different nylons are shown in Table 8.1. An overfeed of 2-3% is normally required but this has to be determined before-hand depending upon the handle and structure required.

On steam injection stenters the heating medium is a mixture of super-heated steam and air. The superheated steam required for the purpose can be generated inside the chamber by injection of saturated steam. In this mixture total heat capac-

TABLE 8.1
Heat-setting Conditions for Different Nylons

Type of nylon	Time of contact (sec)	Temperature of setting (°C)
Nylon 6	15-20	190-193
Nylon 6, 6	15-20	200-230
Nylon 11	15-20	≃ 150
Quina	15-20	190

ity of the medium is increased considerably because the specific heat of steam-air mixture is almost twice the air alone and the fabric can be set at a running speed of 60-70 yds/min. Warp knitted and light woven fabrics require only 3-4 sec compared to 15-20 sec with hot air alone. Apart from this, steam-air mixture also scavange the air from the setting chamber and thus reduce the oxidation degradation and minimise stiffening and yellowing of nylons. However, this system requires a highly efficient insulation of the heat-setting chamber to minimise corrosion.

8.5.3 Texturised polyester and nylon fabrics

The choice of setting conditions for bulked yarn materials depends on the type of bulking process that have been employed. In general, high tension must be avoided during heat-setting process, because of danger of pulling out the bulking effect.

Woven fabrics made from texturised polyester yarns should be heat-set for 20-30 sec at 160°C with slight width extension to remove creases, but without true overfeed so as to avoid the production of rippled selvedges. Higher setting temperatures (e.g. 165-170°C) may be required to control the tendency of some fabrics of tighter construction to crease during jet dyeing, but these temperatures can cause some loss of yarn bulk and tend to give a modified, leaner handle. Knitted goods are composed almost exclusively of textured yarns. Polyester double-jersy fabrics, weft knitted from stabilised bulked filament yarns may be heat-set on a stenter for 30 sec at 150°C. The goods should not be stretched more than 5% wider than the desired end width. An overfeed of up to 20% can be given for knitted goods.

For texturised nylon, after relaxing heat-setting is normally done at 150-160°C for 30 sec in a hot air stenter with an overfeed of 10-15%. The overfeed can be increased to 15-20% depending upon the type of stretch. The heat-setting tempera-

ture is always kept below the temperature of texturisation. Nylon can be heat-set only once [25, 25] and differs in this respect from polyester fibres, which can be repeatedly heat-set at progressively higher temperatures. This is of particular importance in the processing of knitted fabrics produced from textured yarns since such yarns have already been permanently heat-set. For any knitted structure a minimum energy state exists and if a knitted structure is allowed to relax after stretching, it returns to the equilibrium condition [26]. Since the setting effect obtained with fabrics knitted from textured nylon is essentially temporary, ideally the fabrics are set under relaxed conditions. It is not always possible to do this. However, the fabrics may be set within 5-10% of relaxed dimensions which will normally shrink less than 5% [27]. Alternatively, heat-setting in knitted fabrics can be brought about by preventing the changes in length of yarn in each loop and in the shape, curvature or degree of intermeshing of the loops [28].

8.5.4 Acrylic and modacrylic fabrics

These fibres cannot be heat-set in the conventional sense since the fibres are readily stretched or deformed at temperatures above 75°C. The degree of stability, however, can be obtained by passing these fabrics through a hot air stenter at about 120°C. Temperatures above 120°C may cause discolouration of the fabrics. For blended fabrics containing acrylic and modacrylic fibres higher heat-setting temperatures may be required. Knitted fabrics produced from a feeder blend of acrylic and textured polyester fibres, are heat-set at about 160°C for 30 sec.

8.5.5 Cationic dyeable polyester fibre fabrics

Cationic dyeable polyester (CDPET) and regular polyester fibres differ much in chemical properties. Generally, CDPET has a slightly lower heat resistance than the regular PET, so that heat-setting temperature for CDPET is kept slightly lower than that of normal PET. Table 8.2 shows the approximate heat-setting conditions of different polyester fibres.

8.5.6 Triacetate fibres

An important property of triacetate fibres is the ability to undergo structural changes under the influence of heat. Triacetate is not effected by dry heat up to 150°C. The fibre becomes increasingly plastic between 150 to 190°C and at still higher temperatures up to 220°C molecular reorientation occurs to an increasing extent accompanied by increase in crystallinity so that imbibation of the fibre falls from 16 to 10% and there is corresponding reduction in absorption and desorption

TABLE 8.2.
Approximate Heat-setting Conditions of Different Polyesters

Type of Polyester	Heat-setting Temp. (°C)	Contact time (sec)
100% Polyester (normal)	180-220	20-40
CDPET	170-180	20.40
Carrier-free dyeable PET		
(a) Polybutylene terephthalate, Type - 1	160-180	30
(b) Dicarboxylic acid, Type-2	170-190	30
(c) Copolymer, Type-3	190-200	30

of dyes. A permanent change in thermoplastic behaviour takes place and the fibre becomes increasingly less plastic. Table 8.3 shows the extention figures of triac-

TABLE 8.3.
Thermoplastic Behaviour of Triacetate Fibres

Temperature (°C)	% Extention (under load of 0.02 g/den)	
	Normal triacetate	Triacetate after treatment at 200°C for 5 min
20	0.10	0.10
140	0.10	0.10
160	0.15	0.10
165	0.40	0.10
175	1.10	0.20
185	3.00	0.70
190	8.00	1.00

etate fibres. Similar results can be obtained if triacetate is exposed to combined effect of heat and moisture at temperatures lower by 60-70°C than when dry heat is used only.

8.5.7 Polyvinyl chloride fibres

The outstanding property of these fibres is the shrinkage on heating which enables the manufacture of various specialty products. The fabric can be heat-set by

passing it through a hot air stenter with necessary overfeed. Normal feeding, which gives shrinkage in the weft direction, can be done in one passage at 95°C at a speed depending on the fabric construction. Shrinkage can also be allowed to take place during or after dyeing. Materials containing fibres with inherent shrinkage should be processed at temperatures not exceeding 70°C. Pre-shrunk fabric can be wet pre-treated at 96-100°C.

8.5.8 Elastomeric fibres

Fabrics containing elastomeric fibres can be heat-set. A tricot or sleek-knit fabric knitted from nylon 6 and polyurethane may be satisfactorily heat-set at 180-185°C for 20-25 sec. Slightly higher temperatures (190°C) may be used for nylon 6,6. However, the required width and stretch characteristics of the finished fabric determine the precise conditions to be employed with a particular fabric [29].

8.6 Heat-setting of Blended Fibre Fabrics

New fibres and newer blended fabrics have been produced and these are also to be heat-set for successful dyeing and finishing operations.

8.6.1 Polyester / cotton blends

Short staple polyester fibres are often blended with cotton or some other cellulosic fibres. Normally heat-setting in stenter with hot air is carried out at 180°C for 30 secs. Higher temperatures may discolour the cellulosic portion of the material. For increased stability, setting may be carried out even at 200°C for 30 secs without serious risk of damaging the cellulose. The free weft-shrinkage of a typical polyester/cotton shirting fabric is about 4% at its normal setting temperature, but this is restricted to 2-3% (i.e. 1-2% residual shrinkage is allowed) in order to ensure the removal of creases and to get control over weft straightness.

8.6.2 Polyester/wool blends

Polyester/wool blended fabrics are normally heat-set before dyeing. Similar effect is obtained on the wool component on the blend by crabbing. Polyester/wool blended fabrics can be heat-set in a hot air stenter for 30 secs at 180 ±10°C. For worsted-spun goods 3-5% relaxation shrinkage is allowed both warp and weft and for woollen-spun materials 1-2% is allowed. The wool should be allowed the normal moisture regain before heat-setting [30]. For blends containing more than 40% polyester content, heat-setting is done with adequate overfeed to avoid shrinkage during dyeing operations. Top dyed wool rich blend qualities of polyester/wool

fabrics having wool content above 67% need not be heat-set as adequate dimensional stability can be imparted by autoclave decatising popularly known as K.D.Finish. After setting, the goods may be damped or steamed to restore normal equilibrium moisture content of the wool as rapidly as possible. The sequence of operations is slightly different, according to whether a clear-cut or milled finish is required; for clear-cut finishes, heat-setting may either precede or follow dyeing. For milled finish, it is recommended to carry out heat-setting after milling and dyeing. Singeing should follow heat-setting, unless the fabric is to be milled, when singeing precedes heat-setting.

8.6.3 Polyester/linen blends

Polyester/long-staple fibres are also used in the linen industry, where the yarns may be of either the 'stretch-broken' or 'unbroken' type, but are more commonly of the latter. Heat-setting of such fabrics may be carried out at 180°C for 30 secs on the hot air pin stenter, allowing up to 2% weft shrinkage with overfeeding only to compensate for any warp shrinkage that has occured in the previous process.

8.6.4 Polyester/silk blends

Heat-setting of polyester/silk fibres blended fabrics can be carried out on stenter at 190°C for 30 secs. The introduction of up to 50% polyester does not effect the characteristics drape and handle associated with silk fibres.

8.6.5 Polyvinyl chloride/cellulosic fibres blends

For blended fabrics with cellulosic fibres it is possible to produce heat-embossed blend fabrics with 25% polyvinyl chloride fibres. Heat treatment is carried out by one passage on pin-stenter without overfeed at 85-90°C, and if for example a 15-17% shrinkage is to be achieved, the speed of travel is about 10 m/min.

8.7 Effect of Heat-setting on Various Properties of Synthetic Fibres

8.7.1 Structural changes of polyester and nylon

Polyester is not a fast crystallising polymer. The rate of crystallisation is maximum for polyester at around 180°C. The maximum crystallisation rate for polyester is about 0.016/sec, while it is 0.14/sec for nylon 6. The following changes take place as a function of increasing temperature in polyester when heat-set under free to relax conditions (i.e. free annealing) and when held taut at constant length (i.e. taut annealing) :

i) Crystallinity increases with increasing temperature in both the cases, but is more for free or slack annealed samples at all temperatures.
ii) Crystal size increases in both cases.
iii) Crystallite orientation and birefringence increase in case of taut annealed samples, but decrease in case of free annealed samples.
iv) Amorphous orientation decreases in both the cases. In free annealed sample the decrease is greater due to shrinkage allowed.
v) The number of crystals in the fibre increases but at higher temperatures, the crystals fuse together and their total number decreases and crystals become perfect.
vi) Amorphous volume per crystals first decreases and then increases in both the cases.
vii) The glass transition temperature first increases and then decreases with increasing heat-setting temperature.
viii) Increasing tendency for phase seperation at high heat-setting temperatures is possible.

Heat -setting processes result in inner changes in the amine end group content of nylon fibres and such changes will only slightly modify the uptake of acid dyes. The density and crystallinity of nylon increase on setting both in dry heat and in saturated steam. Application of tension assists in the development of crystallinity. When heated under tension orientation increases. The increased orientation is lost, however, by allowing the stress in the fibres maintained under tension to relax. Crystallinity and crystal size increase more readily at a lower temperature for steam set sample compared to dry set samples. The orientation of the crystalline regions resulting from both types of heat-setting show similar trend whereas the orientation of amorphous regions of the wet set material increase rapidly with the setting temperature. The modulus of the fibre increases on dry heat-setting and it decreases on steam heat-setting. Increase in modulus occurs, if heated under tension. Shrinkage of the fibre decreases with heat-setting temperature and is related in an inverse fashion to the crystallinity.

8.7.2 Dimensional stability

The higher the temperature to which the yarn or fabric is exposed, the higher the resultant shrinkage over the temperature range of 100-200°C [31]. Figs. 8-5 and

8-6 illustrate the free shrinkage of a typical unset polyester yarn in hot, dry air and

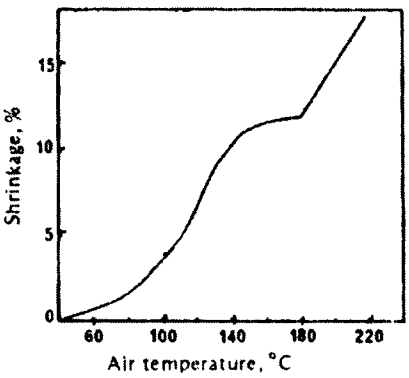


Figure 8-5. Free shrinkage of polyester yarn (medium tenacity), in hot air.

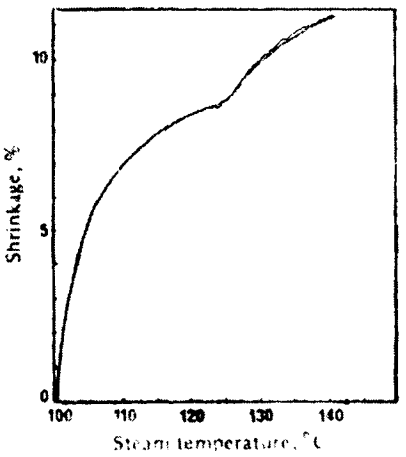


Figure 8-6. Free shrinkage of polyester filament yarn (medium tenacity), in saturated steam.

in saturated steam respectively. As the result of shrinkage, the mechanical properties of the fibre change so that its extensibility increases and breaking load diminishes without appreciably changing the work of rupture. Fig. 8-7 shows the effect

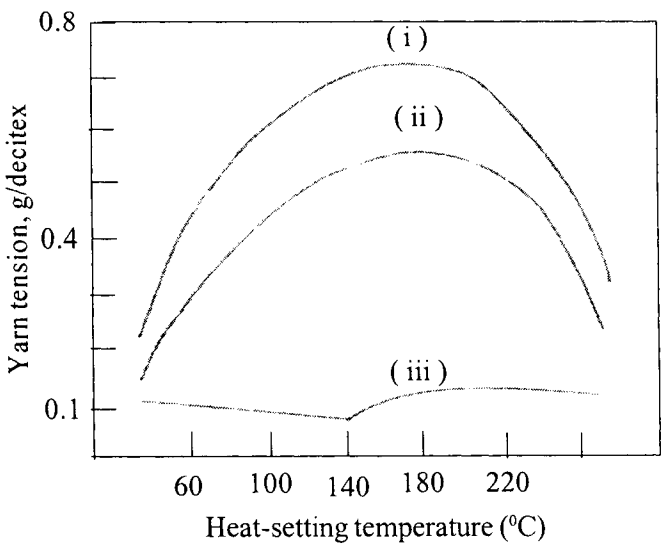


Figure 8-7. Tension produced in heat-setting at constant length. [(i) unset yarn, producer twist, 30 t.p.m.; (ii) unset, thrown, 300 t.p.m.; (iii) steam-set, thrown 300 t.p.m.].

of tension produced in polyester yarn on heat-setting at different temperatures. In general, the tension in the yarn at first increases but temperatures over about 180°C, it decreases steeply. The third curve (iii) of Fig. 8-7 represents the tension produced in a polyester yarn that have been twist set in steam at 110°C and the tension is unlikely to exceed 0.1 g/decitex unless the yarn is deliberately stretched [32].

In general, the higher the setting temperature, the lower is the resultant shrinkage of the heat-set fabric at any given temperature. The shrinkage of unset polyester fabric at 175°C is about 15% as compared to 1% for the same fabric set at 220°C. Fabrics containing both dyed yarns and unset yarn tend to show differential shrinkage effects, and these must be set at the highest temperature permitted by the sublimation fastness of the dyed yarns.

8.7.3 Stiffness

The setting process stiffens the fabric, which is undesirable. Higher the setting temperature, more is the stiffening. A fairly linear correlation exists between the stiffness and setting temperature [31]. The stiffening is due to the formation of continuous film on the fibre surface and high tension developed during setting. The stiffening effect is lost if the fabric is subsequently treated mechanically e.g. by dyeing on a winch. High tensions during setting leads to the production of a thin paper like and impoverished handle while free relaxation gives a soft and silky fabric. However, it is difficult to completely eliminate tensions and full relaxation also leads to considerable loss of yield. Also, tensions have the effect of removing yarn crimp. About 3-4% potential yarn shrinkage is restrained and the rest is allowed to freely shrink in the stenter.

8.7.4 Crease recovery

One of the purpose of heat-setting is to reduce the extent of creasing on subsequent dyeing and washing processes. The higher the setting temperature the less is the wet creasing. The degree of wet creasing, is however also related to fabric construction, for example, open or loose construction fabrics show better crease recovery than dense fabrics. High setting temperature which creates a degree of stiffness in the fabric does not recover well from creasing of dry polyester fabrics. Some compromise is necessary between the temperature necessary for maximum dimensional stability and that for an acceptable dry crease recovery.

8.7.5 Dyeability

Fig. 8-8 shows a typical disperse dye uptake at the boil without carrier in the

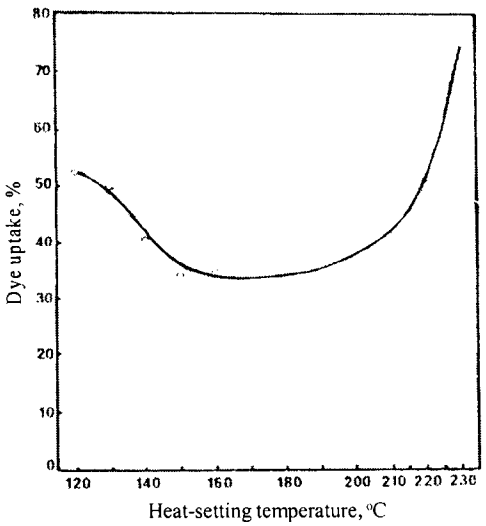


Figure 8-8. The effect of heat-setting temperature on dye uptake when polyester is dyed with C.I.Disperse Red 1 [33].

dyebath in which dye uptake varies with the setting temperature used when polyester is heat-set. Although this pattern of behaviour is general for all disperse dyes applied to polyester, the shape and position of the absorption curve depend on the method of dyeing [34] ; the size, planarity and polarity of disperse dye ; position of substituent groups and solubility of dyes [35]. The absorption of some dyes is practically independent of heat-setting temperature whilst absorption of others is highly sensitive to it [36]. As the setting temperature is increased, the curve shows a reduction in the rate of dyeing for setting temperatures between 130 and 150°C followed by a levelling-off. Above about 190°C, the rate of dyeing rises rapidly and eventually reaches values greater than that for unset cloth. The initial decrease in the uptake suggests that new crystals are formed as setting temperature is increased by coming together of well parallelised chains in the amorphous regions and amorphous volume per crystal decreases so the path for the dye particles through the amorphous region is very tortuous. In the later stages of crystallisation, the crystallites increase in size and also become more perfect. Thus at the higher temperature of setting, the amorphous volume per crystal increases. Chain folding

also occurs giving rise to segregation of crystalline and amorphous regions. This results in less tortuous path for the dye and provide easy passage for the dye molecule. The degree of crystallinity affects the total amount of dye that can be absorbed, whereas the degree of orientation affects the rate of dyeing. Sharp increase in dyeability above 220°C is thought to be associated with disorientation of the fibre and cannot be employed on commercial scale because small differences in temperature may give uneven adsorption of dye and reproducibility of the results would be very poor. In addition tension, moisture and time of contact during heat-setting are also important factors that cause variation in the dyeing properties of the fibre.

The effect of disperse dye uptake on heat-set temperature of polyester is also attributed to the fibre being purified [37]. Purification has been visualised as being either the elimination of di -, tri -, and tetramers or their melting and coalesence to form greater distances between the bonds. The greater bond distances then provide for greater voids causing molecular voids. This is correlated between Tg and apparent transition temperature of dyeing.

Structural changes in nylon due to heat-setting affect the dye uptake. Steam treatments increase the uptake and rate of dyeing whereas dry heat causes some reduction. This increased dye receptivity and hence lower activation energies in steam heated materials may be attributed to the more open structure of set nylons. In the dry setting, the minima observed suggests that at the temperature at which decrease in dyeing properties occurs, the increase in crystallinity is important; however, the increase in dyeing properties at the higher temperatures suggests an opening up of the amorphous structure.

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Chapter 9

MERCERIZATION

9.1 Introduction

Mercerization was discovered by John Mercer in England and the process is named after him : mercerizing. The process of alkaline treatment of cotton was patented in 1850. Later Horace Lowe in England found that the glazing effect became even more pronounced when cold caustic soda acted on cotton under tension. He discovered the actual mercerizing process and applied for its patent in 1890.

Mercerization gives cotton woven cloth a silky lustre, and is the foundation of many improved and beautiful finishes. Sewing and embroidery cotton yarns are mercerized with tension in the form of hank. Stretched yarn can be made by mercerizing without tension [1, 2]. The stretched materials are used for bandages, casual wear (originally garments for skiing), skirts, boat covers etc. The increasing cost of chemicals, machinery, labour, effluent control and recovery of caustic soda make the process of mercerization less attractive now-a-days.

9.2 Conditions for Mercerization

Mercerization is defined as the treatment of cotton textiles with a concentrated solution of alkali consisting the following conditions:

(a) Application of caustic soda solution around 55-60^{0}Tw ($\simeq$ 31 to 35%) at a temperature of 15 to 18^{0}C.

(b) A dwell period of 55 sec on an average, so as to permit diffusion of alkali into the fibre.

(c) Warp tension during alkali treatment and stretching the weft (width) of the fabric during washing are necessary to prevent shrinkage.

(d) Finally, washing-off of the traces of alkali from the treated fibres.

Mercerization may be carried out on grey fibres or after scouring/bleaching. The cloth should be singed before mercerizing to give a smooth surface. If mercerization is carried out in the grey state, complete removal of alkali is not necessary during washing treatment as the residual alkali in the cloth is used for the kier process. However, mercerization is commonly carried out after scouring, but it is preferable to mercerize after bleaching if continuous bleaching plant is available.

Another necessary condition for successful mercerization is the rapid and uniform wetting of the grey cloth. Penetration of alkali is hindered by the high viscosity of the strong caustic soda solution at lower temperature on the one hand and the hydrophobic nature of the fatty matter present in the size coating as well as natural fats and waxes present in the fibre on the other. To obviate these problems a small amount of penetrating and wetting agent is added to the caustic bath, . The wetting agents should be selected so that it should have good solubility and high wetting ability in the alkaline bath, should have no affinity to fibre, low foaming power , good efficiency at low concentration and stability under conditions of sodium hydroxide recovery by centrifuge or vacuum evaporation technique etc. [3]. It is obvious that a single wetting agent does not show all these properties and, therefore, blends of wetting agents are needed to get the optimum effect during mercerization process. Generally, two types of wetting agents are commonly used in mercerizing liquors e.g. cryslic acid derivatives coupled with selected solvents such as triethyl or tributyl phosphate and the other type is non-cryslic type. Mixtures of ortho, meta and para cresols (also called cryslic acid), CH_3-C_6H_4-OH, are not soluble in water, but dissolve in strong caustic soda solutions . Their wetting power is also found to be improved considerably by incorporating methylated spirit, polyhydric alcohols having C_{18} chains , butanol , polyethylene glycol etc, by diminishing the viscosity of mercerizing liquor. Non-cryslic wetting agents include sulphated lower fatty alcohols such as hexyl or octyl alcohol and the addition of polyhydric alcohols, enable the stabilisation of wetting agents while avoiding their precipitation during the process of recovery of sodium hydroxide. A product obtained by the distillation of pine oil as a fraction between turpentine and rosin, has excellent wetting, penetrating and emulsifying properties in mercerizing liquor. Wetting efficiency of non-cryslic type is generally higher than that of cryslic type. In case of mercerization of knit goods which contain paraffin products, the wetting agents used must also possess dispersing power towards these products [4].

9.3 Changes in the Properties of Cellulose Due to Mercerization

Cellulose undergoes chemical, physico-chemical and structural modifications on treatment with caustic soda solution of mercerizing strength [5]. Chemical reactions lead to the formation of alkali cellulose, physical reactions, to a change in arrangement of units of cellulose. The optimum modifications in the properties of

cellulose can be manipulated with the selection of proper concentration of alkali, time, tension and temperature during the mercerizing process.

9.3.1 Swelling and shrinkage of cellulose

When cellulose is immersed in a solution of caustic soda of mercerizing strength, water and alkali diffuses in and the material swells. The fibre hair quickly commences to untwist from its twisted ribbon like form and tends to become cylindrical rod-like surface due to deconvolution. The cross -section of the fibre diminishes, the diameter of the fibre becomes more round. The surface of the nearly cylindrical cotton fibre after mercerizing reflects light more evenly to all sides than the kidney-shaped cotton fibre and the fibre surface becomes more lustrous [6]. As the fibre swells, the fibre shrinks in length [7, 8]. Swelling and shrinkage are more when there is no tension in the fibre, but the alteration in cross-section caused by swelling is more when mercerization is carried out under tension . Under optimum conditions each cotton fibre may contract nearly 9% in length and swell nearly 150% . Swelling of the cotton fibre also has a disadvantage . The fibre becomes more compact in its swollen condition. This compacting diminishes the further penetration of caustic soda into the fibre i.e. penetration slows down and mercerization in the fiber's core is lower than on its surface.

Maximum swelling concentrations of different alkalies depend on the degree of hydration of the alkali ion [9, 10]. Table 9.1 contains data of different kinds of

TABLE 9.1
Effect of Alkali Metal Hydroxides on the Swelling of Cotton Fibre [11]

Reagent	Concentration of alkali at which maximum swelling is obtained		Increase in fibre diameter
	g/100 g of solution	mole/l	(%)
LiOH	9.5	4.0	97
NaOH	18.0	4.5	78
KOH	32.0	5.8	64
RbOH	38.0	3.8	53
CsOH	40.0	2.7	47

alkali metal hydroxides on the swelling of cotton fibre. For small concentration of alkali, the diameter of the hydrated ions is too large to penetrate into the

macromolecular structure of cotton , but as the concentration increases , the number of water molecules available for the formation of hydrates decreases and thus hydrated ion pairs, dipole hydrates (solvated or not) are formed with the decreasing hydrodynamic diameter, are capable of penetrating into the fibre structure of cellulose forming hydrogen bonds with the molecular chains of cellulose . Thus mercerization induces important structural modification of cellulose when interfibrillary swelling takes place. With further increase in concentration of alkali-metal hydroxides in the solution, fibre swelling is reduced due to decrease in hydration of alkali metal ions.

The influence of alkali concentration and temperature of treatment on swelling

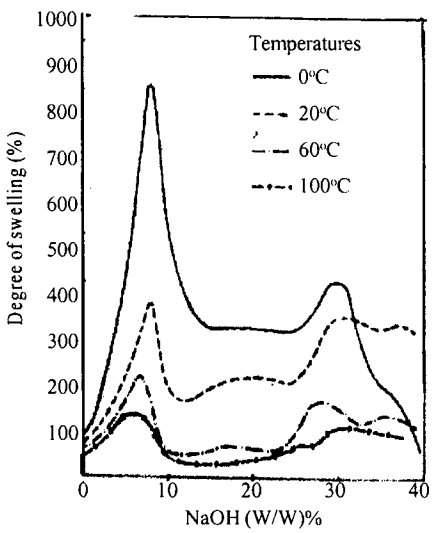


Figure 9-1. Dependence of swelling on temperature and concentration of alkali [12].

of cellulose are represented in Fig 9.1. The extent of swelling depends on the concentration of alkali. In solution with an increasing concentration of NaOH at 20°C, the swelling of cellulose (cotton linters) increases to a maximum value for a concentration equal to 8 to 9% by weight of NaOH ; next it decreases to a minimum (12 - 13% NaOH by wt.) and then slowly increases in higher concentration ranges.

Though 8% NaOH (by wt.) solutions give maximum swelling, commercially mercerization is done at higher concentration of about 31 to 35% which indicates that swelling is not the only determining factor. This is because of preferential

absorption of NaOH during mercerization process. This preferential absorption is associated with the question of compound formation to form soda-cellulose. The amount of alkali adsorbed is very much greater than that of preferentially adsorbed (Fig. 9-2) as a result of very large swelling and adsorption of water in the cellulose. The adsorption of NaOH is found to be constant between certain concentrations of

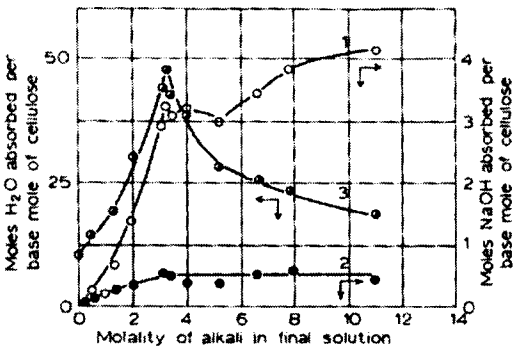


Figure 9-2. NaOH and water absorbed by cellulose sheet at 25°C [13, 14]. 1-total alkali absorbed, 2-preferentially absorbed alkali, 3-water absorbed.

alkali, it is thus assumed that a definite compound is formed with the cellulose molecule. Further water absorption plays a large part and this water absorption fall rapidly after reaching a maximum, thus causing alkali absorption to appear constant.

Two broad explanations are possible for the interaction of cellulose and caustic soda. For the first one, it is assumed that cellulose combines with caustic soda to form alkali-cellulose and swelling is due to the molecular attraction with associated

$$C_6H_9O_4 - OH + NaOH \rightarrow C_6H_9O_4 - ONa + H_2O$$

Alkali-cellulose

hydration. The extent of this combination is governed by the concentration of alkali. It is assumed that alkali-cellulose is more hydrated than the native cellulose. Maximum swelling in particular range of alkali concentration is the result of the attraction of alkali-cellulose on the one hand and the remaining free alkali on the other. The hydration of the cellulose increases with the increased fixation of alkali in solutions of rising concentrations up to a certain limit, after which free alkali exerts a dehydrating effect on the alkali-cellulose to a great extent. The second theory is based on osmotic phenomena. It is assumed that cellulose behaves as a very monobasic acid due to the hydroxyl groups in it and forms an alkali-cellulose

during mercerization with alkali. The excess alkali diffuses into the cellulose according to Donan's theory of membrane equilibrium. The presence of ions in cellulose result in unequal distribution and thus brings about an osmotic pressure. This causes water to enter the fibre until such time as the osmotic pressure is in balance with the restraining or elastic forces of the swollen fibre. When the alkali solution is replaced by a large excess of water, the sodium cellulosate is hydrolysed, osmotic pressure falls, undissociated hydroxyl groups are reformed and the cellulose is recovered chemically unchanged, but permanently distorted if the osmotic pressure is high enough. Another term is transient swelling. When alkali impregnated material is washed with water, increased swelling is observed whilst the alkali is being removed (Fig. 9-3). Water diffuses into the cellulose more rapidly than the alkali ions can diffuse out, and hence, since the activity of the water in the aqueous phase

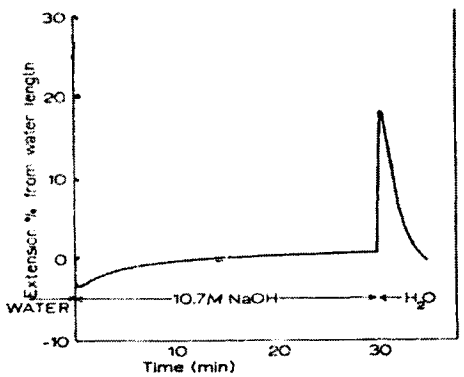


Figure 9-3. Transient swelling of cellulose [15].

is increased, the osmotic pressure is transitorily larger. This greater momentary swelling which occurs for a short period of time decreases as the ions diffuses out of the fibre. If the activity of water in the wash liquor is reduced by the addition of salt, the swelling effects are reduced and the alkali may be removed without undue swelling of the fiber [16].

Swelling of cellulose fibres in alkali increases with a decrease in temperature [17] as the formation of alkali-cellulose compounds is an exothermic process. At 0°C the swelling of cellulose in alkali (8-9% by weight) is about 800% (Fig. 9-1) and swelling decreases rapidly at higher concentration of alkali due to the decrystallisation of NaOH hydrates. The extent of swelling also decreases as the

treatment temperature increases (60°C or 100°C) and maximum swelling is observed at 7-8% NaOH by weight.

Shrinkage of cotton is greatest on swelling in alkali at 15-18°C and the value decreases with increase in temperature. The use of cold (2°C) concentrated solutions of alkali reduce the shrinkage as the solutions become too viscous to impregnate fibres significantly in a short time. The shrinkage of raw cotton fibre is lower than that of scoured cotton [18]. Volume changes are significant ranging from 62cc to 177 ± 8cc in the alkali concentrations ranging from 14.3 to 48.8% (w/w) [7]. The increase is, however, small if treatment is carried out under tension.

9.3.2 Structural modification

Due to swelling of cellulose in caustic soda solution of mercerization strength, many hydrogen bonds are broken, the plane of molecular chains have been moved apart, molecular structure tends to become decrystallised, the chains or spaces within the cellulose structure become more uniform and the chains of glucose residues have been given a slight twist. Because of the distortion of polymer network and changes in crystalline structure, the process of mercerizaation is irreversible [19-23]. Mercerization also affects the size of the crystallites [24] and orientation of the crystalline region [25, 26] and the extent of orientation depends on the tension during mercerization. The influence of alkali concentration on changes in the crystalline structure of cotton yarns mercerized for 60 secs at 20°C with constant length (0% stretch) is illustrated in Fig. 9-4. Soda-Cellulose I is formed with sodium

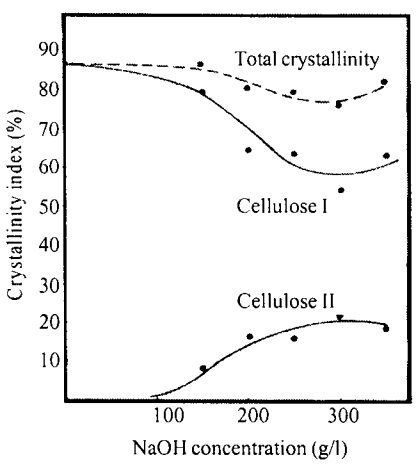


Figure 9-4. Influence of NaOH concentration on the crystalline structure of cellulose fibres [27].

hydroxide at concentrations of 12-19% (by wt.) [28-30], Soda-Cellulose II at concentrations between 20 and 45% by weight. Cellulose I exists in a parallel chain conformation while Cellulose II exists in an antiparallel chain conformation [31]. Soda-Cellulose III is obtained by drying Soda-Cellulose I [32, 33]. For temperature higher than 30°C and in solution 20-25% NaOH (by wt.), the formation of Soda-Cellulose III and II is obtained [34]. Soda-Cellulose IV is obtained by washing Soda-Cellulose I and II in water or in dilute solution of NaOH [35]. Soda-Cellulose V appears between -10 and +20°C in a wide range of NaOH concentrations of about 40-45% (by wt.) [36-38]. However, concerning the formation of Soda-Cellulose compounds there is some approximation the manner in which they form with respect to the nature of NaOH hydrates present in concentrated solutions. Cellulose I content and total crystallinity index decreases as the temperature of mercerization increases, whereas Cellulose II follows an opposite course due to the better penetration of NaOH hydrates. Mercerization without tension allows total conversion of Cellulose I to Cellulose II to take place, whereas when mercerizing with tension, mixtures of the two are formed [39, 40]. Cellulose III, IV and X can also be obtained by treatment of cotton with ammonia at -35°C, hot glycerine and phosphoric acid respectively. The shape of native cellulose crystal (Cellulose I) is monoclinic and the dimensions of monoclinic unit cells of various crystalline forms (Cell I to Cell X) are shown in Table 9.2. Out of various Celluloses, Cellulose II is most stable and the other Celluloses may be reconverted into each other [41, 42].

TABLE 9.2
Dimensions of Unit Cell of Different Celluloses on Structural Modification

Dimensions	Cellulose I	Cellulose II	Cellulose III	Cellulose IV	Cellulose X
a (Å)	8.35	8.14	7.74	8.11	8.10
b (Å)	10.30	10.30	10.30	10.30	10.30
(fibre axis)					
c (Å)	7.9	9.14	9.9	7.9	8.16
β (degrees)	84	62	58	90	75.36

9.3.3 Increased lustre

Unmercerized cotton has a general appearance of a flat ribbon with spiral twists, its surface is rough and non-uniform, its cross-section is irregular and ear-shaped

while the lumen, the central canal, is broad, irregular and resembles a collapsed tube. All these factors result in less lustre. When a cotton hair is brought into an aqueous solution of sodium hydroxide of 18% (40°Tw), cellulose begins to swell immediately, the hair is elliptical in section in a few seconds, and on further swelling becomes circular and the lumen is practically eliminated. The untwisting of the fibre takes place under effect of swelling and increased alignment and packing of the fibres in the yarn also take place. The changes that take place in the cross-sectional shape of cotton fibre during mercerization are shown in Fig. 9.5. Stages 1

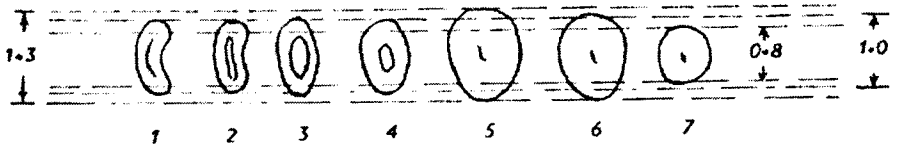


Figure 9-5. Seven successive stages of change in the cross-sectional shape of a cotton fibre as produced during mercerization.

to 5 show the change for a twisted ribbon like fibre to one which is uniformly cylindrical and in its most swollen form at 5. Stages 6 and 7 show some contraction but without loosing its cylindrical form when the fibre is washed with water (6) and then dried (7). During the last three stages, the hair retains the same form of section, but shrinkage proceeds uniformly towards the centre and lumen does not recover its original size. But to secure an increase in lustre the cotton material must be prevented from shrinkage by stretching the yarn lengthwise and the fabric both lengthwise and widthwise during the treatment and washing out of the alkali by water. When cotton is mercerized without tension, the fibre while much smoother and rounder with little or no twist, still show residual creases and wrinkles and there is no appreciable increase in lustre as the cross-section is oval and lumen is contracted but not collapsed. Lustre increases as the tension applied to the fibre during mercerization is increased [43, 44].

Lustre also depends on other factors. Mercerization reduces the axial ratio and increase the light scattering within the fibre (transparency) and thus increases the lustre. The presence of short fibre on the surface decreases lustre and is removed during singeing. Lustre increases from 180 g/l of NaOH solution to a maximum at 260-300 g/l, then decreases slightly [45]. Theoretically lustre increases with an increase in swelling and therefore with a decrease in the temperature of merceriza-

tion [46]. However, if the temperature is decreased, there will be surface dissolution of the fibre which may result in a decrease in lustre [44]. On the contrary, lustre increases with increase in temperature of mercerization [47, 48] inspite of lower swelling value. This may be due to the faster and uniform penetration of NaOH at higher temperature. The staple length of the cotton is also significant since the long staple fibre has the best shape of cross-section. Twisted double yarn is more lustrous after mercerization than non-twisted loose yarn. A face cloth such as sateen will show the greatest increase in lustre and is caused by the long floats lending themselves to the effective tension more readily than shorter crossings of the yarn.

9.3.4 Gain in strength

Mercerization, both slack and with tension, increases the strength uniformity along the fibre length [49], but mercerized fibre with tension shows greater gain in strength than that of without tension. In practice, the improvements in strength are noticed mostly upon yarn treatments, with fabric the major effect is on the surface only. Mercerization increases the tensile strength of cotton fibres by eliminating the weakest points in the fibre [50, 51]. Mercerization increases the cohesion between individual cotton hairs and this closer embedding of the hairs in the yarn not only increases the strength but makes it more uniform in strength and less in diameter.

The physical properties of mercerized fibres are related to the orientation factor; the Young's modulus increases with increase in orientation. The elongation acts in reverse, decreasing as the orientation increases [52, 53]. The increase in orientation of the crystallites with respect to fibre axis can be attributed to such factors as the reduction in crystallinity of the fibre, the decrease in lengths of crystallites and fibre deconvolution [54, 56]. In case of slack mercerized cotton increased strength is accompanied by an increase in extensibility, thus deconvolution is not the only factor influencing the changes in mechanical properties on mercerization apart from decrystallisation and length of crystallites [57].

The twist of yarn plays an important role and low twist appears to be essential for maximum increase in strength. Grey yarn with soft doubling twist gives stronger yarn.

9.3.5 Increased moisture absorption

Mercerized celluloses absorb more water, have higher regains and more easily wet out than unmercerized fibres. Due to caustic soda penetration, many hydrogen

bonds are broken and it is estimated that the number of available, hydroxyl groups are increased by about 25%. Mercerization, thus decreases the amount of crystalline part or increases the amorphous content of the fibre. This increase in the proportion of amorphous part is directly related to the moisture sorption. Moisture is assumed to be absorbed by suitable groups in the amorphous region and on the surface of the crystallites. When mercerization is carried out under tension, the changes in crystalline portion is comparatively lower than that without tension and hence also the moisture sorption. Standard cotton has moisture content of about 7%, mercerized cotton with tension has about 9% and that of without tension about 11%.

9.3.6 Increased dye adsorption

Mercerized cotton shows increased depth of shade, increased rate of dyeing and the irregularities due to neps and unripe cotton are less prominent. Generally immature cotton with large lumen responds particularly well to increased light scattering and hence decreased dye uptake. The greater colour yield on mercerized cotton takes place to different degrees at different depth of colours [58] and the magnitude of increased depth of shade varies for different dyestuffs [59]. The increased depth of shade of mercerized cotton has been attributed to optical effects arising from the modifications of fibre size and shape [60, 61] and to changes in internal light scattering [62], as well as to actual increases in dye content due to increased amorphous part of the fibre. About half the total dye savings is attributed to optical effects. The change in pore volume and reduction in lumen diameter are primary causes of consequent improvement in colour yield and reduced light scattering within the fibre. Mercerization thus lowers the dye costs, savings at 2% depth averaged 40%, while at 6% with the same dyes the average saving is about 60%.

Cotton can be causticized or half-mercerized to increase the dye uptake and economics up to 25% may be realised. Semi-mercerization or causticization is carried out in caustic soda solution between 25 and 30°Tw at a temperature of 20-25°C, sometimes without stretching the cloth to restore original dimensions. Sodium hydroxide solution above 30°Tw the rate of colour absorption decreases. Semi-mercerization is also an important step where heavy shades are required with the expensive vat colours. Better results are also observed with aniline black on goods which have received a semi-mercerization treatment.

9.3.7 Increased reactivity

The reactivity of mercerized cotton is increased by about $1^1/_2$ times at lower temperature in comparison to that of unmercerized cotton. The increased reactivity is not so marked when mercerization is carried out under tension. The reactivity ratio is generally referred to as the ratio of copper number of the mercerized to unmercerized samples. The increased reactivity increases dye absorption, moisture sorption and chemical reaction, but at the same time it also accelerates the reaction with acids and oxidising agents and is susceptible to degradation.

9.3.8 Removal of immature cotton

Mercerization has been recognised as a method for removing immature (dead) fibres to obtain level dyeing effect on cotton fabrics. The dead fibres are underdeveloped and appear as flat or slightly twisted tapes. They are non-crystalline, convolutions are sometimes absent, cell walls are extremely thin and the lumen is collapsed and hence do not contain dye to same extent as matured fibres.

9.3.9 Physical compactness

Mercerization improves dimensional stability of cotton woven fabrics [63]. When knitted fabrics are compared with respect to their relative openness, temperature increases can be said to improve mercerization because when the goods are bleached and then mercerized, the fabric becomes more dense. However, when unbleached fabrics are mercerized, the fabrics become more open [64]. Mercerization also gives moderate improvement in crease recovery of cotton fabrics [65] as well as some protection against the decrease in tensile strength caused by easy-care finishing.

9.4 Mercerization of Remie and Flax Fibres

Remie and flax are often used in the same fabrications and are often blended with cotton to improve its performance. Informations as a result of common conditions of mercerization are of great interest to minimise the variation in dyeing behaviour for the three natural cellulosic fibres. Flax fibres generally possess a high degree of lustre and mercerization is generally done to improve the affinity of dyestuffs, assist in the crease-resisting process, improve abrasion resistance and cover the reediness in cloth associated with yarn unlevelness.

The effects of slack and tension mercerization on the morphology and accessibility characteristics of remie, flax and cotton fibres are compared [66]. Mercer-

ized remie increases in size but not in circularity; mercerized flax fibres do not increase in size or shape; mercerized cotton fibres increase in area and in circularity as a result of swelling in caustic soda. The changes occuring in linen [67, 68] and flax [69, 70] fibres have been reported. Slack mercerizations of remie and flax result in considerable losses in yarn strength, while tension mercerizations result in increased strength. Increased yarn strength is seen in both slack and tension mercerization of cotton yarn. Increases in fibre accessibility are obtained in all mercerized fibres, but the magnitude of change in flax is approximately half of that in remie and cotton. Changes in fibre shape and accessibility characteristics are lower when cellulose yarns are held under constant tension than when they are allowed to shrink freely during mercerizing treatment. Mercerization of remie results in a complete conversion of Cellulose I to Cellulose II and a decrease in the degree of crystallinity to 50% [71]. The orientation of the crystallites in cotton is increased and that of remie is decreased due to intra-crystalline lateral swelling unrestrained by a restrictive primary wall [72]. Structural realignment of cellulose crystals does take place during the NaOH treatment of flax fibre [73].

With the same dyes and conditions of dyeing used for remie, flax and cotton, variations exist in the shade produced. All three fibres can be successfully mercerized to improve dye exhaustion and colour yield, but the extent of increased depth of shade produced on each treated fibre will vary with the specific dye used.

9.5 Mercerization of Blended Fibre Fabrics

Mercerization of blended fabrics containing polyester and cotton is done to improve the low lustre of cotton as compared to polyester and also to secure a more solid dyeing. For such blends the mercerization process is generally carried out in the same way as 100% cotton, but using caustic soda of lesser concentration i.e. 42^0 Tw along with penetrating agent. Hot mercerization has been found to give more uniform results. Under the mercerizing conditions cotton component in the blend undergoes physical and chemical changes, whereas polyester component undergoes a topochemical changes, resulting in surface hydrolysis. This leads to a reduction in strength proportional to the weight loss of the polyester component. The fabric after mercerizing is neutralised and made slightly acidic (pH 6) with acetic acid.

Generally, the blends containing polyester/viscose or polyester/polynosic com-

ponents are not mercerized. Fabrics containing mixtures of cotton and rayon require special precautions as the regenerated fibres, and in particular the viscose fibres show a higher alkali solubility than cotton fibres. Maximum swelling and solubility of viscose fibres occur at room temperature for NaOH concentration on the order of 9-10% by weight (100 - 110 g/l). Actually, viscose rayon withstands the action of alkali of mercerizing strength, but during washing with water, the alkali becomes diluted and at a concentration of about 9-10% (by wt.), the hydrated ion pairs, $20H_2O$ can penetrate the amorphous as well as crystalline regions, causing an unlimited swelling and the fibres are degradated. The loss in strength of viscose fibre, thus, is not during mercerization step, but during the washing-out process. The following approaches can be adopted to minimise the degradation of viscose in the blends:

(i) Alkali should be quickly removed from the fabric after mercerization with a good flow of water at 100°C. The solubility of viscose is less marked at higher temperature.

(ii) If possible, hot mercerization can also be adopted to minimise degradation.

(iii) Addition of electrolyte (e.g. NaCl) in the rinsing bath diminishes the proportion of dissolved viscose. Other protective agents such as sucrose, glycerine etc. are also recommended.

(iv) Additions of electrolyte into the mercerizing liquor are also possible.

(v) Use of KOH or mixture of KOH and NaOH in the similar proportion (ratio) to that of blended fibres in the fabrics is useful. Mercerizing with KOH alone can be done in a solution of 55-60° Tw at 15-18°C with dwell time of 90 sec but is expensive.

Polynosic fibres are more stable than the ordinary viscose fibres in alkaline medium and thus cotton/polynosic blended fabrics can be mercerized without taking any special precautions. However, rinsing process with hot water is also advisable. High wet-modulus (HWM) fibre induces a higher strength loss and thus mechanical degradation can be minimised by applying sufficient tension.

9.6 Mercerizing Machineries

Mercerization with alkali can be carried out in the cloth (woven and knitted) form and in the yarn (hank) form. Mainly two systems i.e. chain and roller mercer-

izing machines are developed for mercerizing cloth in open-width form. There has been a long standing supremacy contest between chain type and chainless mercerizer. One particularly tricky problem is reconciling the need for tension during mercerizing with the undesirability of tension in knit goods. Yarn mercerizing has, of course, been commercially established for many years in the manufacture of sewing threads, embroidery cottons, and lace goods. Farmer Norton, Benninger, Mather and Platt, Machinen, Bobcock, Bruckner, Brugman (Netherlands), Co. Pro. Tex S.r.l. (Italy), Menzel, Kusters, Goller, Dornier, Cibitex, S.r.l., Kleinewefers, Jaeggli and other makers have developed new types of machines with the aim of low mercerizing liquor pick-up, good degree of mercerization, better final width control, increased output and cost reduction. Now-a-days mercerizing units are equipped with liquor concentration regulator, measuring unit, cooling unit, lye recovery unit, purification unit, reciprocating metering pump and unit to dissolve caustic soda. Generally a mercerizing machine consists of four sections which will have different tasks according to the process technique :

i) mercerizing section : impregnation with caustic soda;
ii) intermediary squeezing aggregate : dividing off the mercerizing section against the stabilizing section;
ui) stabilizing section : water treatment and thinning down concentration of the lye;
iv) intermediary squeezing aggregate : dividing off the stabilizing section against the washing section;
v) washing section : washing-off the alkali and neutralisation (if necessary).

9.6.1 Cloth (woven) mercerizing machines

A typical clip chain mercerizing machine for woven cloth is shown in Fig. 9-6. In this type of mercerizing machine shrinkage is allowed in the primary stage of the

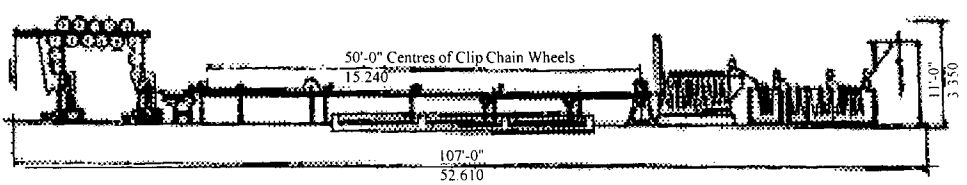


Figure 9-6. Clip chain mercerizing machine (Courtesy of Mather & Platt).

process and tension is applied in the later stage to bring the material to the original dimensions. The cloth is impregnated with cold concentrated caustic soda solution by passing through two 3- bowl padding mangles. Pressure of 10 to 25 tons is applied and more pressure is applied to the second mangle. In between the padding mangles the cloth is passed over timing drums to allow thorough action of alkali on the cloth. Due to higher speed of the second mangle only warp tension can be applied to the fabric and a warp tension indicator is fitted on the drums. On leaving the second mangle, the cloth is led to an open stenter frame for applying tension both the filling and warp direction. After the cloth has travelled about 20 ft in a stretched condition alkali is rinsed from the fabric by overflowing water from a series of cascades. Beneath each of the cascades, vacuum extraction slots are mounted so that as the rinse water overflows it is immediately vacuumed from the underside of the fabric. The washing on the stenter can be carried out in a counter current system. The residual alkali concentration should not be more than 8% on the cloth. After leaving the stenter the cloth passes over compensating rollers which regulate the tension. The cloth then enters the recuperator or the steaming box divided into series of compartments. The residual caustic in the cloth is dissolved under the action of steam and caustic is collected at the bottom of each compartment. On emerging from the steaming chamber, the cloth is squeezed and washed. These washing units are the final portion of the mercerizing range and may be a series of 7 to 8 washers followed by neutralising washer using either sodium bicarbonate or acetic acid. The whole range is about 107 ft long with a standard chain length of 50 ft. The width of the range is 14 ft. Production of this machine is about 55 m/min.

The chain mercerizing machine has one inherent disadvantage. As the force for keeping the material under tension acts mainly on the outer edges and the line of force diminishes towards the middle, a greater elongation takes place at the edges than in the middle of the fabric (Fig. 9-7). Prior to needling up on the chains the warp density, threads per cm over the whole width of the fabric is constant, after stentering it is less at the edges than in the middle. Different measures were tried to avoid this considerable disadvantage but none were really successful. Therefore development took place from chain mercerizing machines to chainless mercerizing or roller mercerizing machines.

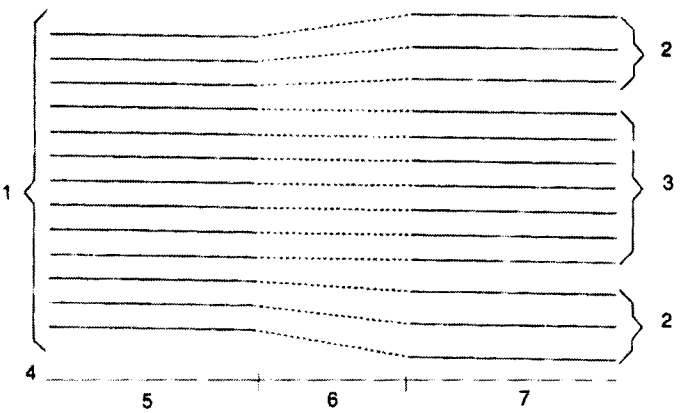


Figure 9-7. Disadvantages of chain mercerizing.
1. normal warp density ; 2. reduced density ; 3. normal density ;
4. difference in warp density ; 5. in front of chain expanding unit ;
6. in the chain expanding unit ; 7. after the chain expanding unit.

The line diagram of a Benninger chainless mercerizing machine is shown in Fig. 9-8. Fig. 9-9 shows a traditional chainless mercerizing machine with the roller

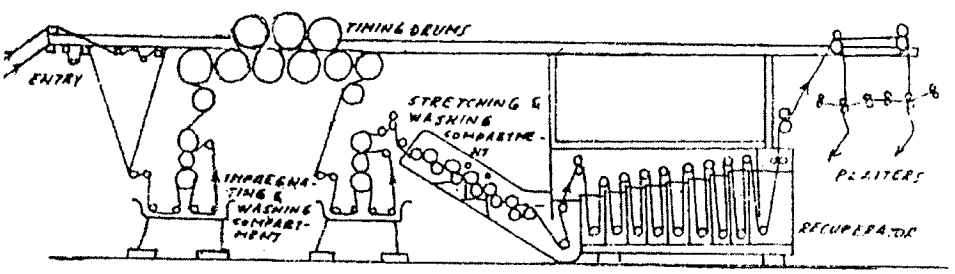


Fig. 9-8. Chainless mercerizing machine (Courtesy of Benninger AG).

arrangement. In this system the fabric is pre-stretched, tension is maintained till the mercerizing process and after-washing are completed. The cloth enters the padding set-up exactly in a similar manner to that of chain type. The cloth after padding with mercerizing liquor is passed through specially curved and specifically dimensioned expander rollers which make possible an even expanding effect over the whole width. The expansion depends on the diameter of the roller, the curvature of the roller as well as the angle of warp. Fig. 9-10 shows the expanding zone

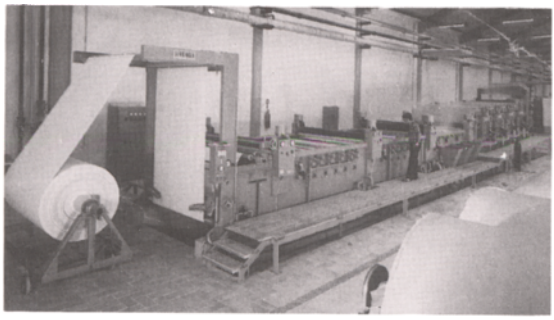


Figure 9-9. Chainless mercerizing machine (Courtesy of Swiss Association of Machinery Manufacturers, VSM).

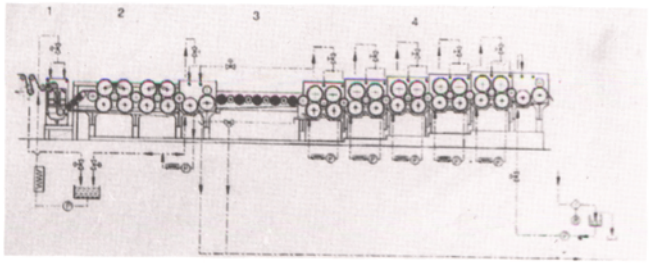


Figure 9-10. Expender zone in the ''Ecomerce'' (Courtesy of Kűsters).
1. ''Flexnip''; 2. Diffusion zone ; 3. Expanding zone ; 4. Stabilizing zone.

incorporated in the "Ecomerce" mercerizing installation and Fig. 9-11 its drive

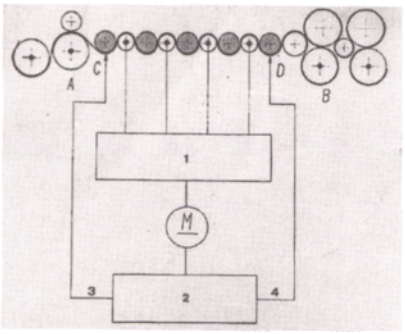


Figure 9-11. Driven system of the expanding zone.
1. Differential gear unit ; 2. Cloth tension control ;
3. Actual value ; 4. Nominal value.

arrangement. The expanding zone consists of a combination of 5 curved expander rollers and 4 driven cylindrical rollers. The drive system is driven by one motor which drives the 4 driven rollers via differential gear unit.

Washing takes place only after the cloth has passed over first few rollers. Normal shrinkage takes place in the washing compartment. The material - at the entry into the mercerizing section - is expanded to its original width at the entry into the washing section by the "mycock" roller arrangement. Fig. 9-12 shows the arrange-

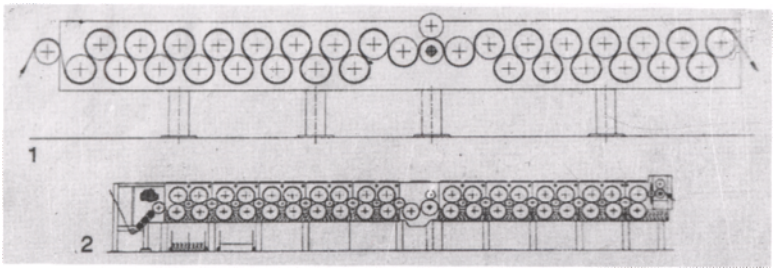


Figure 9-12. Different types of chainless mercerizing installations.
1. traditional roller arrangement ;
2. new roller arrangemnt of the Zittauer Maschinenfabrik.

ment of the rollers in a traditional chainless mercerizing machine as well as the improved arrangement found in the mercerizing machine of the Zittauer Maschinenfabrick. In this the rollers are not situated obliquely to one another but directly one above the other in pairs. The material in this arrangement has a longer contact with each other. The cloth content in the mercerizing compartment is larger, or alternatively, for the same cloth content as in a traditional compartment, this arrangement permits a far more space-saving installation.

Generally, hot water is used for washing. The steaming (recuperator), washing and neutralising steps are carried out in a similar manner mentioned in the chain type of machine. Development of new high efficiency washing units in the mercerizing machines have minimised the amount of water required to adequately remove alkali from the processed fibres [75, 76]. Open-width washing sections with vertical or horizontal cloth run with 15-25 m fabric holding capacity, drum washing section with squeezing units and "Extracta" with efficient predetermined washing effect with low water and steam consumption are some of the washing units frequently used with mercerizing machines. The advantages of chainless mercerizing

system over chain type are less floor space requirement and more production. It is possible to process two, or three cloths superimposed in chainless machine to increase the output.

Mercerizing and causticizing of cotton woven fabrics can also be carried out in batch system for small and medium lots [77]. Figs. 9-13 and 9-14 show the line

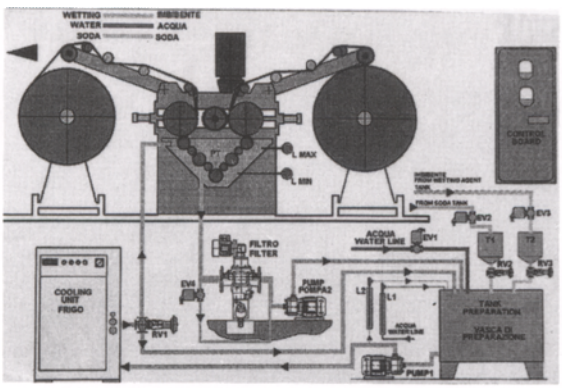


Figure 9-13. Cibitex model C.B. causticizing and mercerizing machine.

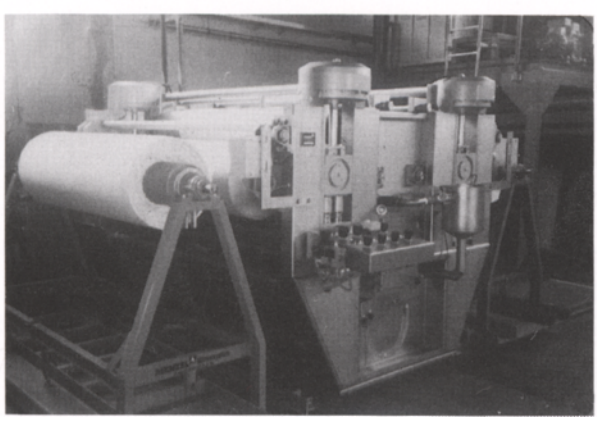


Figure 9-14. Menzel ''minimerce'' range for mercerizing-caustic treatment.

diagrams of "Sodatrice" (Cibitex S.r.l.) and "Minimerce" (Menzel) mercerizing and causticizing machines. In these systems the fabric after impregnation in alkali and extension is wound onto a roll. The caustic soda supply tank is mounted overhead, providing gravity feed to fill the impregnation tank. After the trough has been filled

it is lifted by hydraulic pistons. At the same time the rubber and steel rollers, which are arranged in a V-formation, are pressed from below against the two squeeze rollers (Fig. 9-13). The guide rollers squeeze the goods repeatedly (7 times) below the liquor surface. The high liquor fabric interchange ("sponge impregnation") thus set-up promotes extremely uniform penetration of the textile by the mercerizing liquor. Continuous contact with the guide rollers prevents widthwise shrinkage. The squeeze rollers above the impregnation trough work with a fixed, driven centre roller and two horizontally movable squeeze rollers. The goods are squeezed off to liquor uptake of about 80%. After the impregnation and batching the goods are ready for washing-off and neutralisation, washing-off is a high-temperature operation. Water is continuously sprayed on the fabric during unwinding and stabilisation occurs. The repeated immersion squeeze off promotes rapid removal of the caustic soda solution during washing. The advantages of this system are space saving, best economic efficiency, complete process control, tight-strand fabric guidence with tension control and reduced pollution of environment. The productivity of this type of machine is about 3000 m/h with more uniform mercerization than on continuous ranges and a favourable cost/performance ratio.

Among the various other developments Küster's Ecomerce is a new system utilising the Flex Nip impregnation unit in which the treatment liquor is metered through twin banks of pipes which feed a V-shaped treatment bath (Figs. 9.15 and 9.16). Fabric passes vertically downwards at open-width through the liquor and

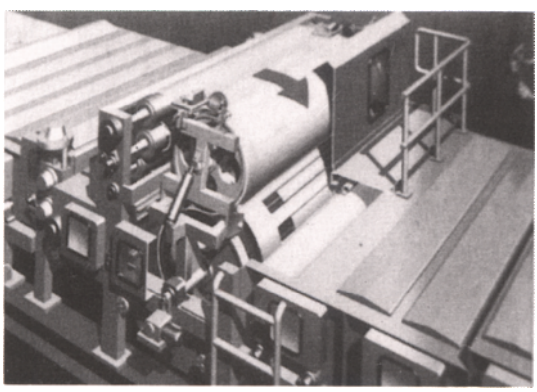


Figure 9-15. Ecomerce Mercerizing machine (Courtesy of Küsters).

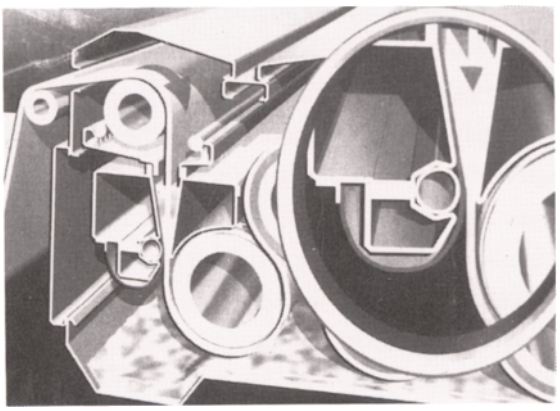


Figure 9-16. Flex-Nip impregnation unit (Courtesy of Küsters).

the fabric is squeezed on exit from the bottom of the V-shaped low liquor capacity bath. "Ecomerce" is designed for hot mercerization in accordance with the wet-on-wet process. The great ecological and economic advantage of the "Ecomerce" process is that the lye circulation contains only approximately 10-20 litre of lye. This chainless mercerizing system maintains a constant fabric tension in both warp and weft directions by the use of differentially controlled stretching zone.

Kleinewefers has promoted the application of reduced pressure to the fabric immediately prior to impregnation using "vacuum cap" unit [78] to facilitate fast, more rapid and complete swelling. In core mercerizing (Fig. 9-17) the impregna-

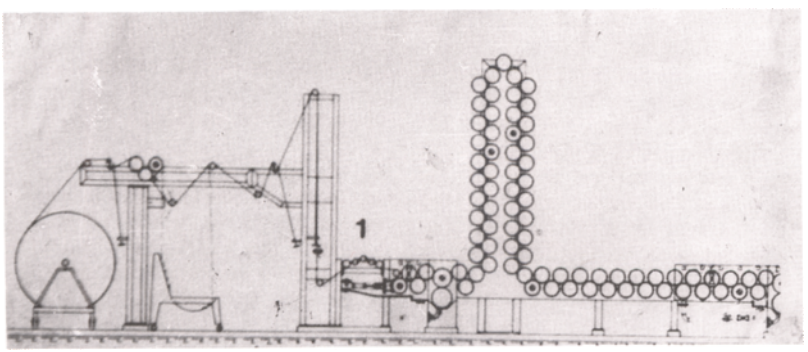


Figure 9-17. Core mercerizing system with vertical reaction section, 1 Vacuum hood (Courtesy of Kleinewefers).

tion and reaction sections constitute the mercerizing compartment. The fabric is impregnated with caustic soda solution in the impregnating section with vacuum hood. At the exit squeeze rollers remove excess liquor from the fabric. Moving on, the fabric runs through the reaction section under positive guidence in the same way as in a conventional mercerizing machine.

The Farmer Norton dual purpose chain mercerizing machine can be used for conventional cold lye impregnation or for hot impregnation. Higher impregnation temperatures are always followed by cooling section to ensure maximum fibre swelling. Farmer Norton (U.K.) has also developed a "Baby Mercerizer" where the fabric passes both direction through the machine. Apart from the low level investment character, this machine is useful for small scale processors.

The Gollar Perfecta chain mercerizer uses two low volume impregnation units with low tension fabric guiding. The Gollar Optima Model MM chainless mercerizing range for single run treatment of woven and knitted fabrics, from pile or large-diameters batch, may be optionally used for impregnation with caustic soda dry-on-wet or wet-on-wet.

Benninger's Dimensa mercerization range (Fig. 9-18) is a combination of

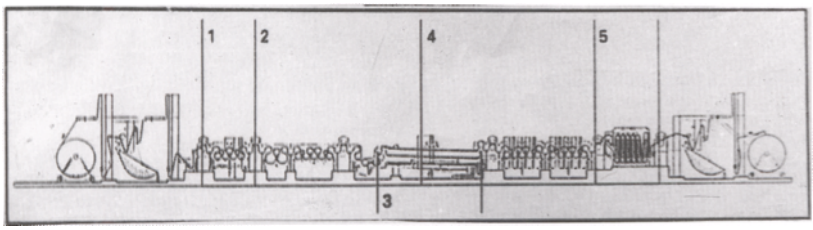


Figure 9-18. Dimensa mercerizing machine : cloth run diagram. 1. impregnating zone ; 2. cooling and reaction zone ; 3. stenter frame ; 4. stabilizing zone ; 5. washing and neutralising zone.

chainless and chain type mercerizing machine. The fabric is first impregnated with hot mercerizing lye in a very short intensive impregnation compartment followed by a cooling and reaction zone. In this area fabric guidence is on the chainless principle. This is followed by a pin stenter section or stabilising zone in which hot weak lye is introduced into the fabric using the chain principle. Ultimate stabilisation is obtained using a conventional, highly effective stabilising compartment with chainless guidence. The final section comprises a high efficiency washing and

neutralising zone consisting of Extracta compartments. Saving on strong lye, water and steam of around 30% and shorter down times are claimed.

Application of foamed alkali liquor on the cloth can produce one sided mercerization and differential dyeing [79].

Some innovative open width washing units are developed in which steam, water and air are projected onto both sides of fabric in any desired combination to generate turbulance and intensive washing of the mercerized fabrics.

9.6.2 Yarn mercerizing machines

Many machines for mercerizing of cotton yarn in the form of hank are developed. The yarn mercerizing machine usually available may be single sided or double sided with about 5 to 10 kg per batch per pair of rollers. Almost all the yarn mercerizing machines have similarity in design. Mather & Platt, Bertshinger, Kleinewefer, Noubold, Jaeggli and others are well known makers of yarn mercerizing machines. Useful summeries of the state of the art of yarn mercerizing have been presented [80-82]. A typical two sided yarn mercerizing machine (double arm type) is shown in Figs. 9-19 and 9-20. The machine is provided with pairs of

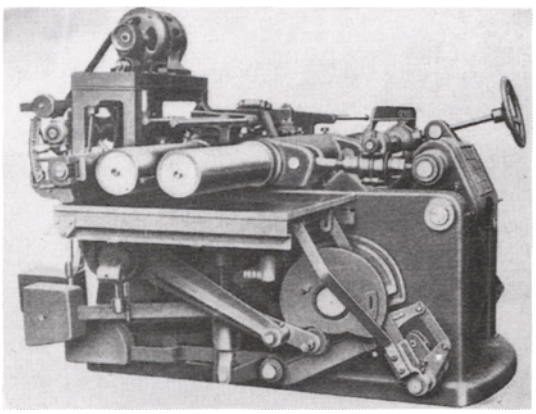


Figure 9-19. Yarn mercerizing machine (Courtesy of Mather & Platt).

rollers and one roller is fixed and the other is movable (B) (Fig. 9-20). Yarn is laid on the rollers and then caustic soda solution of 25% strength at 20°C is applied by raising the trough, F. The rollers are caused to rotate and the yarn is allowed to shrink during impregnation process to ensure penetration of alkali. It is arranged to bring the rollers somewhat closer together while they still continue rotating. Squeez-

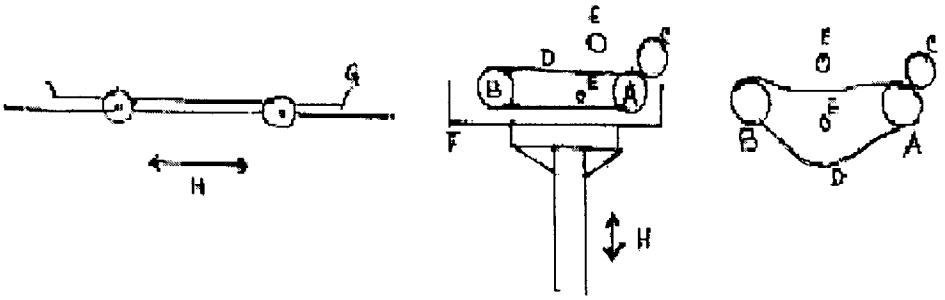


Figure 9-20. Line diagram of yarn on rollers (a) water trough on trolly ; (b) in stretched state ; (c) in slack state.

A – Stationary roller	E – Spurt pipe
B – Movable roller	F – Caustic soda trough
C – Squeezing roller	G – Water trough on trolly
D – Yarn in hank form	H – Rail

ing roller (C) above the fixed roller also assists penetration of alkali. The yarn is then stretched during which the rollers are made to move away from each other steadily thus extending the length of the skiens and stretching the yarn to about its original length. The excess alkali is squeezed out. The alkali trough (F) then goes down and the water trough (G) is brought into position. The yarn is washed by spraying hot and cold water through spurt pipe and the yarn is still under tension and is squeezed. During mercerizing and washing the direction of the rotation of rollers and thus the skiens are periodically reversed which ensures even penetration. Finally, the supporting arms go down, tension is released, rollers come closer together, squeezing rollers are lifted up, hanks are removed from the rollers and then neutralised with acid and again washed in other apparatus. The complete cycle takes 5 min out of which alkali treatment lasts for 2.5 min. The whole cycle occurs in one complete revolution of the cam shaft. Machinery developments of interest include the cone-to-cone continuous yarn mercerizing machine from Jaeggli with highly developed automatic control [83]. Various studies have been carried out to examine the potential for mercerized rotor yarns [84, 85].

9.6.3 Knit goods mercerizing machines

The traditional machines used for mercerizing woven fabrics are inadequate to treat circular knit fabrics. Owing to knit structure, such fabrics are easily deformed, distorted and extended on stretching during mercerization and washing. These dis-

tortions become permanent and have adverse effect on the elastic properties of the fabric structure [86, 87]. The existing chainless mercerizing machines can be modified to suit the knit goods either by installing tension controlling device [88, 89] or by processing between conveyer belts [90, 91]. However, the main disadvantages of open width knit goods mercerizing are edge creases of the flattened tube and variation in several characteristics from edge to centre. To eliminate edge creasing problem air is introduced into the fabric by means of jets to balloon the tube [92] and several manufacturers have produced machines for knit goods mercerization.

A typical Dornier continuous mercerizing range for tubular knit goods is shown in Fig. 9-21. Fig. 9-22 shows the line diagram of similar Sperotto Rimar Knit goods

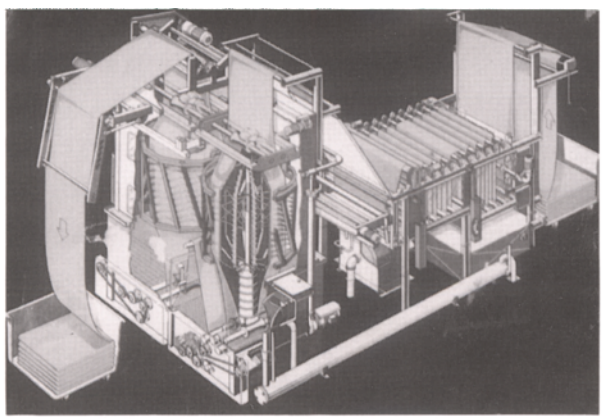


Figure 9-21. Knit goods mercerizer (Courtesy of Dornier, GmbH).

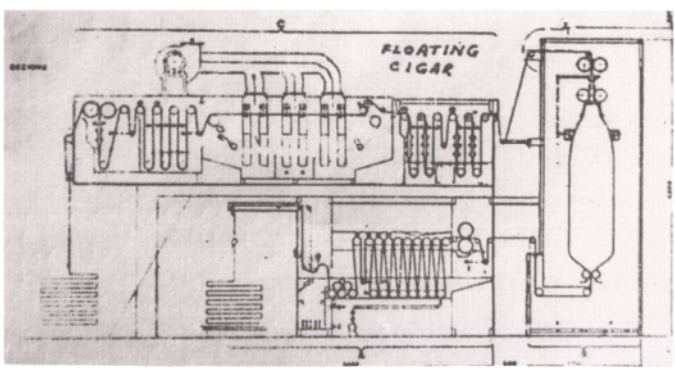


Figure 9-22. Sperotto Rimar Knit goods mercerizing range.

mercerizing range. Other machinery manufacturers offering equipment for tubular fabric mercerizing include Jaeggli [93], Caber [94], Pegg-Whiteby [95,96] etc. Dornier's tubular mercerizing range consists of a flat tubular impregnation zone followed by opening of the fabric using a circular expander with rolling friction and pressure compensation. Thus a higher spreading tension can be achieved with almost constant traction force, i.e. longitudinal tension. Motorised adjustment of circular and flat tube expanders drastically decrease the setting up times, and the water used in rinsing is recycled and passed through a heat recovery system.

The sperotto Rimar MT-15 tubular cotton knitted fabric mercerizer consists of three units, an impregnation/reaction tank, a stabilisation and reduction tower and a washing and rinsing tower. To achieve tension in the width steel spreaders (called cigars) are necessary, these being placed inside the circular knit fabric enabling stretching during passage of the fabric both in the first phases of hot washing and in the following cooling phases. In case of MCS machine this frame is flat and horizontal, but the other manufacturers produce vertical frames of tubular design.

Knit goods mercerization can also be done in batches by rinsing the knitted fabrics after impregnation and winding onto a perforated beam [97] or by carrying out the stabilisation by water spraying during batching after impregnation [98, 99].

Based on the tubular fabric mercerizing machine, Dornier, GmbH, has developed a combinable mercerizing and bleaching concept for tubular warp knitted fabrics. The combined mercerizing/bleaching machine (Fig. 9-23) comprises im-

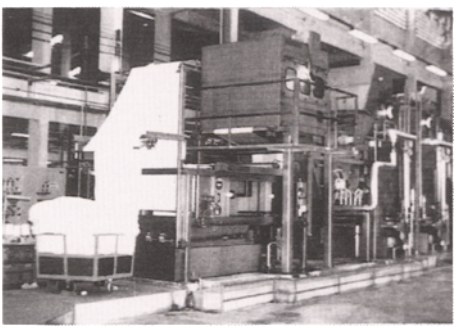


Figure 9-23. Combined mercerizing/bleaching machine for tubular warp knitted fabrics (Courtesy of Dornier, GmbH).

pregnating, reaction and scouring sections in the mercerizing unit, and is comple-

mented by a heating and dwell zone for peroxide bleaching. A combined after-washing section can be integrated, enabling fluorescent brighteners to be applied, including a neutralising bath and treatment trough located after the scouring unit. The metering cycles are controlled, automatically regulated and partially monitored.

9.7 Hot Mercerization

Since the beginning of the sixties, mercerization with hot caustic soda at a temperature between 60-70°C has become known as hot mercerization. In classical cold mercerizing, processing takes place at temperatures of 15 to 18°C with 31 to 35% caustic soda solution with a dwelling period of about 50 seconds. At that range cotton swells best but also fastest. The fast swelling increases the outer edge density of the fibre also rather swiftly. The viscosity of the caustic solution is also such that the penetration into the grey fabric becomes even more difficult. These result in poor mercerizing of the core and lack of uniformity as the reaction is restricted mainly to the surface of the yarn or fabric. To increase the penetration into the fibre alkali stable wetting agents are necessary and are expensive. In addition, the effluent load is considerable and ecologically critical.

In hot mercerization process, with caustic soda at 60-70°C the cotton swells more slowly. The outer edge density of the cotton fibre is not increased as fast as in cold mercerizing. At 60-70°C, the viscosity is considerably low. Thus the penetration of alkali is extremely rapid with improved core mercerization and consequently results in better uniformity of alkali treatment. Due to higher temperature and higher diffusion into the core the dwell time of the material in the mercerizing section can be reduced from 50 sec (cold) to 20 sec (hot). In other words, the mercerizing installation for the same production speed is shorter than the one based on cold mercerizing. Fig. 9-24 shows the interrelations between the necessary dwell time and the temperature of the lye. Cold mercerizing requires about 55 sec to reach a nominal concentration of 300 g/l on the material. Hot mercerizing at 60-70°C achieves the same possible effect already in 20 seconds.

In hot mercerization fabric is either padded through hot caustic solution or at ambient temperature and then passed through steamer where the fabric is steamed. The process sequence of two step hot mercerization is as follows :

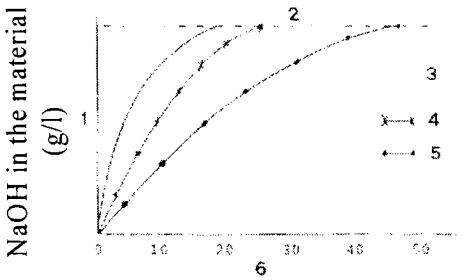


Figure 9-24. NaOH concentration in the textile fabric in relation to dwell time in the lye and lye temperature. 1 NaOH in material (g/l) ; 2 nominal concentration (approx. 300 g/l NaOH) ; 3 ''Flexnip'' addition mercerizing 60 .... 70°C ; 4 hot mercerzing 60 .... 70°C ; 5 cold mercerzing 10 .... 15°C ; 6 dwell time in NaOH.

i) Saturation of cotton material with sodium hydroxide solution of mercerizing strength preferably under relaxed condition at temperature between 60°C and boiling point with an impregnation time ranging from 4 to 60 sec.

ii) Controlled hot stretching following the saturation. The material being stretched 2-20% of its original dimensions.

iii) Cooling the stretched material to a temperature less than 25°C which completes the swelling effect.

iv) Tension controlled washing to NaOH solution of 6% (stabilisation).

v) Final washing or neutralisation under normal condition without tension being applied to the fabric.

Another possible method of hot mercerization consists of wet-in-wet impregnation of fabric immediately after washing at 95°C and a subsequent hot squeezing with high speed steam injected. The heated fabric is then impregnated with caustic solution at 30°C in the first step and 20°C in the second step. These offer the stabilisation. Sequence is normally carried out under tension controlled condition.

The various factors changing the properties of cotton due to hot mercerization are slightly different from that of conventional mercerization. The degree of swelling of individual fibre is lower at higher temperatures [100] as the process is an

exothermic one. The conversion of the crystalline structure from Cellulose I to Cellulose II is retarded at higher temperature and reveals a skin-core appearance [101]. Mercerizing at elevated temperatures can lead to improvements in lustre and shrinkage, has no adverse effect on strength, and under certain recommended conditions, can result in a softer handle [102-105]. However, the improvement in lustre is contradictory which may be due to the fact that the double treatment during hot mercerization produces a different response compared with that of the single stage process in cold mercerization. Temperatures upto 45°C can be used without any deterioration of lustre [106], but on the other hand no substantial improvement in lustre is found as a result of double mercerization [107].

The following advantages can be detailed for the hot mercerizing process :

i) Due to higher and rapid penetration of alkali, level and uniform mercerization can be obtained with lesser contact time resulting in greater productivity with more compact unit.

ii) At higher temperature (about 100°C) the shrinkage is nearly half as compared to conventional mercerization and the shrinkage does not vary with dwell time.

iii) The necessary and expensive alkali resistant wetting agents needed in cold mercerization are not necessary for the hot mercerizing process. Production costs are reduced and the environment load is lowered.

iv) In hot mercerization the freed reactive heat is used to raise the temperature of the lye to about 40°C. The further increase in heat to about 60-70°C is done in a moderately priced heat exchanger.

v) The fibre and fabric structure become more pliable and less elastic.

vi) Higher tensile strengths are obtained due to greater degree of stretch and modification of cellulose while saturated with hot caustic soda solution. These lead to a greater orientation of molecular structure and increased cohesion between fibres.

vii) Hot mercerized fabrics have better wet crease recovery than conventionally mercerized fabrics. It induces easy care finishing characteristics. Hot mercerized fabrics are flatter and less crumpled when drip dried.

viii) Hot mercerized cotton fabric gives uniform application of dyes. Though the total uptake is better, but the colour yield is less pronounced than con-

ventional mercerized cotton. The colour yield decreases as the temperature of mercerizing treatment increases [108].

ix) The combined mercerizing and desizing, and mercerizing and scouring processes minimise the energy conservation and can lead to cost saving. In combined processes a steaming step is inserted between hot alkali saturation and stabilisation [109]. The steaming time is about 10 min at atmospheric pressure and about 5 sec under pressure at 130 - 140°C.

x) Hot mercerizing technique also reduces the inventory and pollution problem.

9.8 Liquid Ammonia Mercerization

Some twenty years ago it was found in systematic research work that a treatment of cotton fibre with liquid ammonia produces effect similar to that obtained with caustic soda. Liquid ammonia treatment was first developed by the English firm Coats in the mid-1960s. Coats developed a process with which it was possible to treat cotton yarn in a continuous manner and the firm Platt Saco Lowell Ltd., Accrington, England acquired the world wide licence for this process called ''Prograde''. The firm Cluett, Peabody & Co., known for its process of compressive shrinking (Sanforising), has in 1973 registered two trade marks : ''Duralized'', name for a material treated with liquid ammonia and ''Sanfor-Set'', name for a material treated with liquid ammonia as well as by compressive shrinkage, system Cluett. The liquid ammonia treatment is widely accepted for yarns used in sewing threads and for special fabrics such as denims, corduroys, chambays, pillow material, materials made of cellulose, linen, jute and mixtures of cellulose with polyester or nylon.

Among various amines, the liquid ammonia appears to be unique in its swelling action on cellulose and its effect on crystal structure. Anhydrous liquid ammonia, being smaller molecule, penetrates cellulose very rapidly and complexes with hydroxyl groups of cellulose after breaking hydrogen bonds in crystalline regions and increases distance between cellulose chain in crystallites [109-115].

The ''Prograde'' process requires the addition of selected amines to improve the original ammonia system. In this process (Fig. 9-25) yarn is treated in liquid ammonia at its boiling point (–33°C or –28°F) for less than a second, then subsequent immersion of yarn under tension in hot water for about 0.1 sec to produce a 40%

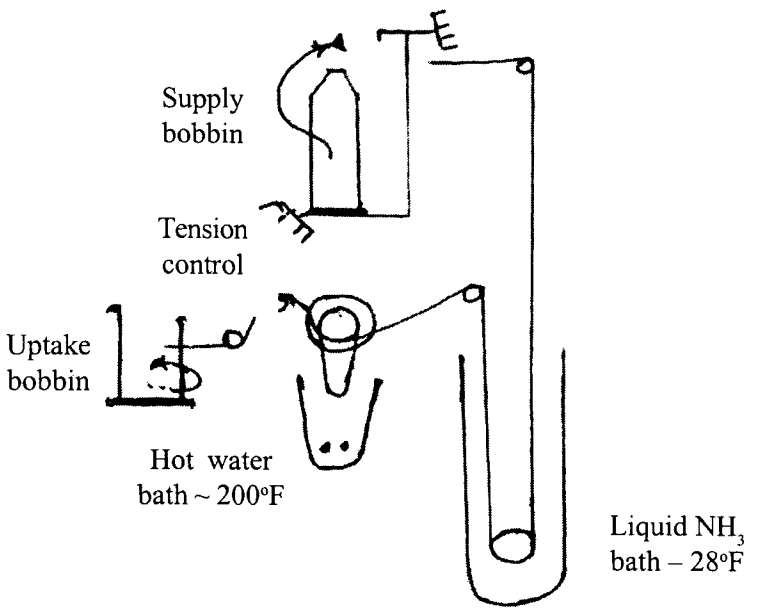


Figure 9-25. Diagram of the "Prograde" process [116].

increase in tensile strength, improved lustre etc. In this process the yarn after ammonia treatment is stretched and subsequently ammonia is removed by hot water washing.

"Sanforset" represents a combination of exclusive liquid ammonia processing and controlled compressive shrinkage to provide no iron characteristics without strength loss on cotton denims, plus an unusually soft and supple handle. The installation for ammonia treatment on woven and knitted fabric is shown in Fig. 9-26. Fig. 9-27 shows the fundamental construction of such an installation for the ammonia process. After the entering process (1) the material passes over five predrying cylinders (2) and then through a cooling station (3). The drying cylinders reduce the moisture content of the material to below the normal humidity, whilst the cooling station it is being cooled. The material then passes through a lock (4) into the actual treatment chamber (5) where it is impregnated with liquid ammonia in a trough (6). Finally it is squeezed off in a padder which can be determined by looping (7). The ammonia is driven off in two felt calenders. In this heat treatment some 90-95% of the ammonia is removed. The rest, which is chemically bound to

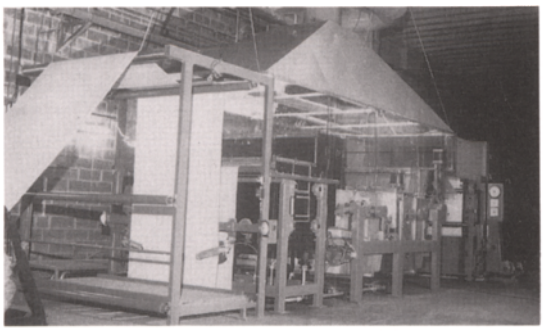


Figure 9-26. Installation for ammonia treatment on woven and knitted goods (Courtesy of Veramtex S.A/N.V.).

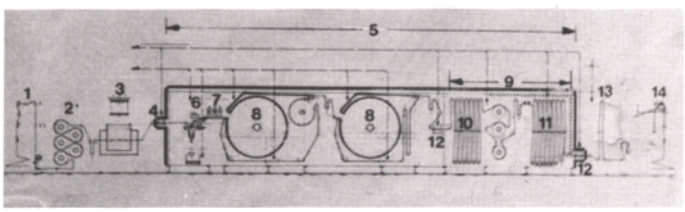


Figure 9-27. Sanfor-set treatment range (Courtesy of Monforts, Germany).

the cellulose is removed in a steaming compartment (9) consisting of a pre-dwelling zone (10) and a steaming zone (11). The entering and exit ends of the steaming compartment are again sealed by locks (12). An after dwelling zone (13) and the take-off device (14) complete the installation. The treatment chamber is kept under slight vacuum to prevent ammonia gas from escaping. The evaporated ammonia is led to a recovery unit where it is compressed, cooled and liquidized, to be led to a storage tank for later perusal. The chemically bound ammonia is removed from the material seperately. It is possible to dissolve it in water and reuse it as a chemical or as manure. It can also be heated until it escapes and is oxidised. In all cases care is taken that no pollution occurs.

The properties and swelling processes of cotton fibres after treatment with liquid ammonia are compared with conventional and hot mercerized cotton in Table 9.3. The nature of the improvement in properties resulting from the treatment of cotton with liquid ammonia depends on the conditions of its removal from the fibre. Dry removal of ammonia after treatment converts Cellulose I to Cellulose III,

TABLE 9.3
Comparison of Various Swelling Processes [117]

	Mercerization		Liquid ammonia treatment	
	Conventional	Hot	NH_3/H_2O	NH_3/dry-steam
Characteristics of swelling processes				
Speed	Relatively low	Relatively fast	Very fast	Very fast
Degree	High	Decreases with temperature	Somewhat less than hot caustic	
Evenness	Uneven in tightly constructed fabrics	Good	Good	Good
Shrinkage forces	Relatively small shrinkage forces and exhibit good extensibility in swollen condition.		High shrinkage forces, may lead to difficulties in maintaining exact dimensions.	
Properties				
Lustre	Large increase	Improved	Improved but not quite as high as mercerization.	Only slightly increased.
Dye take-up	Strongly increased	Not quite as high	80-90 % compared to conventional mercerzation.	Slightly or no improvement.
Strength	Improvement in the treatment of yarn or knit goods, none in the treatment of fabric. Similar effect for all methods.			
Dimensional stability	Similar effect by all methods. On heavy and tight fabrics, NH_3 treatments have the advantage.			
Resistance to deformation	Relatively stiffer and harshes	Somewhat softer hand	Similar to hot mercerzation	Softer and more resilient.
	Dry crease recovery angle (C.R.A.) is scarcely altered.			Distinctly increase dry C.R.A.

and there is hardly any increase in dye diffusion. The ammonia-water system gives an improvement in colour yield in subsequent dyeing which is only slightly less than that obtained by mercerizing [118]. This has been attributed to the changes in internal volume after ammonia treatment [49]. The moisture regain and water absorbancy of fibres treated with liquid ammonia are increased compared with values of untreated fibres, whereas both these parameters and dyeing properties of mercerized cotton are adversely effected by liquid ammonia treatment. ''Sanforest'' process produces a shrinkproof material which does not only shrink in domestic washing (as is the case with Sanforised material) but also not during drying in tumbler dryers. The treatment with liquid ammonia produces non-iron properties without loss of strength, such as one must put up with in the so-called non-iron finishing processes. At the same time the wearing properties of the material are improved ; it acquires a smoother surface, better uncreasing angles and soft and pliable handle (Table 9.4). The stretching of the fabric with 60-80% ammonia not only avoids shrinkage during the treatment but also compensates for shrinkage during scouring and bleaching. The ashing shrinkage potential is greatly reduced and fabrics treated in this manner are more resistant to shrinkage through repeated washings (Fig. 9-28). Liquid ammonia treatment prior to resin application will improve the relationship between strength and crease recovery and increase resistance in most cases to tensile, tear strength and abrasion (Table 9.5). Liquid ammonia is found to reduce fibrillation in the laundering of resin-finished goods. A combination of slack mercerization and liquid ammonia treatment for the production of cotton stretch fabrics have been reported [124]. It is also possible to combine liquid ammonia treatment with dyeing into a single operation as in the case of ''Rapid anhydrous method''. Liquid ammonia treatment is found to have less pollution problem but comparatively an expensive process. The most important cost element is the recovery of ammonia which involves refrigeration. The liquid ammonia treatment can also be applied in the pre-and after-treatments with organic solvents, since no water is used and the liquid ammonia can be largely recovered. There is no danger of the personnel being troubled by smell, etc., since the machines are hermetically sealed and the process is carried out in a closed system which is under slight vacuum.

TABLE 9.4
Mechanical Properties of a 100% Linen Fabric for Garments

Properties	Conventional finishing	Finishing with dry condensation		Finishing with damp reticulation	
		Without NH_3	With NH_3	Without NH_3	With NH_3
Shrinkage after 5 washings at 40°C					
Warp	– 8%	– 3.50%	– 1.10%	– 4.20%	– 1.20%
Weft	– 8%	– 3.50%	– 2.00%	– 4.00%	– 1.50%
Creasing angle (Warp + Weft)					
Dry	127°	170°	250°	145°	240°
Wet	124°	165°	235°	170°	265°
Wash-and-Wear behaviour (Monsanto)	1.5	3	4.3	3.5	4.5
Abrasion resistance (Accelerator 3'000 rpm/120')	– 10%	– 32%	– 16%	– 26%	– 10.50%

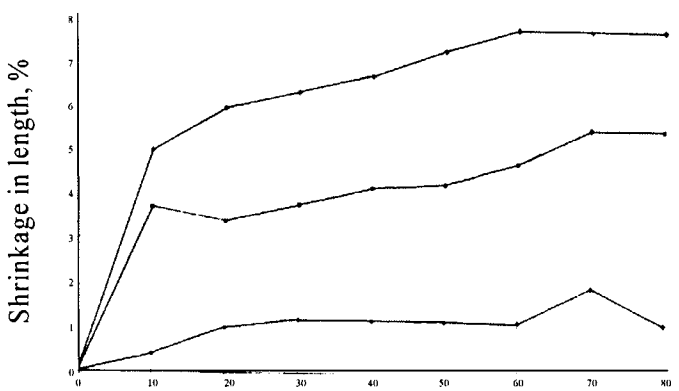


Figure 9-28. Shrinkage after multiple washings ; cotton fabric for professional clothings, 290 g/m².
1 Bleached ; 2 Bleached + NH_3 ; 3 Bleached + NH_3 + Resin.

TABLE 9.5
Results of the Ammonia Treatment on Cotton Fabric [120-123]

	Grey fabric	Bleached sample	Bleached + NH_3	Bleached + NH_3 + resin
Tensile strength				
Warp	1191.9 N	1267.5 N	1393 N	896.6 N
Weft	890.7 N	864.3 N	879 N	662.2 N
Elasticity				
Warp	16.30%	10.20%	11.20%	12.40%
Weft	11.10%	15.60%	20.80%	13.80%
Tear strength				
Warp	50.2 N	29.3 N	30.8 N	48.3 N
Weft	48.1 N	24.0 N	28.2 N	40.2 N
Creasing angle				
Dry		183.6°	193.2°	220°
Wet		128.8°	143°	235°
Creasing angle (3'000 rpm/90s)		4.40%	3.60%	3.90%

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Chapter 10

OPTICAL BRIGHTENING AGENTS

10.1 Introduction

Textile fibres do not appear perfectly white due to the presence of certain coloured impurities. During chemical bleaching, coloured impurities are either destroyed or decoloured by oxidation or reduction. Over-bleaching may reduce the fibre strength. Even well bleached fabrics possess a slight yellowish appearance. This yellowish hue of the materials can be eliminated by whitening with optical brighteners or fluorescent brightening agents (OBA or FBA). Sometimes blueing agents are also used. In 'blueing' the initial yellowish shade of the textiles is covered by the blue dye and a bluish white results. However, the corresponding blue dye itself absorbs in visible light and thus the total amount of reflected light is smaller than in the case of unblued material, so that the blued mjaterial is less bright i.e., it is dull, or grey-ish.

The optical brighteners counteract the yellowness of the fabric by increasing the reflection of blue light rays. They convert invisible short-wave ultraviolet rays of sunlight into visible blue light and has a degree of whiteness which is comparatively more intense. Fig. 10-1 illustrates a comparison of the possible spectral

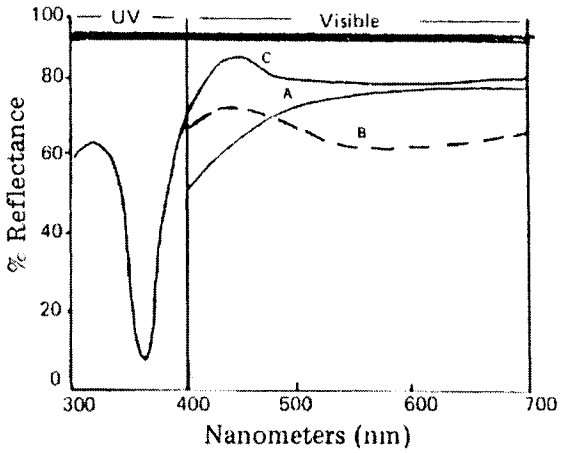


Figure 10-1. Reflectance of a bleached cotton fabric (A), after adding a blue tint (B) and after adding a fluorescent brightener (C) [1].

reflectances of a fabric after bluing and optical whitening. The 100% reflectance

which represents a pure white light is shown as a straight line parallel with the horizontal co-ordinate. Curve A which represents the bleached cotton deviates from the ideal, while the fabric with blue tint (Curve B) is apparently whiter although there is some loss of intensity and less reflectance. The fabric treated with whitening agent (Curve C) improves the distribution over the spectral reflectances and also add to the total amount of light reflected, thus giving whiteness of outstanding brightness. One possible reason for high reflectance in the visible region is that the fluorescing material does not absorb light in the 400-500 nm region and exhibits the effects of emission. The whitening effect given by the optical brightener is thus an additive effect, while that produced by 'bluing' is a substractive effect.

10.2 Chemical Constitution of Optical Brighteners

The production and consumption of optical brighteners are constantly increasing and the annual increase is amounted to about 10-12%. In addition to textile, detergent and paper industries (Table 10.1), optical brightening agents are also used

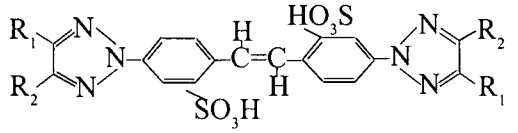
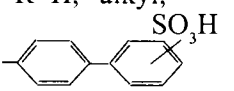
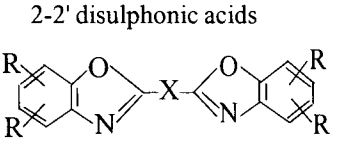
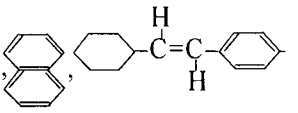
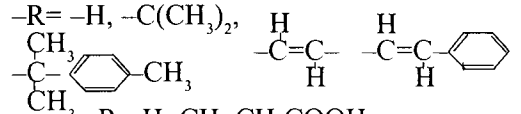
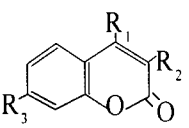
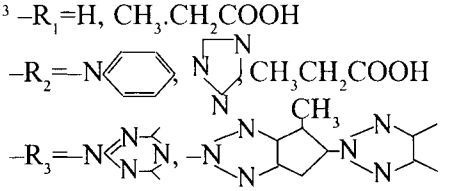
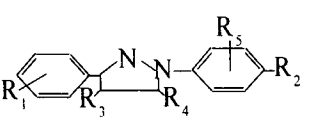
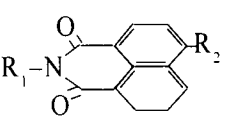
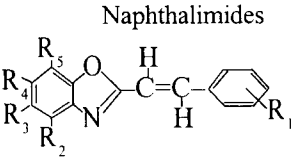
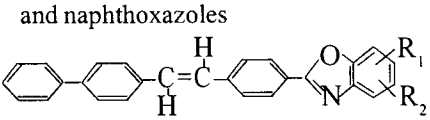
TABLE 10.1
Consumption of Optical Brightening Agents

Branch	Consumption (%)
Detergent mixture	40
Paper	30
Textiles	25
Synthetic fibres & plastics	5

for the brightening of feather, fats, gelatine, wood shavings and sand dust, for the brightening of paints, leather, furs, straw and in the photographic industries.

Fluorescent brightening agents are organic compounds, which when present on textile fibres, exhibit fluorescence. FBAs resemble dyes in all respects except that they have no visible colour and are thus called colourless dye. They are substances normally having a system of conjugated double bonds [2] and must be essentially planer and should contain electron donating groups such as OH, NH_2 etc. and be from electron accepting groups such as NO_2, –N=N– etc. Table 10.2 contains a selection of important basic structures with reference to the main field of their derivatives. The majority of the compounds are built up from aromatic and heteroaromatic structural elements which are reconnected together either by direct

TABLE 10.2
Chemical Constitution of Some Important Optical Whiteners [3, 4]

Fields of application and substrates	General basic structures	Substituents
Textiles, detergents Polyamide (T,W).	 4, 4'-bis-(γ-triceol-zoyl) stilbene-2-2' disulphonic acids	–R=H, –alkyl, 
Textiles, detergents, Spinning solutions/ melts, plastics Polyamide (T,W), Polyester (T,W,S), Polyvinyl chloride (K), Polystyrene (K), Polypropylene (K), Triacetate (T,S).	 bis-(benzoxazolyl)– derivatives	–X=   –R_1=H, CH_3.CH_2COOH
Textiles, detergents, Spinning solutions/melts, plastics Polyamide (T,W), Polyester (S), Polyacrylonitrile (T), PVC (K).	 Coumarins	
Textile, detergents Wool (T), Silk (T), Triacetate (T), Polyacrylonitrile (T), Polyamide (T,W).	 Pyrazolins	–R_1= –N, –Cl –R_2=Cl, –SO_3H, –SO_2NH_2. –SO_2NH, SO_2CH_3 –R_3, –R_4=–H, Alkyl–  –R_5=H, –Cl
Textiles Polyester (T), Polyacrylonitrile (T), Sec. acetate (T), Triacetate (T).	 Naphthalimides	–R_1=alkyl, –$(CH_2)_3N(CH_3)_2$ –R_2= –O alkyl, –SO_3H, –$NHCOCH_3$
Textiles, detergents Polyamide (T,W), Polyester (T,W).	 2-styryl-benzoxazoles and naphthoxazoles	–R_1=CN, –COO alkyl, –Cl –R_2+R_3=  –R_3,–R_5=H, –alkyl –R_4=H, –alkyl– 
Textiles, Spinning solutions/melts Polyester (T), Polyamides (S).	 4-phenyl-4'-benzoxazolyl stilbene	–R=–H, –Cl, alkyl –SO_2CH_3

T = Textiles, W = Detergents, P = Paper, S = Spinning solutions, K = Plastic.

bonds or by ethylene bridges. These latter serve as π-electron bridges and connect the resonance systems without interrupting the continuous conjugation essential to the whitener molecule (Table 10.2). By far the greater number of compounds are derivatives of stilbene, benzidine, benzthiozole, benzaminazole, benzoxazole, coumarin, pyrazolines etc. [3]. About 80% of all optical brightening agents produced are derived from stilbene. The world market now carries more than 2500 trade marks, representing 200 various products belonging to more than 15 structural types [4].

10.3 Mechanism of Fluorescent Whitening

When a specimen transforms a part of the absorbed light into light of another wavelength instead of into heat (as is the case with normal dyed specimens), it is called fluorescent specimen. FBAs absorb ultraviolet light in 300-400 nm region from day light and emit it in the visible region (400-460 nm) at the blue-violet of the spectrum. The emitted blue light compensates for yellow tints of fibres and at the same time they also increase the luminosity of the goods. The emission spectrum is characteristics of a particular agent on a given substrate. Depending on the energy distribution of the spectrum, the fluorescent light emitted is blue-violet, blue, blue-green [5]. According to Stoke's law the shape of the fluorescene band can be predicted from the shape and the position of the absorption band, and the colour of the fluorescence can thus be determined. The relative distribution of the emitted light within the emission band is also important.

The mechanism of optical brightening is also explained on the basis of quantum theory of light and electronic structure of atoms and molecules [6, 7]. In the fluorescent substance molecules which have absorbed radiation (light) of short wavelength can pass into an excited state of higher energy. These excited molecules then return to the ground state of lower energy with re-emission of light quanta only slightly smaller than those absorbed i.e., of lower energy and longer wavelength (visible light). The average mean life of excited molecules is 10^{-8} to 10^{-9} sec and in general the shorter this life the less difference will be there between the wavelength of fluorescence and emitted light and greater will be the fluorescence as there will be less time for dissipation of energy as heat.

10.4 Factors Influencing the Functions of Optical Whiteners

Optical brighteners are applied to substrate as a seperate after-treatment process

or are incorporated into bleaching and finishing baths. Since the fluorescent brightening agents behave like dyestuffs, their efficiency and effectiveness are influenced by various factors that are important in application.

10.4.1 Substrate

The brightening effect is dependent on the nature of the substrate. For example, a very strong reflectance is observed with whitened cotton, but it is weaker in viscose and wool. All synthetic fibres absorb strongly in the near ultraviolet region. Since the fluorescence produced by optical brightening agent is added to reflectance of the substrate, the maximum fluorescence effect is achieved on those substrate whose ability to absorb the ultraviolet region is suppressed by chemical brightening. In the absence of sufficient affinity of brighteners, the application results in yellow to green colour yield.

10.4.2 Saturation

There is a saturation limit for each optical whitening agent. Above certain concentration on the fibre a yellow colour is superimposed on the flourescence resulting in decrease in whiteness. This is because at higher concentration of brighteners a protective optical layer (filter) is formed on the surface of the substrate which prevents the extinction of the molecules of the brightening agent in deeper layers (so called self-quenching, concentration quenching of fluorescence or filter effect).

10.4.3 Method of application

The saturation limit of an optical brightening agent, however, is also dependent on the method of application to the substrate. Usually exhaust application process gives higher whiteness value then it does when applied by padding technique for a given amount of whitener.

10.4.4 Time

Generally optical brightening agents have high rate of exhaustion on the substrate and therefore great care is to be taken to avoid unlevel application. Slow exhaustion rate and increased migration time is necessary to produce level whiteness on the fabric.

10.4.5 Temperature

The optimum temperatures of optical brightening agents on cellulosic fibres are usually between 40 and 60°C and further rise in temperature tend to lower the exhaustion. However, for synthetic fibres higher temperature is needed for good penetration of the brighteners.

10.4.6 pH

The chemical stability, solubility and affinity of optical brightening agents depend on effective pH value in solution. For example, for wool and polyamide fibres, optimum pH is on the acidic side for better exhaustion.

10.4.7 Salt

Generally salt is added in the application bath to promote and also to control the rate of exhaustion of the brighteners on cellulosic fibres.

10.5 Application of Optical Brighteners

The application of fluorescent brightening agent depends on the kinds of fibres on which it is applied and accordingly can be classified as direct (or substantative), disperse and cationic types. The direct brightening agents are mostly derivative of 4, 4'-diaminostilbene-2, 2'-disulphonic acid and are used mainly for the brightening of cotton, paper, viscose, linen and polyamides. Acid optical brightening agents contain free sulpho groups and serve mainly for the brightening of silk and wool. Basic optical brighteners contain amino groups and include mainly coumarin and pyrazoline types. They are used primarily for the brightening of natural and synthetic polyamides. Disperse optical brightening agents are water insoluble compounds of various structures and are used mainly for the polyester, cellulose acetate and polyacrylonitrile. They are mainly triazolyl stilbenes, bis (benzoxazolyl), ethylene coumarins etc. Often mixtures of optical brightening agents with violet and blue/green type are used to get a natural white fluorescent effect [8], Cation -active optical brighteners are compounds mainly of the methane ethanine type, which are used mainly for the brightening of polyacrylonitrile fibres.

Optical brightening agents may be obtained as powders, pastes, liquid water-insoluble forms or stable dispersion. The stabilised dispersions are suitable only for insoluble disperse optical brighteners. Generally the liquors of the brightening agents are not stable to light and should not be stored for a long time or exposed to light. They undergo cis-trans isomerisation in addition on exposure to light resulting in a compound which has practically no fluorescent effect. They also accelerate the photodegradation of textile materials on exposure to sunlight. An optical brightener should not be used on dyed materials because it flattens the shade.

Optical brightening agents are applied to textiles at the time of scouring, bleaching or finishing. When chlorite bleaches are used anti-chlorinating measures must

be taken. The fluorescent brighteners should be stable in the bleaching bath and also should be stable on the fibre at the thermosoling temperature in the case of polyester. In continuous processing when sodium chlorite is the bleaching agent, then fluorescent brighteners must be applied after bleaching in the wash-off, but with hydrogen peroxide bleaching it can be included in the peroxide bleach liquor. Fluorescent brighteners can be applied to cotton materials prior to resin treatment or it can be added to the resin formulation bath. However, proper selection of catalyst is needed since certain catalysts impair the light fastness of the treated fabric. Sometimes optical brightening agents are added during polymerisation of synthetic fibres to impart a reddish to neutral bluish tinge to fibre [9, 10]. Mass brightened material gives equal fluorescence intensity throughout the fibre, while the textile brightening effects have a ring of bright fluorescence with little intensity in the centre of the cross-section. For blended fabrics, a mixture of two whiteners that are suitable for both the component fibres is used.

10.5.1 Cellulosic fabrics

Optical brightening agents when applied to cellulosic fibres behave like direct cotton dyes and their uptake is influenced by temperature, electrolyte concentration and liquor ratio etc. The links between fibre and brightener involve hydrogen bonds, Van der Waal's forces and interactions of the dipoles of the brightener. The brightener penetrates the fibre in a monomolecular form, and having expelled a part of water in it, aggregates there, and takes on a greater volume, where it can no longer so easily leave the interior of the fibre.

Optical brighteners can be applied on cellulosic fibres either by exhaust or padding methods. In the exhaust method, goods are entered into the cold liquor containing optical brightener (0.5-0.6%, o.w.f.) and electrolyte (5 g/l) and then the temperature of the bath is raised to optimum slowly over a period of 15 min. When required temperature (depending upon the brighteners used) is reached, a further 30 min of running is sufficient for complete exhaustion.

When padding methods are used, the fabric is padded with a solution containing 0.05 to 4 g/l brightening agent in a two-bowl mangle at room temperature keeping 80-100% expression. The material is dried and stored in dark. To achieve good diffusion, full fluorescence and complete development of the brightener, a subsequent heat treatment on stenter or in curing unit may be given.

The light fastness properties of the direct optical brighteners used for cellulosic materials are medium i.e. of the order of 2-3. Other fastness properties are good to water and washing at 40°C, medium to good to washing at 95°C and medium to heat treatment at temperatures above 150°C and to sanforising.

10.5.2 Woollen fabric

Wool fibres have amphoteric properties rendering them capable of combining with both acidic and basic substances. However, wool contains more number of basic side groups which enable them to combine with acid type optical brighteners containing sulphonic or carboxylic groups. The most common brighteners for application to wool are a selected range of dastriazine derivatives with certain pyrazoline derivatives. The mechanism involves salt formation with amino groups of the polypeptide chains in the wool structure. In addition to this hydrogen bonds are also formed depending on the structure of the brighteners.

The goods are treated with a solution containing 0.02 to 0.2% fluorescent brightening agent and 2-4% acetic acid (40%) or 1-2% formic acid (85%) to maintain the pH of the exhaust bath 3 to 5. The treatment time is about 20 min at 40°C. A final rinsing with water completes the process.

Optical brighteners are often applied to wool with a reductive bleacher under acid or alkaline conditions. Wool after peroxide bleaching, a reductive bleaching is carried out for 1-3 h at 50-55°C, during which optical brightening agent may be added. It is usually added into the neutral reducing bath after 75% of the reduction time. When all the dithionite has been consumed, a 2% formic or acetic acid is added to complete the exhaustion of the whitening agent. Brightening in an acid bath alone does not give much good results.

The main problem of wool is its creamy colour and yellowing on exposure to sunlight. Both the bleaching and fluorescent brightening of wool accelerate the photo-yellowing and also photo-tendering [11]. These yellowing and tendering of wool have been shown to depend on the spectral distribution of light (affected by glass etc.), the pH [12], the moisture content of wool, the temperature [13] and the nature of chemical pre-treatment [14]. Photo-tendering is caused by oxidative and hydrolytic cleavage of the protein chains and the disulphide bonds [15]. The anionic degradation of protein fibres has been associated with photochemical reactions of the tryptophan, histidine and tyrosine residues [16, 17]. The fluorescent

brightening agents present on the fibre absorb uv light and thus accelerates the yellowing. The chemical structures of chromophores found during photo-yellowing have been reported, with amino acid dityrosine being identified on irradiated wool [18, 19].

A number of chemical treatments have been suggested to reduce the photo-yellowing of bleached and whitened wool. Tetrakishydroxymethyl phosphonium chloride, thiourea (alone or as a formaldehyde condensate) and some mercaptans and reducing agents [20, 21] and the reaction of wool with sulfamic acid [22] have been shown to offer some protection against photo-yellowing, particularly on wet wool.

10.5.3 Silk fabric

In contrast to wool, in silk the acid nature of the proteinic substance (fibrion) predominates, which can permit whitening with acid and basic type of brightening agents. However, for silk direct brightening agents are preferred.

After degumming of silk, a peroxide bleaching is given and the brightener is added in the subsequent reductive bleaching bath containing 0.5 to 4% optical brightener and 2-5 g/l reducing agent and treated for 45 min at 70°C. Then the pH of the bath is adjusted to 3.5 with formic acid and the treatment is continued for about 15 min, rinsed warm and cold.

Silk is generally brightened by exhaust method because higher degree of whiteness can be obtained in this case than by padding method. In the padding method, fabric is padded with a solution of 5 to 20 g/l of optical brightening agent along with 1 g/l wetting agent at room temperature, squeezed to approximately 100% pick-up and then dried at 100 to 120°C.

Like wool, yellowing is also a problem with silk. Fluorescent brightening agent accelerates the photo-degradation of silk, resulting in greater yellowing and losses in strength, especially in the presence of moisture [23-25].

10.5.4 Polyester fabric

Polyester fibres have no affinity for the water soluble optical brightening agents and thus water insoluble compounds are applied to polyester from dispersion in the same manner as disperse dyes by the formation of a solid solution in the fibre. These brightener particles penetrate into the fibre in a state of molecular dispersion and they are held in the fibre by Van der Waal's forces. A part of the finely dis-

persed particle forms a molecular solution in the bath. Only this proportion which has dissolved in the bath penetrates into the outer layer of the polyester, from where it diffuses slowly into the interior of the fibre. Diffusion within the interior of the fibre is essentially a function of the temperature and the concentration of the brightener in the interfacial zone.

In carrier method of application by exhaust process the polyester fabric is entered into a bath containing 0.5 to 2.0% optical brightening agent, 1 g/l dispersing agent, 2-4 g/l suitable carrier and acetic acid to maintain the pH around 5 to 6. The goods are run through the solution at 40°C for 15 to 30 min, the temperature of the bath is then raised to boiling in 30 min, and the treatment is continued for at least 90-120 min at the boil. Compounds such as diphenyl and chlorinated hydrocarbons are suitable carriers. The goods are then rinsed with hot water and dried.

In the thermofixation process the fabric is padded with 5-25 g/l dilute suspension of optical brightening agent at room temperature with a liquor pick-up of approximately 50%, dried at about 120°C in an open stenter and then heated for 30-60 sec at 190-200°C. Finally, the goods are washed and dried. This process makes possible higher thoroughput of material with superior dimensional stability.

In the pad-steam process the goods after padding with a liquor pick-up of about 80% are steamed at 100-101°C for 2-3 h or under pressure (1-1.5 kg/cm^2) for 25-30 min. Alternatively, the goods may be thermofixed by superheated steam at 150-170°C for 3-5 min.

10.5.5 Nylon fabric

Optical brightening agents of acid dyeing type are applied to nylon from an acid bath. Direct cotton dyeing type of brighteners vary in their affinity for polyamides. Cationic optical brighteners show affinity at low temperature, but maximum yield and fastness is not developed below 70°C [26]. The disperse optical brighteners are applied to nylon at boil in presence of dispersing agent (0.5-1%) at pH 5 to 6. They exhibit better light fastness (3-4) and washfastness (4-5 at 60°C) then acid dye type of brighteners.

With acid dyeing type, the goods are treated on jiggers or winch beck with a solution containing high affinity type brighteners (0.05 to 0.5%) and acetic or formic acid (pH 3.8 to 4.5) at 40°C for 10 min and then the temperature is raised to boil in 15 min and the treatment is continued for 30 min. The goods are rinsed and

dried. The light fastness of the anionic product is of the order of 1-2 but yellowing does not occur as in wool fibre. Nylon can be brightened by the hydrosetting process in HT equipment. The bath is set with 0.2-2% optical brightening agent, 0.5% sodium hydrosulphite, 0.1-0.5 g/l sequestering agent and 0.5 g/l surface active agent. The bleached goods are treated at 40°C for 10 min and hydrosetting is carried out for 15-20 min at 120-130°C (120°C for nylon 6, 130°C for nylon 6, 6). The treatment liquor is cooled to 80-85°C and then the goods are rinsed and dried. The improved light ($\simeq$ 3) and wash ($\simeq$ 5) fastness can be obtained.

Selected acid and disperse type of optical whitening agents can be applied to nylon by continuous or semi-continuous process. In the pad-roll process, fabric is padded with 10-20 g/l optical brightening agents at 50-70°C with padding mangle expression at 60-70% and then kept in a chamber for 1-2 h at 90°C. Acid conditions are maintained by adding ammonium chloride in the pad-bath solution. In the pad-steam process, the padded goods are steamed for about 3 min at a steaming temperature of 105°C. In the acid-shock process, the fabric after padding with cold solution containing brighteners are then treated in a boiling bath containing formic acid in an open width soaper, washed and dried. Certain acid type brighteners (pyrazolines and 1 : 2 : 3 triazoles) can be applied to polyamide by the thermosol process at 170-190°C. Heat fastness during heat treatment and fixation, however, is medium.

10.5.6 Polyacrylonitrile fabric

The acrylic fibres are normally white, but variations in degree of yellowness and stability to thermal degradation with fibres from different sources can be minimised by application of whitening agents [27, 28]. The Neochrome process involves applying brightener during the gel stage of fibre production. Though chlorite bleaching removes yellowness but certain fibres such as Courtelle cannot be bleached with chlorite because of subsequent degradation of the fibre. Furthermore, the nature of copolymer also determines the affinity of fibre for various optical brighteners. Mostly, polyacrylonitrile containing anionic groups confers an affinity for cationic type optical brighteners. These types of brighteners have either a heterocyclic nitrogen or external amino group with cationic character.

In the exhaust method, the fibre material is introduced into a bath containing cationic brightening agent and 3-5% formic acid (85%) to maintain the pH 3 to 4 at

about 70°C. The liquor is then brought to the boil in 30 min and held at that temperature for a further period of 30 min. The bath is finally cooled and the material is washed or rinsed.

The one bath two stage bleaching and brightening of acrylic fibres is quite popular. In this procedure, the material is boiled with chlorite, using oxalic acid as an accelerator for about 30 min, the bath is cooled to 80°C and excess chlorine is eliminated with sodium hydrosulphite. In the second phase, the optical brightening agent is added and the bath is again heated to the boil in 30 min and the material is treated at this temperature for further 30 min. The material is then worked up in the usual manner.

Non-ionic brightening agent can also be taken up by the fibre from suspensions. The fibre material is treated with a solution containing disperse type brighteners and 2% formic acid (85%) (pH 3 to 4) at 100°C for 30 to 40 min. Exhaustion can be accelerated by raising the temperature of the bath to 110°C.

There are certain type of acrylic fibres that can be whitened by padding techniques. The three methods of padding are pad-roll, pad-steam and acid-shock process. In the pad-roll process, the fabric is padded with a solution containing optical brightening agent, formic acid, dispersing agent and thickening agent, at room temperature to a mangle pick-up of 80-85%, batched, stored on roll in a chamber set at 100-105°C for 2 h. In the pad-steam process, the padded fabric is steamed in a saturated steam for 5 min at 105°C. In the acid shock process, the fluorescent brightening agents are applied to the material by mechanical pick-up and white is developed by acid treatment in a seperate bath.

10.5.7 Cationic dyeable polyester fabric

Cationic dyeable polyester possesses anionic group and hence cationic brighteners can be applied as in the case of acrylic fibres. However, the effect of cationic brighteners on acrylic fibres cannot be reproduced on anionically modified polyester [29]. This proves the fibre-brightener inter-relationship. Disperse brightener can also be applied to cationic dyeable polyester. The optical brightening agent can be applied to cationic dyeable polyester in a chlorite bath. The brighteners are applied at 98°C in presence of carrier based on dichlorophenyl or biphenyl. Suitable brighteners are chlorite resistant types based on benzofuranyl and benzoxazoyl – benzimidazole. Certain brighteners can be applied by thermosol method at 200°C.

Soft disperse brighteners can be applied at 160°C. The light fastness ratings of cationic brighteners on cationic dyeable polyester are higher than on acrylic. Non-ionic brighteners give poor ratings than on normal polyester.

10.5.8 Polyvinyl chloride fabric

The low melting types of PVC permit a maximum temperature of 60°C during optical brightening and thus carrier must be used in the application bath. The heat resistant types of PVC can be brightened either in presence of carrier at 65 to 75°C or without carrier in a boiling bath. Brightening is generally done during bleaching with sodium chlorite and optical brighteners, carrier, dispersing agent and cross-linking agents are added in the bleach bath. The bleaching bath is heated to 55°C and worked at this temperature for about 45 minutes. The material is then washed with cold water.

10.5.9 Other synthetic polymers and plastics

The use of fluorescent brighteners in whitening of polyolefins, polycarbonates and poly (methyl methacrylate) are reported [30]. The increasing demand for many new applications for plastics and trends for recycling have created a demand for the use of special optical brightening agent. Long life expectations for children's playing things, refrigerators and rainwear need a long life of optical brightening agents. New stilbene derivatives and addition of stabilisers improve the brilliance and high long life. These compounds also prevent yellowing of plastics during thermosol processing, giving a better white based material.

10.5.10 Blended fibre fabrics

The polyester/cotton blended fabrics can be optically brightened to the same degree of intensity and brilliance as pure cotton fabric. Normally, after application of disperse type optical brighteners for polyester fibre, either by exhaustion or padding method, the usual direct optical brighteners are applied to cotton by exhaust method. An intermediate treatment with hydrosulphite is necessary to remove polyester brightener deposited mechanically on cotton portion during padding operation. Optical brightening of polyester/cotton blends can be combined with bleaching. In the combined proicess, the goods are treated in a bath containing 1-5 g/l sodium chlorite along with 0.5-1.5% fluorescent brightener (o.w.f.) and acetic acid (pH = 4) at boil about an hour. The bath is then drained and the goods are given treatment with an optical brightening agent for cotton. In the continuous process of

application, the blended fabrics are padded with a solution containing disperse and cellulose brighteners along with dispersing agent. After padding and drying, the white is developed by baking for 20-30 sec at 150-200°C. The fabrics are then washed-off with detergent (2 g/l) and soda ash (1 g/l) at 50-60°C for 15 min, rinsed and dried. Pad-steam process can be applied to polyester/cotton blends in the same way as for 100% polyester by the inclusion of the pad bath of a suitable concentration of a cellulose brightener. In another method, the optical brighteners for polyester/cotton blends may be added in the resin finishing bath. In this method, the goods are padded with a solution containing cross-linking agent, catalyst, softener, fluorescent brightener for both polyester and cotton and wetting agent, dried and cured at 140-150°C for 4-5 min. A final scouring followed by washing process completes the process. Although the process is economical, the brightening effects obtained are not very intense.

The most efficient process for optical brightening of polyester/wool blended fabrics is to brighten polyester content first and then bleach wool portion with peroxide and brighten the wool in a reducing bleach following peroxide bath. However, the two bath process is time consuming. In one bath process, the goods are treated with a bath containing the optical brighteners for wool and polyester, carrier, dispersing agent, a protective agent for wool and acetic acid (pH $\simeq$ 5) at 95-100°C for 20-30 min, cooled the bath, rinsed and washed with non-ionic detergent (2-3 g/l) at 40-45°C for 15 to 20 min. However, the one bath process suffers from the disadvantage of possible staining of the wool by the carrier and polyester brightener not being removed by a simple scour.

The blends containing polyamide/cellulose can be optically brightened with a solution containing selected cellulose brighteners by adjusting the temperature and pH of the application bath. The brighteners which show little change in uptake on nylon by change in pH should be selected. Likewise, raising the temperature increases the uptake on the nylon relative to cellulose. The temperature of the bath is raised to 95-100°C over 30 min and the fabric is treated for 30-40 min and then rinsed well and dried.

For polyamide/wool blended fabrics fluorescent brightening agents (1-2%) are applied following hydrogen peroxide bleaching in presence of stabiliser (3-5 g/l). The treatment is carried out at 70-75°C for 45-60 min and then rinsed and dried.

For brightening of acrylic/cellulose fibre blended fabrics the compatibility of the brighteners for each fibre is most important. If the two classes of brighteners are not compatible, then a two-bath process is necessary, first applying the acrylic brightener and, then in a fresh bath the cellulose brightener. Peroxide/hypochlorite bleaching of acrylic/cotton or combined bleaching techniques can be used. Chlorite stable products should be applied from the bleach bath. Another requirement is wet light fastness in presence of perborate containing washing agents. Garments made from PAN or their blends on drying in sun, after washing with washing powders containing perborate, are observed to show yellowing.

For acrylic/wool blends, the acrylic portion is brightened in the normal way and then the wool is bleached with hydrogen peroxide and subsequent reduction bleaching is done in a bath containing suitable brightener (1-2%) and stabilised sodium hydrosulphite (3-5 g/l) at 85°C for 30 min. The fabric is then rinsed and dried.

For polyamide/acrylic blends, both the fibres can be brightened by using suitable disperse type brighteners at 95-98°C for 30-60 min, cooled, rinsed well and dried. Where bleaching is necessary, a suitable brightener stable to chlorite may be included in the bleach bath.

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Chapter 11

COMBINED PRE-TREATMENT PROCESSES OF TEXTILES

11.1 Introduction

Now-a-days all efforts in the field of pre-treatment processes of textiles are directed towards shortening and simplification of the treatment. In the conventional preparation, the desizing, scouring and bleaching processes are carried out seperately at high temperatures, requiring the use of large amount of thermal energy. In order to minimise energy consumption it has become necessary to combine several pre-treatment stages by reducing number of operations or by shortening the reaction time. Although several new processes and some continuous and semi-continuous machineries have been developed, the ideal of a truely single stage process employing only one desizing cum bleaching stage suitable for all qualities of cloth and end uses, has not been developed so far. Process integration to enable integrated desizing/scouring, scouring/bleaching or desizing/scouring/bleaching continues by boosting the chemical recipe to improve the removal and decolourisation of impurities. Low energy chemical pre-treatment of textiles using higher concentrations of chemicals in order to integrate the processes can work well if the process is carefully controlled. Many methods have been reported and a number of low temperature (25-45^{0}C) batch scouring and bleaching processes are available [1-10] combining two or all the three stages into two stage or single stage process. In all these accelerated processes, cost savings are obtained in steam, water, electricity and labour with little increase in chemical costs. The brief account given in this chapter aims at presenting a bird's eye view in the area of combined pre-treatment processes.

11.2 Combined Scouring and Desizing

Many combined scouring and desizing processes are developed but these processes are particularly useful if the sizes are not intended to be recovered [11-13]. Alkaline hydrogen peroxides and peroxy compounds such as persulphate, perphosphate, peroxydiphosphate can be used as oxidative desizing agent and free radicals are produced favouring size degradation rather than bleaching. However, some bleaching does also take place under these conditions.

A combination of peroxy compound and caustic soda at elevated temperature can effectively combine desizing and scouring conditions. In this process, the fab-

ric is treated with a solution containing 0.2% potassium persulphate and 4% sodium hydroxide and then steamed in J-Box at 95°C for 85 min, washed and dried. This combined process of cotton fabric is more or less adequate with a fluidity of about 1.8.

In the pad-steam process, the fabric is padded with a solution containing 70 g/l caustic soda, 3 g/l sodium persulphate and 10 g/l non-ionic detergent at 40°C with a wet pick-up of about 80% and then the fabric is steamed for 12 min at 102°C. The fabric is then washed thoroughly in an open soaper with a temperature of about 98°C in the first and second, 80°C in the third and 60 and 50°C in the fourth and fifth compartments respectively.

Grey fabric can be simultaneously desized and scoured by making use of a suspension of enzyme, a chlorinated solvent and surfactant solution (Markal II process, Chapter 4).

11.3 Combined Scouring and bleaching

Single stage bleaching processes using hydrogen peroxide require some additional chemicals that can act as activator, stabiliser, surfactant and scouring agent. Strongly alkaline solution of hydrogen peroxide has been advocated for such combined processes. Sodium persulphate and potassium persulphate boost the single stage operation in presence of hydrogen peroxide. Other compounds which accelerate the peroxide reactions are urea, methylcarbonate and tetra acetyl ethylenediamine. However, such chemicals increase the chemical cost. Generally, in traditional kier bleach the cost of utilities is nearly 3.5 to 4 times the chemical cost and in continuous bleach it is about twice to $2^1/_2$ times the chemical cost.

A combined process (ATIRA) can be carried out in a kier with a bleach liquor containing hydrogen peroxide (50%) 1.5%, sodium hydroxide 1.5%, sodium meta silicate 1%, sodium tetrapyrophosphate 0.5%, emulsifying agent 0.5% and wetting agent 0.1% with a liquor ratio of 2.5:1 at 60°C. The liquor is circulated through the material for about 12 h. A low temperature catalyst (''Urjal'') developed by ATIRA avoids the use of sodium silicate in the bath and also bleaching with hydrogen peroxide may be possible even at room temperature.

In another process [14,15], the kier circulation is reduced by using emulsified solvent systems (Chapter 4). Emulsified solvent system consists of blends of emulsifier and solvents like chlorinated hydrocarbons, mineral oils etc., which stabilises

or emulsifies oils, fats and waxes from the raw cotton and enhances the action of other chemicals like hydrogen peroxide. This system may be used in kier boiling or J-Box or thermofixation chambers. In this process, the desized and washed cotton fabric is treated in open kier boiling for 4 h with a liquor containing hydrogen peroxide 1%, emulsified solvent 0.3%, caustic soda 0.3%, soda-ash 0.5%, sodium silicate 2.5%, magnesium sulphate ($Mg\ SO_4.\ 7H_2O$) 2.4% and wetting agent 0.1% at 90°C. The treated fabric is then washed, soured and washed. The use of magnesium sulphate is made use for this treatment for stabilising hydrogen peroxide bath by the formation of magnesium silicate which is the actual stabiliser. This system is well suited for polyester blended fabrics because the use of caustic soda is restricted. The high concentration of caustic soda at high temperature may damage the polyester component in the blends.

In order to reduce the peroxide consumption, the fabric can be treated with sodium hypochlorite prior to peroxide treatment to increase the initial whiteness [16]. In this process, the desized fabric is first chemicked by pad-store method using sodium hypochlorite (3 g/l available Cl_2), 3 g/l soda-ash and wetting agent with pad pick-up of 100% and dwelling time of 30 min at 30°C. In the second stage, the washed and dried goods are padded with a liquor containing hydrogen peroxide (1.2%), sodium hydroxide (2.5%), potassium persulphate (50%) (0.4%) and magnesium sulphate (1.5%) at 100% pick-up. The padded fabric is then batched for 7 h followed by a hot wash at 80°C or higher for 1 min.

Sandoz has recommended two recipes (Table 11.1) for combined scouring and bleaching. The desized goods are impregnated wet-on-wet (drying after desizing and before steaming is omitted). This process demands continuous feed of a strongly reinforced feed liquor and systematic control of the concentration of H_2O_2 and caustic soda. The cloth is impregnated in a U-Box system container for 45 min at 100°C with the liquor of recipe I. In another process the cloth is padded with liquor of recipe II at room temperature (add-on 30%), batched for 40 min at 100° C and rinsed thoroughly. The result of this treatment greatly depends on the duration of reaction. The longer this is, the better the results.

In an energy saving and trouble free combined scouring and bleaching system [17], the goods are padded with a bleaching formulation containing sodium chlorite (0.85-1%), formaldehyde as catalyst (3 g/l), sodium carbonate (3 g/l) and an

TABLE 11.1
Recipes for Combined Scouring and Bleaching

Ingradients	Recipe I		Recipe II	
	Impregnation liquor (ml/l)	Feed liquor (re-inforced 3.5 times) (ml/l)	Impregnation liquor (ml/l)	Feed liquor (ml/l)
H_2O_2 (35%)	30	105	70	105
NaOH (36°Be')	20	70	22	77
Sodium silicate (38°Be')	8	28	–	–
Sandopan SF (wetting agent)	12	42	–	–
Sandopan CBN liq.	–	–	4	14
Stabiliser SIF liq.	–	–	8	28
Magnesium Chloride	0.3	0.4	0.4	0.4

emulsified solvent (pentachloroethylene) based scouring agent (2%) at 30°C and batched for 6-8 h and then washed.

11.4 Combined Desizing, Scouring and Bleaching

Many continuous processing machineries have been developed over the past few decades by which cotton and polyester/cotton blended fabrics can be desized, scoured and bleached in one single operation.

As ASISA shock system for continuous desizing, scouring and bleaching in open width gives result within few minutes without any need for previous pad-batch process. The reaction time is only 2 min.

Du Pont has developed a 2 min bleaching process for heavy fabrics using H_2O_2 at specific pH value employing a special formulation to prevent undue decomposition of peroxide and damage to the fabric under process.

ITCO process deals with a six sectioned J-Bbox system and the treatment is continuous with complete saturation and counter-current flow of water.

The Farmer-Norton steam-purge system is extremely effective in promoting a thorough saturation of the fabric with chemical pre-treatment liquors.

In the vaporloc machine full bleaching can be obtained in one passage of 90 to 120 sec duration at a temperature of 134°C (30 p.s.i.).

The ICI Markal III process combines bleaching with scouring and desizing by using an emulsion of aqueous H_2O_2 in trichloroethylene-surfactant solution, followed by steaming and washing-off.

An example of latest preparatory equipment for one step desizing, scouring and bleaching is the Reco-Yet from Ramisch Kleinewefers [18, 19]. With the Reco-Yet a heated aerosol of steam and chemicals, including a new multi-functional auxiliary agent and thermal energy, is applied to the fabric simultaneously in a reaction time of one to three minutes.

Benninger has developed ''Ben-Bleach-System'' for desizing, scouring and bleaching in one operation. The system comprises four models : Ben-Injecta for desizing, Benm-Impecta for impregnation, Ben-Steam and Ben-Extracta for washing. With the aid of individual dispensing system, the feed – to each module – of chemical can be controlled. In the steamer, the tight-strand fabric is plaited on a roller-bed permitting a dwell time of 1-60 min.

In the Flexnip (Kusters) cotton fabric can be processed by a single stage process and a reduction in energy and water used is claimed.

Dip-Sat Vario unit (Goller, Germany) uses a single stage process in which high degree of humidity is generated on cotton fabrics leading to efficient swelling of fats, waxes and cotton seeds, producing good whiteness with low fibre damage.

The C.R.C. process (Caustification Reductrice a chaud i.e. causticizing, Reductive, hot) from Sandoz is a simple and economical method of pre-treatment by which cotton is desized, scoured, bleached and causticized in one operation. The flow sheet diagrams of C.R.C. process equipment are shown in Fig. 11-1.

The combined desizing, scouring and bleaching is mainly achieved by the addition of a second peroxy compound to hydrogen peroxide or sodium chlorite bath when its reactivity is boosted synergistically during bleaching. In the case of H_2O_2, tetra potassium peroxydiphosphate as booster along with stabiliser and non-ionic wetting agent in the bath can act as a substitute to conventional process with savings in water and energy. The effectiveness of the system used under alkaline conditions can be interpreted in terms of free radical formation.

A number of patents are available on the use of emulsified solvents in combined

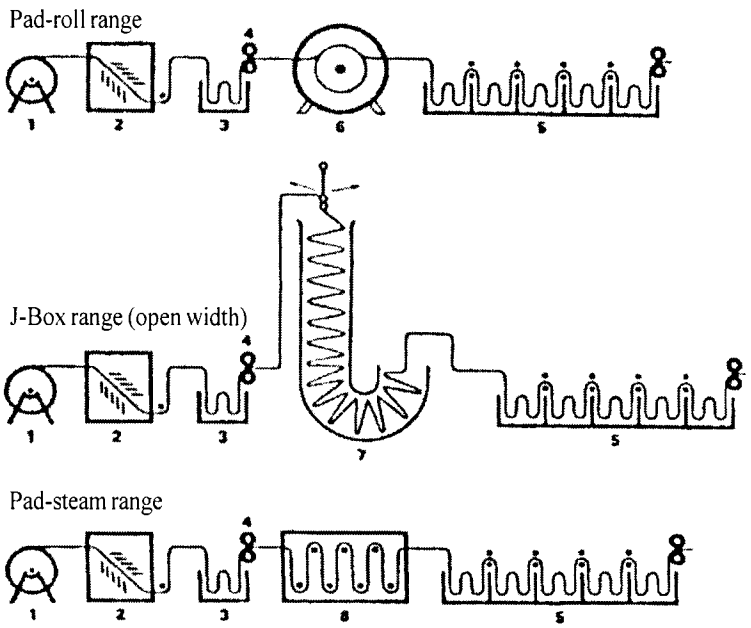


Figure 11-1. C.R.C. (Sandoz) processs equipment.
1 Grey goods from the loom (cotton or polyester) ;
2 Singeing unit ; 3 Impregnation bath at 20-40°C ;
4 Padding mangle (80-100% pick-up) ;
5 Washing compartments (95, 95, 70, 50, 30°C) ;
6 Pad-roll chamber (60-120 min at 90-95°C) ;
7 J-Box (20-60 min at 95-100°C) ;
8 Steamer (5-20 min at 100-107°C).

desizing, scouring and bleaching. In one process, the cloth is padded with an emulsion comprising of aqueous solution of alkaline compound emulsified in chlorinated hydrocarbon with selected emulsifier at 25-60°C, dried and steamed to remove chlorinated hydrocarbons. In another process, the singed and desized cotton fabric is padded with ethylene carbonate, peracetic acid and emulsifier in trichloroethylene followed by heating at 95°C for 10 min. Solvent assisted combined desizing, scouring and bleaching process using a mixture of 4% scouring agent [a mixture of pine oil (50 parts), non-ionic emulsifier (40 parts), perchloroethylene (10 parts)], H_2O_2 (100%) 1%, sodium silicate 2% and activator 2% is reported [20]. The fabrics are padded with the mixture and batched for 12 to 24 h at 40 to 60°C.

Single stage preperatory processs for cotton using sodium hypochlorite is optimised [21, 22]. A process based on emulsified solvent system as scouring agent along with sodium hypochlorite as a bleaching cum desizing agent at pH 11 is reported [23, 24]. Around 30-35% more hypochlorite is required in the single stage process compared to conventional bleaching.

A fast desizing, scouring and bleaching system using sodium chlorite for cotton-based textile material is reported [25]. In this process, the fabrics are padded in a solution containing 20 g/l $NaClO_2$, 0.05 g/l $KMnO_4$ and 2 g/l wetting agent at pH 10 to a wet pick-up of about 80%. The treated fabrics are then exposed to 90°C for 30-60 min and washed and dried.

Another approach is the combination of an enzyme treatment with hydrogen peroxide [26]. By combining enzyme treatment (a simultaneous treatment of pectinase and cellulase), or alkaline boil-off, with an alkaline peroxide bleaching, the total degree of whiteness is reported to be higher in combination with enzyme treatment. The combined process, including an enzyme treatment, deliver results comparable with those of alkali treatment [27].

A single stage preparatory process on polyester/cotton blended fabrics can be carried out using peracetic acid as an oxidising agent. The fabric is treated with a solution containing peracetic acid 5-6 g/l, tetrasodiumpyrophosphate 1 g/l, bacterial type desizing agent 1 g/l, common salt 2 g/l and non-ionic wetting agent at pH 5 to 6 (m : l :: 1 : 3 to 1 : 5) at 75-80°C for 90 min. The treated fabric is then washed with hot water and finally with cold water.

Solar water heating system for single stage preparation in a kier and pad-batch systems with a process cost savging is possible [28, 29]. Solar heat may be utilised to the maximum extent for drying the fabric to reduce consumption of fuel.

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Chapter 12

DEGRADATION OF FIBRES ASSOCIATED WITH CHEMICAL PRE-TREATMENT PROCESSES

12.1 Introduction

Faultless pre-treatments of textiles are very essential for the quality of the final products. Faulty pre-treatments impair the reproducibility of the desired effect with an increased amount of rejects. Generally, the defects can be classified into two broad classes namely, grey mill defects and defects during chemical processing. The grey mill defects are arisen from yarn defects, warp-wise weaving defects, weft-wise defects and general defects. The defects in chemical processing may be classified as chemical damage, mechanical damage or operation faults. Chemical damages are caused by the improper application of pre-treatment processes, erroneous concept of procedure, faulty operation of machines, faulty feeding of chemicals and haphazard work. Excessive tension or stretch may often be the cause of mechanical damage.

Degradation or damage depends on chemical structure of individual fibre and pre-treatment history. Degradation also involves changes in molecular structure of the fibre. Further, the strength of cotton yarns depends not only on the strength of the fibres, but also on the twist and the lubrication of the fibres. Similarly, high and low crimp wool fibres, as a result of the influence of nutrition levels, have different levels of degradation during chemical processing [1]. Molecular orientation in a synthetic fibre, fabric thickness and spacing in a weave can also modify the way in which fabric is degraded by abrasion. Degradation may also arise as a result of storage, maintanance procedure, exposure to ultra-violet sources, weathering, fungi or other microbiological attack, heat and acid and alkaline hydrolysis of fibres.

12.2 Degradation of Cotton During Desizing

Desizing is carried out to remove the sizes and its degradation product is removed from the fabric before subsequent processing. In rot-steeping, the cloth is allowed to lie for about 24 h and the fermentation is not controlled. The degradation of cellulose may occur as a result of cross infections e.g. of mildew. The loss in weight in acid steeping is slightly higher than with water steeping. Cotton fabrics treated with dilute sulphuric acid at room temperature show little degradation, the

fluidity increases from 4 to 5.8 rhes in 4 h and about 70% of the starch is removed. Generally dilute solutions of mineral acids and acid producing salts such as $ZnCl_2$ and Al_2Cl_6 have little action on cotton fibre provided they are washed out before the fibre is dried [2-4]. If washing is not done, hydrocellulose, a break down product of cellulose, is produced with consequent tendering of the fibre [Fig. 12-1].

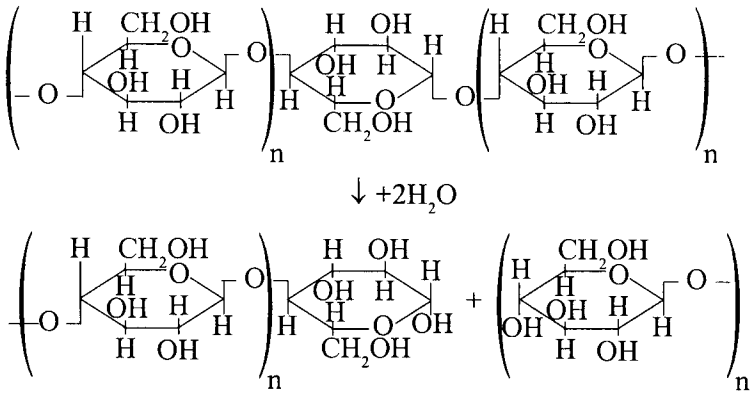


Figure 12-1. Mechanism of hydrolysis of cellulose molecule.

Due to partial hydrolysis of the cellulose molecule, the average molecular length is reduced. The appearance of additional –CHOH end groups increase the reducing power because they can undergo tautomeric change in the formation of aldehyde

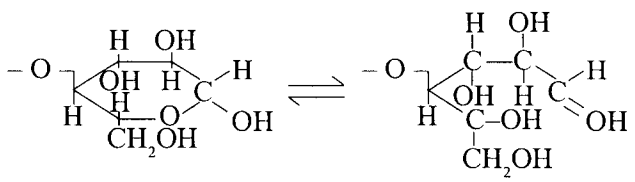


Figure 12-2. Formation of aldehyde group on hydrolysis.

[Fig. 12-2]. Most organic acids in dilute solution have little effect on cotton even if dried in, but oxalic, citric and tartaric acids are liable to cause tendering [5].

When sodium bromite is used as a desizing agent for cotton fabric by continuous and discontinuous processes, the concentration of bromite should be restricted to ensure that the oxidaiton of cellulose is kept to a negligible proportion.

In enzymatic desizing, the time, temperature and pH of the desizing bath is well controlled. Furthermore, the action of enzyme is restricted only on the sizes present on the fabric and thus degradation of the fibre due to enzymatic desizing is few and

far between. Repeated treatment of cellulase enzymes from Penicillium funiculosum [6] and trichoderma endocellulase enzymes [7] leads to extensive fragmention of cotton fibres. Repeated enzyme treated cotton shows Cellulose I pattern with the absence of 101 plane similar to that of drastically acid hydrolysed cotton [8]. This confirms that enzymatic hydrolysis of cotton fibres proceeds preferentially along the orientation, which is a cleavage phase. Morphological changes take place during the phases of degradation. Acid hydrolysis causes localised degradation whereas enzymatic hydrolysis is uniform. There are changes in moisture regain, crystallinity of the hydrolysates and weight loss due to enzyme hydrolysis.

12.3 Degradation of Cotton During Scouring

Scouring of cotton is generally carried out under mild concentration of alkali. The scouring treatment increases the wettability of the fibre, but it induces fibre degradation under severe conditions by creating crevices in fibre or dissolution of cuticle or primary wall [9, 10]. The main changes in cotton during scouring process are loss in weight (about 5-10%), loss in length due to shrinkage and alteration in count affected by both losses and changes in tensile strength (generally an increase) [11, 12]. Since the scouring treatment contributes to the dissolution of a portion of shorter cellulosic chains, it bestows on cotton an average DP higher than that of native cellulose. The alkali treatment of scouring condition does not induce pronounced changes in the fine structure of fibres and has a small effect on the degree of crystallinity [13].

The degradation of cellulose in alkali solution depends on the concentration of alkali and on the presence or absence of oxygen. In the absence of air cellulose is slowly attacked by hot alkali in a stepwise fashion at the reducing end of the cellulose chain [14] resulting in a loss of material. The entrapped air should be sweeped out before kier boiling under pressure. The cotton must be entirely covered by the scouring liquor as otherwise part of the fibre exposed to the air loose strength and result in unevenness in dyeing. Fig. 12-3 shows the role of pH in the endwise depolymerisation of hydrocellulose from cotton by treatment in NaOH solution (0.5 to 18.6 N) at 120°C. The curve shows a pattern similar to the degree of swelling of cellulose in alkali. The number of carboxyl groups increases with increasing [OH] ion concentration, with a rapid rate between 6 and 8.5 N, but the viscosity decreases only slightly, which implies the loss of low molecular weight compo-

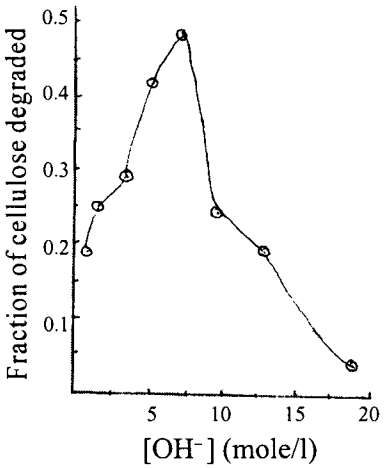


Figure 12-3. Effects of alkali concentrations on the extent of hydrocellulose degradation at 120°C for 1 h [15].

nents. The loss in weight, however, increases with temperature of the alkaline solution [16]. The reaction scheme of this kind of degradation is represented in Fig. 12-4 by the formation of peeling-off centres on the cellulose i.e. aldehyde

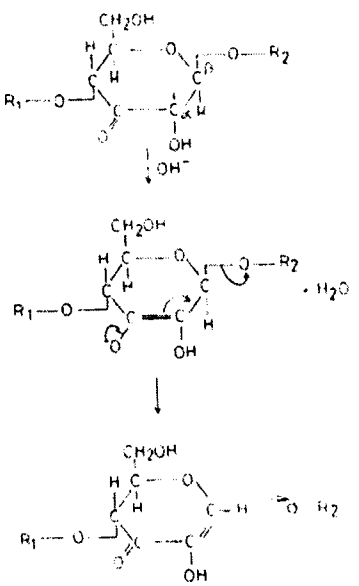


Figure 12-4. β-alkoxy elimination reaction [21].

groups, by β-alkoxy elimination reaction from the reducing ends of the chains, by the formation of carbonyl groups containing coloured products and yellowing [17] and by the formation of metasaccharinic acid at the end of the chains [18-20].

In the presence of air i.e. the reaction of oxygen with cellulose in presence of strong alkali (above 40 g/l), the degradation can be very serious and the oxidative attack may likely to follow the pattern suggested for alkali cellulose [22]. The attack of oxygen at 20°C is slow, rapid at 40-50°C and is 1000 times higher at 95°C than at 20°C [22]. A theory based on free radical intermediates i.e. the oxidative degradation which occurs with chain scission is shown in Fig. 12-5. It is shown that

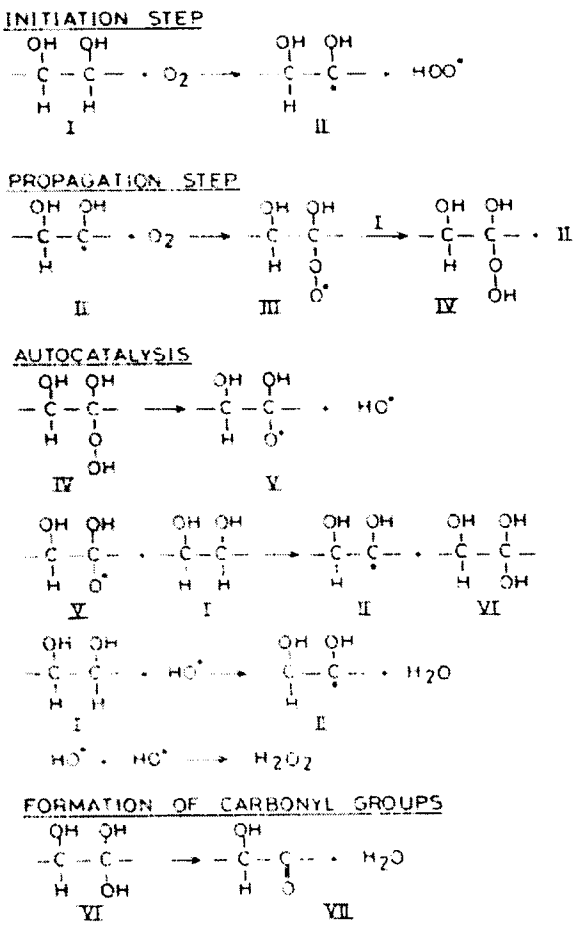


Figure 12-5. Free radical mechanism of alkali cellulose auto-oxidation [22].

hydrogen peroxide is always present during cellulose auto-oxidation. Oxygen may attack on hydrogen atom at C_2 or C_3 position to produce a radical II in the cellulose. Radical II may then rapidly take up oxygen forming a peroxide type radical III which may react with other groups in cellulose to give hydroperoxide IV and the original radical II. Thus, a chain reaction may be set up. Hydroperoxide IV gives a hydroxyl radical and a new radical V, which may abstract hydrogen from cellulose to give compound VI and the original radical II. The hydroxyl radical may attack cellulose to give new type II radicals (in autocatalysis). Hydroxyl radicals may also combine to form hydrogen peroxide. Compound VI finally loses water with the formation of carbonyl group in the cellulose chain compound (VII) and thus chain scission may occur by β-alkoxy elimination. The rate of reaction of alkali cellulose with oxygen increases with the number of reducing end groups.

An ionic mechanism (Fig. 12-6) is also proposed for the auto-oxidation of al-

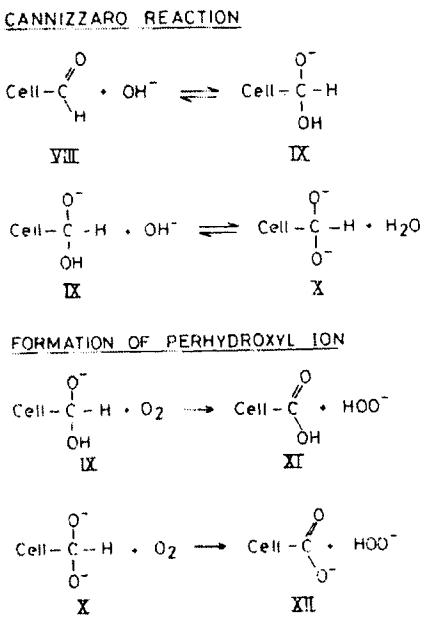


Figure 12-6. Ionic mechanism of alkali cellulose auto-oxidation [23].

kali cellulose [23]. The reducing aldehyde groups in cellulose under strong alkaline condition form Cannizzaro intermediates such as IX and X which is auto-oxidisable.The initiation step of auto-oxidation reaction consists of the formation

of the perhydroxyl ion. The propagation step is the attack of cellulose by the perhydroxyl ion with rupture of the cellulose chain and is similar to the degradation mechanism during bleaching with hydrogen peroxide.

12.4 Degradation of Cotton During Bleaching

Bleaching agents commonly used are mainly oxidising agents which react with cellulose forming oxycellulose with accompanying tendering of the fabric. The rate of decomposition of bleaching agent and also the rate of attack on cotton depends on concentration, pH, time and temperature of the bleaching bath and also on the soils present in the fabric. Over bleaching takes place due to lack of proper control of these parameters and oxidation proceeds at a faster rate and fabric is destroyed. Tendering takes place if bleaching is carried out in presence of metals which act as catalysts in accelerating the oxidation process. Tendering also takes place if the removal of bleaching agent during washing treatment is incomplete. Generally, bleached cloth is soured with HCl (1.5%) or H_2SO_4 (1.0%) to remove calcium carbonate or metallic composition deposited in the cloth. Tendering due to acid may also occur if the acid is not properly washed-off after the goods are soured. Hydrocellulose may form due to acid action on cellulose on storage.

Yellowing of the bleached fabric is another defect. Yellowing of the cotton fabric is caused by improper control of bleaching condition parameters, faulty working of the kier during boil-off operation, poor circulation or filtering of some cotton impurities and defective circulation of bleach liquor. The yellower the substrate, the higher is the oxycellulose present and the more susceptible the fabric to after-yellowing on storage.

12.4.1 Sodium hypochlorite bleaching and damage

Bleaching of cotton with sodium hypochlorite solution is done in alkaline condition (pH 8.5 to 10) by the the addition of sodium carbonate. Maximum damage to the fabric takes place in the neutral region of pH (Fig. 12-7). Around pH 7.0, the hypochlorous acid and hypochlorite ion are present at approximately the same concentrations and hence the rate of attack on cellulose is greatest in this region. The degree of degradation is demonstrated by increase in fluidity which also shows a maximum at approximately pH 7.0. The temperature of the liquor should be kept as low as possible and also direct sunlight should be avoided to ensure minimum oxycellulose formation. Bleaching with sodium hypochlorite can be done at 20°C

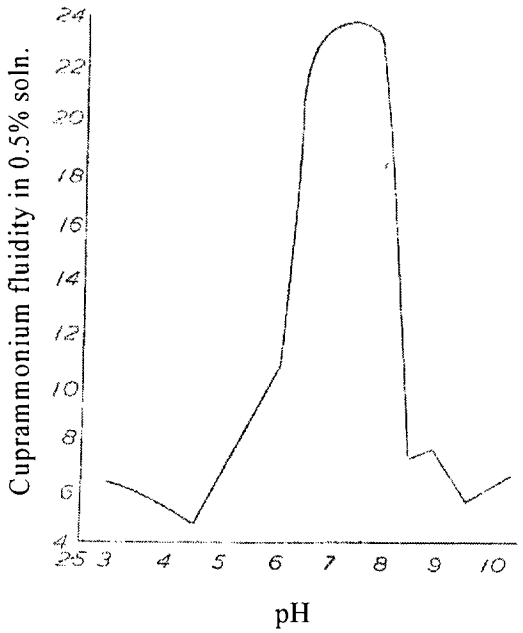


Figure 12-7. Degradation of cotton with self-buffered hypochlorite solution (3 g/l av. Cl_2) after 5 h treatment [24].

for a treatment time of 16 h, but the same result can be obtained for 30 min at 60°C without appreciable increase in damage to cellulose [25, 26]. The degradation of cotton at elevated temperature proceeds faster than that of impurities, but the effect is dependent only on the effective hypochlorite consumption. Certain metals such as mercury, copper, cobalt, nickel and iron should be absent in the bleach bath as the oxides and hydroxides of these metals are able to catalyse the decomposition of hypochlorite solution and the liberated oxygen converts the cellulose into oxycellulose. Certain yellow and orange vat dyes also accelerate the rate of oxidation accompanied by degradation of cellulose under combined action of hypochlorite solutions and light [27].

The reaction of hypochlorite with cellulose is non-specific i.e. not confined to a particular hydroxyl group. The degradation is located mainly on the surface of the fibre as the reaction is heterogeneous nature. Hypochlorite may attack and convert the accessible hydroxyl groups of cellulose into carbonyl groups (i.e. aldehyde and ketone groups) and carboxyl groups with subsequent chain cleavage. Strength loss,

in the early stages, is accompanied with slight weight loss but stength decreases rapidly with continued oxidation [28]. The formation and extent of carboxyl contents (determined by methylene blue absorption) and aldehyde groups (determined by Copper No.) depend on the pH of hypochlorite solution during the treatment (Fig. 12-8). Under acidic pH reducing type (aldehyde and keto groups) and under

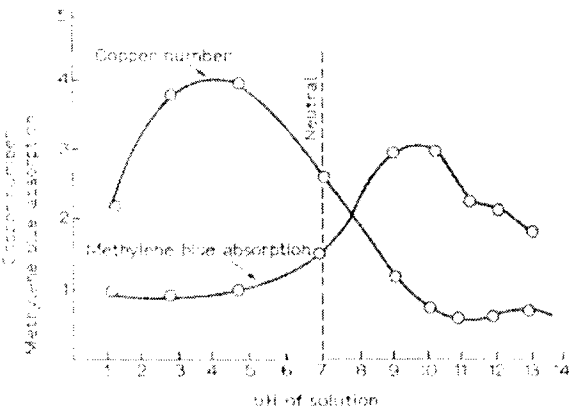


Figure 12-8. Effect of pH of hypochlorite solutions on the copper number and methylene blue absorption of oxycellulose [29].

alkaline pH acidic type (carboxyl groups) of oxycelluloses are formed. The changes in pH modify the rates of reactions but do not alter the mechanism for them [30]. The oxidation may be progressive and proceeds along a course known as β-elimination [Fig. 12-4]. Bleaching with hypochlorite is done in alkaline pH and hence oxycellulose of the acidic kind are insensative to alkali, but when in the free acid form, the hydrogen ions from the carboxyl groups catalyse hydrolysis of the adjascent glucosidic linkage. A sequence of reactions is shown in Fig. 12-9 and 12-10 [30].

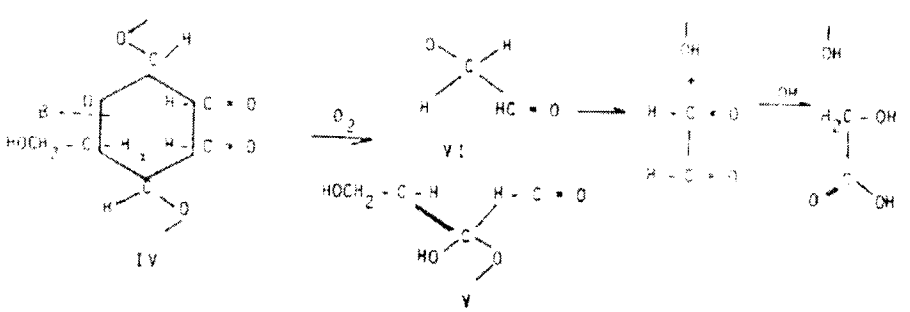


Figure 12-9. Oxidation with periodate [30].

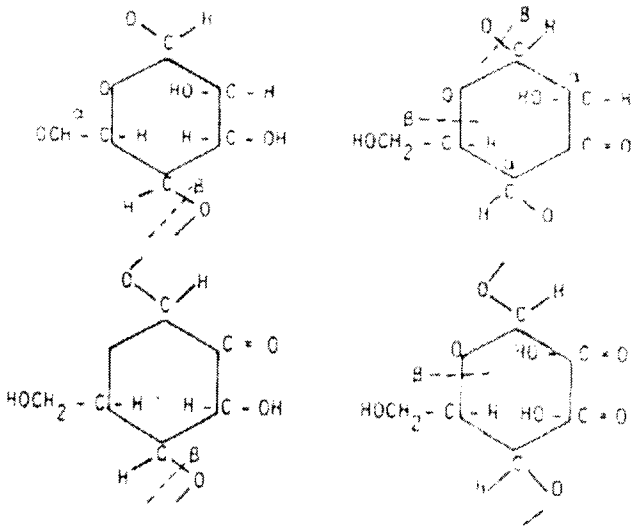


Figure 12-10. General reactions with non-specific oxidising agents [31].

Apart from degradation of fibre, the increase in the number of aldehyde and carboxyl groups also increase the dyeing and finishing problems.

12.4.2 Hydrogen peroxide bleaching and damage

Bleaching of cotton with hydrogen peroxide is carried out under alkaline condition along with sodium silicate which acts as a stabiliser. However, the use of sodium silicate is liable to cause deposition of silicon compounds on the cloth and also form hard crystalline deposits on plants and machineries which may cause abrasion damage to the fabric. This defect may be avoided if addition of alkali in the ratio of Na_2O : SiO_2 within the region of 2.25 : 2.75 is used. It is also recommended to use a mixture of equal proportion of NaOH and Na_2CO_3 instead of NaOH alone as only NaOH may cause initial degradation. The silicate concentration may be reduced further by the use of organic stabilisers which tend to have lubricating effect.

The damage of cotton during metal catalysed bleaching with hydrogen peroxide is a serious problem. There are various sources by which the bleaching bath can be contaminated with metal particles. The raw cotton contains high metal content because of the use of pesticides, fungicides and weed control agents in cotton-growing [32, 33]. During open end spinning, soil particles which are rich in metal containing compounds, are deposited in the rotor chamber and after temporary re-

moval get into the yarn [34]. By increasing the spinning and weaving speeds the contamination of metal particles may also increase due to friction from machinery components [35]. Metal ions present in chemicals used for bleaching can also cause problems [36].

The influence of the concentration of iron ions on decomposition of hydrogen peroxide in bleaching liquor is shown in Fig. 12-11. The influence of the concentration of complexing agent on decomposition of iron complexing peroxide bleaching liquor and cellulose is shown in Fig. 12-12. The rapid release of large amount

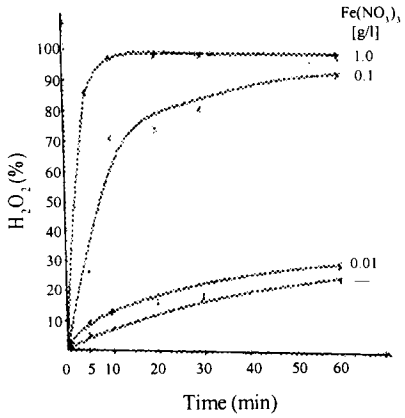


Figure 12-11. Decomposition curve of H_2O_2 in bleaching liquor at various $Fe(NO_3)_3$ concentration [37].

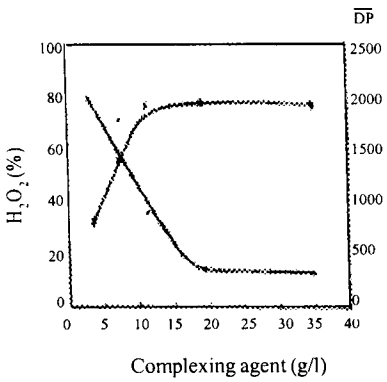


Figure 12-12. Decomposition of H_2O_2 and damage to cotton as a function of the concentration of the complexing agent, falling curve H_2O_2, rising curve $\overline{DP}$.

of oxygen species causes rapid and significant oxidative degradation of cotton cellulose in the immediate vicinity of the metallic particle. The decomposition effect of water soluble catalysts on peroxide and cellulose can be suppressed by increasing the complexing agent concentration. The catalytic damage that occurs during peroxide bleaching is due to the metallic particles trapped in the fabric and the decomposition of H_2O_2 is thought to be catalysed by metal ions present near the surfaces of the metallic particles [38]. The catalytic damage caused by metal salts is most striking in a long liquor bath and least with the pad-batch method.

12.5 Damage of Wool During Pre-treatment Processes

Boiling water can gradually break down the wool keratin and the fibre can loose

its strength. Dilute acids, however, have little effect on wool, but 20% HCl can hydrolyse wool. Cold concentrated mineral acids can dissolve wool fibre [39]. Dilute solutions of caustic alkalies rapidly disintegrate wool at a rate depending upon the temperature and concentration employed. Soda-ash and sodium carbonate have much less destructive effect and hence are used in scouring of wool fibres. Borax, soap and ammonia behave similarly.

Carbonisation of wool can cause localised damage. Wool undergoes some hydrolysis between acidising and drying steps, even at room temperature [40]. The surface acid remaining after carbonising is unevenly distributed in the wool mass and consequently localised damage is caused [41]. There is a critical point at a temperature of 70°C in the drying stage and 120°C in the baking stage above which wool hydrolysis increases significantly. Oxygen is not directly involved in hydrolysis damage to wool during carbonising. Lower drying temperatures before baking in carbonising minimise damage to wool fibres. The addition of surfactant in the carbonising bath results in the even distribution of the acid as a film over the entire surface of the fibre and can protect wool during carbonising [42].

Sometimes carbonising is done during dyeing with 1 : 1 metal complex dyes under strongly acid conditions, but this method may produce severe fibre damage and requires careful control of dyeing conditions. Fibre damages may also occur by decatising the dyed fabrics under pressure and hence decatising at atmospheric pressure is recommended [43].

Modern methods of bleaching wool is directed towards the control of chemical damages during the treatment. Chemical damage generally occurs due to excessive rapid decomposition of H_2O_2. The reaction of wool with H_2O_2 is relatively slow in acidic condition than that of alkaline condition. The presence of activating reducing agents (metal salts) can also enhance reactivity of the normal wools in presence of H_2O_2 and can lead to fibre degradation. The precautions are exactly the same as those needed in the bleaching of cotton with H_2O_2.

During oxidative damage to wool some of the cystine cross-links (the number depending on the conditions) are split and are oxidised to cysteic acid which can be regarded as a measure of the degree of damage [44, 45]. A possible mode of attack has been suggested for the reaction of persulphate ions with the peptide groups [46]. The reaction of wool with peracids and probably hydrogen peroxide is con-

sidered to yield S-monoxycystyl and S, S-dioxycystyl residues [47]. Although sulphite ions react with wool to split the disulphide linkages, dissolution does not occur. The reaction is reversible and the maximum extent of reaction takes place at pH around 3 to 4 [48]. The mechanism of reaction seems to be nucleophilic attack of the disulphide bond by either the bisulphite (HSO_3^-) or the sulphite (SO_3^{--}) ion.

12.6 Damage of Silk During Pre-treatment Processes

There may be three types of damages of silk during the pre-treatment processes. Repeated processes and improper handling may cause mechanical damages due to chafing at the silk fibre surface. Biological damages may occur on storage, especially in a non-degummed state, due to bacteria. Chemical damages may occur due to improper control of the various parameters during degumming and bleaching treatments.

The chemical behaviour of silk towards acid is somewhat like wool except that it is more readily attacked by strong acids. Silk is more resistant to all alkalies except caustic soda and caustic potash. Prolong boiling of silk fibres in water alone will produce slow degradation and hydrolysis. In acid or alkali, hydrolysis of the peptide chain occurs with loss of tensile strength of the fibres. The extent of degradation depends on the pH of the solutions and is minimal between approximately pH 4.0 and pH 8.0. Uneven degumming causes spotted batches due to uneven weft material. Lime soap residues may be present on silk due to hard water and poor rinsing showing metal spots and rust particles.

Uncontrolled oxidation of bleaching baths can attack the silk fibre. Hypochlorite, chlorine dioxide etc. can cause discolouration of the fibre probably due to the oxidation of the tyrosine residues. Hypochlorite solutions render both fibrion and sericin insoluble to an extent depending on the pH, being more effective in alkaline solution (pH 10.3), slightly less in mildly acid (pH 4.0), and not at all in strongly acid.

When silk is immersed in hydrogen peroxide solution, the latter is absorbed to an extent which is independent of pH in the range 2.5 to 9.0. This may be due to the fact that the peroxide combines with amino groups and peptide bonds of silk fibres [49]. Peroxide also causes reduction in tyrosine content presumably due to the scissioning of peptide bonds at linkages involving tyrosine [50]. Oxidation of peracetic acid causes scission at a greater rate than by hydrogen peroxide, but loss

in weight for a given rise in fluidity is greater with hydrogen peroxide than peracetic acid [51]. This is because tyrosine in silk is oxidised to acidic groups.

12.7 Damage of Polyester During Pre-treatment Processes

Polyester is highly resistant to acids but alkali can hydrolyse polyester fibres. The fibre surface is not damaged by treatment for 5 min at sodium hydroxide concentration as high as 38.9 g/l or at 5.2 g/l for 2 h, but damage does occur if fibres are treated with a 9.1 g/l sodium hydroxide for at least 2 h [52, 53]. The number of hydroxyl groups increases due to alkaline hydrolysis, but there is some damage to the fibre surface. The fibre cross-section becomes more complex and its area decreases [54]. Due to alkaline hydrolysis weight loss occurs, together with an increase in density, crystallinity, amino acid content, dye uptake and abrasion resistance, and a decrease in intrinsic viscosity, as the concentration of alkali is increased [55]. In addition, aminolysis of ethylamine proceeds by permeation of the reagent into the fibre and causes degradation, which affects the brittleness, flexural fatigue resistance, and tensile properties of the polyester [56]. These changes are explained in terms of crystallinity and crystallite size. As the treatment time increases, decrease in crystallinity and crystallite size become more pronounced. On extensive treatment, the propagation stress cracks on the fibre surface and finally results in fibre breakage [57]. The addition of cationic surfactant, dodecyldimethylbenzylammonium bromide, reduces the alkaline hydrolysis of polyester fibres subjected to NaOH treatment by reducing the concentration of alkali [58, 59, 53].

Heat-setting of polyester fibre with steam always leads to low molecular weights than occur with conventional setting. However, the cleavage of polyester fibres by hydrolytic degradation on exposure to steam occurs only after very severe exposure to steam. Generally, cleavage takes place predominantly across the fibre axis to give irregular lengths between scissions and the cleavage does not appear to be related to the significant physical phenomenon [60-62].

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Chapter 13

CONSERVATION OF ENERGY AND WATER, ECONOMY AND EFFLUENT CONTROL IN PRE-TREATMENT PROCESSES

13.1 Water Consumption in Textile Industry

Textile industry is a leading consumer of water and it ranks among ten top water consuming industries [1]. Table 13.1 shows the approximate consumption of water for the processing of various textile fibres. Cotton fibres require the largest amount of water for its preparation. In general, the water consumption in a process house is about three times the consumption of all other units put together (Table 13.2). The water consumption in the bleaching section is highest. The conventional

TABLE 13.1
Water Consumption by Textile Industry in Various Processes [2]

Substrate	Water consumption kg/kg of fabric
Cotton	250-350
Wool	200-300
Nylon	125-150
Rayon	125-150
Polyester	100-200
Acrylic	100-200

TABLE 13.2
Water Consumption Pattern in Textile Mills [3]

Process	Water consumption (% of total)
Bleaching, Finishing	38
Dyeing	16
Printing	8
Boiler House	14
Humidification (spinning)	6
Humidification (weaving)	9
Sanitary, Domestic etc.	9

preparatory processes of textiles namely, desizing, scouring, bleaching, and washing are highly water consuming operations and consequently energy-intensive (Table 13.3).

TABLE 13.3
Consumption of Water and Energy in Kiers and J-Box Processes [4]

	Process	Consumption of water l/kg	Consumption of steam kg/kg
	Desizing	3	0.25
	Washing	20	0.35
J-Box	Scouring	2	1.75
Bleaching	Washing	20	0.30
	Bleaching	2	1.00
	Washing	40	0.60
	Total	87	4.20
Conventional kier-boiling		100	5.10

13.2 Impurities in Water

The quality of water to be used in a process house decides the ultimate quality of cloth like whiteness, brightness of colour etc. The main impurities in water are turbidity and colour, iron and manganese, alkalinity and hardness. The quality of water received in the textile mills depends on their history. Moorland water is acidic in nature. Colour and turbidity in water may stain the fibre. Inpurities in water may deactivate enzymes during desizing and insolubilise starch material which may deposit on the fabric. The Ca^2 and Mg^2 ions from $Ca(OH)_2$, $Mg(OH)_2$, $CaCO_3$ and $MgCO_3$ present in water may combine with soap during scouring. The alkali salt have no or very little aqueous solubility and once deposited the handle, sewability, knittability and water absorbancy of the scoured fabric and yarn will be impaired. Besides dirt will be more difficult to remove from the textiles in hard than in soft water. Ions of heavy metals (iron, copper, manganese) act as catalyst in the decomposition of bleaching agents and cause activated attack with subsequent degradation of fibre. If the iron content of the water supply for reservior or deep wells is high, oxidation and filtration units must be installed to reduce its content below 0.1 p.p.m., otherwise suitable bleaching auxiliaries must be added to the bleach bath.

In the aeration technique, the water is pumped through the aeration apparatus [5], the metal is oxidised to its insoluble form and precipitates from the water. Improper water may insolubilise metal oxide during mercerizing and reduce absorbancy and lustre. In the dyeing stage, metal ions may combine with some dyes and cause dulling of shade. Impurities in water may also lead to precipitate on to boiler tubes forming scales. As boiler scale forms, heat transfer and boiler efficiency is reduced forming hot spots which in turn cause weakening of the boiler tubes leading to pipe blow-outs and failures.

The quality of water is judged by total dissolved solids (TDS) and hardness which generally varies depending on the locations and regions. Table 13.4 shows

TABLE 13.4
Acceptable Water Content for Processing [6]

Impurities	Parts per million
Silica	0.5-3
Total hardness ($CaCO_3$)	0-25
Total alkalinity ($CaCO_3$)	35-64
Dissolved solids (TDS)	65-150
Iron (Fe), Cu, Mn	0.02-0.1
Colour	Transperant
Turbidity	Clear
pH	7-7.5

the approximate idea of the limit of water quality suitable for wet processing of textiles. Water hardness is caused mainly by calcium and magnesium bicarbonates, chlorides and sulphates which can have been absorbed by rain water as it percolates through the various strata. When hard water is boiled, the bicarbonates are decomposed and precipitates as carbonates and the hardness due to these salts largely

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2 + 2CO_2$$

disappears. This type of hardness is called "Temporary hardness" and is the major cause of scale formation in boilers. "Permanent hardness" is associated with metal salts such as nitrates, chlorides, sulphates and phosphates which are soluble in water

and are not decomposed by heat. The sum of the temporary and permanent hardness is called ''total hardness''. Hardness is usually expressed in degrees and is described in terms of equivalents of calcium carbonate or oxide. It is generally considered that the maximum permissible level of TDS and hardness to be used in wet processing should be about 25 and 500 p.p.m. respectively. Water containing 0-5° English hardness is considered to be soft and over 15° is hard.

1° English hardness = 10 mg/l of $CaCO_3$ in 0.71

1° American hardnesss = 1 mg/l of $CaCO_3$

1° German hardness = 10 mg/l of CaO or 7.9 mg/l MgO

13.3 Water Purification

Conventional softening treatment plant may not remove the impurities in water to the recommended permissible level. Demineralised or reverse osmosis technique is needed for removal of TDS from water but is costly. Water purification in the process house normally consists of floculation, sedimentation, filtration and ion-exchange. Hard water is normally softened using one or combination of methods the details of each process is given in many text books.

13.3.1 Soda-alum process

Hard water is first pumped into the reaction tank and then aluminium sulphate is added to it as floculant. About 20-30 min is allowed to react and then the impurities are allowed to settle for about 30 min before filtration. Many floculants need alkali

$$4H_2O + 3Na_2CO_3 + Al_2(SO_4)_3 \rightarrow 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2 + H_2O$$

as an assistant floculant. If additional alkali is not added, the total alkalinity is reduced and part of aluminium sulphate, being water soluble may pass through the filter. As aluminium hydroxide and metals precipitate downwards, clear water arrives at the top and is decanted.

13.3.2 Lime-soda process

In this process lime and sodium carbonate are added to precipitate the calcium and magnesium salts as temporary hardness.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + 2CaCO_3 + 2H_2O$$

For permanent hardness the reactions are :

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

The softened water is usually slightly alkaline with 1-4° residual hardness.

13.3.3 Base exchange process

When hard water is passed through a bed consisting of zeolites, which are synthetic material systems composed of complex sodium, aluminium and silicate salts (Na_2Z), the calcium and magnesium ions are exchanged. The displacing reactions for temporary hardness are :

$$Ca(HCO_3)_3 + Na_2Z \rightarrow CaZ + 2NaHCO_3$$

$$Mg(HCO_3)_3 + Na_2Z \rightarrow MgZ + 2NaHCO_3$$

For permanent hardness the reactions are :

$$CaSO_4 + Na_2Z \rightarrow CaZ + Na_2SO_4$$

$$MgSO_4 + Na_2Z \rightarrow MgZ + Na_2SO_4$$

The process is reversible and the bed (Na_2Z) can be regenerated by passing concentrated salt solution. This method of water softening yields a very soft water (0.5-1° hardness).

$$CaZ + 2NaCl \rightarrow CaCl_2 + Na_2Z$$

Water softening by demineralisation systems can be accomplished using either mixed bed (both cation and anion resin in one bed) or two bed system (resins remain seperated according to their charges). The active sites of the resins are limited and the sites are filled when water passes through these columns and must be regenerated again. Their ion-exchange capacity is greater than that of zeolite.

13.4 Economy Through Energy Conservation

The textile industry consumes both electrical and thermal energy. All the four major commercial energy sources i.e. coal, electricity, oil and gas are utilised. Power from hydroelectric, nuclear power and natural gas also contributes important source of energy, solar energy, bio-gas may be used for textile drying, for heating water, singeing, desizing, kier-boiling etc. [7-11]. About 55 to 60% energy consumed in the textile industry is used in various pre-treatment stages. Table 13.5 shows the pattern of steam consumption in a composite textile mill. Wet processing of textiles consume only a small proportion of electrical energy ($\simeq$ 15%) mainly for running various processing machineries. Fuel in terms of coal or oil is used extensively in the textile industry and thermal energy in the form of steam generated in the boiler is supplied to the various equipment through pipes. Several plants/machin-

TABLE 13.5
Steam Consumption in a Composite Textile Mill

Department	Steam consumed (%)
Humidification	10
Sizing	15
Boiler house (auxiliaries, blow down etc.)	05
Leakage and avoidable wastages	10
Wet processing	60

ery developments and technological advancements have been witnessed over the last decade to meet the challanges for conserving both thermal and electrical energy. Some of the important approaches are given below.

13.4.1 Efficient generation of energy and minimum consumption

The boiler itself should be very efficient to generate steam and for this preparation of oil, air to fuel ratio, stack temperature of flue gases, conversion of furnace oil to LSHS oil, maximum condensate recovery, cleaning of the fire side, replacement of old boilers etc. are the various important factors to be taken care-of. Factors responsible for optimum consumption of steam such as supply of steam at correct pressure, provision of pressure reducing valves, water separators in steam lines for supply of dry steams at requisite pressure, selection of trap of right type and size for efficient recovery of condensate etc. should be considered for the saving of thermal energy.

13.4.2 Mechanical removal of water before drying

Use of squeezing systems to pick-up 40-50% water by using Kuster mangle [12], Rotomat washing machine [13], Kleinewefers Jaeggli Bioflex [14], Aquilan air cushion squeezing [15] and Roberto rolls in place of rubber rolls [16] are some of the machineries related to efficient removal of water/process liquids or controlled application. Use of vacuum impregnation technique [17, 18] and vacuum roller extractor [19] claim 75% fuel saving by the use of vacuum for expulsion and expansion of air from the fabric for better and uniform impregnation. Use of suction slot for mechanical removal of water for fuel saving is also reported [20].

13.4.3 Increased efficiency of drying and heat-setting

The total energy consumed in wet processing may be in heating water, 35-65%;

drying, heat-setting or baking, 25-60% ; liquor circulation, 10% ; the rest is consumed in moving and handling fabric and so on. Increased efficiency of drying is achieved by improved thermal insulation, reduced leakages, appropriate steam pressure and proper steam line distribution. Use of radio-frequency technique in drying can be used as low energy electromagnetic radiation. High speed heat-setting system can be developed by the use of mixture of air and superheated steam and swelling compounds like polyethylene glycollic ether in place of conventional hot air can be used and 60-70% saving in thermal and electrical energy is thus, possible.

13.4.4 Reduced liquor to material ratio

Generally, machines with bigger trough sizes cause major wastage of water and chemicals. V-shaped troughs give better impregnation time with low liquor ratio and the quantity of steam required for heating the liquor is also less. Further, switching over to semi-continuous or continuous operations can also lead to reduced liquor ratio, time and cost. The spraying of liquor, nip padding, foam application, minimum application techniques etc. are also the various approaches in this direction.

13.4.5 Efficient heat recovery

In the process house water is generally heated from room temperature to 80-90°C and at the end of the process water is run away into the drain. This is absolutely uneconomic. Many of the modern machine is equipped with effective heat-exchangers, in which the outflowing hot water heats up the inflowing cold water and is only then discharged into the drain.

Another possible source of recoverable heat is the waste heat contained in the condensate. Owing to the condensation problems, the flue gas temperature is around 200°C. If the flue gases are cooled down from 200°C to 50°C by boiler feed water or processing water, the result is considerable saving in energy.

Exhaust air heat recovery units can also be employed as the energy carrier may be gas or air. During heat-setting of textiles on stenter frames emission of compound capable of vaporisation may occur and the flue gases is escaped from the chimney. The air exhausted from the stenter is fed through an insulated air duct into the boiler house, where together with the quantity of air required for combustion, is passed through a blower system into the the boiler. When the boiler comes into operation, clean flushing energy is drawn-in through an intake via a switch equipped with an automatic drop flap. The switch changes over to exhaust air after the burn-

ing unit has ignited. Above the roof is an open buffer chimney, through which the excess exhaust air can escape or the fresh air required for further combustion can be drawn-in [21].

13.4.6 Heat recovery from process effluents

Textile processing houses discharge a lot of contaminated hot waste water and emit smoke, which are sources of water and air pollution. There is an inter-relationship of energy recovery and environmental protection. Increased temperature have negative effect on the organisms living in water and destroy the ecological system. The waste water and exhaust gas can be used to heat up clean, cold water and this can be returned to the production process.

13.5 Economy Through Water Conservation

It is always essential to use less quantity of water with proper quality for a particular process. The cost of water is increasing and in order to conserve energy it is necessary to reduce the water consumption in the process house. This is expected to result in savings of chemicals, water, reduce the effluent quantity and related problems of treatment and disposal. Machineries with new designs and new process techniques are developed for minimising the requirement of water.

13.5.1 Minimising liquor to material ratio

Reduced liquor ratio not only reduces water consumption but also reduce the quantity of effluent to be treated. The liquor ratio in kier and peroxide boil, usually ranges from 2.5 to 4. In pressure boils, the water consumption for cooling and washing is found to vary from 6 to 9 litres/kg of cloth. It is possible to reduce the water consumption by about 25% by regulating the water particularly at the time of cooling and washing operations with the help of water meter or timer. The aspect of liquro ratio is already discussed while describing the conservation of energy through plant and machinery modification.

13.5.2 Minimising wash liquor

Washing machines are the major consumer of water. Generally old type of washing machines like slack and tight rope require more quantity of water for washing. Counter-current principles of washing, aquatex washing, beam and suction washing, powerful jet with pumps and vibrators, horizontal or inclind washers etc. will not only increase the washing performance but also decrease the water consumption.

13.5.3 Re-using rinsing bath water

Water and heat energy consumption, together with effluent accumulation can be reduced in batch type bleaching of textiles by re-using rinsing and treatment baths on the counterflow principle [22]. This system has been patented under the name Bleachstar. Due to the better usuage of the individual baths, large quantities of clean water and heat energy are saved.

13.5.4 Direct steam injection

For reducing fresh water requirement in a boiler, direct steam injection in jiggers and other equipment may be replaced with indirect heating system. The continuous machines offer, besides reduction in quantity of water with better washings and labour requirement, produce more even quality of fabric. By proper cleaning and sequencing one can avoid down time during continuous processing operations.

13.6 Economy Through Process Modification

Process modifications/developments for minimising energy consumption in the pre-treatment processes are very important and some of the major developments are briefly mentioned.

13.6.1 Mather and Platt's Vaporloc bleaching

Vaporloc system is a continuous washing and bleaching unit with a reaction chamber for scouring under steam pressure of about 30-40 p.s.i. at 130-140°C for 60-80 sec, followed by washing and peroxide bleaching in another chamber. Considerable savings in steam, time, labour are achieved. Only 3-7 min is required for scouring and bleaching. Reducing the time of treatment by modifying the pressure kier boiling for 2-6 h at 15-25 lb/in^2 in presence of sodium sulphite in the scouring bath is recommended [23].

13.6.2 J-Box bleaching

Du Pont Co. has developed a two minutes bleaching process [24] for heavy fabrics using H_2O_2 at very high pH values using a special formulation to prevent undue decomposition of peroxide and damage of fabric during the process.

13.6.3 Solvent Scouring

''Markal Process'' developed by ICI for desizing and scouring of fabric involves the treatment of a suspension of enzyme, TCE and surfactant solution [25]. The material after treatment for 10-20 sec passes through a steaming chamber where the solvent is flashed-off. About 80% saving in steam consumption is reported.

13.6.4 Cold bleaching

A cold bleaching method is reported in which decomposition of $NaClO_2$ is caused by acidification or by addition of reducing agent [26]. Sodium hypochlorite is an intermediate in the release of active chlorine dioxide. A combination of bisulphite with an aldehyde is said to initiate the cold bleaching action and practically no thermal energy is required. The use of azetropic/emulsion based scouring cum bleaching formulation helps in processing at room temperature. This process uses a hot wash at not less than 70°C to achieve the required result. In the cold pad-batch method, the use of peroxide, sulphates and some accelerators like urea, glucose, penta-acetate etc. can cause considerable savings in energy, water and labour.

13.6.5 Combined processes

Several single stage combined pre-treatment processes are discussed in Chapter 11 to minimise the energy consumption. In recent years there has been a trend to save labour and energy by combining different processes with dyeing operations. The combined mercerizing and scouring process consists of impregnating the fabric with caustic soda of mercerizing strength at elevated temperature with a steaming unit within the hot mercerizing section [27]. In the Bruckners Remaflame Process [28] for combined drying and finishing, a mixture of methanol and water is applied to the fabric along with finishing solutions. As the fabric is moved rapidly upward through the drying chamber, methanol is ignited, the solution burns away and the fabric is left with lesss than 4% moisture. Remaflame dryers have been claimed to give fuel efficiency as high as 72% as compared to 50% for conventional dryers.

13.6.6 Shortening of process sequence

The time of various pre-treatment processes can be reduced by judicious approach of the shortening of process sequence without compromising the quality of goods. The heat-setting speed can be improved by making use of super-heated steam and some swelling compounds instead of hot air. Grey mercerization can reduce the number of drying operations. Running two or more ends side by side or superimposed on machines like shearing, cropping, chainless mercerizer, cylinder drying range etc. can increase the production. Hydrosetting of synthetic fibres and its blends at HT/HP beam dyeing machine can reduce the energy consumption. Combined optical brightening and heat-setting for synthetic fibre fabrics and combined bleaching and optical whitening are commonly employed.

13.7 Pollution Aspects in Pre-treatment Processes of Textiles

13.7.1 Water and air pollution

The two main sources of pollution in chemical pre-treatment of textiles are water pollution and air pollution. Water pollution is mainly attributable to the various waste stream coming out of the pre-treatment operations like desizing, scouring, bleaching etc. Moreover, the blow down water from the boilers and the effluent discharged from the water treatment plants also contribute to the water pollution. Air pollution mainly comes from the boilers which are used to produce heat energy requirements for wet processing. The extensive use of coal, oil, gas for industries has led to the air pollution. Polluted air contains cotton dust, CO, nitrous oxide (NO_x), sulphur oxides (SO_x), CO_2, CH_4, chemical vapour, various oxidation colours, chlorine vapour, kerosine, various hydrocarbons and particulates in the atmosphere. The worst condition for human health is the combination of particulates containing SO_2. Generally, air pollution from industrial fuel burning and processing emission contribute to about 30% of total air pollution. In case of industries situated near housing colonies, the permissible limit of any harmful material in air is mentioned as $^1/_{100}$ of the MAK value. If the values are higher than this permitted level, an air purification system will have to be installed. Usually the emissions are ducted away by means of a tall chimney to minimise the impact of air pollutants. Green house gases like CO_2, CH_4 and N_2O etc. trap the earths heat, raising atmospheric temperature. The impact would be varied and unpredictable. A key effect may be rising of sea level by around 50 cms by 2100 because of expansion due to heat and melting of glaciers. This may become a cause of submersion of low lying areas and displacement of around 80 million people. The main culprit causing global warming is CO_2, whose contribution is about 87% and hence CO_2 emission is required to be contained. Table 13.6 summerises the possible problems in environmental control likely to be caused by individual steps in the production of textiles. Air pollution due to scouring and bleaching operations are considered to be negligible as not many volatile products are used at high temperatures. Actic acid is volatile and readily eavporated in the chamber. It can be replaced by citric acid which is non-volatile and also will be required in a lesser quantity.

To minimise waste water pollution some of the most frequently used chemicals have already been either banned by law or voluntarily withdrawn. The red listed

TABLE 13.6
Environmental Problems at Various Stages of Chemical Processing of Textiles [29]

Processing step	Waste water pollution	Air pollution
Spinning/Texturising (yarn production) dry step	No	Heat energy given out
Weaving (winding/dry) (warping/dry) (sizing/wet) Drying	Leads to pollution later on desizing	Heat energy
Chemical processing		
Singeing	No	Heat energy
Desizing	50% total load	No
Scouring/bleaching	20% total load	No
Dyeing	Dyes, Chemicals	Some
Printing	Dyes, Chemicals, Thickeners	Some
Finishing (Conventional/ special)	Natural and synthetic polymers, chemicals	Appreciable

chemicals, whose presence on a textile product considered as dangerous can be divided into following groups :

(i) Pentachlorophenol – used as preservatives for gums, sizing agents, fungicides, rot proofing agents. Its range limit is 0.05 p.p.m. to 0.5 p.p.m.

(ii) Heavy metals – present in buttons, dyes, antiseptics, fungicides, auxiliaries, after-treating agents. Its range limit is 0.0001 to 100 mg/kg.

(iii) Toxic pesticides – to prevent pest attack in cultivation of wool and cotton, 0.5 to 5 mg/kg.

(iv) Formaldehyde – resin finishing, dye after-treatments, printing assistants etc., 20-300 p.p.m.

(v) Azo dyes – those which could release listed carcinogenic amines, during reductive cleavage (Banned).

(vi) Halogen carriers – used in the dyeing of disperse dyes on polyester, 200 mg/kg for volatile organic helogens.

(vii) Chlorine bleaching – to be avoided under some eco levels.

13.7.2 Parameters for assessment of harmful materials in waste water

It is an established fact that industries produce significant quantities of contaminant waste water which are discharged to municipal gutters, open lands, rivers, nullah and ponds and ocean and cause considerable pollution problems. Pollution in some parts of the world has reached a level close to ecological catastrope and all countries are tightening control on environmental pollution. It is now essential that the waste water be treated before being discharged to the sewerage system and has to be biologically degradable. These harmful substances are assessed together as some parameters (Table 13.7) which can be evaluated by standard test methods.

TABLE 13.7
Parameters for Assessment of Harmful Materials in Waste Water [30]

Parameter	Estimation method	Concentration (unit)
BOD	Oxidation by aerobic micro-organism	mg O_2 / l
COD	Oxidation with $K_2Cr_2O_7$	mg O_2 / l
TOC	Catalytic burning	mg C / l
DOC	Catalytic burning	mg C / l
AOX	Adsorption on active carbon	µgx / l
N total	Colorimetric estimation	mg N / l
P total	Precipitation	mg p / l

Physical, chemical, physico-chemical and biological treatments are used to test the nature of textile effluents. The physical characteristics include temperature, pH, colour etc., whereas chemical characteristics include the nature and quantity of organic and inorganic compounds and dissolved gases. The biological characteristics include different types of micro-organisms or microbs that are present in the effluent. These characteristics are determined in terms of BOD (biological oxygen demand), COD (chemical oxygen demand), THOD (theoretical oxygen demand) and TOC (total organic carbon) etc.

The tolerance limits (Indian Standard Institute) for industrial effluents, textile industry raw waste water characteristics are given in Table 13.8. The tolerance limits are different for different receiving bodies. Such regulations are imposed to facilitate further purification of water by sewerage authorities, which can then be discharged into river or other major water sources. Table 13.9 lists some typical

TABLE 13.8
Tolerance Limit for Industrial Effluents [31]

Characteristic	Tolerance limit, mg/l			
	A	B	C	D
Suspended solids	100	600	200	100
Dissolved solids (inorganic)	2100	2100	2100	–
pH Value	5.5-9.0	5.5-9.0	3.5-9.0	5.5-9.0
Temperature, °C	40	45		45
Oils & Greases	10	20	10	20
Total residual chlorine	1	–	–	1
Ammoniacal nitrogen (as N)	50	50	–	50
Total Kjeldahl nitrogen (N)	100	–	–	100
Free ammonia (as NH_3)	5	–	–	5
Biochemical oxygen demand (5 days at 20°C)	30	350	350	100
Chemical oxygen demand	250	–	–	250
Lead (as Pb)	0.1	1	–	1
Cadmium (as Cd)	2	1	–	2
Hexavalent chromium (as Cr^{+6})	0.1	2	–	1
Total chromium (as Cr)	2	2	–	2
Zinc (as Zn)	5	15	–	15
Percent sodium, max.	–	60	60	–
Residual sodium carbonate	–	–	5	–

A – Effluents discharged into inland surface waters
B – Effluents discharged into public sewers
C – Effluents discharged on land used for irrigation
D – Effluents discharged into marine coastal areas

ratios of general effluents. Generally, the treatability of the effluent is illustrated by ratio of COD to BOD. COD quantifies the total oxidisable portion of the effluent. BOD is a measure of the biologically oxidisable portion of the effluent. The higher the ratio of COD/BOD, the less treatable the effluent. The organic carbon is oxidised to CO_2 which is expressed as TOC [33]. A strength and treatability similar to domestic sewage is the objective.

TABLE 13.9
Typical Ratios of General Effluents [32]

Operation	Typical COD/BOD ratio
Domestic sewage	2.1
Brewing	1.6
Textiles	1.6-6.0 (average 3.0)
Chemical manufacture	3.6
Abattoir	1.9

13.8 Pollution Loads in Pre-treatment Processes

The nature of textile effluents is very complex as various types of fibres and chemicals are employed in preparing the textiles. Further the process sequence and chemicals employed in the pre-treatment processes vary from fibre to fibre. The quantities of pollutants that form the pollution load going into the waste water thus depend on the amount and kinds of fibres, type of manufacturing operation employed and water consumption practices.

Approximately 45 million tons of fibres, of which over 50% are cotton, are consumed each year for textile purposes [33]. Although synthetic fibres do not contain any natural impurities, they produce considerable amount of pollutants during wet processing. Table 13.10 gives the characteristics of different processes wastes

TABLE 13.10
Pollution Loads of Cotton and Wool in Pre-treatment Processes [34]

Process	Water required (l / kg)	BOD (mg O_2 / l)	COD (mg O_2 / l)	Pollution load (%)
Cotton				
Desizing	15-20	3000-6000	4000-6000	>50
Scouring	4	8000-14000	7000-12000	10-25
Bleaching	150-180	800-1200	80-150	3
Mercerizing	7	7-50	10-70	<4
Wool				
Scouring (raw wool)	10-40	22000	42600	–
Milling	5-18	4000-24000	6000-4300	75
Carbonising	30-80	200-500	200-700	1

from different stages in pre-treatment of cotton and wool fibre/fabrics. In case of cotton sizes are the major factor being responsible for almost 75% of the pollution load. In case of wool, however, the natural impurities in the unwashed fibre amount for 30-50% of the pollution load. The agents used in synthetic fibres which also cause water pollution are listed in Table 13.11. The materials which can cause sig-

TABLE 13.11
Characteristic Effluents from Processing of Synthetic Fibres [35]

Fibre	Water consumption l / kg of fibre	pH	B.O.D. p.p.m.	Pollutant	% o.w.f
Viscose Rayon	45	7-9.5	1200-1800	Sulphonated oil,	2.0
				Antistatics,	2.0
				Detergents,	3.0
				NaCl.	10-30
Acetate Rayon	85	7-9.5	500-800	Sulphonated oil,	2.5
				Antistatic,	1.5
				Detergents,	1.0
				Softeners.	2.0
Nylon	140-200	7-9.5	300-500	Sulphonated oil,	2-4
				Antistatics,	1.5
				Detergents,	1.0
				Fatty matter.	1.0
Polyacrylics	140-200	1.5-3	500-700	Formic acid,	3.6
				Copper sulphate,	3.0
				Antistatics,	1.5
				Detergents,	5.0
				Carriers.	2-10
Polyesters	140-200	1.5-3	300-800	Antistatics,	1.5
				Detergents,	3.6
				Acetic acid,	4.0
				Carriers.	6-40

nificant water pollution in synthetic fibre wet processing are spin finishes, coning oils, anti-static agents, synthetic detergents, sizes, thickeners etc. The waste water

of synthetic fibres are highly variable and a general characterisation of these wastes is useful only as an approximate indication of their consumption [36].

13.8.1 Desizing effluents

Sizing agents and lubricants are needed for producing textile materials. Sizes used for weaving can be generally classified into four main classes i.e. starch, PVA, CMC, acrylates and others. During the desizing process they get into the effluent. The effluent is further loaded by the chemicals (enzymatic or oxidative) used in desizing apart from the sizes and lubricants [37]. Additional effluent loads during desizing are also produced by fungicides which are mixed in with the sizing agents to preserve them. Size has also a tendency to cause mildew, algae etc., to form in ponds and in slow moving streams. Thus, the discharged effluents account for approximately 50% of the COD level in pre-treatment processes. The proportion of water consumed in this process is comparatively small. Significant characteristics of the effluents of this process are high BOD, high TDS and some suspended solids, which are sometimes in colloidal form. However, the nature of sizing agent used decides the BOD of the wash liquor (Table 13.12). Native and depolymerised

TABLE 13.12
Oxygen Demand of Various Types of Sizes

Type of size	BODs mg O_2/ kg	Oxygen consumption kg O_2 per 1000 kg of textile material
Corn starch	810,000	477
British gum	690,000	690
Methyl cellulose	1,600	1.6
C.M.C.	10,000	9.0
Poly (vinyl) alcohol	1,600	1.6

starches as well as esterified are easily biodegradable. But other products such as CMC or PVA are not satisfactorily degraded and are present a more or less persistant form of pollutant in the upper layers of waste water (Fig. 13-1) [38, 39]. A possible solution to reduce the oxygen demand of starch sizes is the use of persulphate to replace enzyme degradation. Unmodified polyacrylates are also difficult to be degraded biologically and remain as polyelectrolytes in the aqueous phase. By intro-

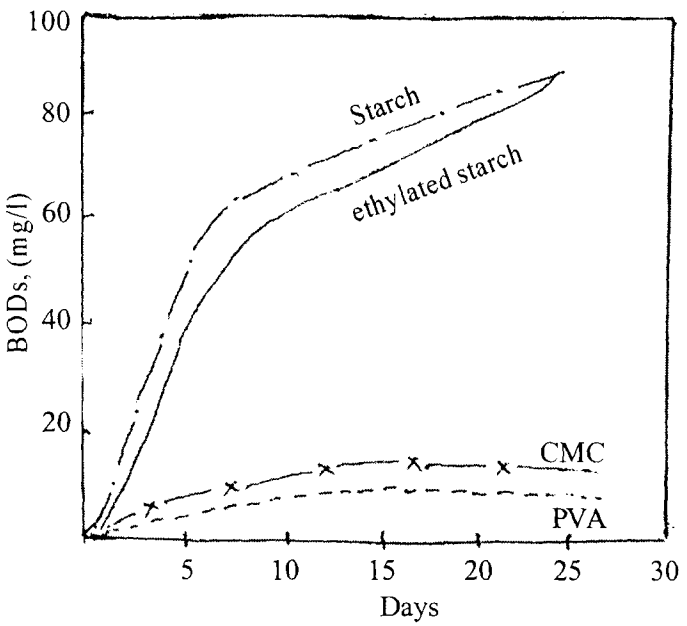


Figure 13-1. Oxygen demand of various types of sizes [40].

ducing the hydrophobic groups, a satisfactory elimination from the aqueous phase is possible biologically. Another approach to minimise the pollution problems is to use a mixture of modified natural polymers with good biodegradability and synthetic polymer with ease of recovery and re-use. Cationic modified product and guar gums are easily degraded by microorganisms and their mixtures with suitable starch derivatives (1 : 4).

13.8.2 Scouring effluents

The chemicals used in the scouring process are mainly, alkalies, wetting agents, detergents, sequestering agents etc. About 25-40% of total water used in a composite mill is consumed in this section. In the scouring process impurities are removed from the fabric depending on the kind of fibre. Generally, oil, colouring matter, detergent, antistatic, lubricants, solvents, oligomer etc. in the presence of alkali contribute to water pollution. Significant characteristics of effluents discharged from scouring section are high BOD, high temperature (70-80°C), very high pH (10-12) and high TDS.

Non-biodegradable branched chain anionic surfactants are now replaced by readily biodegradable straight chain compounds and thus pollution load in waste

water is reduced [41]. Non-ionic ethoxylated alkyl phenols which are extremely used for scouring are difficult to biodegrade at low temperature. Excessive foam of the surfactants may seriously affect the efficiency of biological waste water treatment.

Conning oils, solvents and antistatic agents removed from the fabric during scouring are generally inert to biological treatments [42, 43]. Coagulation with calcium chloride is useful for removing conning oil or alternatively floatation method can be used.

Scouring of wool is mainly done by detergent and solvent. The main components of wool scouring waste water are wool grease, suint and dirt and excrement. Table 13.13 shows the pollutant load of the wool scouring effluent. The detergent

TABLE 13.13
Pollutant Load of Wool Scouring Effluent [44]

Parameter	Concentration unit
COD	60,000-90,000 mg O_2 / l
BOD	30,000-50,000 mg O_2 / l
Pesticides as total of individual pesticides	0.4-1 mg / l
AOX, adsorbable helogenated hydrocarbon	cα.1.0 mg / l
Nitrogen, Total of ammonical, nitrate and nitrite N_2	1000-1500 mg / l
Phosphate	20-30 mg / l

process involves washing of greasy wool with hot water in the presence of non-ionic detergents and sodium carbonate. The characteristics of the discharge are generally affected by both the wool origin and the pre-treatment system which is used to extract the grease and wool waxes. Grease causes big problems as it is not biodegradable. It is possible to reduce the concentration of grease by recovery, but it will still remain high for biological systems.

13.8.3 Bleaching effluents

Generally, the bleaching waste liquor in cotton processing is alkaline in nature with BOD 3.5% of the total load. Hypochlorite is still used as a bleaching agent for cotton due to its bleaching power at low temperatures and its relatively low cost. However, the formation of highly toxic chlorinated organic by-products (AOX) during the bleaching process has limited its use because these types of compounds

are a potential hazard to the drinking water resources when discharged [45, 46]. Table 13.14 shows the typical data on the total AOX and $CHCl_3$ concentrations in

TABLE 13.14
AOX and $CHCl_3$ Concentrations in Bleaching Liquid (p.p.m.)

Toxic by-products	NaOCl stage	H_2O_2 stage	Rinse 1	Rinse 2
AOX	105	19	5	2
$CHCl_3$	11.5	1.1	0.3	0

spent hypochlorite bleaching liquids and rinse solution. Chloroform can be reduced to victually zero by subsequent peroxide bleaching and hot washing. Generally bleaching with H_2O_2 is less harmful as far as AOX content in the waste water. H_2O_2 decomposes into water and oxygen and leaves little dissolved solids or objectionable residue behind except small amounts of sodium silicate and alkali that is added to peroxide liquor. The commonly used stabilisers like DTPA or phosphonates are not easily biodegradable. A new class of sugar acrylate complex sequestering agents are developed for ecological alternative for the present range of products used [47].

Peracetic acid is environmentally safe since it decomposes to acetic acid and oxygen [48, 49]. However, acetic acid contributes slightly to higher BOD levels of waste water in the order of magnitude of 20-40 mg BOD/l. Bleaching of synthetic fibre does not create a major water pollution problem. In case of sodium chlorite bleaching, the sodium nitrite added to the bleaching bath causes water pollution. The sodium sulphite used as an antichlor is also not desirable in water. A low concentration of optical brightening agent do not create any special pollution problem, although most of the agents are not biodegradable within 5-10 days of waste water biological treatment [50]. In contrast, however, some of the intermediates used for the production of optical brightening agents are more or less toxic.

13.8.4 Auxiliary effluents

The consumption of surfactants in textile wet processing is very high and thus large number of surfactants find their way into waste water. Textile auxiliaries used in pre-treatment have relatively lower pollution loads. The ethylene oxide/propylene oxide condensates of fatty alcohols and alkyl phenol ethoxylates (Fig. 13-2) are most commonly used product groups for wetting/detergency. However, during the last few years, it has been shown that during biological degradation of alkyl

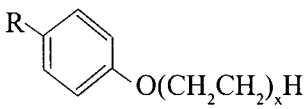


Figure 13-2. Structure of alkyl phenol ethoxylates

phenol ethoxylates, metabolates are produced which are toxic to fishes. By careful selection of alkyl phenol ethylene oxide it is possible to achieve a degree of biodegradability, but the decomposition products are still phenolic and therefore toxic to fish. Fortunately, non-ionics like ethoxylated fatty alcohols (Fig. 13-3), are more

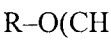


Figure 13-3. Structure of ethoxylated fatty alcohol.

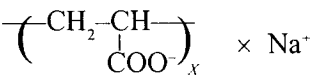


Figure 13-4. Structure of polyacrylate.

degradable and whose metabolites are non-toxic. Another eliminable dispersing agent is low molecular weight polyacrylate (Fig. 13-4). The fat emulsifying power of Lauryl Alcohol Ethoxylates is of importance in pre-tratment of fabrics as chlorinated products are discharged. In order to remove fatty stains, the emulsifying power has to be higher than 10% of fat quantity. Lauryl Alcohol Ethoxylates have a higher foaming tendency and the problems are aggravated in the presence of sizing polymers which have a foam stabilising effect. Anionic alkyl benzene sulphonates are hard compounds in the sense that they are resistant to break down by bacteriological action in waste treatment plants. The low rate of biodegradability is due to the presence of branched side chain. If the linear side chain is present, the rate of degradation increases markedly. Cationic surfactants are used in small quantities for specialised purposes. These are neutralised or rendered non-surface active by reaction with anionic substances which are present in most effluents from textile works.

13.9 Waste Water Treatment From Pre-treatment Plants

Selection of the appropriate method of treatment is influenced by a large number of factros related to each effluent characteristic, such as relative costs, levels of treatment required or site restrictions etc. The composition of a textile effluent depends not only on the type of mill but also to a great extent on the processes involved. Various mechanical, physical and chemical methods can be used, depending on the composition of the effluent. These methods are summerised in

Fig. 13-5. By several techniques and treatments, passing through several stages of

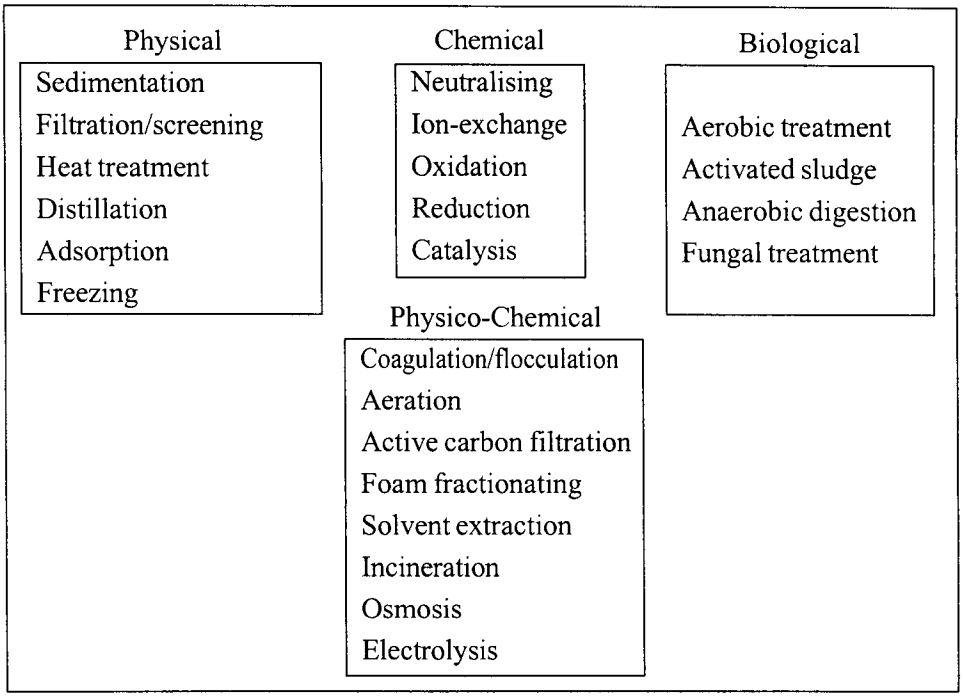


Figure 13-5. Physical, Chemical and biological treatments.

purification, it is possible to obtain water sufficiently clean to be recirculated in a textile mill, as in other spheres of industry. Generally, there are four stages of effluent treatments – namely, preliminary treatments, primary treatments, secondary treatments and tertiary treatments.

Preliminary treatment processes remove grit and solid matters. This include screening, sedimentation, floatation and flocculation. Primary treatment processes are intended to fit effluents for admission to secondary treatments. It includes equalisaiton, pH adjustment, neutralisation and posssible disinfection. These preliminary and primary treatments of the effluent are necessary whether the discharge is to the municipal treatment works or direct to a water course (Fig. 13-6). The variations in loading are eliminated by mixing highly concentrated waste with very dilute waste i.e. equalisation. Neutralisation is done by adding H_2SO_4 or HCl or using flue gases [52] to pH 7. If neutralisation is done by using HCl, sodium chloride is formed, which cannot be dumped in rivers due to salt burdening of river

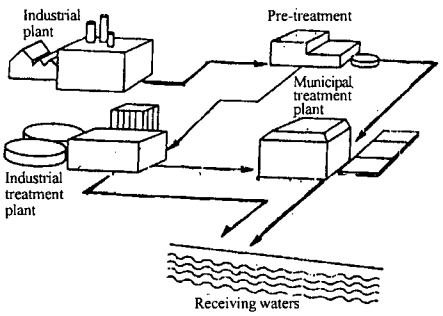


Figure 13-6. Waste water management activities [51].

water. In addition the building structures and production equipment are subjected to corrosion by acid vapour. The H_2SO_4 leads to the formation of sulphate which has adverse effect on concrete. The use of flue gas has several advantages over mineral acids [53]. Flue gas is easily available from boiler firing installation. During neutralisation bicarbonates are formed which are advantageous to the environment. A process for the treatment of effluents using flue gas is shown in Fig. 13-7.

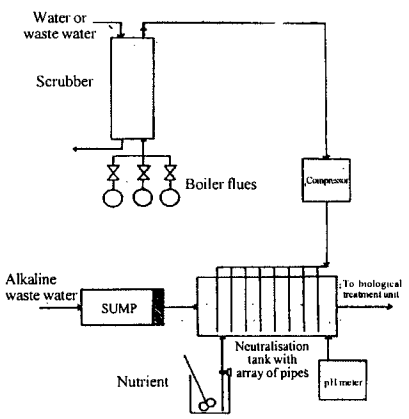


Figure 13-7. Process flow diagram for neutralisation of flue gas.

The secondary treatment methods are used to reduce the organic load of textile effluents. It consists of aeration, chemical coagulation and biodegradation. Aeration helps in reducing the possibility of odour formation and sludge production. Effluent contains impurities in dissolved, colloidal and suspended form. Precipitation and coagulation of these impurities to produce microflocs is done either by pH adjustment (such as acid cracking), or by inorganic coagulants (multivalent metals)

or by organic coagulants. Acrylic acid base size can be completely removed from effluent by precipitation. Commonly used coagulants are lime, ferric sulphate, ferric chloride, ferric alum, calcium chloride, aluminium sulphate, sulphuric acid etc. Organic coagulants are low molecular mass, highly charged polyelectrolytes that are usually cationic, and can be used either as an alternative to, or in conjunction with, inorganic coagulants. Their mechanism can be explained in terms of the charged patch model (Fig. 13-8). When the impurities in the waste water are in the form of

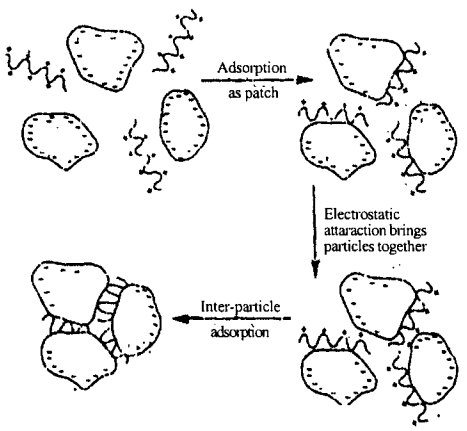


Figure 13-8. The 'charge patch' coagulation model.

microflocs and other suspended solids, the second stage of flocculation aggregates them into larger agglomerates. Flocculation involves adsorption of the polyelectrolyte onto particle surfaces. These form loops and tails which act as physical bridges across the particles, thus binding them together into a polymer-particle matrix or floc i.e. a bridging mechanism (Fig. 13-9). A substantial proportion of colloidal

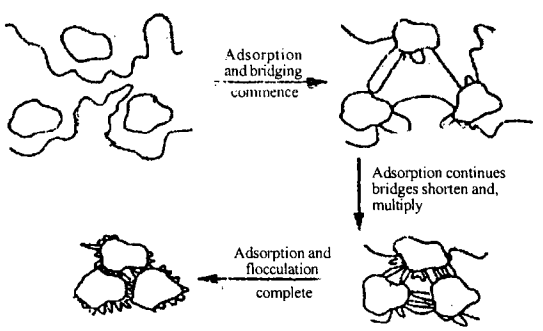


Figure 13-9. The 'bridging' flocculation model.

dirt (stabilised by detergent) from wool scouring effluent can be removed by flocculation process (Fig. 13-10) with high molecular mass bridging flocculant like

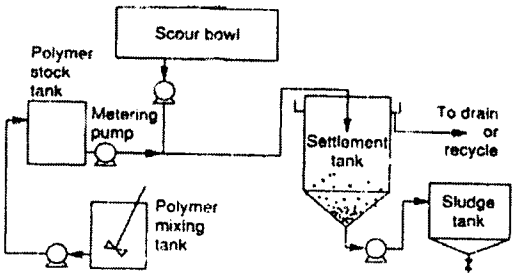


Figure 13-10. Flow diagram of a typical wool-scour treatment plant.

polyelectrolyte with slight anionic or cationic charge depending on the particular characteristics of the liquor to be treated. Recycling of the liquor to the scouring bowls is also possible. Conventional centrifugation, floatation or settling is broadly used for grease and suspended solid removal from wool scouring waste water. Hot acid cracking also increases grease removal. Grease removal before biological treatment will greatly increase the load removal. Typical reductions in suspended solids (and the accompanying reduction in COD) are shown in Table 13.15. Grease re-

TABLE 13.15
Typical Data from Treatment of Wool Scour Effluent

Treatment	COD		SS	
	(mg/l)	Reduction (%)	(mg/l)	Reduction (%)
Untreated	100490		30950	
Centrifugation 60 mg/l Zetag 92	91500	9	26200	15
Centrifugation 100 mg/l Zetag 92	60460	40	19370	37
Centrifugation	50650	50	13400	57

covery by centrifugation is usually less than 50%. Another system of wool scouring waste water treatment is by land irregation [54]. The treatment steps are, storage and aerobic digestion by static aeration, land farming and evapotranspiration of land farming leachate.

In biodegradation, the micro-organisms are utilised to degrade the organic ma-

terials in the waste stream. Aerobic bacteria requires oxygen while anerobic bacteria thrive in the absence of oxygen. Microbes consumes organic matter giving out finally gaseous products. The most common aerobic biological treatment processes are activated, trickling filters [55]. A schematic flow chart for activated sludge treatment is shown in Fig. 13-11. The activated sludge process involves mixing of

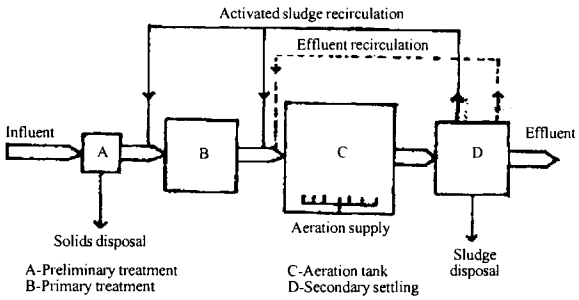


Figure 13-11. Activated sludge plant.

incoming waste water with biologically active sludge or suspensions of microorganisms. The mixture is then aerated with compressed air or mechanical aerators for the desired length of time before transferring the same into another tank where the aerated sludge is seperated by sedimentation. The treated effluent is then discharged to the natural streams. Biological systems as activated sludge and aerobic filters have been widely used to achieve strict standards in wool scouring waste water treatments. The removal of sizing agent by aerobic biodegradation is restricted almost entirely to natural products like starch. The starch is usually decomposed by bacteria with the aid of specific enzymes into its fundamental building blocks i.e. water, CO_2 and NH_3. Considerable amount of biomass i.e. sludge, are thus produced and must be disposed of.

Tertiary treatment processes are used only to eliminate materials which are not amenable to secondary treatment. A treatment method for wool scouring effluent has been developed, consisting of evaporation and incineration plant in combination with a biological plant [56]. The resulting condensates from the evaporation plant and the incineration residues are recycled so that the water, ammonia and scouring aids are returned to the production plant [57].

Organic removal processes are achieved by adsorption, foam seperation and chemical oxidation. In adsorption activated carbon, silica gel, chitosan fibre, fullers earth etc. are used to absorb impurities from waste water. The sizes from the

textile effluents can be removed by bioelimination i.e. adsorption by sludge. Acrylic acid and polyacrylate sizes can be readily disposed of by adsorption by the sludge. CMC cannot be eliminated in water treatment plants, whether by biodegradation, adsorption on the sludge or precipitation. Foam seperation treatment involves the passing of compressed air through the waste water containing surface active agents and the foam rich in surfactant is seperated. Chemical oxidation is used for decreasing the BOD. Ozone, H_2O_2, manganese perchlorate are generally used for this purpose.

Inorganic removal processes are achieved by anerobic denitrification, algae harvesting, electrodialysis, ion-exchange resins, solvent extraction etc. The electrochemical technology is very effective in the reduction of colour. Ozone treatment is also applied primarily for discolouration, but it can also improve the quality of effluent in many other ways. Gamma radiation-induced oxidation appears to be effective in discolouring refractory dyes. Freezing, ammonia stripping, distillation are also employed to remove impurities from effluents.

The recovery of caustic from the mercerization process is a common practice in the textile industry. Mercerizer rinse water is normally recovered when its concentration is above 2-3% and below this concentration it is discharged to waste treatment. An alternative to this procedure is to use an ultrafiltration membrane to filter caustic rinse water before the solution goes to the evaporator. A flow sheet diagram of caustic recovery solution is shown in Fig. 13-12. The clarified and concentrated solution is then ready for re-use and consumption of caustic is significantly decreased [59].

The recovery of sizing agents by means of ultrafiltration has become very popular as a result of environmental legislation [59-61]. The recovery of chemicals, energy and water for reuse is more econimical today. Recovery of PVA was one of the first recycle processes to be used by textile industry [62]. A diagram of PVA recovery system is shown in Fig. 13-13. An important factor is that when size is recovered, 60,000 gallons of discharge from each range per day is eliminated from the waste stream.

Hyperfiltration or reverse osmosis is a seperation process involving the filtration of aqueous solutions by membranes capable of removing not only suspended particles but also substantial fractions of dissolved impurities, including organic

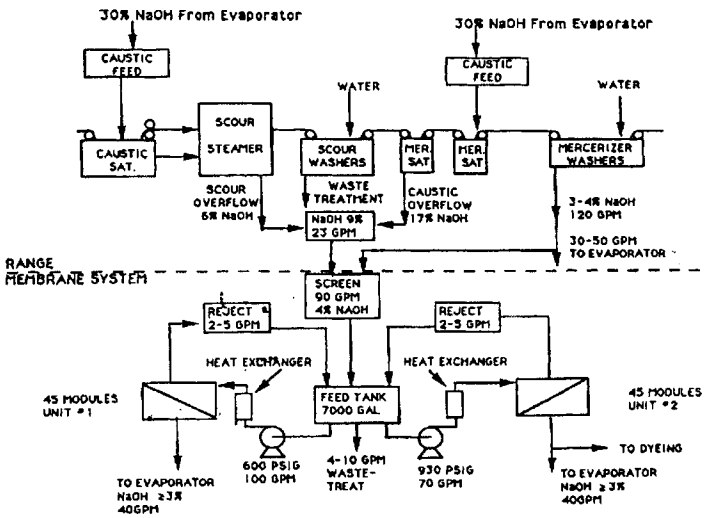


Figure 13-12. Caustic recovery system [58].

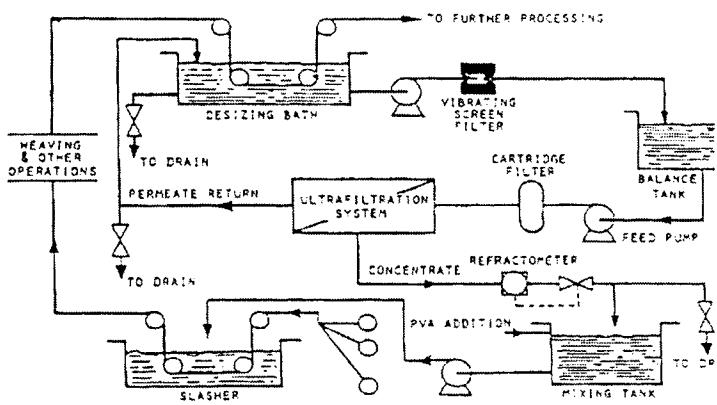


Figure 13-13. PVA recovery system [63].

and inorganic material. The use of reverse osmosis alone or in combination with other treatment is suggested for recovery of sizes [64-66]. In this method, water and soluble salts are selectively removed from the desizing liquor by passing it through ultrafiltration membrane. This is a system for making sizing agents more concentrated and recycle the reclaimed liquor in a continuous cycle during sizing and weaving. Fig. 13-14 shows a simplified line diagram of a system of making sizing agents more concentrated. With ultrafiltration, the membranes, which may

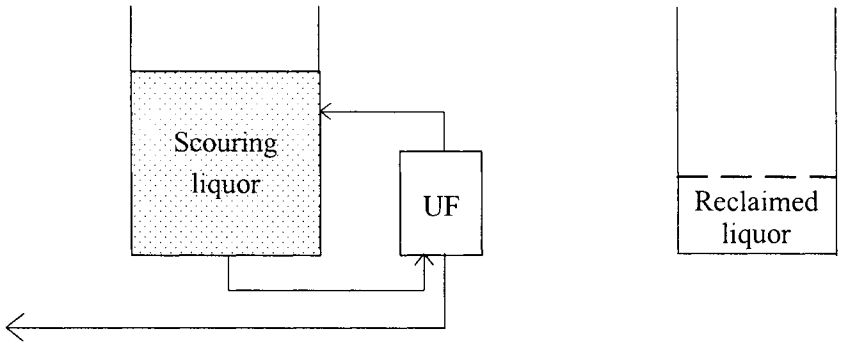


Figure 13-14. Increasing the concentration of sizing agent [66].

either be in the shape of tube or coil, retain the removed substances from a certain molecule size onwards. Technical details on ultrafiltration is presented in Table 13.16. An average permeation rate of 20-25 l/m²h is attained in increasing the con-

TABLE 13.16
Recycling Sizes by Ultrafiltration [67].

Initial concentration (%)	1.5
Final concentration (%)	8.1
Permeation rate	
Initial (l/m²h)	130-150
Final (l/m²h)	8-10
Average (l/m²h)	20-25
Retentivity (%)	95
Temperature (°C)	80

centration of acrylic acid base size in washing liquors to a value of about 9%. With ultrafiltration the size containing scouring liquor is circulated until the cycle liquor reaches a desired concentration [68]. The regenerated size is reused per se or mixed with original product (10-20%). Recovery rates of 70-85% in recycling PVA sizes have been reported [69].

The recovery and reuse of size mixtures containing CMC, PVA, polyacrylates are studied by ultrafiltration technique [70]. Fig. 13-15 shows the extent to which different groups of sizing agents can be recycled. The influence extended by the

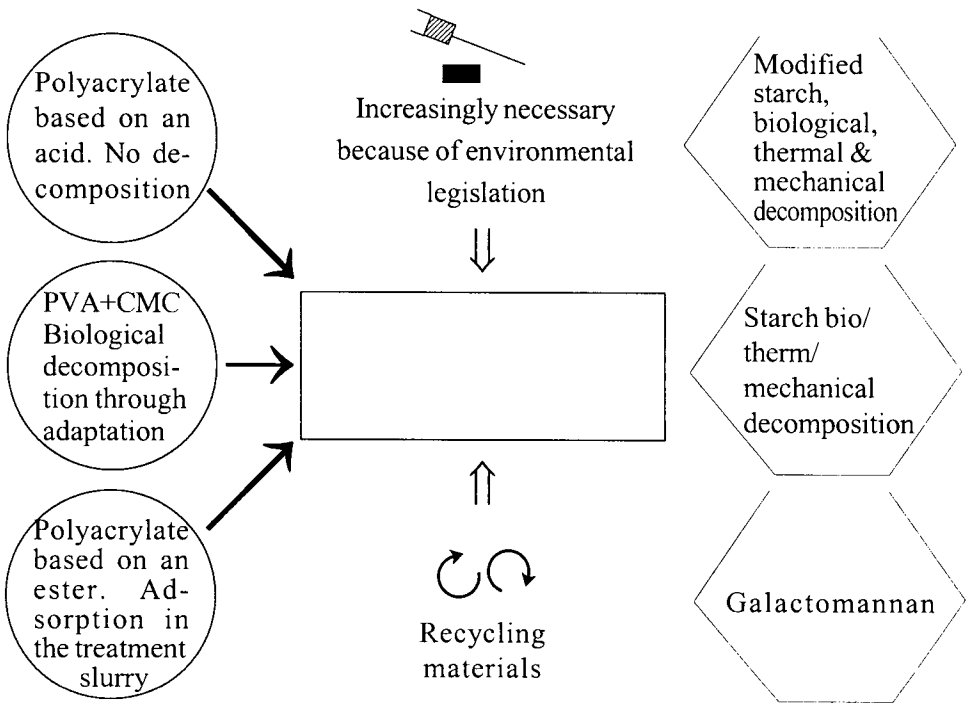


Figure 13-15. Recyclibility of various groups of sizing agents [66].

salts commonly used (particularly Ca^{2+} ions), the thermal, mechanical and biological stability and the eliminability of these size mixtures are investigated [71]. It is found that size mixtures containing polyacrylate show marked advantages over mixtures of CMC and PVA. It is claimed that yarns sized with recycled liquor performed better during weaving than warp sized with the original liquor. This is because the short chain molecules are removed from the particular sizing agent during ultrafiltration. These are found again in the permeate. The improvement is the result of the size becoming more uniform. Modern techniques for recycling sizing agents are one way of reducing effluent loads in the textile industry. But the main difficulty is, the commission finisher has no reliable informations concerning the size content of the grey fabrics he has to finish [72, 73].

Every effluent treatment plant will produce solid waste, which has to be disposed off properly, as it contains hazardous chemicals. Some of these materials are highly toxic, others are corrosive, flammable, irritants, explosive, infectious etc. Disposal of these solid wastes always presents a problem. Waste disposal systems

commonly practised are landfill either on site or to municipal operation, incineration, ocean damping, spray irregation or hauling to municipal treatment plant. Most of the countries have approved landfills for various types of wastes with proper precautions. The incineration of textile waste is not usually recommended due to air pollution and the ash which has high concentration of heavy metals.

13.10 Protective Measures for Ultraviolet Radiation

The problems of ozone depletion in the upper atmosphere have led to increased problems of exposure of the skin to solar ultraviolet radiation [74]. Ultraviolet radiation to earth, due to the above effect could gradually affect human's immune system. Ailments like cataract, lung diseases and skin cancer would increase. Approximately 90% of non-melanoma and 65% of melanoma skin cancers have been attributed to ultraviolet exposure.

The UVR band has been identified as consisting of three regions, namely, UVA from 320 nm to 400 nm, UVB region from 290 nm to 320 nm and UVC from 200 nm to 290 nm. The regions of utmost concern for skin cancer are the UVB and UVA regions [75]. UVC, UVB and UVA radition are usually absorbed by the ozone layer, with no UVC and only half of the UVB reaching the surface of the earth. The size and depth of the Antarctic ozone hole has caused concern particularly in Australia, where it has been suggested that a decrease of 1% in ozone would lead to increase in the ultraviolet radiation at the earth's surface and may eventually lead to a 2-3% increase in skin cancer [76].

Protection from UVR is available through the use of sunsceens and clothing. Sunscreen lotions contain UVR absorbers and sun blockers contain pigment that physically blocks UVR. Hats, sunscreens, sunglasses and clothing can be used to decrease the exposure to ultraviolet radiation by a factor of 10 or more, as well as by people avoiding exposure to the sun at its maximum [74].

This opens up another area of opportunity for textile fabric and garment producers to manufacture comfortable ranges of clothing for leisure and for outdoor workwear that offer significant enhanced protection against ultraviolet radiation. The appropriate selection of dyes, fluorescent brightening agents, and particularly UVR absorbers should enable cotton finishers to provide the high levels of protection demanded [77, 78]. The importance of assessing the protection afforded by apparel fabrics is recognised and there is much research being conducted on the

manner in which different fibres, fabrics, fabric construction, colorants, additives, etc. influence the UV protection of textiles [79-82]. The cover factor of a fabric (the percent of open spaces to closed spaces) has been identified as an important determinant in protectiveness against UVR transmission and SPF (sun protective factor) [83]. Sun protection factor (SPF) of fabrics is improved by applying UV absorbers to fabrics [81]. Woven fabrics usually have higher cover factors than knit due to the yarns in woven fabrics lying closely together and minimising spaces between the yarns and thus the application of a reactive UV absorber performance depends on the fabric [84]. Pale shaded fabrics of cotton, silk, polyamide show little protection against intense UV radiation. The darker shade of any colour shows higher protection provided from sunburn [80].

Two additional considerations in evaluating textiles as protection from UVR are wetting and stretching. It is shown that the SPF of fabrics is reduced when the fabrics are wet [84, 85]. A decrease in SPF values of fabrics as a function of stretching of fabrics is observed [85, 86].

SPF is the ratio of the length of time of solar radiation exposure required for the skin to show redness (erythema) with and without protection. The term SPF or UPF (ultraviolet protection factor) has been introduced such that a garment of UPF 15 will provide the same amount of protection against solar ultraviolet radiation as a sunscreen of SPF 15. Garments with a UPF value of 20-29 offer high protection (UVR transmission 5.0-3.3%). A UPF value of 30-40 (UVR transmission 3.3-2.5%) offers very high protection and a UPF value of 40 + offers maximum protection with a UVR transmission of 2.5%.

The protectiveness that fabrics and garments can afford against UVR is of great importance to consumer throughout the world and a systematic research is yet to be performed on each of the variables that has been identified as impacting on SPF of fabrics.

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Chapter 14

PRE-TREATMENT OF TEXTILES UNDER PLASMA CONDITIONS

14.1 Introduction

To - date, the required surface modification of the fibre is mainly accomplished by wet chemical processes. An appropriate alternative to its conventional techniques is given by the pre-treatment of textile fibres with low temperature glow-discharge plasma in air [1-10]. There is also an increase in patent applications on the latest developments in plasma technology [11-14]. Physico-chemical method of modifying the surface of polymer substrates without changing the nature of the bulk of the substrate has been of great interest. Particularly in the area of pre-treatment of textiles, this technology which is relatively new to the textile industry, seems to bring about obvious advantages in relation to the conventional technique. The reason for this interest is the intriguing possibility of modifying polymers and obtaining new and interesting properties leading to better performance.

Conventional wet pre-treatment processes of textiles are generally energy consuming process. Plasma modification of textiles saves large quantity of water, chemicals, and electrical energy. Ecological and economical constraints which are imposed on the textile industry to an increasing extent, call for the development of environmentally friendly and economic finishing processes. Large savings are possible since the plasma process does not produce large volumes of waste or toxic by-products [9].

14.2 The Concept of plasma

Plasma is known as the fourth state of the matter. Plasma is partially ionised gases, consisting of ions, electrons and neutral particles. These gases are produced by electrical discharges. The plasma state has played a key role in the evolution of life on earth and holds a great potential for future. Apart from the process of nitrogen fixation which goes on year after years during thundering of clouds, lightning and the rains, it is believed that the first ''live'' molecule namely the amino acids were synthesized under the conditions of plasma. During the primitive days of earth, nitrogen and hydrogen combined to produce ammonia, then coupled it to methane and carbon dioxide to synthesize amino acids. In spite of such a long history, the phenomenon of electrical discharges has been used for polymer modi-

fications over the last thirty years or so [15-17]. Particular mention may be made of pioneering work done by Goodman [18], Kassenbeck [19], Pavlath [20], Split [21] and others [22,23], for polymers.

Generally speaking there are various forms of an electrical discharge which differ in their external appearance and the temperature, depending on the pressure and the voltage source connected to the gas section. This current flow is brought about by ionisation through a gas, whereby the current flow is produced by applying high voltages. For textile fields of application, fundamentally only ''cold'' plasma and in particular the corona and glow-discharge are of interest. ''Cold plasma'' are unbalanced plasma or low temperature plasma. The electron energy is up to 100 times greater than the energy of the gas partcles. ''Hot plasma'' are known from nuclear fusion. The energy of electrons and gas particles is equal.

14.2.1 Corona discharge

This is generated at gas pressures equal to or near to the atmospheric pressure with an electromagnetic field at high voltage (>15 kV) and frequency in the 20-40 kHz range for most practical applications today. It develops when a high voltage is applied to electrodes, but the ignition of a spark between them is prevented by an insulator. In order to trigger a corona discharge, a high field strength must be produced at one electrode. Through high voltage, the electrons are accelerated in the direction of the insulator. The insulator is situated directly under the substrate to be treated. On their way to the substrate, the electrons collide with air molecules and form ozone and nitric oxides in the process. The electrons which reach the substrate are due to their high energy (approx. 5eV) and able to split covalent linkages. In doing so, radicals are created on the fibre surface which react with ozone or nitric oxides, i.e. the fibre surface is being oxidised and thereby becomes more polarized.

14.2.2 Glow - discharge

This is generated at gas pressures in the 0.1-10 MPa range with an electromagnetic field in a lower voltage range (i.e. 0.4-8.0 kV) and a very broad frequency range (0-2.45 GHz). Glow-discharge has found practical use in fluorescent tubes. A glow - discharge is brought about when an increased voltage is applied to two electrodes which are spatially seperated in a container with reduced pressure (approx. 10^{-3}-10^{-4} bar). Due to the possibility of feeding in different gases, the surface of a

substrate to be treated can be modified in a chemically specific manner.

Both forms of discharges are regarded as a 'low temperature plasma', but the term 'plasma' is used to describe the glow-discharge only. Corona discharges are generally suitable for flat products and subsequent processing is done immediately after the treatment. In contrast to corona discharge, the electrons produced in the glow-discharge are of high energy, as they are not slowed down by colliding with air molecules (corona discharges originate in an air atmosphere). Glow-discharges are suitable for all kinds of textile products and their efficiency does depend on the time elapsed between the treatment and further processing. The electrons having been created in glow-discharge can also better penetrate the fibre surface and thereby also alter the fibre surface more intensively.

Uneven finishes cannot be ruled out in the case of dense and heavy fabrics. In heavy fabric, for instance, the water contents at the cross-over points of the individual yarns are very high, while non-overlapping areas of the yarns have relatively low moisture contents. The same applies to the individual fibres in the yarn structure. As the conductivity of the wool being an insulator in its dry state, increases with its moisture content, greater voltage gradients may occur in the ''fibre-free areas'' than at the cross-over points of the fibres and yarns respectively during a corona discharge. This does not apply to fabrics of low fibre density, as here no such large moisture differences occur within the fabric structure and thus corona treatment is the method to be chosen. It can be applied in a more cost-effective manner than the glow-discharge which must be carried out in a vacuum. An even treatment of fabrics having high weights of surface or of combed sliver, however, is only possible with the aid of the glow-discharge. The pressure reduction in the treatment chamber being necessary for the production and maintenance of the plasma, leads to drying of the material and thereby to the equilisation of moisture differences. In addition to that a homogeneously distributed ''plasma cloud'' also develops between the individual fibres which allows an even treatment in the dense fabric structure.

14.3 Generation of Plasma and its Action

Plasma may be produced by :

(i) thermal ionisation at high temperatures at normal gas pressures, or

(ii) by using electrical discharges-the frequency of the electrical energy vary from zero (d.c.) to 10^{11} Hertz (microwaves).

These may be subdivided as : (a) electrode discharges (glow, plane, point, corona etc.) and (b) electrodeless discharge using radio frequency (RF) at low gas pressures. The use of RF has a further advantage that it can be used to bring about RF heating. Various types of electrode assemblies can be used for initiating plasma.

14.3.1 Machine performance for producing plasma

The field of industrial plasma engineering has grown in recent years. The uses are motivated by plasma's ability to accomplish industrially relevent results more efficiently and cheaply than competing processes. The research program concerning plasma treatment of textile materials was launched at the Polish Textile Institute in 1973 to improve the soil release properties of double jersey fabrics from texturised polyester yarns. The first experiments with wool date back to 1980 to replace the chlorination in fabric preparation for printing. Three machines for continuous plasma treatment of wool top have been developed as follows :

- 1983 First laboratory device with capacity of ~ 2kg/h
- 1986 First machine with capacity of ~ 20 kg/h
- 1992 First machine with capacity of ~ 40 kg/h.

For example, the shrink proofing of wool using corona discharge has already reached a stage of commercial production [24].

It is necessary to recognise the difference between polymer forming plasmas and non-polymer forming plasmas in order to understand the true meaning of the processing factors of glow-discharge polymerisation. Not all glow-discharges yield polymer deposition. Plasmas of Ar, Ne, O_2, N_2 and air are typical non-polymer forming plasmas. In case of polymer forming plasmas there is pressure change that occurs before, during and after the glow-discharge. In the other case no pressure change occurs. Although a number of methods can be used to generate plasma, the methods utilised in surface modification of textiles are more or less limited to some kind of electric discharge. The volume of glow-discharge as well as intensity of glow are highly dependent on the mode of discharge, the discharge power and pressure of the system. The chamber where the polymer is modified is known as the reactor. The volume and intensity will affect the rate of polymer modification, depending on the geometric factors of the reactor. Electric discharge can be obtained

in number of ways and numerous combinations of factors are involved in the design of reaction vessel. The type of electric power source and mode of coupling also play an important role. Based on this R.F., low frequency or D.C. source can be used for excitation and coupling can be either inductive or capacitive.

Figs. 14-1 to 14-5 describe the typical reactors of different kinds for producing plasma. The description given in the caption is self-explanatory. Fig. 14-1 shows

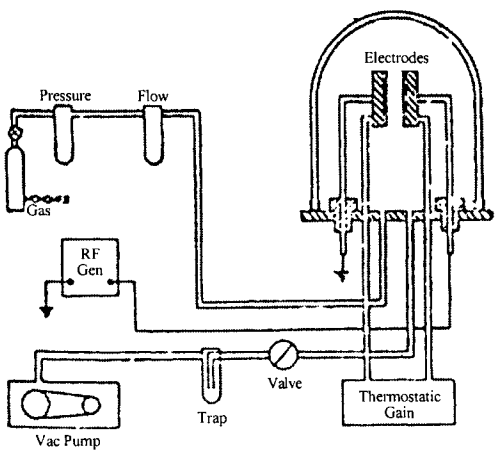


Figure 14-1. Typical laboratory equipment for glow-discharge experiments [25].

the schematic representation of glow-discharge reactor with internal electrodes. The two copper electrodes in the glow-discharge chambers are 1 cm apart and the fabric samples are held rigidly between these electrodes. Power is supplied by 500-W 3.14 MHz generator. The chamber is evacuted to 10^{-3} torr and if required monomer is then introduced at the ambient temperature, its pressure and flow being regulated by valves.

Fig. 14-2 shows the experimental arrangement that is necessary to be made for producing plasma. It consists of a cylindrical glass chamber having arrangements for connecting to vacuum pump, an inlet and outlet for gas and an inlet to introduce monomer for the purpose of grafting experiments. A radio frequency oscillator, operating at 18 MHz can be used as a source to produce electrodeless discharge. The power output can be varied from 100 to 250 watts. The gas pressure inside the tube may be maintained at about 0.1 mm of Hg. A special glass holder is designed to introduce the sample into the plasma chamber. The samples are subjected to plasma treatment for various durations of time. Occasionally a D.C. power supply

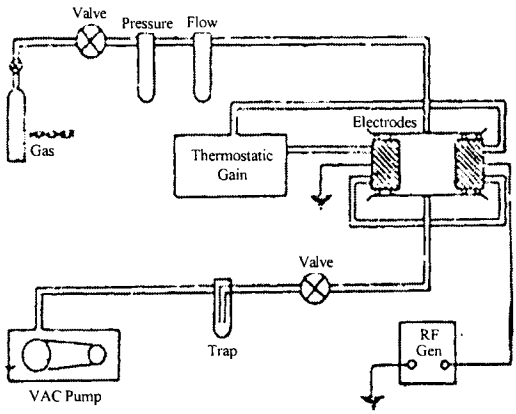


Figure 14-2. Schematic representation of a glow-discharge reactor with internal electrodes

operating between 400 -2000 volts is used to produce gas discharge.

Fig. 14-3 shows schematic representation of glow-discharge reactor with exter-

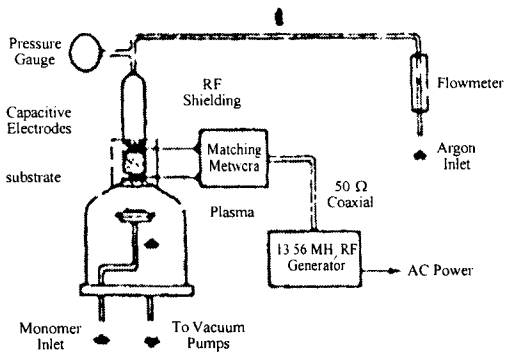


Figure 14-3. Glow-discharge reactor with external electrodes.

nal electrodes. A substrate is placed in the tall frame portion. Figs. 14-4 and 14-5 show the schematic representation of corona reactors. Fig. 14-5 shows the corona reactor with a rotating drum on which substrate is placed. The type and rate of polymer formation depend very much on the type of reactor.

The practical advantages of textile plasma exposure have been documented by Rakowski [9], who compared conventional chlorination process with a new process based on the exposure of wool to a low pressure plasma using the apparatus shown schematically in Fig. 14-6. Wool tow is fed continously into a vacuum

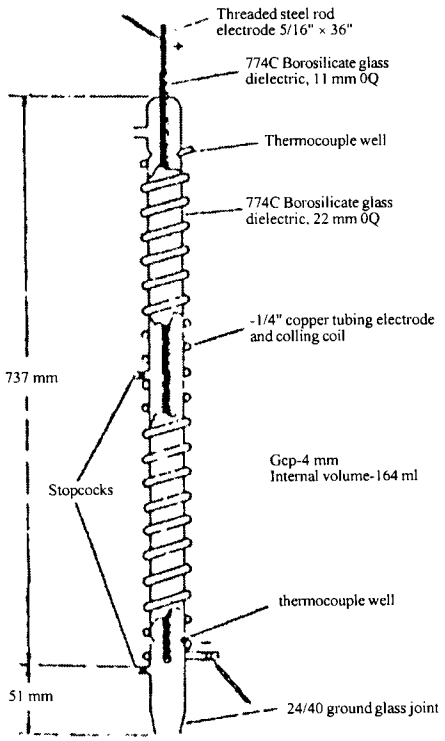


Figure 14-4. Schematic representation of corona reactor.

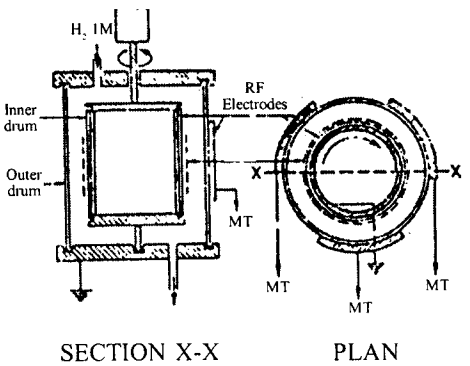


Figure 14-5. Schematic representation of corona reactor with a rotating drum on which the substrate is placed.

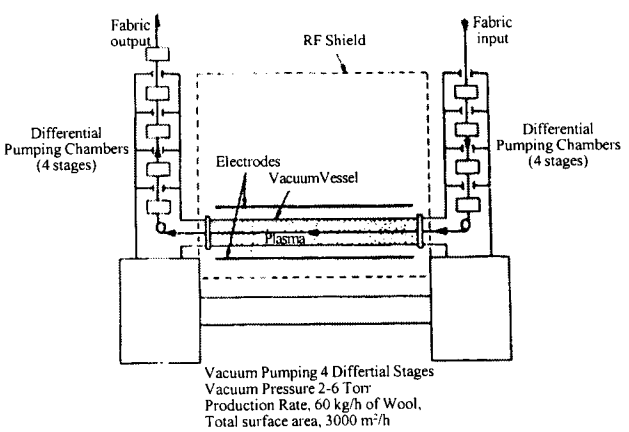


Figure 14-6. Apparatus for low pressure plasma treatment of wool [9].

chamber operating at pressures of 2 to 6 torr, where a glow-discharge plasma provides active species to which the wool is exposed. A novel feature of this approach

is the continuous feeding of the wool tow into and out of the vacuum system through several differential stages of vacuum pumping.

More recently, a group affiliated with Sofia University in Japan [26-28] has reported the generation of both filamentary and glow-discharge plasmas at one atmosphere of pressure in such gases as helium, and argon with an admixture of acetone. Similar work is also originated independently in the UTK Plasma Science Laboratory at the University of Tennessee in Knoxville [29-34]. A schematic diagram of the one-atmosphere glow-discharge plasma reactor system developed at the UTK Plasma Science Laboratory is shown in Fig. 14-7. The reactor volume is

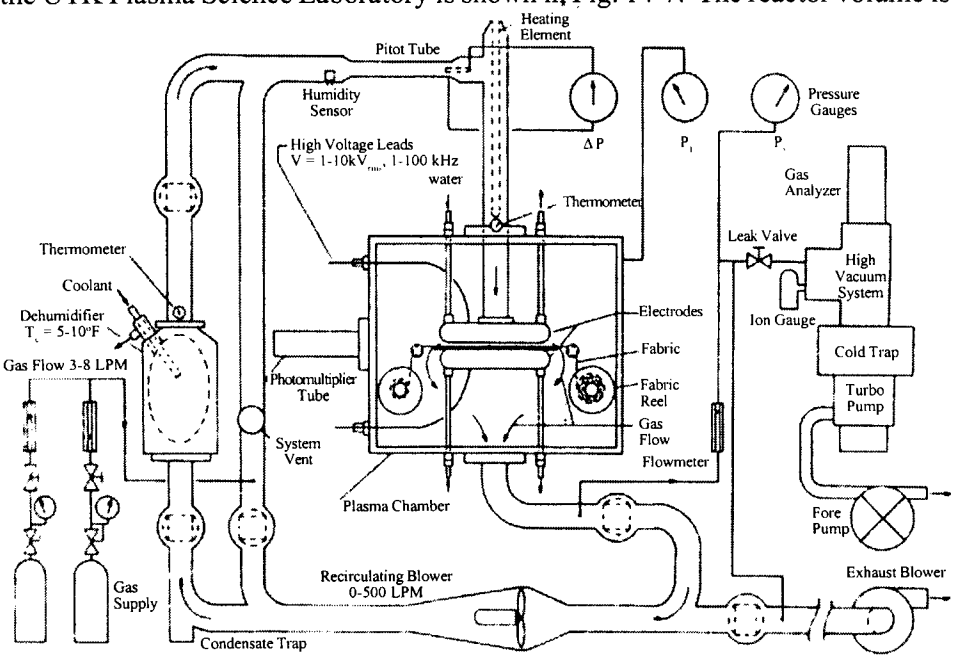


Figure 14-7. Schematic drawing of the one-atmosphere glow-discharge plasma reactor [35].

bounded by two plane, parallel plates across which a kilohertz electric field is imposed. The electric fields must be strong enough to electrically break down the gas used, and are much lower for helium and argon than for atmospheric air. The parallel face electrodes constituting the discharge region are placed in a Plexiglas enclosure. The working gas is recirculated and chilled to remove moisture, and reheated as required. The lower electrode has a solid stainless steel face and is covered with a 3.2 millimeter thick Pyrex insulating plate. The upper electrode has a perforated face of stainless steel with 650 holes 3.2 millimeter in diameter. Gas

flow is introduced on the back side of this electrode and flows downward through the perforated face of the electrode. Fig. 14-8 is a schematic diagram of the upper

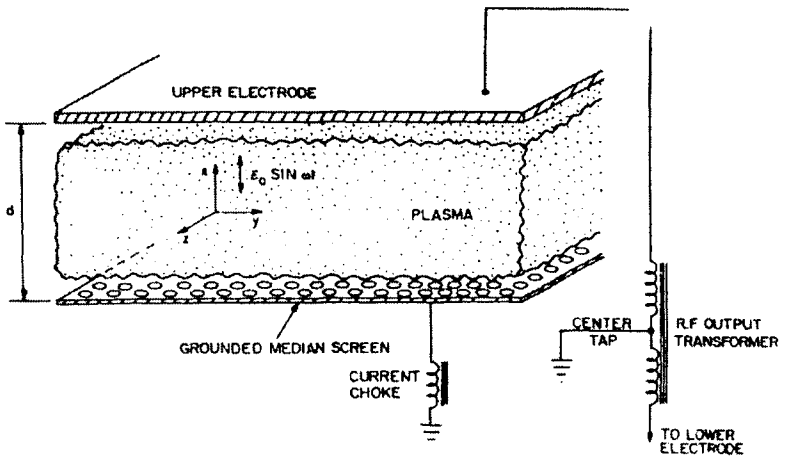


Figure 14-8. Electric field of a radio frequency power between upper and grounded midplane electrodes [35].

chamber of one-atmosphere glow-discharge plasma reactor. The lower boundary of this space is the midplane screen, the floating potential of which should remain near ground if the power supply output is connected as a push-pull circuit to the two electrodes with a grounded center tap. This reactor does not require any vacuum system, and only a simple enclosure is needed if one wishes to operate with gases other than atmospheric air.

The discontinuous (batch) machine (Fig. 14-9) for fabric treatment developed

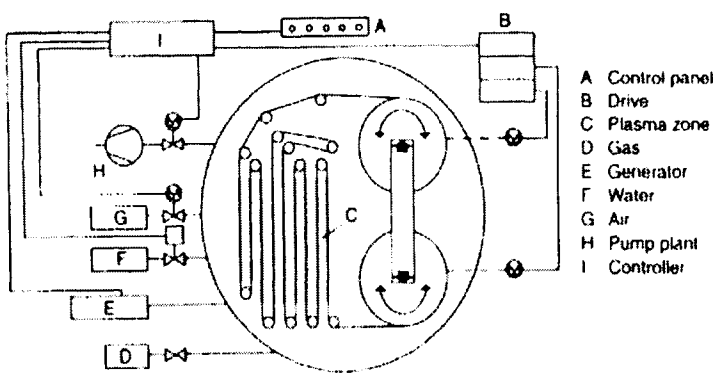


Figure 14-9. Batch plasma machine KPR-180 for fabric treatment [36].

by the Tecnoplasma SA consortium in Switzerland, based on research and construction work performed in Niekmi, Russia, for the last 16 years, has recently become available as production equipment.

The most recent machine for continuous plasma treatment of wool top developed at the Textile Institute in Lódz consists of (Fig. 14-10) a vacuum generation

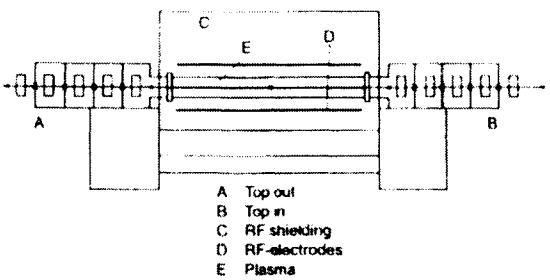


Figure 14-10. Prototype machine for continuous plasma treatment of wool top [36].

unit, a plasma generation unit, a top transport and collecting system. The glow-discharge is generated in a 45.8 litres processing chamber at 13.56 MHz and average RF energy density of 0.12 W/cm^3, provided that there is good coupling of the RF generator and plasma generation circuit. The machine capacity is estimated as ~ 40 kg/h.

14.3.2 The interaction of plasma with substrate

The interaction of plasma with materials can be roughly divided into three different classes [37] :

(i) Reactions due to formation of ions which would lead directly to a new chemical product like formation of NH_3, NO_2, ozonisation etc.

(ii) The second type of plasma reaction is the initiation of polymerisation i.e. deposition of thin uniform polymer film on the electrodes. Organic monomers in the vapour phase, like other gases, are ionised by bombardment of electrons under the discharge conditions. Such ions when neutralised have energy which leads of rapid polymerisation. Films having good stability, insulating properties, free of holes and uniform thickness can be obtained at a rate of few grams per kwh. Continuous movement of textiles, paper etc. through flat plate electrodes (0.1 m separation) for coating is possible. Manufacturing of thin film for capacitors, coating of cans or metal surfaces has been achieved.

(iii) The third type of plasma reaction is concerned with effects produced at organic polymer surfaces in contact with plasma. This type of reaction forms the basis of major developmental work on textiles. The energic ions from the plasma break organic bonds with the evolution of gaseous products (for e.g. hydrogen from hydrocarbons) and the formation of carbon free radicals. These radicals can in turn lead to chemical reactions at the surface of the substrate [38,39].

The essential plasma processes are presented in Fig. 14-11. The process which

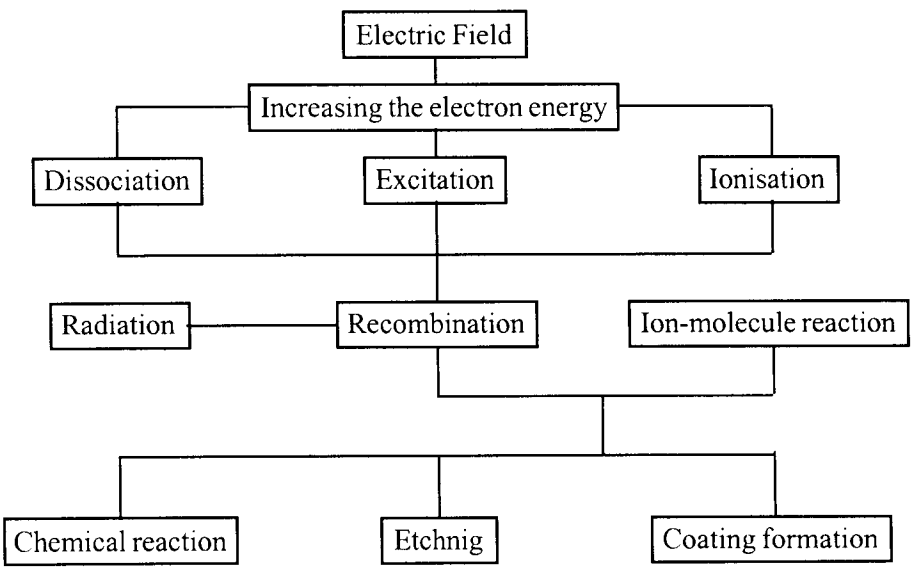


Figure 14-11. Basic process in plasma (Courtesy of Amann und Söhne GmBH).

can occur are cross-linking, solid-state polymerisation, etching action, radical formation and degradation. Which of these processes are predominant, however, strongly depend on the nature of gas, pressure and the power used for the glow-discharge. These reactions may be discussed under separate categories.

Recombination : When the rate of producing surface radicals is high and air is excluded, a tough cross-linked shell is formed that can offer protection against solvent attack, penetration by vapours or ions in solution or thermal disorientation. This type of surface cross-linking can be useful for : (a) limiting of plasticizer loss and extending the life of polyvinyl chloride tiles or other plasticized products, (b) rendering water soluble products like polyvinyl pyrolidene partially water resistant for time delay encapsulation.

Oxidation, Oxidative degradation : In oxygen containing plasma, surface excitation leads to absorption of oxygen and formation of polar surface of ketone, hydroxyl, ether, peroxide and carboxylic acid groups that are much more hydrophilic (wettable) than the untreated surface. Thus articles like flannel, polypropylene non-woven fabrics, PE film, and Teflon have shown marked increase in wettability after exposure to air discharge. Corona discharge treatment is routinely applied to PE film to make it printable. Plasma treatment can also lead to improved adhesion properties (through mechanism discussed below).

Peroxide formation : A high proportion of reactive sites is converted to peroxide form when a typical textile or plastic substrate is exposed to Argon plasma and then to air. If R-H represents carbon-hydrogen bonds susceptible to the dissociation by exposure to plasma, then

$$\underset{\text{(polymer with C–H bonds)}}{\text{R–H}} \xrightarrow{\text{Argon discharge}} \text{R}^* + \text{H}^* \rightarrow \text{H}_2$$

$$\downarrow \text{air}$$

$$\text{R–O–O}^* \text{ (peroxy radical)}$$

$$\text{R–O–O}^* \xrightarrow{\text{R–H}} \text{R–O–O–R} + \text{radicals} + \underset{\text{(peroxide)}}{\text{R–O–O–H}}$$

Since peroxides are known to act as initiators for vinyl polymerisation, it follows that under suitable conditions a vinyl monomer will react with peroxide group to produce a graft copolymer with the substrate, e.g.

$$\underset{\text{peroxide site}}{\text{R–O–O–H}} \xrightarrow[\text{(acrylic acid)}]{\text{CH}_2=\text{CH–COOH}} \text{RO–CH}_2 + \underset{\text{(propagating radical)}}{^*\text{CH–COOH}} + {}^*\text{OH}$$

Since peroxide groups are indefinitely stable under ambient conditions and thus, they can be stored as reactive sites and used at a later time. These surfaces also show improved adhesion in different circumstances.

Initiation for grafting : The free radicals formed on the surface of fibre by exposure to plasma can be used directly to initiate polymerisation, with new polymer bonded firmly to the surface by carbon linkages. Thus, a new polymer can be applied in the following manner :

$$\text{R} - \text{H} \xrightarrow{\text{discharge}} \text{R}^* \xrightarrow{\text{Acrylic acid}} \begin{matrix} \text{RCH}_2\text{CH} - \text{COOH} \\ \text{CH}_2.{}^*\text{CHCOOH} \end{matrix}$$

14.4 Surface Modification of Fabrics Under Plasma Treatment

The plasma-induced surface modification of textile substrates has gained increasing importance over the last few years [40]. Probably the most advantage behind this renewed interest in plasma technology is the restriction of the concentration of AOX compounds in the discharged effluents to 0.5 mg/l [41]. The other reason for this interest is the intriguing possibility of modifying properties leading to better performance. The range of applications is diverse and modifications of surface of various materials like cotton, wool, silk, polyester have been reported. Plasma treatment generally takes place in dry conditions, thus the fibres are not swollen. The changes in properties induced by plasma treatment are therefore restricted to the surface and any damage to the interior of the fibre is very unlikely. The physico-chemical nature of the modified fibre surface has a tremendous influence on the following important phenomenon:

i) Static electricity build up and dissipation.
ii) Moisture transport and comfort.
iii) Oily stain adsorption and release in detergent solution.
iv) Soil deposition, release and redeposition in detergent solutions.
v) Wettability and adhesion.
vi) Scourability and bleachability of textiles.
vii) Wettability and dyeability

Form the physical point of view, roughening of fibre surface as seen by atomic force microscopy is responsible for changes in the coefficient of friction, top cohesion, spinnability, yarn strength, etc., as well as for increase in felting resistance of wool. From the chemical point of view, the oxidation of the fibre surface and interaction with polymeric materials are the main factors responsible for improvements in various properties of plasma treated materials.

14.4.1 Plasma treatment of wool

The effects of a plasma treatment on wool such as anti-felting effect, degreasing, improved dyestuff absorption and increase in wetting properties have been documented in numerous publications [42-46]. Other changes in wool properties are summerised below :

(i) Plasma treatment increases the fibre/fibre friction as measured by Röder method [47], but reduces the differential friction effect (DFE) as defined by Mercer [48] and Lindberg [49].

(ii) Plasma treatment does not change the strength and elongation; the breaking force in loop form is slightly reduced.

(iii) The plasma treatment increases the top cohesion by a factor of 1.5-2.0; this increased cohesion remains stable after prolonged storage.

(iv) The specific electrical resistivity does not change considerably after plasma treatment.

(v) The fatty matter content in wool is reduced by about one-third due to plasma treatment.

(vi) The water content of the wool top is reduced by about 3% due to plasma treatment.

(vii) There is changes in spinning behaviour of plasma treated wool [50,51]. The spinning aids applied on the first drawing frame are carefully selected. The rubbing intensity or twist of the slubbing should be increased. Reduction in breaks rate at ring spinning frame is usually observed and an increase in yarn tenacity by 20-25% is observed for all yarns.

The normal process of preparing light weight woollen fabrics has involved a chlorination operation. However, this leads to difficult working conditions, rapid corrosion of equipment and has a bad effect on the local ecology. Plasma treatment is a good alternative for chlorination treatment although two problems remain : namely the efficiency of plasma/polymer system itself and the ways and means to improve the fabric handle [52]. However, plasma treatment considerably reduces the felting potential for any product obtained from the modified wool. The reduction in the content of covalently bound highly hydrophobic methylicosanoic acid and increase in content of oxidised sulphur species are the main factors responsible for improvements in dyeing and shrinkproofing of plasma treated wool.

Plasma treatment of wool followed by polymer application has also been studied [36]. Almost all polymers used currently on pre-chlorinated wool cannot be used on plasma-treated top. Silicone resins applied to plasma-treated wool increase the shrinkage over that for untreated wool. However, the combined plasma/ PMS/Hercosett treatment encompassing the top treatment gives excellent shrink resistance [53]. The polymer after-treatment reduces both relaxation and felting shrinkage almost independently of plasma treatment time.

There is more even and quicker penetration of dyestuffs and chemicals on plasma-

treated wool than the untreated reference sample. Fig. 14-12 shows the fibre cross-

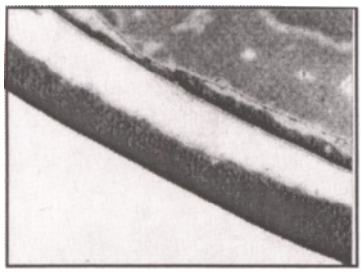


Figure 14-12. Fibre cross-section of the untreated wool (enlargement 30 000X).

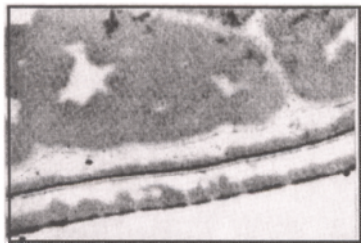


Figure 14-13. Fibre cross-section of the wool following plasma treatment (enlargement 30 000X).

section of an untreated wool fibre with the fibre stem (cortex) and the scale layer (cuticula), which is made up of the A-and B-layer of the cystine rich exocuticula and the cystine poorer endocuticula. Essentially A-layer of the exocuticula is changed by the plasma treatment. Fig. 14-13 reveals that the A-layer of the combed sliver is attacked to a different extent by the plasma treatment (glow-discharge) [54]. This manifests itself in a partially much reduced contrastability and gives the A-layer a ''pearl-necklace like'' appearance in the electron microscope. The increased dyes and chemicals affinity is presumably attributed to the plasma induced oxidation of the cystine in the A-layer of the exocuticula and thereby to a reduction of the wetting bridge density in the fibre surface.

Surface analyses of wool fibres treated with different plasma gases reveal that the wettability, wickability, printability and surface contact angle of the materials are significantly changed in a direction that may lead to new uses for these materials. Several aspects affect the web wettability, such as pore size, fibre diameter, fibre surface roughness and fibre surface chemical composition. Chemical composition of the fibre surface is most important as it determines the surface bonding forces with water, i.e. disruption force, polar force, and H-bonding force. Surface roughness is not a primary reason for improved wettability, but it may increase it [35].

Plasma treatment increases the hydrophillic groups in the wool fibre and the cystine present in the surface layer is converted to cysteic acid [55, 56]. The

endocuticle and the intercell membrane complex and the density of cross-links in the surface layer is decreased by the reactive species in the plasma gas and thus facilitate diffusion of dyes and chemicals [57]. The internal lipids of cell membrane complex are also modified to a certain extent [58]. These changes in the interior of the fibre are presumably caused by the short wave ultra-violet radiation which is produced by the low temperature glow-discharge plasma apart from the chemical active species such as electrons, radicals etc. [59,60].

Woollen sliver and yarn have been treated in low temperature plasma in a vacuum chamber for times from 20 to 30 min [61]. There is a significant increase in the strength which lead to better stability of the material during subsequent processing. Fabrics made from treated wool do not felt and also the shrinkage is reduced e.g. from 37% to 3-5%.

Plasma treated wool may exhibit more or less firm or harsh handle because of surface roughening. This property is very important for hand-knitting yarns or yarns for underwear fabrics. Softeners generally deteriorate the shrink resistance imparted by plasma treatment or plasma plus polymer after-treatment quite heavily [36]. The enzyme treatment is capable of improving the handle of plasma treated wool as well as plasma treated and polymer after-treated hand-knitting yarns without imparting their shrink resistance [62].

14.4.2 Plasma treatment of other fibres

Plasma may be used for removing the contaminants, finishing and sizing agents from the fabric. Desizing of polyester fabric that used polyvinyl alcohol as the sizing agent can be removed by plasma treatment [63].

The efficiency of scouring, mercerizing etc. depends on the penetration of water into the fibre and thus its wettability The wettability of cotton and silk is increased a few fold due to its pre-treatment by N_2 plasma. In case of polyester fabrics also the wettability increases significantly.

The effectiveness of treating grey state and mercerized cotton and polyester/ cotton blends in a low temperature plasma before dyeing is reported [64]. Both air and oxygen plasma treatment allowed the scouring process to be eliminated before dyeing.

A process has been developed for bleaching textile materials containing cellulose activated by microwave radiation [65]. High degree of whiteness and capil-

lary sorption are obtained. The bleaching can be carried out without silicate stabilisers with no increase in oxidation damage to the cellulose.

The hydrophobic effect on a woven cotton fabric can be obtained by surface treatment. Plasma treatment with acid as a component of original gas will result in a hydrophilic surface [66].

Polyester fibres can be effectively modified by low pressure plasma treatment. For yarns the plasma should be capable of being incorporated into the finished yarn production process, depending on the end-use of the yarn, alternatively it should be possible to add on a plasma treatment [67]. Treatment of polyester fibres by glow-discharge in air or oxygen causes a partial degradation of the fibre surface together with an increase in the capillary sorption of iodine or cations in aqueous solution [68]. Wetting out properties of polyester can be achieved by treatment of polyester with plasma and corona discharge [69]. The fabric can be processed without the use of a wetting out agent. Generally, polyester has a very hydrophobic surface because the surface is made up of ether oxygen (C-O-C) linkages while the hydrophilic ester oxygen (C = O) is facing towards the core of the fibre. When surface is treated by plasma either the ester oxygen (C = O) comes closer to the surface as a result of etching or some new C = O bonds are formed due to oxygen ions present in the plasma chamber.

Soiling of fabrics is another important aspect. Treatment of polyester with air plasma considerably decreases the soiling. During plasma treatment fabrics get negatively charged. The soils are also generally negatively charged and therefore there is increased repellency. The plasma etching increases the hydrophilic nature and therefore the soiling decreases. Etching by air plasma causes greater weight loss of nylon, cotton, silk or wool fibres than does etching by carbon tetrafluride or nitrogen plasma, The degree of surface modification is lower for plasma etched nylon or polyester fibres than for cotton or wool fibres [70].

A small scale method for the preparation of linen fabric is described which practically eliminates the use of chemical reagents [71]. The grey fabric is treated in a glow-discharge plasma in air and then washed in hot water. The process maintains the strength of the fabric, does not affect the natural colour of linen and does give fabric a high degree of hydrophilicity [72].

The electron microscopic studies provide additional information regarding mor-

phological changes as a result of plasma treatment. Due to very low range of penetration the bulk structural property such as crystallinity of the sample is not much affected. Plasma etching alters the surface structure of cotton and silk considerably. The fibrillar structure is apparent only on the uppermost surface, whereas deep down it disappears. The surface of the polyester is very smooth initially, but plasma treatment produces a typical ''sea-shore'' structure. In addition in most of the fibres the plasma treatments give rise to the formation of some cracks, voids etc. The type of surface structure produced depends on the type of gas and pressure. For example, the use of nitrogen, oxygen, air and carbon dioxide for polyester gives distinct surface structure with striations and depressions. The use of CO_2 produces even more single crystal structures. On the other hand, the use of He, Ar, NH_3 gives low profile surface structures.

14.5 High Energy Radiation to Textiles

Energy sources fall conveniently into two groups, viz. high energy ionising radiation (X-rays, alpha particles, protons, deuterons, γ-rays and electrons) and low energy radiation (gas discharge and ultraviolet). In the case of radiation processing of textiles, only γ-rays from radioactive isotopes and high energy electrons (β-rays) from machines are needed to be considered. γ-rays are high energy electromagnetic waves and have great penetrating power. Among the radioactive materials recommended are Cobalt - 60 and Cesium - 137. 1-MeV gamma photons lose half their initial energy after passing through 10 cm of material of unit density. Only a small amount of available energy is in general utilised when textile materials are irradiated. The maximum dose rate from a powerful Cobalt - 60 source is about 2 M rad/h, and since several M rads are needed to effect significant changes in the material, long reaction times are generally needed. The irradiation source dictates the time of exposure. For example, radiation using ultraviolet lamp requires substantially longer times. However, the amount of radiation dosages depends on the kind of fibre (Table 14.1). It varies from 2 M rad for cellulosic fibres to that of about 40 M rad for polyester fibre (1 M rad = 10^8 erg/g of substance). With high energy radiation elaborate screening and safety measures are essential, capital costs are high, and the active material must be replaced from time to time. Nevertheless, γ-radiation is useful when low dose rates are required and when thick materials or rolls of fabric, are to be irradiated.

TABLE 14.1
Guide Values of Irradiation Dosages [73].

Substrate	Radiation dosage M rad
Cellulose	2-3
Cellulose/synthetic	2-3
Polyamide	5
Polyacrylic	5
Polyester	40

Certain fibre forming polymers have been reported to degrade and to cross-link on exposure to high energy radiation. The relative extent of degradation and cross-linking varies from fibre to fibre and is dependent upon radiation dose, temperature, and whether air is excluded during irradiation [74-77]. Degradation predominates in cellulosic fibres, cellulose acetates, wool, poly (vinylidine chloride) and polytetrafluoroethylene, whereas polyethylene, polypropylene, polyamides, polyesters and polyacrylonitrile are more susceptible to cross-linking [78].

The result of the introduction of radiation with a polymer is the creation of free radicals. These frequently result from the of breaking C-H bonds leaving a polymer radical. The latter usually abstracts another hydrogen forming hydrogen gas and another polymer radical. The fate of the radicals determines whether the polymer chain degrade or form cross-link. The mechanism by which these cause effective cross-linking is not clear but presumably the monomer adds to the macromolecule before cleavage, just as in the grafting process [79].

The use of high energy radiation for the bleaching of textile materials has been patented [80]. A wide range of possibilities exists for modifying both the physical and the chemical properties of textiles. Bleaching of textiles can be done either by radiating the bleach bath before the entry of the fabric into the bleaching solution or the fabric may be exposed to radiation and stored and then bleaching is carried out. The bleach bath containing sodium chlorite (5 - 110 g/l) can be activated by high energy radiation, with pH adjusted to 9 to 11. The application baths also contain other usual additives such as optical brighteners, wetting agents and auxiliaries and bleaching can be done using continuous or batch methods at or below normal pro-

cessing temperature. The free radicals are formed when textile materials are subjected to moderate amounts of radiation (1-2 Mrad), so that the fibre degradation can be kept to minimum.

The potential of ultra-violet or electron beam curing treatments on textiles needs further investigation as such treatments have been used in surface coating treatments in the packaging industry [81]. The use of appropriate polymer systems with appropriate functional performance properties for use with such treatments may be particularly valuable for surface treatments using UV curing, although electron beam curing is an expensive technique [82-84].

Gas phase or vapour phase treatments is not yet popular in wet processing of textiles. However, in the area of garment finishing, the difficulties of treatment by any other method potentially render gas phase treatments attractive, particularly for treatment of a composite multiple layers of fabrics, such as in a garment [85, 86].

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Chapter 15

APPLICATION OF BIOTECHNOLOGY IN THE PRE-TREATMENT PROCESSES OF TEXTILES

15.1 Introduction

Biotechnology can be defined as the ''application of scientific and engineering principles to the processing of materials by biological agents to provide goods and services''. The earliest evidence of biotechnology include baking of bread using yeast by the ancient Egyptians and brewing [1]. Early methods of producing coloured pigments from natural viable sources may also be cited as primitive technology [2-6]. Today enzymes have been used on a large scale in medicine, food analysis, genetically modified food, transgenic animals and plants and also in the domestic detergent fields. The discovery of chemical structure of DNA has led to genetic engineering, DNA finger-printing, rapid gene sequencing and host of related technologies such as process engineering, fermentation, enzymology, downstream processing, microbiology, biochemistry, process control, reactor design, immobilised cells and enzymes, biosensors, biopolymers and biotransformation [7]. Modern genetic technology is constantly producing new types of application potential which will continue in the future. Biotechnology is also increasingly gaining importance in bioremediation and in the clean up of polluted environments.

15.2 Enzymes for Textile Application

In textile application, the knowledge of specific action of enzymes-amylases for starch splitting began around 1857, when malt extract was used to remove size from fabrics before printing [8]. The use of enzyme in pre-treatment processes of textiles has found much broader acceptence. At present the priority areas are scouring and bleaching of cellulosic fibres and carbonising, bleaching and shrink-resist treatment of wool. Enzymes have traditionally been used for stone washing and bio-polishing of cotton fabrics and garments. Also enzymes have been incorporated in detergents to remove fibre fuzz and brighten the colour of the fabric. In contrast to cellulose and woollen fabrics, the other market segments includes a spectrum of fibres from linen to lyocell (Tencel), rayon (viscose) and cellulose acetate and a multitude of blends, weights and fabric constructions. With the apparel industry trend towards increasing use of cotton knits for achieving novelty finishes is observed.

15.2.1 The chemistry of enzymes

Enzymes are naturally-occuring proteins capable of catalysing specific chemical reactions and being catalysts, facilitate the reaction without being consumed. After catalysing the chemical reaction, therefore the enzyme is released and is able to catalyse another reaction-and so on.

Enzymes have a protein like structure with primary, secondary, tertiary and quaternary structures and are susceptible to denaturing (degradation due to temperature, ionising radiation, light, acids, alkalies and biological effect factors). The textile and clothing sector is now a major user of enzymes during manufacturing and after-care. Table 15.1 summerises some of the already important established en-

TABLE 15.1
Important Enzymes for Textile Application [9]

Enzymes	Origin	Effect
Amylase	Bacillius Subtilis Bacillius lickerinforms	Desizing of starches. Desizing of jeans. (AQUAZYM) makes denim streak-free, softer and more uniformly faded.
Cellulases and Hemicellulases	Trichoderma raesci Aspergillus niger	Desizing of CMC, stylish effects on cellulosic fibres, Non-stone treatment for jeans.
Pectinase	Aspergillus niger	Scouring of vegetable or bast fibres like jute, hemp, flax, remie etc.
Proteases	Bacillius subtilis B. Licheniformis B. Oryzaeof	Scouring of animal fibres, or degumming of silk, modification of wool properties.
Lipases	Aspergillus niger Muco javanicus	Elimination of fats and waxes.

zymes. Cellulases are widely used in textile application. Cellulases are high mo-

lecular colloidal protein catalysts in metabolic form and are commonly produced by soil-dwelling fungi and bacteria [10]. Industrial cellulases are complexes of a number of cellulases, cellobiase and related enzymes in non-uniform composition, with molecular weight ranging from 10,000 to 4,00,000 [11]. Cellulases comprise a multicomponent enzyme system, including endoglucalases (EGs) that hydrolyse cellulose chains randomly, cellobiohydrolases (CBHS) that split cellobiose from cellulose ends, and cellobiases that hydrolyse cellobiose to glucose. EG or EG-rich preparations are best for aging and defibrillation of fibre surfaces, while complete cellulase systems are best for cleaning and depilling effects [12, 13]. In general, there are two major commercial classifications of cellulase enzymes based on optimum ranges : 'acid cellulases' exhibit the most activity within the pH range 4.5-5.5, at a temperature of 45-55°C ; while 'neutral cellulases'', are more effective in the 5.5-8.0 pH range at 50-60°C. Currently, acid cellulases and neutral cellulases are more commonly used. With alkaline cellulases, there is a possibility of applying the enzymes in combination with reactive dyes from a dyebath.

15.2.2 Mechanism of enzyme action on cotton textiles

Enzyme's effect mechanism, i.e. enzyme catalysis, operates first of all to form an enzyme substrate complex [14]. Direct physical contact of enzyme and substrate is required to obtain the complex. The current proposed mechanism of cellulase action is illustrated in Fig. 15-1. However, the mechanism of enzymatic hy-

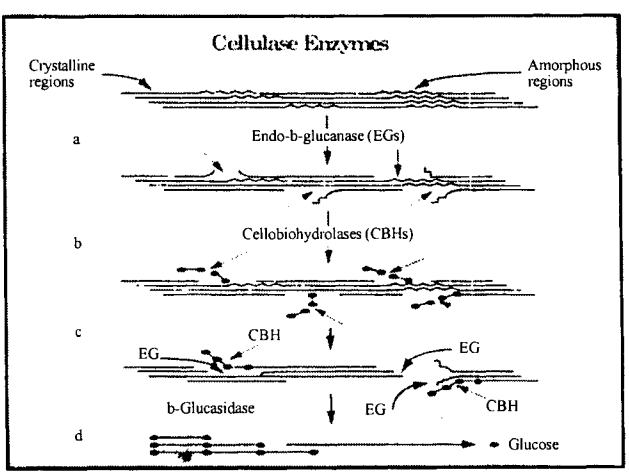


Figure 15-1. Schematic representation of synergistic action of enzymes on cellulosics [15].

drolysis of cellulosic materials is complicated and not yet fully understood [16-18]. Enzymes contain true activity centre in the form of three dimensional structures like fissures, holes, pockets, cavities or hollows. Endoglucanases or endo-cellulases hydrolyse cellulose polymers randomly along the chains, preferably attacking non-crystalline region [19]. Cellobiohydrolases or exo-cellulases, attack the polymer chain ends and produce cellobiose [20]. Coupled with the binding domains associated with the enzyme, exo-cellulases may assist in degradation of cellulose by disrupting the local crystalline cellulose structure, which makes the region more susceptible to subsequent hydrolysis by endo-cellulases [21]. Fig. 15-2 shows the reducing and non-reducing end groups by the action of cellu-

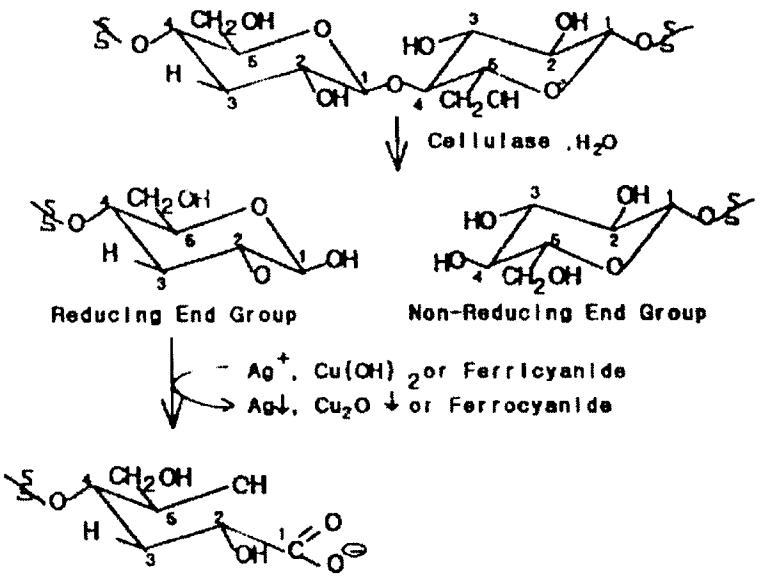


Figure 15-2. Enzymatic hydrolysis of cotton cellulose [22].

lase on 1, 4-β-glycoside bond of the cellulose molecule. β-glucosidases hydrolyse small chain oligomers, such as cellobiose into glucose. The three types of cellulase component act synergistically in degrading cellulose to glucose. Synergism of different components in the cellulase complex and inhibition mechanisms further complicate the reaction [23, 24]. Enzyme diffusion plays a much more decisive role in the heterogeneous system of soluble enzyme and solid substrate. The kinetics of reaction therefore depend on the diffusion of enzyme to and into the solid phase of

the substrate and the diffusion of the reaction products out of the solid phase into the liquor. For cotton, the restriction of the enzyme to the fibre surface is easily achieved because cellulose is a highly crystalline material and possesses only small amorphous areas, making the diffusion of enzymes into the interior of the fibre nearly impossible. Thus, by regulating enzyme dosage and choosing the right type of enzyme, the catalytic action of the enzyme can be confined to the surface of cotton and to the amorphous regions, leaving the fibres, as a whole, intact [25].

15.2.3 Parameters governing the cellulase treatments

The cellulase multi-enzyme complex is completely non-uniform. Added to that is substrate specificity in the form of a selective suitability for enzymatic degradation, due to non-uniform structure of collulose. Yarn type, structure and textile substrate also influence the break-down effect. Fine yarns and open material constructions, particularly any freely accessible projecting fibres, are specifically susceptible to degradation. Prior to enzymatic treatment any impurities or additive present have to be removed first. In particular, the substrate must be free from any enzyme toxins. Some of the enzyme toxins recognised are formaldehyde containing finishing agents, tannic acids like natural tannin or polyphenolic fastness after-treatment agents, proteases, specific surfactants and microbiocides. Denaturing can occur through specific storage effects. In general buffered granulates are more stable for storage. The presence of chemical substances such as organic salts, iron, magnesium and zinc ions etc. can either enhance or inhibit enzyme activity [26].

Both pH and temperature are critical factors affecting cellulase treatment (Fig. 15-3 and Fig. 15-4). A particular type of cellulase will only operate under a specific pH and temperature optima and its activity will decrease sharply on both

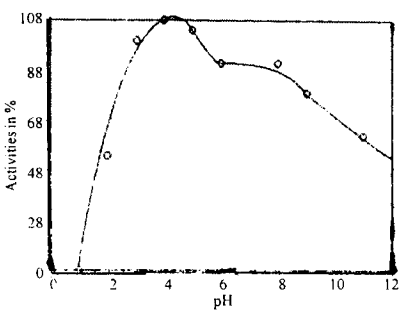


Figure 15-3. pH dependency of cellulase activity.

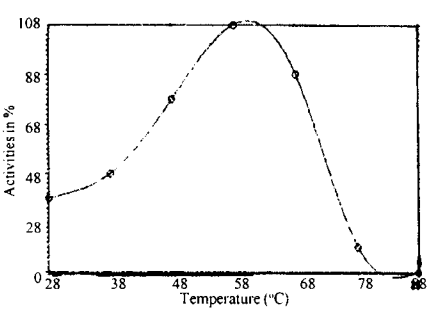


Figure 15-4. Effect of temperature on cellulase activity.

sides of the optimum range. Neutral cellulase is advantageous as it is stable over a broader range. Generally, a treatment time of 45-120 min is appropriate as prolonged treatment time may increase the fibre loss significantly. Similarly, excessive cellulase dosage may also increase the weight loss %. The degree of agitation also considerably increases the weight loss. Machines with vigorous action such as a launderometer cause a much greater weight loss than does hand stirring. The decrease in bursting strength is roughly proportional to the weight loss of the fabric. The decrease in drape co-efficient and the flexural rigidity are apparent and hence leads to the improvement in the handle of the cotton knits after cellulase treatment.

15.2.4 Changes of structures and morphology of fibres by enzymatic hydrolysis

The cellulase complex diffuses through the pore system to the microfibrils, attacks the cellulose chains and hydrolyses each chain to the end. The differences in the efficacy of cellulases on various fibres are dependent on number of factors such as the amounts of non-cellulosic wood pulp-derived matter, the degree of polymerisation, the type and degree of crystallinity, and the type and number of chemical substitutions to the cellulose [27-30]. Key features for the cellulose substrate are crystallinity, accessible surface area and pore dimensions [31]. Variation of any of these factors, e.g., structural changes of cellulose substrate by pre-treatments, will influence the course of the entire degradation process [32, 33].

Viscose rayon is inherently a weak fibre, particularly when wet, therefore it is highly susceptible to damage if enzymatic hydrolysis is not controlled. The enzymatic hydrolysis of viscose fibres causes a decrease of the intrinsic viscosity from 250 to 140 ml/g and an increase in crystallinity from 29 to 39% after 44 h [34]. Strong changes of the structure, however, are not typical for the enzymatic hydrolysis of cellulosic materials. Neither cotton nor wood pulp show an essential decrease of the DP during enzymatic hydrolysis [35-37]. The kinetics of the enzymatic hydrolysis of regenerated cellulose fibres before and after acid prehydrolysis changes the kinetics from a monophasic to a biphasic first order reaction [38].

Bast fibres like linen and remie are multiple cellular systems, in contrast to cotton, which consists only of a single cell. Multicellular fibres contain natural gums and resins that keep the cell together. Crystallinity indices of cotton, linen, remie and viscose fibres do not change after the enzymatic hydrolysis, nor does accessibility to moisture [39]. Consequently, neither the ratio of crystalline to amorphous material nor the DP of the residue changes significantly [40].

15.2.5 The uses and advantages of enzymatic processing

Recently enzymes are used in textile application. The use of enzyme in degrading starch has been known. Enzyme technology is of great interest in the chemically demanding pre-treatment of cotton, wool and silk fibres. Cellulases can be used to finish treatments of cotton pertaining to fabric softness, good performance and fashionable looks as well as the potential to simplify and cheapen manufacturing processes. Popular uses perhaps are stone-washing of denim jeans and bio-polishing. Enzymes are also used for degumming of silk and bast fibres, removal of skin residues and vegetable matter from wool and anti-felting and surface modification of wool. Cellulases show great promise in terms of effectiveness and the entire pre-treatment processes do not appear to be beyond the bounds of possibility in the future. In some of the processes the enzyme treatment is combined with mechanical action to enhance the accessibility of cotton substances. Another approach is the combination of plasma treatment with enzyme treatment [41].

The following points are achieved in practice :

i) The enzymatic process removes the small fibre ends found in yarn surface which eventually lead to pilling on the fabric surface.

ii) Knitted fabrics treated with cellulases are free from surface hairiness, neps, fluff and knops with much improved handle and flexibility.

iii) The material sticking (the burr effect) is prevented particularly with mercerized knitted fabric. Material texture relaxation takes place and improve sewability.

iv) The effect of treatemnt is long lasting. The colour of the dyed goods become brighter with a visual improved colour yield.

v) The process is particularly suitable for the pre-treatment of napped, knoppy goods when there are no suitable cleaning, beating, brushing and shearing machines available.

vi) Complete or partial replacement of pumice stones by cellulase enzymes for the effect of 'stone-washing' on denim is well established and the concept of 'bio-polishing', which originateed in Japan has been extended to knitted structures and blended fabrics.

vii) Cellulases have been incorporated in detergents to remove the fibre fuzz and this means brighten the colours of the fabrics.

viii) Another advantage of enzymatic processes is that they can be adopted to run on equipment already existing in textile plants.

ix) The method is of interest from the view point of energy savings, pollution control and safety. Because the cellulase enzyme, being a biocatalyst, offers advantages such as energy savings through lower treatment temperatures of 40-50°C. The enzymatic pre-treatments of textiles are not so aggrasive to fibres and environment. The 'clean chemistry' aproaches is an advantage in comparison to the powerful alkalies, acids, oxidisers and reducers needed in traditional processes, tending to attack the textile material as well as causing considerable contamination in the environment. After the enzyme stops, residues are present only in the primary strucutre, while there is no chemical residues likely to affect the skin. Besides, they will not leave chemical residues on the processed materials and the colour change on the dyed goods is minimal.

The disadvantages still unsolved in the practical application of the cellulase treatment are that the cellulase catalytic reaction rate is affected appreciably not only by pH and temperarture, but also by coexisting chemicals such as dyes or surfactants in the treatment solution or on the substrate.

15.3 Treatment of Cotton with Enzymes

The cotton fibre has a single biological cell. The layers in the cell structures are from the outside of the fibre to the inside, cuticle, primary wall, secondary wall, and lumen. These layers are different structurally and chemically. The primary and secondary walls have different degrees of crystallinity as well as different molecular chain orientation. The cuticle, composed of wax, proteins and pectins, is 2.5% of the fibre weight and is amorphous. The primary wall is 2.5% of the fibre weight, has a crystallinity index of about 30%, and is composed of cellulose. The lumen is composed of protoplasmic residues. Additionally, sizes and soilings are added to cotton fibres. The total material added to the fibre is up to 20% of the fibre weight. Traditionally, the absorbancy of cotton is improved by alkaline scouring and whiteness is improved by oxidative bleaching. The intensive basic research currently being conducted opens up interesting possibilities for the use of enzymes for gentle removal of cotton's attendent material without the hitherto necessary use of alkalies and other dubious effluent content.

15.3.1 Enzymatic desizing of cotton and silk fabrics

Malt extract was used originally for the desizing of amylaceous sizes from the fabric. Later, around 1900, Diastafor was found more efficient for starch desizing. Rapidases were introduced in 1919 and cause the liquefaction of starch in compounds soluble in water. At present a variety of these products are available commercially. They are mainly based on amylopectic enzymes. These enzymes do not damage the cellulose. These enzymes are effective at various temperatures ranging from 20 to 115°C covering all means of applications [42]. Now-a-days special attention is paid towards the development of simultaneous desizing and scouring in an alkaline medium replacing two-stage process.

Degumming of silk to remove the sericin is an important step. Soda-ash and sulphides used in conventional degumming process not only reduces the fabric strength but also causes pollution problem. Enzymatic degumming on the other hand, offers a very safe and simple method of degumming. Apart from sericin the silk fabric also contain about 2% oil to facilitate weaving. Enzymes not only dissolve the gummy portion but also dissolve the oil at the same time. The method of application is either cold water soaking for 12 to 16 h or warm water (50-55°C) soaking for 3 to 4 h with appropriate enzyme solution. The application of serine protease (Bactosol SI) combined with hydrogen peroxide bleaching in the presence of detergent provides efficient desizing of sericin in 1 hour [43].

15.3.2 The use of enzymes in mercerization

The effect and action of enzymes seems to be very limited because of the stronger conditions of alkali of mercerizing strength. Enzymatic hydrolysis is accelerated when mercerization is carried out without tension [44]. The greater accessibility and lower crystallinity of cellulose mercerized without tension is a decisive factor in the enzymatic hydrolysis process. Mercerized cotton is generally more prone to enzymatic modification than untreated cotton.

15.3.3 Application of enzymes in scouring and bleaching of cotton

To achieve good absorbancy of cotton, dirt, sizes and natural impurities are usually removed by alkaline scouring. If these impurities are not removed, can lead to the formation of AOX in the effluent when NaOCl is used as a bleaching agent [45].

Enzymatic treatment of unscoured cotton fabric can be done with pectinase,

cellulase, protease, lipase and other enzymes [46]. Cellulases are especially suited to scouring of cotton fabrics [47]. The degree of whiteness of a cotton sample treated with cellulases only is lower by 8-10% than the degree of whiteness of alkaline boiled-off treatment. Pectinolytic enzymes can be used for enzymatic degradation of pectin adhering to cotton [48]. Cotton fibres or their blends with other fibres can be treated with aqueous solutions containing protopectinases for 18 h at 40°C to give scoured yarns with good tensile strength retention [49]. Pectinases and cellulases are very effective compared to the proteases and lipases [50]. The most significant results of various enzymes are listed in Table 15.2. The change in the water absorbancy of cotton is rapidly catalysed by pectinases, cellulases or their

TABLE 15.2
Summary of Results and Conditions of Enzymatic Treatments for Adequate Absorbency of Cotton [50].

Fibre/Fabric	C_1	C_2	C_3	P_1	P_2	P_3
Fibre						
Cotton weight, g	0.2	0.2	0.2	0.2	0.2	0.2
Enzyme units	–	40	30		4	4
Concentration, %	0.1	0.44	0.023	0.025	0.0067	0.0017
Treatment time	10 min	10 min	10 min	2 hr	10 min	10 min
Weight loss, %	3.900	2.266	3.044	2.571	1.642	1.898
Fabric						
Fabric weight, g	0.4-0.5	0.5	0.5	0.4-0.5	0.5	0.5
Enzyme units	–	<60	<45	–	<16	<16
Concentration, %	0.15-0.2	<0.66	<0.0345	0.1	<0.0268	<0.0068
Treatment time	20 min	20 min	20 min	3 hr	20 min	20 min

Note : C_1, C_2 and C_3 are cellulases, P_1, P_2 and P_3 are pectinases.

mixtures. Pectinases can destroy the cuticle structure by digesting the inner layer of pectins in the cuticle of cotton. Cellulases can destroy the cuticle structure by digesting the primary wall cellulose immediately under the cuticle of cotton. By combining the enzyme treatment (a simultaneous treatment of pectinase and cellulase), or the alkaline boiled-off, with an alkaline peroxide bleaching, the total degree of whiteness is higher in combination with enzyme treatment. Cellulases break the

linkage from the cellulose side and the pectinases break the linkage from the cuticle side. The result of the synergism is a more effective scouring in both the speed and the evenness of the treatment.

Natural pigments present in cotton are responsible for greyness of the substrate before bleaching. Motes are swollen in alkaline scouring and removed or rendered colourless in oxidative bleaching. In the Synbleach project [51] natural fibres are bleached with hydrogen peroxide followed by enzymes, photosensitisers and UV light. Methods of bleaching of paper pulp and deinking printing paper using enzymes have been reported [52]. A friction treatment is suggested before the enzymatic treatment to remove the pigment more easily and ensure that cellulase and hemi-cellulase are effective [53].

The cellulase, xylanase and pectinase enzymes have tremendous effect on processing of jute. The treatment of enzyme before bleaching of jute improve whiteness whereas due to backstaining at optimum pH, there is decrease in whiteness and increase in yellowness index, if treatment is carried out after bleaching. The enzyme action is more on 4% NaOH scroured fabric. Scouring causes higher hemicellulose loss producing open structure and thus larger surface area of lignin is accessible to hydrogen peroxide resulting in higher whiteness [54].

15.3.4 Bio-polishing

Surface modification of cellulosic fabrics to improve their cleaner surface conferring cooler feel, brighter luminosity of colours, softer feel and more resistance to pilling using cellulases is often known as bio-polishing [55, 56]. This treatment can be applied to knit and woven cellulosic fabrics such as cotton, viscose and linen and their blends [57-60]. The elimination of superficial microfibrils of the cotton fibre through the action of cellulase enzymes is obtained by the controlled hydrolysis of cellulose leaving the surface of the fibres free and conferring a more even look [61-63]. The effect of cellulase enzymes on fabric hairiness is shown in Fig. 15-5. The picture on the left shows an untreated woven 100% cotton fabric, while on the right the same fabric appears after enzyme treatment. These improvement in fabric softness and smoothness are permanent in contrast to the softeners applied to the fibre surface. Further the water regain is not decreased by the enzymatic treatment [64, 65].

A number of patents are obtained to obtain softening effect by enzymatic treat-

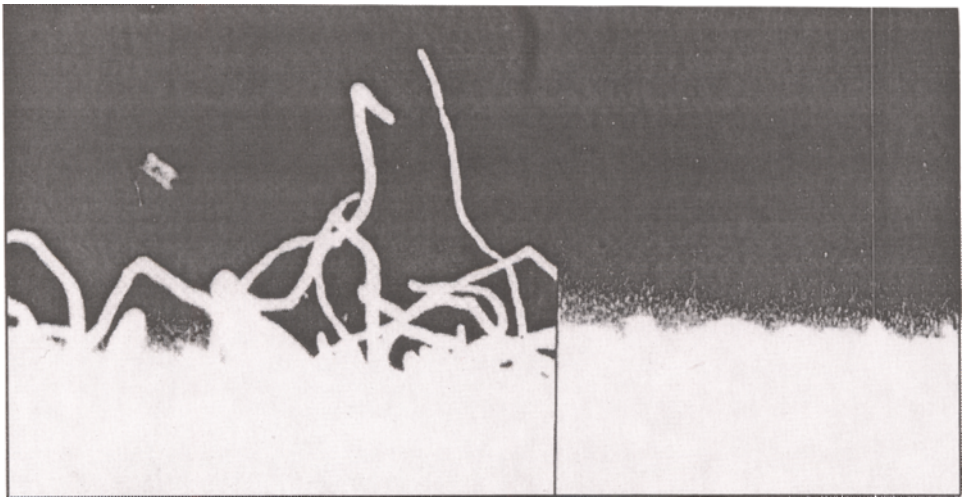


Figure 15-5. The effect of cellulase on fabric hairiness.

ment of cotton textiles [66-71]. Although bio-polishing may be carried out at any time during wet processing, it is most conveniently performed after bleaching. Fabrics may be treated in either piece or garment form and the treatment can be combined with another process or kept as a single operation. Batch processing, using washers, jets, becks and winches is extremely suitable as pH and temperature can be controlled easily.

Controlled finishing with cellulase enzymes optimises the surface properties of the fabric, but decrease in tensile strength [72]. Commercial processes aim for 3-6% weight loss after hydrolysis and a maximum of 10% loss in strength is considered acceptable [73, 70]. The strength/weight loss relations of remie and linen differ from those of cotton and viscose rayon [39]. The mechanical properties before and after enzymatic hydrolysis of different fibres are compared in Table 15.3. For all the fibres after 6 hours' treatment there is significant reductions in tensile energy (WT) and tensile linearity (LT), while tensile resilience (RT) is increased, indicating that the fabrics become less stiff, easier to stretch and looser in structure. However, after 48 hours' treatment, shear hysteresis (2 HG) values are markedly lower than those of controlls, indicating yarns have become more mobile in the fabrics.

Anionic dyes such as direct and reactive dyes and cationic and anionic surfactants inhibit cellulase catalytic reaction appreciably resulting in decreased weight loss, whereas non-ionic dyes such as vat dyes and non-ionic surfactants do not

TABLE 15.3
Comparison of Mechanical Properties of Cotton After Enzyme Treatment [39].

	Enzyme treatment for			
Fabric	0 hours	6 hours	24 hours	48 hours
Cotton				
WT, cm^2	4.86	3.47	3.11	2.13
LT	0.87	0.77	0.83	0.78
RT, %	41.85	48.61	46.29	49.09
2HG, g/cm	7.04	7.29	5.12	3.36
Linen				
WT, cm^2	5.65	3.00	3.93	4.07
LT	0.72	0.66	0.71	0.69
RT, %	42.14	48.93	42.00	44.05
2HG, g/cm	0.83	1.02	0.56	0.29
Remie				
WT, cm^2	5.45	2.45	2.40	2.30
LT	0.85	0.63	0.69	0.73
RT, %	52.70	65.69	67.87	68.76
2HG, g/cm	4.59	4.16	3.84	3.36
Cotton/linen (warp)				
WT, cm^2	1.61	1.02	1.25	0.84
LT	0.81	0.69	0.72	0.75
RT, %	44.87	50.27	57.82	46.73
2HG, g/cm	1.08	0.94	1.14	0.97
Cotton/linen (filling)				
WT, cm^2	2.22	1.96	1.84	1.51
LT	0.85	0.84	0.86	0.81
RT, %	56.39	51.24	58.72	57.98
2HG, g/cm	1.08	0.94	1.14	0.97

show remarkable inhibition [74-76]. The planner structure of vat dyes with larger molecular sizes than indigo dye play an important role in their inhibitory effect [77]. DMDHEU treated fabric shows a slower progress of enzymatic cleavage on

cross-linked cellulose. The degree of inhibition depends on class of dye and dye concentration. The inhibitory effect may be due to the ionic interaction between cellulase and anionic dyes with sulphonate groups, the cross-linking ability of bi-functional dyes or the large planner structure of vat dyes.

15.3.5 Effect of cellulase treatment in washing processes

There are three methods to remove surface fibres from 100% cotton woven and knit goods, namely singeing in the greige state and bio-polishing. The third method is home laundering the fabrics using detergent that contains a cellulase enzyme.

Laundering of knit fabrics with detergent containing cellulase enzymes help to maintain a clean surface appearance and the appearance of the fabric look better even after multiple launderings [78]. Today's detergents contain a sophisticated cocktail of enzymes designed to breakdown stains and assist the cleaning process at low wash temperature. Proteases, lipases and amylases are generally used to increase the efficacy of removal of stains. Cellulases assist in the removal of particulate soils by removing microfibril from the cotton fibres, which initially form the pills and which scatter incident light [79, 80]. Generally the detergents for this purpose rely on a mixture of enzymes, strong sequestrants and soil-release polymers to provide satisfactory stain removal and soft finish.

The short fibre ends emerging from the fabric surface is enzymatically hydrolysed, but an additional mechanical treatment is necessary to complete the process, to remove the fibres normally leading to pilling for example, rotating drum washers and jets [81, 82, 10, 12]. Increasing the degree of mechanical agitation increases the extent of the hydrolysis [83]. Prior mechanical agitation makes cellulosic chains more accessible for cellulase hydrolysis [84]. The cellulase treatment and the further washing process show similar effects to that of one step process, but with smaller changes, which confirms the role of simultaneous mechanical agitation in cellulase textile process [85]. The cellobiohydrolase rich enzyme mixtures produce more soluble reducing sugars, which can also reduce the indigo dye and increase backstaining. In the two-step process of washing, the total loss of colour is about 20%, while the one step washing process yields a loss of colour of about 40%, under the same conditions [10].

15.3.6 Stone washing

Stone and denim washed garments, generally cotton, show a characteristics well-

worn look and are very popular with young people. In the stone washing process, the finished garments, whose fabric had been dyed with sulphur, or reactive dyes or indigo are subject to the eroding action of pumice stone in a washing machine in the presence of an oxidiser, usually potassium permanganate. The treatment results in uneven decolourisation, without excessive loss of fabric strength. The blue denim is faded by the abrasion action of pumice stones.

Cationisation of the cotton surface by a treatment with 1, 1-dimethyl-3-hydroxy-azetidinium chloride (DMA-AC) followed by dyeing with reactive dyes can develop the appearance of a denim type effect on specially constructed fabric [86].

In the same way, wash-out and stone-wash effects can be produced on dyed jeans by subjecting piece goods to a bio-finish process with suitable cellulase complexes without pumice stone and bleaching agents [72, 87]. Complete or partial replacement of pumice stones by cellulase enzymes for the effect of stone-washing on denim is well established and hundreds of looks can be generated from any piece of standard denim fabric [87-90]. The enzymes or combination of enzymes eliminate partially projecting dyed fibres, exposing the undyed material underneath. This forms the uneven, colour-flecked surface of wash-out article, but with no material surface damage and with an elegent fabric appearance. The surface frictions play an important role in the enzymatic decolourisation of cellulosic fabrics [84]. The mechanical action opens the outermost layers of the cellulosic crystal, thus increasing the part of the cellulose accessible to enzymes, and allowing the enzymatic removal of the dye.

The use of acid cellulases are recommended for fast treatments and neutral cellulases for more severe treatments when marked effects are required [56, 91]. Endo-enriched acid cellulase is found to be best for easily weekened fabrics such as linen and viscose rayon. Standard whole acid cellulases are best for sturdy fabrics such as lyocell, modal rayon and heavy weight cotton [92].

15.4 Treatment of Protein Fibres with Enzyme

Enzymatic pre-treatments to protein fibres are generally concentrated on wool and silk. It is possible to remove skin residues, skin grease and vegetable matter of wool by enzymatic degradation method. Furthermore, the wool surface can be modified, and felt free finishing with simultaneous improvement of lustre and handle of woollen fabric is possible by enzyme treatment.

The two major morphological parts in the structure of wool are cuticle and cortex. The epi-cuticle of wool fibres surrounds each cuticle, it consists of approximately one-quarter fatty acid and three-quarters protein by mass. The hydrophobic epicuticle acts as a barrier to dyes which enter the wool fibre between cuticle cells through the highly cross-linked cell membrane complex (CMC). Enzyme from the liquor can diffuse into the interior of the fibre and hydrolyse parts of the endocuticle and proteins in the cell membrane complex, completely damaging the fibre if not controlled. In contrast, the catalytic action of enzyme on cotton is confined to the surface and the amorphous region only.

Enzymes such as proteases, lipases, lipoprotein lipases and proteolytic enzyme derived from the bacterium Streptomyces fradie (known as SFP) is capable of attacking natural keratin hydrolysing some peptide linkages. However, proteases are most widely used.

15.4.1 Wool carbonising

Vegetable matters of wool are normally removed by a process known as carbonising. Carbonisation of wool with inorganic acid may cause some degradation of the fibre. The replacement of carbonisation by the use of enzymes, such as cellulases, ligninases, hydrolases, lyases and oxidoreductases are reported [93]. A biochemical alternative using complex combination of enzymes to the chemical process of carbonising with sulphuric acid is also reported [94]. The amount of sulphuric acid required for carbonisation can be reduced by the action of cellulolytic and pectinolytic enzymes [95].

Natural soilings on wool such as vegetable matter and skin flakes can also be enzymatically modified [96]. Burr removal becomes easier after lubricating wool with cellulases due to weakening of the cohesion between burr and wool [97]. Lignin of the burrs in wool can be degraded by the use of lignin peroxidases [98].

15.4.2 Wool bleaching

Bleaching of wool is necessary for the enhancement of whiteness and lustre. Using proteolytic enzymes alone [99] or in combination with peroxide [100], the degree of whiteness and hydrophilicity of the fibres are increased, compared with the oxidative treatment alone [99]. Serine protease stable to hydrogen peroxide is active in an alkaline medium and its activity increases with increasing peroxide level [94]. Higher whiteness index is caused by the decolourising action of the enzyme on natural colorants present in the wool fibre [100].

15.4.3 Shrinkproofing and hand modification of wool

Wool fibres have a tendency to felt and shrink due to its scaly structure. The differential frictional effect (DFE) causes the fibre to move towards their root end when mechanical action is applied in the wet state. Generally shrinking of wool is done either by oxidative or reductive methods and/or by application of resin. The most frequently used commercial process consists of chlorination, followed by dechlorination and polymer application. Among the various processes, nickel-catalysed surface degradation by hypochlorite [101-103] and the use of 'second generation' chlorination equipment [104] are commercialised. Though such descaling is expected to improve the handle of the wool fibres by making them smoother, the handle is actually made harsher, perhaps because the fibres become sized by degraded protein. However, the softness of the fabric can be improved as a final application of a silicone microemulsion [105], but expensive equipment are needed.

It is possible to limit chlorination and other oxidations to the cuticle layer to remove the fibre from the surface of the fabric without damaging the fibre and thus increases its softness too. Consequently, in addition to the antifelting effect achieved by the pretreatment and processing of wool fibres, a soft handle is also obtained. Of all the enzyme processes available for wool, only a few are 'pure' enzymatic processes. The majority of enzymatic processes published are combined processes. In most of the treatments for improving the handle of wool, reduction of the fibre diamerter is done by complete descaling which produce a non-tolerable weight loss of the fibres. Descaling is generally performed by pretreating the fibres with potassium permanganate as a preoxidising agent [106] or by gas chlorination (the Chlorzym process [107]) or by hydrogen peroxide (the Perzym process [108]) and subsequent treatment with a proteolytic enzyme [109]. Thus it is possible to remove the scales by using much less than 5% chlorine if the process is followed by an enzyme.

Protease, trypsin or papain are commonly used as enzymes for wool fibres. Protease is quite unreactive unless acted upon by a mild reducing agent, i.e. bisulphite or cysteine, so as to split disulphide to sulphydryl groups [110-113]. Other enzymes have been proposed [114, 115], including bacterial alkaline proteases of the type used in washing powders. In some processes proteases are used to cut-off damaged fibres [116] or to achieve certain texturising effects [117, 118].

Descaling is also achieved by the applicaiton of heat-resistant neutral protease, resulting in cashmere-like feel [119]. The combined use of the chlorinating agent, dichloroisocyanurate and proteolytic enzyme can improve handle properties [120, 121].

Physical, as well as chemical, pretreatment processes have been combined with the enzyme treatment of wool. A low-temperature plasma is applied to the fibres prior to treatment with polymeric shrinkproofing agent [122]. Combined protease and heat treatment with a saturated steam [123] and the use of high frequency radiation on enzyme treated materials are reported.

15.5 Bio-technology and Effluent Treatment

Environment friendly pre-treatment processes of textiles are the need of the day due to tremendous awareness of chemical pollution and mounting legislation to limit the chemical burden of the factory effluent. Biotechnology can be used for the treatment of wastes which can solve the problem either partially or totally. The applicaiton of biotechnology is mainly attributed to the removal of colour from the dyehouse effluents. Living organisms is used to bind and degrade colour (e.g. artificial reed beds) or dead organisms (e.g. straw, chitin/chitosan, microfungal hyphae etc.). Selected microbes or isolated enzyme may be used to assist specific areas. The discharge of dyestuffs into the environment is not solely an aesthetic matter and many dyestuffs are identified to be mutagenic [123]. Biosorption has the potential to remove metal ions such as chromium [124], which are used in the manufacture and application of mordant dyes. The enzymatic bleaching of released dye reduces process time and the amount of energy and water needed to achieve a satisfactory textile quality [125]. However, the type and the concentration of dyes as well as the amount and type of substrate used are found to play a major role in dye adsorption [126, 127]. Chitosan is found to be most efficient in absorbing dyes of small molecular size [128].

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Chapter 16

ANALYSIS AND TESTING IN PREPARATORY PROCESSES

16.1 Introduction

The objective of chemical pre-treatment of textiles is to obtain uniform effects as regards to size removal, absorbancy, whiteness, absence of husks, dye affinity ; high dependency of results ; minimum fibre damage and favourable cost performance relationship. The factors which affect the pre-treatment are goods (printed or dyed), machinery, dispensing system, dependability of results, end use, customer requirements, economical and ecological aspects etc. The potential defects during pre-treatment processes are inadequate or uneven desizing, incomplete removal of greases and wax, poor or uneven absorbancy, unlevel mercerization, inadequate or unstable ground white, poor mechanical strength, low DP value, catalytic damage and creases etc. In the case of synthetics that are heavily oiled prior to or during knitting, dye spots and speckiness later attribute to poor dyeing practices. Improper size removal is the major cause of unlevelness encountered in thermosol or range-dyed goods.

It is thus necessary to optimise the effects of various pre-treatment chemicals, focusing on fabric physical properties such as tensile strength, weight loss, fuzzing, hand, copper number, moisture regain and colour change (in the case of dyed fabrics).

This chapter is devoted to evaluate the usefulness of measurement of different physical and chemical properties of textile fibres before and after chemcial pretreatment to provide a direct assessment of effects of different chemicals. Such information about a property that is immediately and directly affected by chemical reaction will help to optimise the process conditions, whereby the desired effects can be achieved while minimising the undesired effects such as excessive strength loss etc.

16.2 Analysis of Water

To calculate the hardness of a particular water the concentration of actual magnesium or calcium salt is converted to an equivalent weight of calcium carbonate. Hardness is generally expressed as equivalent parts per million (p.p.m.) of calcium carbonate irrespective of the actual salt present. By defination, 1° English hardness

is 10 mg of $CaCO_3$ in 0.71 and 17 mg per 0.71 = $\frac{17}{10}$ = 1.7° English hardness. Similarly 1° US hardness is 1 mg/l of $CaCO_3$ and so 24 mg/l = $\frac{24}{1}$ = 24° US hardness.

16.2.1 Suspended matter

2 litres of water are filtered through previously weighed filter paper. The residue is dried and weighed (x g). The results are expressed as

$$\text{p.p.m.} = \frac{x \times 10^6}{10^3}$$

16.2.2 Total soluble salts

First of all the dirt and suspended materials are removed from the sample water as described above. 250 ml of this water is put on dried platinum dish and heated on iron plate. The dish is then transferred on a hot water bath when some quantity of water remains in the dish. Finally, the content is dried to constant weight in the oven, cooled in a desciccator and wighed (x g). The results are expressed as

$$\text{p.p.m.} = \frac{x \times 10^6 \times 4}{10^3 \times 1}$$

16.2.3 Total hardness

The total hardness of water can be determined either by using standard soap solution or by using EDTA reagent.

In the first method, 100 ml of water is placed in a 200 ml stoppered flask. 1 ml of standard Wanklyn's soap solution is added at a time until a lather is obtained on shaking which persists for one minute. If the titre on 100 ml of water is T ml, since 1.0 ml of standard soap solution ≡ 1.0 g $CaCO_3$.

$\therefore$ 100 parts of water contain 0.001 T parts of $CaCO_3$

and 1,000,000 parts of water contain 10T parts of $CaCO_3$.

$\therefore$ Total hardness = 10 T p.p.m. as $CaCO_3$.

In the second method, 100 ml of sample water is pipetted into a 250 ml conical flask. 2.0 ml of ''balanced'' buffer [50 ml HCl (Sp. gr. = 1.18) is added to 400 ml distilled water. 310 ml ethanolamine is slowly added with constant stirring, followed by 5.0 g of magnesium disodium EDTA. The content is diluted to 1 litre] is added, mixed and then added one or two drops of indicator solution [5.0 g

Solochrome Black WDFA (C. I. Mordant Black 11) is dissolved in a mixture of 75 ml triethanol amine and 25 ml alcohol]. The content is titrated with EDTA solution (0.02 N) until last reddish tinge disappears. Let the titre obtained be T ml. Since 1.0 ml of 0.02 N EDTA solution $\equiv$ 1.0 mg $CaCO_3$,

$\therefore$ Total hardness = 10T p.p.m. as $CaCO_3$.

16.2.4 Calcium hardness

100 ml of the water sample is pipetted into a flask and 1 ml of 4N-sodium hydroxide and one tablet of calcium hardness indicator (BDH) is added. The content is titrated with 0.02 N-EDTA solution until the solution becomes violet (0.1 ml causes no further colour change).

$\therefore$ Calcium hardness = 10T p.p.m. as $CaCO_3$.

16.2.5 Magnesium hardness

This is obtained by difference as follows :

Magnesium hardness = Total hardness – Calcium hardness

(all values expressed as p.p.m. $CaCO_3$)

Magnesium hardness (p.p.m. $MgCO_3$) = 0.84 × magnesium hardness (p.p.m. $CaCO_3$).

16.2.6 Temporary and permanent hardness

100 ml of water is titrated with 0.02 N-EDTA solution as described above.

Another 100 ml of water is boiled gently for 10 min in a 250 ml flask. This will decompose bicarbonates. The content is cooled, filtered and the filtrate is diluted with distilled water to make up the volume to 100 ml and then titrated with 0.02 N – EDTA solution to obtain permanent hardness.

Temporary hardness = Total hardness – Permanent hardness

(all values expressed as p.p.m. $CaCO_3$).

16.3 Analysis of Non-Cellulosic Residues

Such analysis is useful as a diagnostic aid in finding the cause of poor preparation or may be required for specific end uses, e.g. surgical cottons.

16.3.1 Ash content (mineral matter)

The ashing of a yarn or fabric can be used to determine inorganic residues like silicate, phosphate, calcium, copper and iron contents on the fabric.

Approximately 5 g of dried samples are placed in a weighed crucible. The material is slowly ignited over a Bunsen flame and then the crucible is placed in a

muffle furnace maintained at a temperature of 750°C for 1 h or until constant weight is obtained.

$$\text{Ash content (\%)} = \frac{100 \times b}{a}$$

where a = dry weight of the sample,

and b = weight of ash.

Typical values for grey cotton are 0.5-1.0%, which drops to 0.2-0.5% after scouring and bleaching.

16.3.2 Silicate and phosphate

Approximately 5 g sample is ashed as above and cooled. The content is then mixed with 5-6 times the amount of sodium-potassium carbonate (made by mixing equal weights) and then heated until a clear melt is obtained. On cooling, the solidified melt is then dissolved in distilled water and granular ammonium molybdate is added to it. Then the content is acidified with nitric acid (20%). In the presence of silicate an intense yellow colour or a yellow, crystalline precipitate is produced.

For testing phosphate contents in the sample, the ash is dissolved in 10 ml nitric acid (20%), filtered and the residue is mixed with 5-6 times the amount of sodium-potassium carbonate and then continue as above.

16.3.3 Calcium and magnesium

5 g sample is ashed and the ash is mixed with hydrochloric acid (10%) and ammonium chloride. Ammonia (Sp. gr. 0.88) is added until the solution is alkaline. The ammonical filtrate is acidified with acetic acid and calcium is precipitated with oxalic acid as calcium oxalate. The presence of calcium is indicated by a characteristic red flame colour placed in a bunsen flame.

For quantitative analysis of calcium, the filtered calcium oxalate is washed with little distilled water and then taken up in warm sulphuric acid (20%) and titrated against 0.1N $KMnO_4$ solution.

The concentration of calcium and magnesium, expressed as a percentage on weight of raw cotton is usually in the following ranges :

Calcium 0.43 – 0.15%

Magnesium 0.046 – 0.11%

Calcium and magnesium may be taken up by the fibre during growth or from the liquor during wet processing, where they are present as hardness formers.

16.3.4 Iron and copper

The presence of compounds of iron and copper can cause fibre damage during bleaching, by so-called ''catalytic tendering''. It is important to know if such contaminants are present and remove them prior to bleaching.

0.5 – 1.0 g fibre is spotted with 1-2 drops of nitric acid (5%) and allowed to stand for 2-3 min so that any iron present is oxidised to ferric ions. Then 2-4 drops of potassium thiocyanate solution (10%) are added and a red colour indicates ferric ions. The intensity of colour indicates the amount. The test can be carried out on an ashed sample.

In another method, the fibre is spotted with hydrochloric acid (10%) and the acidified area is spotted with 1% potassium ferrocyanide. A dark blue colour indicates the presence of iron.

For testing of copper, the ash is spotted with 5-10 drops of nitric acid (10%) and then dilute ammonia (1:1) is added until the ash is alkaline. A blue colour shows the presence of copper. For fabric, the sample is first spotted with dilute nitric acid and then after neutralisation with ammonia, 1-2 drops of diethyldithiocarbamate solution (0.1%) are spotted on to the same area. A yellow colour shows the presence of copper.

Metal contents may also be determined on the ash by emission spectroscopy or atomic absorption spectroscopy.

16.4 Evaluation of Wax Content on Cotton

Soxhlet extraction is the usual procedure for seperation of the wax from the cotton, with percentage composition being obtained by gravimetric means after the evaporation of solvent. Different values are sometimes encountered for the same source of cotton when different solvents are used. Solvents commonly used are ethanol, ether, benzene, benzene-methylene chloride, chloroform, carbon tetrachloride and acetone. The results of the cotton wax extracted by the above process are reported in Table 16.1. Modern analytical techniques such as gas chromatography, mass spectrometry and X-ray defraction can be used for detection of the individual wax components. It is confirmed that a waxy substance is present within the crystalline cellulose chain. Cuxam is used to dissolve the cotton fibre, the wax portion is separated through the use of organic solvents, and greige cotton is found to contain approximately 2% wax. By continuing the extraction process, an additional

TABLE 16.1
Composition of Cotton Wax [1]

Wax	Percentage
Wax ester	22
Phytosterols	12-14
Polyterpenes	1-4
Hydrocarbons	7-8
Free-wax alcohols	42-46

1% wax is detected, even though normal extraction processes had suggested that this batch of cotton contained only 0.6 - 0.7% wax.

16.5 Evaluation of Lubricants

Sizing materials for both filament and spun yarn usually contain additional film modifiers to produce a product with improved sizing qualities. One such compound is lubricants. Lubricants can be divided into two basic groupings, saponifiable and unsaponifiable. The saponifiables are easily removed and can, in fact act as emulsifiers for the unsaponifiables [2]. The unsaponifiables, such as paraffin waxes, are considered to be the best friction reducers. Tallow, bleached tallow, hydrogenated tallow glycerides, and fatty esters are used as fats and fatty components. Crude-scale paraffin wax, slack paraffin wax, refined paraffin wax and some polyethylenes are used as unsaponifiable materials. In general practice, there are three general categories of lubricants, or kettle waxes : water soluble, water dispersible, and size dispersible. Wax concentrations on cotton yarn increase weave efficiency when used at a concentration of up to 5%. Above 10-15%, no increase in efficiency is achieved and desize problem can occur.

16.5.1 Total fatty matter

8-10 g of sample is weighed in a dry conical flask and about 50 ml of 2N sulphuric acid is added. The contents are refluxed for 2 h using a water condenser. After cooling the fatty matter is extracted with 50 ml of ether twice in a seperating funnel. The combined ether extracts are washed with water till free from acid. The ether extract is transferred to a weighing beaker, the ether evaporated using a water bath and the residue dried in an oven at 110°C and weighed after cooling.

$$\text{Total fatty matter (\%)} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

16.5.2 Saponification value of an oil

0.5 g of the sample is weighed into a conical flask and 50 ml of 0.5N alcoholic potassium hydroxide solution is added to it. The contents are boiled under reflux for 2 h. After cooling the excess alkali is back-titrated against 0.5N HCl using Methyl Orange as an indicator. A blank is also run (without tallow sample).

1.0 ml of 0.5 N HCl solution = 28.05 mg KOH

x ml of 0.5 N HCl solution = 28.05 x mg KOH

W g of sample requires 28.05 x mg KOH

$$\therefore \quad \text{Saponification value} = \frac{28.05\ x}{W}$$

where, x = (blank reading – sample reading)

16.5.3 Unsaponified matter

The solution preserved after the determination of saponification value is extracted with petroleum ether, evaporated and dried in an oven. After cooling the residue is weighed.

$$\text{Unsaponified matter (\%)} = \frac{\text{weight of residue}}{\text{weight of sample}} \times 100$$

16.6 Determination of Moisture Content [3]

The amount of moisture in a textile material can be determined directly or indirectly and may be expressed either as ''moisture content'' or as ''moisture regain''. In the direct method the amount of moisture in a definite weight of material is driven out, usually by heating in an oven at 105 - 110°C (for cotton) for a period of 4 h, at the end of which the sample is cooled in a desciccator and the loss in weight is determined. In the indirect method, a property of the material, usually its electrical conductivity or resistance, which is dependent on the moisture content of the material, is made use of. The moisture content, is defined as the moisture present in the sample and is expressed as percentage of the original weight of the sample in the condition in which it is received for test, whereas moisture regain is expressed as a percentage of the oven-dry weight of the sample. The two quantities can be expressed as follows :

$$\text{Moisture content (M.C.)} = \frac{a-b}{a} \times 100$$

$$\text{Moisture regain (M.R.)} = \frac{a-b}{b} \times 100$$

where 'a' and 'b' represent original weight and the oven-dry weight of the sample.

16.7 Tests and Analyses of Sizes

The warp size, once applied to the yarn and dried, increases the tensile strength and abrasion resistance of the yarn. This minimises down time or ''breakouts''. The sizing formulations may consist of natural and synthetic polymers, gums, starches, metal-to-fibre lubricants, preservatives, and defoamers. The solution, after impregnation into the warp yarns at a level of 10-15% (o.w.f.) for cotton [4] and cotton blends, and at a level of 3-5% on filament synthetics, is dried in continuous form over drying cylinders and then wound onto large goods called beams. The compounds commonly used for filament sizing and spun yarn sizing are shown in Table 16.2 and 16.3 respectively. In desizing operation the size is removed and the effectiveness of the removal of size can be tested depending on the kind of size used.

TABLE 16.2
Filament Sizing Materials

Fibre	Basic size
Nylon	Polyacrylic acid
	Polyvinyl alcohol
Polyester	Acrylic copolymers
	Alkali soluble polyvinyl acetate
	Linear polyester
	Stymer (styrene – maleic anhydride coplymer)
	Gelatin
Viscose rayon	Polyvinyl alcohol
	Amylose derivatives
	Carboxymethylcellulose
	Blends
Glass	Polyvinyl alcohol
	Dextrins
	Amylose derivatives
	Blends

TABLE 16.3
Spun Yarn Sizing Materials

Fibre (100 % or blends)	Basic size
Cotton	Starches : corn, potato, tapioca
Rayon	Unmodified – pearl
Nylon	Acid modified, 20-60 fluidity
Polyester	Oxidised, several fluidities
Acetate	Dextrinized – British gum
Acrylic	Derivatized
Wool	Acetate, Hydroxyethyl ether, Acrylate, Styrene, Cross-linked, Cationic, High amylose, Polyvinyl alcohol, CMC, Blends and other polymers

16.7.1 Identification of sizes

Starches are hydrolysed by acids, alkalies or by enzymes during desizing process. Acid hydrolysis of starches yield mixtures of saccharides or glucose. Enzymatic (β-amylase) hydrolysis of starches yield maltose and amyloglucosidase yields D-glucose. All these products give different coloured residues on treatment with iodine. Because of the hydroxyl content of the cellulose, reaction can occur with many different compounds. The identification of different sizes with the help of different reagents are summerised in Table 16.4. Starch apparently contains two fractions, a soluble amylose (10-20%) and an insoluble residue, amylopectin (80-90%), account for the violet colour and blue colour that are yielded on treatment with iodine. Amylose gives the blue colour and amylopectin gives the violet to red-violet colour. In enzyme hydrolysis of starch, amylose is completely hydrolysed to amylase [4], whereas only 60% of amylopectin can be hydrolysed. Table 16.5 shows the assessment of pre-treatment effects on desizing starch size from cotton fabrics. Poor removal of size during desizing may effect in warp stripeness, stains during dyeing and printing, uneven mercerization and uneven absorbancy.

Normally extraction techniques are useful for assessing the rinsing effectiveness and size residue. Sequential extraction technique with solvent and enzyme [5] or water, enzyme and solvent [6] or solvent, water and enzyme [7] is used.

TABLE 16.4
Identification of Sizes

Sizes	Reagents	Procedure	Reaction	Notes
Starch	iodine/potassium iodide solution.	1. apply solution dropwise, 2. rub in gently, 3. assess colour reaction.	colourless = no starch size present, blue violet = starch present, brown = modified starch or mixture with PVA present.	cool material and test ; neutralise alkaline goods with acetic acid.
Polyvinyl alcohol (PVA)	iodine/potassium iodide solution, boric acid soln.	1. apply iodine/potassium iodide solution dropwise 2. apply boric acid solution dropwise to the same spot as the I_2 / KI soln.	colourless = no PVA present, blue = PVA present.	colour intensity depends on amount of size.
Polyvinyl acetate	iodine/KI solution.	1. spot with I_2 / KI solution.	deep reddish brown = polyvinyl acetate present.	colour intensity increases on hot washing.
Starch + PVA	I_2 / KI solution, borax.	1. Treated with warm (70°C) water, 2. aqueous extract is tested with I_2/borax.	blue solution or precipitate = PVA.	colour intensity depends on PVA.
CMC + Acrylate	copper-II-sulphate solution.	1. cut up the sample, 2. add water at ratio 40:1, 3. boil up for 10 min, 4. filter off liquor and cool, 5. add 5 drops solution to the liquor, 6. assess reaction.	clear liquor = no CMC or Acrylate present, white turbidity/ precipitation = CMC or Acrylate present.	distinguish between CMC and Acrylate by adding 2-3 drops acetic acid 80% to the liquor, Reaction : ppt. dissolves = CMC, ppt. undissolved = Acrylate.

TABLE 16.5
Assessment of Starch Size on Desizing

	Extraction content (water extract)	TEGEWA violet scale
Grey-state fabric	6-10%	1
Pre-treatment, good	0.1-0.4%	6-9
Pre-treatment, poor	more than 0.5%	2-5

16.7.2 Percentage size by ordinary method

The weighed cloth is first washed in water and then boiled in caustic soda solution (2%) for about 30 to 40 min. The sample is washed again in water and boiled for 60 min in a solution of hydrochloric acid (1%), adding water as it evaporates. The sample is washed, dried slowly and weighed. The difference in weight indicates the loss of sizing material. In normal practice allowance of 1 to 2% for weight loss by removing natural impurities is allowed during the boiling.

16.7.3 Estimation of total size by Soxhlet method

5 g of accurately weighed sample is extracted with chloroform in a Soxhlet extractor for about 1 h at a minimum rate of 100 drops per min. The sample is then dried in air and washed in hot water several times and then rinsed by hand 12 times. The material is then treated in 0.5% diastase solution (20 to 30 times the weight of cotton) at 70°C for 1h and then washed in hot running water, dried at 110°C and weighed. Side by side a sample is also tested for moisture determination.

$$\text{Apparent size (\%)} = \frac{100 - (a - 1.03b)}{a} - k$$

where, a = dry weight of sample,
b = weight of desized sample, and
k = desizing blank.

In the absence of unsized control, k may be taken as 3% of the desized and dried sample. No correction is required for bleached and dyed cloth. For total size content the ash content (%) of the desized sample is to be added.

16.7.4 Total size by enzyme method

The material is desized by using 5 g/l diastase and 10 g/l NaCl at 70°C (pH 6.5 to 8.5) for 1 h, liquor ratio 40 : 1. The sample is washed thoroughly in hot and cold

water and dried. Either the loss in weight is determined or the carbohydrates in the extract is estimated by oxidation with potassium dichromate under acid conditions.

16.8 Determination of the Efficiency of Scouring

Immediately following the desizing, the yarns and fabrics are washed with detergents and alkalies by a process known as scouring. The efficiency of scouring are assessed by the removal of various types of impurities from the cotton material, e.g. loss in weight, changes in protein content (determined by nitrogen analysis), residual wax content, absorbance etc. Apart from these the decrease in Methylene Blue absorption is indicative of the removal of pectic substance and that of copper number of the removal of hemicelluloses and sugars.

16.8.1 Measurement of weight loss

5 g of dried sample is treated with 200 ml of 1% NaOH for 1h at 80°C, after which the sample is well rinsed and run out in hot water. It is then treated in 200 ml of 0.5% HCl at 80°C for 1h, after which the sample is once again rinsed, boiled for $^1/_2$ h in distilled water, dried and weighed. Weight loss on scouring is normally 6-9%.

16.8.2 Measurement of residual wax content [8]

A known weight of oven dried sample is placed in the Soxhlet extractor and refluxed for 3 h in chloroform (solvent) for cellulose and petroleum ether for polyester blends. The solvent is distilled-off and the flask containing the sample is reweighed. The difference in weight will give the fat and wax contents. For well bleached cotton, the fats and waxes should be below 0.2%. Knit goods should have an acceptable value higher than 2% as processing is designed to aid sewability.

16.8.3 Practical test of absorbancy

Fig. 16-1 shows the technique for evaluating wetting speed by the standard Draves wetting test [9]. Wetting and scouring are normally associated as being

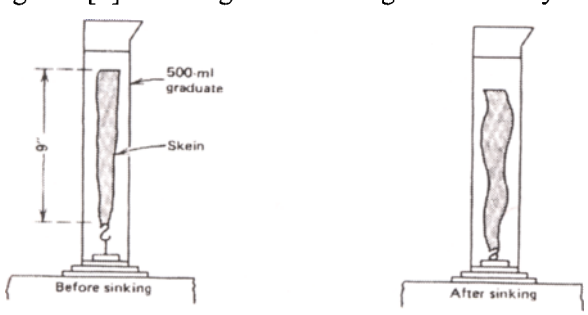


Figure 16-1. Apparatus for running Draves wetting test (Courtesy of Union Carbide).

synonymous, however, this unfortunately is not true. Experimental data indicate that the best wetting agents are usually non-ionics with low ethylene oxide content, whereas the best scouring compounds generally have a long chain hydrophile and hydrophobe.

However, the absorbancy of fabrics can be estimated by a test in which a drop of distilled water is allowed to remain in contact with the scoured cloth for 30 sec. If the drop is absorbed in this time, the material is judged to be absorbant and suitable for bleaching and dyeing. In the case of printing cloth, the time of absorption of the drop of water must be lower than 1 sec. The assessment of pre-treatment effects by absorbancy test is given in Table 16.6. Poorly pre-treated goods will have increased amount of dye on the fibre surface as a result of inadequate

TABLE 16.6
Assessment of Pre-treatment by Absorbancy Test

	Spot	Wicking test		Wicking rate		
	test	5 min	10 min	1 cm	2 cm	3 cm
Pre-treatment Good	1-5"	30-50 mm	50-90 mm	3-5"	10-30"	40-70"
Pre-treatment Poor	more than 10"	< 30 mm	< 50 mm	> 10"	> 30"	> 100"

penetration, poor fastness properties and unlevel dyeing.

16.8.4 Removal of motes (kitties)

This is done visually by observing the kitties present on the prepared samples, and the ratings on an arbitrary scale of 1-5 are given. A rating of 5 may be given to the sample with no kitties present on the fabric.

16.9 Testing and Evaluation of Bleaching Agents

Although it is generally accepted that an improvement in whiteness is one of the basic requirements in bleaching it is by no means the sole objective. Now-a-days with the increased production of polyester/cotton blended fabrics, polyvinyl alcohol, CMC and starch or their blends are used as sizing agents. During enzymatic desizing starch sizes are being solubilised, but the PVA and other polymers will be ineffective. Therefore, one of the major purposes of bleaching is the removal of these polymers apart from the degradation of the naturally occurring pigments in

the fibre. Also extremely high whiteness is not worthwhile if it is obtained at the expense of degrading the material being bleached. It is impossible to give strict guidelines for the optimum bleach bath because of the nature and quality of the goods to be bleached, the amount of bleaching required and the availability of equipment in which bleaching is to take place. The evaluation of effective bleaching can be done by measuring the absorbancy, fluidity, whiteness and analysis of impurities which should be 2-3% or less with an ash content of 0.20-0.25%. However exact control on the concentration of bleaching agents is most important along with the treatment time, temperature, pH and stabilisation of the bleach bath. The processed fabric should be absorbant, clean, white, uniform bottom for dyeing and printing.

In the textile industry, it is quite common to check the strengths of solutions by means of normality, molarity, specific gravity, density, percentage and g/l of available chlorine. Bleach liquors, mercerizing liquids and resin solutions are checked with hydrometer for determining specific gravity and strength is expressed in terms of degrees Twaddell (°Tw). Sometime Baume (°Be') is also used to express the strength in solution. The relations among the three common methods for expressing the density of solutions can be simplified by arithmetical expression for quick routine checking.

$$\text{specific gravity} = \frac{145}{145 - {}^{\circ}\text{Be'}}$$

$${}^{\circ}\text{Be'} = 145 - \frac{145}{\text{specific gravity}}$$

$$\text{specific gravity} = 0.005\ ({}^{\circ}\text{Tw}) + 1$$

$${}^{\circ}\text{Tw} = 200\ (\text{specific gravity} - 1)$$

$$\text{precent by weight} = \frac{\text{g/l}}{10\,(\text{specific gravity})}$$

$$\text{pounds per gallon} = \text{g/l} \times 0.008345$$

The relationship between °Tw and strength of bleaching powder solution is shown in Table 16.7. These methods of expressing strengths of solutions, however are far from accurate and hence quantitative estimation by titration for practical control of bleaching operation is preferable.

TABLE 16.7
Fresh Bleaching Powder Solutions [10]

°Tw	Available chlorine, g/l
0.5	1.40
1	2.71
2	5.58
3	8.41
4	11.41
5	14.47
6	17.36
7	20.44
8	23.75
9	26.62
10	29.50
15	45.70
20	61.50

16.9.1 Analysis of bleaching powder

5 g sample is made up to 500 ml in a volumetric flask. 50 ml of this solution is pipetted out to a 250 ml conical flask and 25 ml of distilled water is added followed by 20 ml of KI solution (10%) and 10 ml of glacial acetic acid. The liberated iodine is titrated against N/10 sodium thiosulphate solution using starch solution as indicator towards the end point when the blue colour will be discharged.

$$Ca(OCl)_2 + 4KI + 4CH_3COOH \rightarrow CaCl_2 + 4CH_3COOK + 2I_2 + 2H_2O$$

$$2I_2 + 4Na_2S_2O_3 \rightarrow 2Na_2S_4O_6 + 4NaI$$

1 ml of 0.1 N $Na_2S_2O_3$ = 0.00355 g available chlorine

$$\% \text{ available chlorine} = \text{B.R.} \times \text{Normality of } Na_2S_2O_3 \times \frac{\text{Eq. wt. of } Cl_2}{1000} \times \frac{500}{50} \times \frac{100}{\text{wt. of sample (W)}}$$

$$= \text{B.R.} \times \frac{3.55}{W}.$$

16.9.2 Analysis of sodium hypochlorite

The estimation by above method expresses chlorates as well as hypochlorites as available chlorine. The errors due to chlorates can be avoided by titration with an N/10 solution of sodium arsenite (Na_2HAsO_3)

1 ml of 0.1N Na_2HAsO_3 = 0.003546 g chlorine.

16.9.3 Analysis of sodium chlorite

2 g sample is made up to 500 ml in a volumetric flask. 25 ml of solution is pipetted out and then 25 ml of 10% KI solution and of 10% H_2SO_4 are added. The content is titrated against 0.1N $Na_2S_2O_3$ solution using starch as an indicator till blue colour disappears completely.

$2NaClO_2 + 8KI + H_2SO_4 \rightarrow 2NaCl + K_2SO_4 + 8I + H_2O$

1 ml of 0.1N $Na_2S_2O_3$ = 0.00226 g $NaClO_2$

$$\% \ NaClO_2 = B.R. \times \text{normality of } Na_2S_2O_3 \times \frac{\text{Eq. wt. of } NaClO_2}{1000} \times \frac{500}{25} \times \frac{100}{W}$$

$$= B.R. \times \frac{4.52}{W}.$$

16.9.4 Analysis of hydrogen peroxide

10 ml of sample solution is diluted to 1000 ml with distilled water. 10 ml of this solution is pipetted out into a conical flask and 10 ml of 10% H_2SO_4 is added to it. This solution is then titrated against 0.1 N $KMnO_4$ till pink colour of permanganate solution persist.

$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

1 ml of 0.1N $KMnO_4$ = 0.0017 g H_2O_2

$$\% \ H_2O_2 = B.R. \times \text{Normality of } KMnO_4 \times \frac{\text{Eq. wt. of } H_2O_2}{1000} \times \frac{1000}{10} \times \frac{100}{10}$$

$$= B.R. \times 1.7$$

Generally, H_2O_2 concentration is expressed in volume. 10 volume H_2O_2 = 10 times its volume of O_2 which corresponds to 3% solution by weight of H_2O_2. To convert % H_2O_2 into volume of H_2O_2 following calculations can be used :

$$\text{Volume of } H_2O_2 = \% \text{ of } H_2O_2 \times \frac{112}{34}.$$

16.9.5 Analysis of stabilisers for peroxide bleach

The efficiency of a stabiliser for peroxide bleach is tested by titrimetric determination of the speed of decomposition of H_2O_2, in the presence and absence of stabiliser, during the bleaching of cotton. Bleaching baths containing 10 ml/l H_2O_2, 5 ml/l NaOH (67°Tw) and 0, 0.25, 0.5 and 1 g/l stabilisers are prepared by adding stabiliser, caustic soda and H_2O_2, in that order, to water. Cotton cloth pieces (5g) are bleached in this solutions at 90°C for 90 min, material to liquor ratio being 1:50. After replenishing water lost due to evaporation, about 25 ml samples are withdrawn after 0, 30, 60 and 90 min, cooled in ice water and a 5 ml aliquot is pipetted from these for analysis. It is diluted with 50 ml of distilled water, acidified with 10 ml of 2N H_2SO_4 and titrated with 0.1 N potassium permanganate to a permanent pink colour.

In the case of stabilisers which consume permanganate under these conditions, the determination is done iodometrically by adding 1g KI to the acidified solution and titrated the iodine liberated, after keeping in dark for 10 min, with 0.1N sodium thiosulphate using starch as an indicator.

1 ml 0.1 N $KMnO_4$ = 0.0017 g H_2O_2

1 ml 0.1 N $Na_2S_2O_3$ = 0.0017 g H_2O_2

16.9.6 Analysis of sodium hydrosulphite

2 g sample is dissolved in a mixture of 10 ml HCHO and 25 ml water in a 250 ml volumetric flask. The stoppered flask is allowed to stand for 5 min and the volume is made up to the mark. 25 ml of this solution is pipetted out and titrated against 0.1N I_2 solution using starch solution as an indicator till blue colour persists.

1 ml of 0.1 N I_2 = 0.00435 g $Na_2S_2O_4$

$$\% \, Na_2S_2O_4 = \text{B.R.} \times \frac{4.35}{W}.$$

16.9.7 Analysis of sodium bisulphite

10 g sample is accurately weighed and dissolved in 1 litre distilled water. To 10 ml of this solution 5 ml acetic acid is added and then titrated against 0.1 N I_2 solution using starch solution as an indicator. End point is judged when the colourless solution turns blue.

$NaHSO_3 + I_2 + H_2O \rightarrow NaHSO_4 + 2HI$

1 ml of 0.1 N I_2 = 0.0052 g $NaHSO_3$

% $NaHSO_3$ = B. R. × 52.

16.9.8 Estimation of sodium silicate

In a commercial sample of silicate, Na_2O (total alkali) and SiO_2 (silica) are determined. 5 g of sodium silicate is dissolved in 100 ml water. 10 ml of this solution is titrated against 0.5 N H_2SO_4 using Methyle Orange as an indicator.

1 ml 1N H_2SO_4 = 0.031 g Na_2O

For determination of silica, 20 ml of silicate solution is kept in an evaporating dish and then 20 ml of N HCl is added to it. The content is evaporated to dryness with constant stirring. After cooling 10 ml of N HCl is added and again evaporated to dryness. The content is baked (over a sand bath) at about 130°C to convert the silicic acid into silica. After cooling water is added to dissolve the soluble matter and then filtered through a weighed-ash filter paper, washed free from chloride (test the filtrate with dilute $AgNO_3$ solution). The content is incinerated and weighed as silica.

16.10 Assessment of Damage of Cellulose During Pre-treatment Processes

The damages that occur during various pre-treatment processes of cellulosic fibres can be detected by various chemical tests like fluidity, copper number, Methylene Blue absorption and silver nitrate staining etc.

16.10.1 Determination of fluidity of cellulose

The extent of chemical damage to cellulosic fibres is usually expressed from fluidity measurements, although with oxidative damage some problems arise. Fluidity is the inverse of viscosity of cellulose solution and is measured as rhes. Oxycellulose or hydrocellulose has equal effect upon viscosity and give overall degradation of cellulose. Degradation is always accompanied by a decrease in DP, therefore higher the viscosity the less is the damage which has been inflicted upon the fibre. Viscosity changes do not give a straight line plot in relation to loss of tensile strength. When fluidities are used, however, the curve is near enough to a straight line for all practical purposes.

Among the various solvents suggested for dissolution of cellulose, cuprammonium solution is recommended as a general solvent having 15 ± 0.1 g/l Cu, 200 ± 5g/l NH_3 and less than 0.5 g/l nitrous oxide. The fluidity in this solvent of the solution of cotton is given by

$$F = \frac{c}{t}$$

where, c is the viscometer constant. If it is necessary to apply kinetic energy correction, k,

$$F = \frac{c}{t - \frac{k}{t}}$$

The kinetic energy correction is unnecessary for times of flow greater than 200 sec. In actual practice 0.5 g of finely cut dry cotton sample is dissolved in 100 ml of standardised cuprammonium hydroxide solution. The viscometer (Fig. 16-2) is

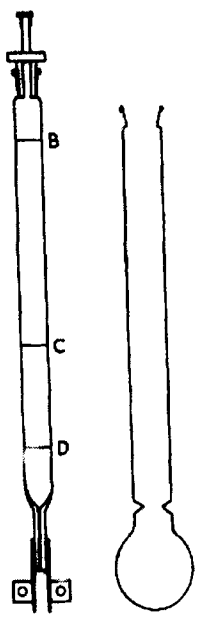


Figure 16-2. Shirley X-type viscometer and jacket.

used for dissolving as well as flow time of cellulose solution. The viscometer tube is calibrated. The three marks on the tube are timing marks. The ratio of the time of flow from BC to CD should be near unity. The viscometer is then wrapped with black cloth and wound on a cycle wheel which rotates at 4 r.p.m. overnight. Steel cylinder or Hg placed inside the cylinder falls from one end to the other during rotation. The established procedure [11,12] involves long agitation of cellulose with the solvent. A modified method is also described which gives only slightly less accurate results in a much shorter time [13].

Chemically undamaged cotton has a fluidity of 3 to 5. A value of 10 or more can be taken as an indication of excessive degradation during chemical pre-treatment processes. It is usual to work with 2% solution in the case of regenerated cellulose. Unprocessed viscose has a fluidity of 10 to 12. The fluidity values can be expressed in terms of DP of cellulose by the following equation [14]:

$$DP = 2160\ [(\log\eta_r + 1) - 0.267]$$

where η_r is the relative viscosity of 0.5% solution of cellulose in Cuoxam compared to the viscosity of the solvent. When the fluidity measurements in different solvents are compared, it is observed that the apparent DP of the degraded (oxidative) cotton is dependent on the alkalinity of the solvent [15] :

$$DP_{EWNN} < DP_{CUEN} < DP_{CUOXAM} < DP_{NO_3Al}$$

Fluidity results determined in Cuxam and Cuen for chemically damaged cotton are correlated with viscosity values obtained in Cadoxen and FeTNa solvents [16]. The comparison and conversion of the viscosity values to apparent cuprammonium fluidity is a quick method of determining degradation of cotton occured in pre-treatment processes [16].

16.10.2 Determination of copper number

Copper number is an expression of the reducing power of degraded celluloses. Oxidation of cellulose can produce ring fission of the glucose residues, resulting in the formation of aldehyde groups at carbon atoms 2 and 3. The aldehyde groups can reduce Fehling's solution to cuprous oxide. The latter may be determined quantitatively by allowing the oxide to reduce ferric alum to the ferrous state and determining the latter by titration with ammonium cerric sulphate. The copper number is thus the weight of copper from Cu^{2+} to Cu^{+} state by 100 g dry cellulose and is a measure of its inter and intra chain break down. Pure cellulose has a copper number of 0.2 - 0.3 and when fully degraded may be as high as 14. The importance of copper number has suffered a decline because it has been demonstrated that there is a poor correlation between increase in copper number and decrease in tensile strength.

Four solutions are prepared as follows :

Solution A : 100 g pure $CuSO_4$ dissolved in 1 litre H_2O.

Solution B : 50 g $NaHCO_3$ and 350 g Na_2CO_3 dissolved in 1 litre H_2O.

Solution C : 100 g ferric alum and 140 ml pure concentrated H_2SO_4 dissolved in 1 litre H_2O.

Solution D : N/100 cerric sulphate.

Solution A and B are mixed in proportion 5 to 95 and the mixture is boiled. 0.125 g finely cut dried sample is kept in a pyrex test tube and 100 ml of the mixture (A and B) is added to it. The test tube is immersed in a constant level water bath which is kept boiling. The test tube is covered with loose glass bulb during boiling. After 3 h test tubes are taken out, cooled and transferred onto Gooch crucible and filtered with suction. The sample is washed, first with dilute sodium carbonate solution (5 g/l) and subsequently with hot water . The residue is then washed with solution C twice with about 5 ml each time. The residue is then finally washed with about 10 ml of 2N H_2SO_4. Distilled water is added. The filtrate and washings are collected and then titrated with N/100 cerric sulphate solution using ferroin (2-3 drops) as indicator until the colour changes from red to pale blue.

1000 ml of N/100 cerric sulphate = 0.000635 g Cu (reduced)

$$\text{Copper Number} = \text{B.R.} \times 0.000635 \times \frac{100}{0.125}$$

$$= \text{B.R.} \times 0.508$$

The cuprous oxide reduces ferric alum as follows :

$$Cu^{+} + Fe^{3+} \rightarrow Cu^{2+} + Fe^{2+}$$

and final titration with cerric sulphate involves the oxidation $Fe^{2+} \rightarrow Fe^{3+}$ [18].

16.10.3 Methylene Blue absorption test

Methylene Blue test can also be used to differentiate between oxycellulose and hydrocellulose. Methylene Blue is a cationic dye. Standard cellulose generally has no affinity for Methylene Blue, but oxycellulose with the formation of carboxyl groups confer an affinity and can be sorbed onto cotton. For this purpose, Methylene Blue absorption tests are carried out both at pH of 7.0 and at a pH of 2.7 (acidic). Two pieces of fabrics to be tested are taken and treated one with Methylene Blue at a pH of 2.7 and the other at pH 7.0. If oxycellulose is present, the material will absorb less dye in the acid than in the neutral solution, whilst reverse is the case if hydrocellulose is present. The degree of staining will indicate the extent of degradation.

In another method, 1g cation free sample is treated with 100 ml of Methylene Blue solution (10 m. moles/l) buffered in presence of potassium dihydrogen phosphate (0.625 m. moles/l) and NaOH (0.4 m. moles/l). The contents of the flask are agitated for about 18 h at room temperature. The solution is poured off from the

cellulosic sample and preferably centrifuged. The supernatent solution is suitably diluted to determine the absorbance at 620 nm. The loss in concentration of the dye in the treating solution is found out by referring to the calibration graph and the carboxyl content of the cellulose sample is calculated and expressed as m.eq/100g dry cellulose.

If a dyed material is under test, the stripping of dye will be necessary before the test can be carried out. Alternatively, degradation can be determined by titration using an anionic dye which precipitates Methylene Blue from solution.

Scoured and bleached American cotton have carboxyl contents of 0.8-0.9; Egyptian cotton 1.16-1.74. Unbuffered Methylene Blue solutions give lower values viz., 0.45 and 0.65 respectively. Methylene Blue absorption of cotton depends on the ash alkalinity of the cotton and the value decreases as the ash alkalinity decreases.

16.10.4 Silver nitrate test

This qualitative test is also referred to as Harrison's test since he was the first to describe it in 1912. The test specimen is either boiled or padded with a reagent containing a mixture of silver nitrate (1%), sodium thiosulphate (4%) and sodium hydroxide (4%) and then steamed. Those parts where degradation takes place due to oxycellulose or hydrocellulose in a fabric will be stained black or dark grey due to the formation of silver by reduction.

16.10.5 Determination of acidic groups by iodometric method

1 g of bone dry cation freed sample is treated with 50 ml solution [NaCl (A.R.) 50 g, KI (CP) 83 g, KIO_3 (CP) 21.4 g, sodium thiosulphate crystals 4.96 g dissolved in 2 litres of water] in a stoppered flask. To this 25 ml of CO_2-free distilled water is added. A current of CO_2-free air is also bubbled through the solution and water washing the bubbling glass tube with 25 ml CO_2-free distilled water, the flask is stoppered and kept for 24 h. The contents in the flask are titrated with 0.02 N iodine solution using starch indicator. The end point is indicated by the appearance of a faint blue colour.

$$\text{Carboxyl content (m. eq. COOH/100g)} = \frac{1 \times (a - b) \times N \times 100 \times 1000}{1000 \times W}$$

where, a and b are the titration readings for blank and sample,
N = normality of iodine solution,
and W = bone dry weight of the sample.

16.11 Assessment of Damage of Wool

Wool fibre during its various pre-treatment stages also undergoes some kind of damage, the extent of which may be assessed by both physical and chemical methods. The very multiplicity of tests available is in itself evidence of the lack of a universal method for assessment of damage [19].

16.11.1 Microscopic test

Modification of the external scale structure of wool by chemical treatment can be examined visually with the aid of microscope.

Wool is immersed in a dilute solution of Methylene Blue (0.4 g/l) for 1 min and washed in water for 5 min and finally dried. The stained fibres are then cut into short lengths of about 1 mm and then mounted in a liquid paraffin and examined under microscope of about × 200. The degree of damage is then expressed in comparative numerical terms depending on the extent of staining.

Alternatively, damage to the outer layers (epicuticle) may be revealed by means Allwörden reaction [20]. When wool fibres are immersed in chlorine or bromine water, bubbles or blisters known as Allwörden sacs are formed on the surface. Damage to the fibre surface may show up by lessening the size of or eliminating altogether, the blisters. This test is particularly useful when damage caused by alkali treatment is severe.

16.11.2 Swelling test [21]

Wool fibre is immersed in a solution of sodium monohydrogen and dihydrogen phosphate at a pH of 5.95 for 1 h at 20°C. The samples are then centrifuged to remove the entrained liquor and then weighed wet and afterwards dried thoroughly and reweighed. The ratio of the weight of absorbed water to that of dry fibre i.e. retention of water will give the degree of swelling. The alkali solution will rupture the disulphide bonds in the polypeptide chains and thus the extent of swelling will give some idea of damage in wool.

16.11.3 Solubility test

In this method the amount of wool capable of being dissolved with a solution, which rupture the disulphide cross-links, is determined. Essentially it is a test which detects main chain breakage caused, most often, by action of acids on wool [21,22].

1 g wool (oven dry) is treated with 100 ml of 0.1 N solution NaOH at 65°C for 1 h. The sample is then rinsed with 2 litres of distilled water and dried to constant

weight at 105°C. The alkali solubility is then determined as the loss in weight of the test specimen expressed as percentage. Normal wool is expected to have about 12-13% solubility and values greater than 18% may be taken as suggesting that the sample has been damaged.

In the Krais-Viertel reagent test the wool is immersed in a solution of ammonia in caustic soda [23]. The test entails timing of the appearance of the characteristic swellings in this reagent. When the fibre has been damaged with acid, the time for appearance is decreased.

In the urea-bisulphite solubility test [24], wool is treated with a solution of urea (50%) and sodium bisulphite (3%) (pH adjusted to 7) at 60°C for 1h and then the residue is washed and dried till constant weight is obtained. Urea breaks the hydrogen bonds and bisulphite attacks the disulphide bonds in wool. Solubility in this method depends on the wool which had been treated in acidic or alkaline pH.

16.11.4 Spectrophotometric test [25, 26]

1g sample is extracted with 10 ml solution comprising isopropanol : pyridine : water 5:5:90. 2 ml of the wool extract solution is then reacted with 2 ml of ninhydrin solution (21.02 g NaOH, 62.4 ml propionic acid and 30 ml distilled water. After cooling 125 ml of methyl cellosolve and 18.75 ninhydrin is added and dissolved and the solution is made up to 250 ml) in capped test tube at 100°C for about 8 min. After reaction the solution is made up to 50 ml and the absorbance is measured in spectrophotometer at 570 nm against blank ninhydrin solution that contain no wool extract solution. The absorbance reading for the extract from the original clean wool is zero. The absorbance reading for the ninhydrin/wool extract reaction is directly related to the damage caused by sulphuric acid. The results correlate well with both alkali solubility and tensile strength test methods.

16.12 Determination of Degree of Mercerization

The effect of mercerization depends on the conditions of mercerization. A quantitative assessment of the degree of mercerization is carried out mainly in three different ways i.e. variation in the mercerized product, external appearance (lustre) and internal appearance (x-ray diagram) etc [26].

16.12.1 Determination of deconvolution count [27]

In this method cotton hairs are cut in large number of hair fragments 0.2 mm long. They are then mounted in liquid paraffin on a microscopic slide, and then

counted the proportion of fragments free from twist on convolution during mercerization. The result is expressed as percentage and is called "Deconvolution Count". If the figure is above 20, the fabric is mercerized. The ratio of the two sets of data may be used to estimate the degree of mercerization. The disadvantage of this method is that the extent of deconvolution is influenced by the maturity of cotton and by the structure of material that is twist of the yarn or weave of cloth.

16.12.2 Determination of swelling index [28]

Untwisting number of single yarn can give reliable means for estimating degree of swelling of cellulose in non-polar liquids such as carbon tetrachloride and benzene. Strong alkali solution and cadoxen (cadmium ethylene diamine complex of 3.6%) also causes large amount of untwisting. In this method, the yarn together with the weight (0.8 g) is hanged into the measuring cylinder containing sufficient amount of solvent as to dip the upper end of the yarn. The yarn is then allowed to untwist and the number of revolutions made by weight are measured for 3 min.

$$\text{Swelling index} = \frac{\text{Untwisting number in solvent}}{\text{Untwisting number in water}}$$

Swelling index increases with degree of mercerization. In this method there is no necessity of untreated sample.

16.12.3 Benzopurpurine test

In this method mercerized and unmercerized cotton samples are treated in a 0.5% solution of Benzopurpurine for 30 min at boiling temperature. The treated samples are then washed, dried and compared visually or spectrophotometrically. The mercerized sample is always more deeply dyed than the unmercerized. However, it is recommended that a standard swatch be calibrated so that the actual degree of mercerization can be assured.

16.12.4 Sodium hydroxide spotting test

In this method the undyed fabric is spotted with 30% solution of caustic soda and then both mercerized and undyed spotted fabric samples are dyed by using Benzopurpurine. If the fabric is fully mercerized, the spots will not be evident after dyeing. On the other hand, if the fabric is not mercerized or semi-mercerized, dark spots will be evident and the degree of mercerization can be evaluated on comparing the spots.

16.12.5 Goldthwait Red-Green test [29]

In this test a mixture of red and green direct dyes is used to compare the maturity of cotton fibre samples. Immature fibres dye red, and mature fibres green. Mercerization increases the fibre's affinity for green compound and ''causticization number'' can be assessed related to the strength of the green hue. Fabric treated with liquid ammonia ''under industrial mill condition'' dyes red.

16.12.6 Staining test

The fibre is immersed in iodine solution (20 g iodine in 100 ml of standard KI solution) for 3 min and rinsed thoroughly. Mercerized cotton is stained bluish black and unmercerized cotton remains white. Cotton fibres in the yarn bundle can be counted using a microscope and the ratio of dyed to undyed fibres can be used to determine the degree of mercerization. The iodine sorption value shows the largest increase for those samples treated in liquid ammonia with NH_3 removal by evaporation, followed by caustic mercerized samples, and last by those samples NH_3 treated and water quenched. Generally only minor differences in iodine sorption value are found between samples mercerized slack or under tension.

In another method [30] fabrics treated with several concentrations of NaOH are immersed in a mixture of 1.3 g/l Telon Fast Red AF-3G 150% (BAY), a low molecular weight acid dye, C.I Acid Red 151 and 1.4 g/l Benzo New Blue GS 140% (BAY), a large molecular weight direct dye, C.I. Direct Blue 10, liquor ratio 70:1 at pH 2 using H_2SO_4 for 10 min cold followed by washing off. Untreated cotton is stained red and becomes progressively bluer with increase in NaOH concentration.

16.12.7 Barium activity number [31-33]

Mercerized sample absorbs barium hydroxide (alkali) to a greater degree than sodium hydroxide and from practical point of view, barium hydroxide is more easy to estimate. The ratio of uptake for this reagent has been referred to barium activity number.

2 g mercerized and unmercerized samples are placed separately in two conical flask containing 30 ml of N/4 barium hydroxide and left for 2 h or preferably overnight. 10 ml of clear solution is withdrawn and titrated against N/10 HCl using phenolphthalein as indicator. A blank titration is also carried out on the measured barium hydroxide solution using Methyl Red as indicator.

$$\text{Barium activity number} = \frac{b - s}{b - u} \times 100$$

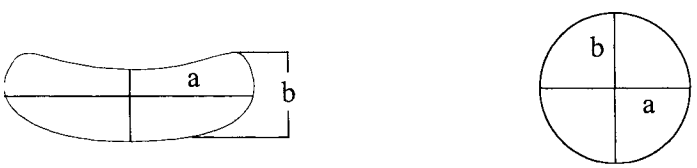
where, b = ml required for blank test,
s = ml required for mercerized cotton,
u = ml required for unmercerized cotton.

For exact estimation, correction should be made for the moisture regain of the sample. Barium activity number of unmercerized cotton is considered as 100 and semi-mercerized cotton ranges between 115 to 130 and that for completely mercerized cotton is about 155.

16.12.8 Determination of lustre [34, 35]

Pulfrich photometer, the Gorez Glarimeter comparative glass method and microscopic examination of cross-section of fibre are the qualitative methods for the assessment of degree of mercerization.

Mercerization increase the lustre and reduces the axial ratio (Fig. 16-3). Micro-



Before mercerization After mercerization

Figure 16-3. Cross-section of cotton fibre before and after mercerization.

scopic examination shows that the corss-section of the cotton fibre changes from eliptical to circular form due to mercerization. This can be measured as a ratio of two axes 'a' and 'b'. The axial ratio (a/b) of unmercerized cotton is about 2.2 to 2.6, whereas that of mercerized cotton is about 1.5 to 1.6. Caustic mercerized samples appear to give superior lustre than ammonia treated fibre.

The measurement of specular reflectance is considered as an accurate evaluation of lustre. Lustre can be determined from reflectance measurements with incident light inclined at 45°, the reflected light is measured either perpendicularly to the surface of the material (diffuse reflectance) or viewed at 45° symetrically to the incident light (specular reflectance). Lustre is therefore defined by the contrast ratio of the specular to diffuse reflectance [36, 37].

16.12.9 X-ray analysis

X-ray photograph of native cellulose (unmercerized) reveals the presence of two arcs close together and inside the prominent 002 arc. These reflections are

from $10\bar{1}$ plane and 101 plane, the latter being nearer the centre of the photograph. They are not as intense as 002 arcs. In case of completely mercerized or regenerated cellulose, X-ray photograph shows a change in position of two shorter arcs. The $10\bar{1}$ arc is much nearer to 002 arc and 101 arc is nearer the centre of the photograph. On the basis of this estimations it is estimated that mercerizing efficiency seldom exceeds 60-70% for yarn and 35-40% for cloth.

16.12.10 Infra-red analysis

Determination of infra-red crystallinity index at different wavelengths (1429 cm^{-1}/893 cm^{-1}) by the usual base line technique can be used [38]. When cellulose-II samples are considered, the 1372 cm^{-1}/2900 cm^{-1} ratio is more reliable index [39, 40]. A rapid method for estimation of the degree of mercerization has been developed using a near IR diffuse reflection technique [41].

16.13 Evaluation of Whitening Efficiency of Optical Brighteners

The estimation of optical whiteners in substrate is really a difficult problem, but the qualitative and quantitative estimation of fluorescent brightener in solution by examination of absorption and/or emission spectra have been detailed [42-46]. Since the brightener will differ in substantivity for a particular substrate with differences in their chemical structure, cost comparisons of performance can only be based upon evaluation of the treated substrates. Various techniques for such evaluation have been described [46-51].

16.13.1 Visual assessment

Visual assessment of a white object is based on a comparison of the test sample with a standard sample. A viewing angle of 45° is generally recommended and the position of the samples are changed several times during the test. Out of many white scales, Ciba-Geigy's ''Cotton white scale'' occupies a prominent position [52].

16.13.2 Extraction method

Generally optical brighteners on cotton are extracted from the fabric by suitable solvent like pyridine. The absorbance of the extracted solution of optical brighteners of unknown concentration is determined by using a uv-spectrophotometer, and by referring the calibration graph, the unknown concentration is determined. Optical brighteners can also be determined by extraction with alkaline cadoxen solution within narrow limits [53] and with relatively large errors (> 20%) in the uv range

[54]. This must place some doubt on results of fluorescent brightening agent concentrations determined in this way. A similar technique is also used to determine fluorescent brightening agents on nylon and acetate fibres [55]. A m-cresol-methanol mixture is used as solvent for nylon fibres and DMF for the acetate fibres. Extraction with a DMF-water mixture is recommended for cellulosic fibres.

16.13.3 Instrumental assessment

Thin-layer chromatography, tristumulus filter photometer and spectrophotometer are the most popular techniques for seperation, identification and quantitative analysis of fluorescent brightening agents, although some other instrumental techniques have been developed [56]. Spectrophotometers simply measure spectral reflectance, from which tristumulus values are calculated on the basis of spectral energy distribution of the light source and the C.I.E. spectral tristumulus values function . The L*, a*, b* values for the standard reference substrate and the sample are determined. The former values are substracted from the latter to get ΔL^*, Δa^* and Δb^* values. This determines the whiteness and tonal differences. The results obtained by this method are not always with full agreement with the results of subjective evaluation, and therefore it is used as an auxiliary method, especially in the determination of the concentration of the brightening agent on fibres.

16.14 Determination of the Degree of Heat-setting

16.14.1 Shrinkage test

Normally a square area is drawn on the heat-set material and measured. The marked cloth is boiled in soft water in the washing wheel for 30 min, centrifuged and air dried. The dimensions of the square are measured without ironing the dried fabric and the shrinkage is determined. A well set fabric should not show more than 1% residual shrinkage.

16.14.2 Crease-recovery angle

The determination of crease recovery angle before and after heat-setting of the fabric is done. The extent of crease-recovery of heat-set fabric before and after setting at and above 170-175°C will give idea of the degree of heat-setting.

16.14.3 Assessment of handle

Assessment of handle before and after setting gives an idea of the degree of heat-setting. In general, fabric becomes stiff after heat-setting. Stiffness is measured by bending length and compared with that of the unset fabric. The narrower

the difference of bending length between the set and unset fabrics, the better the setting.

16.14.4 Iodine absorption method

The degree of heat-setting of polyester fabrics can be correlated with their iodine absorption value. Heat-setting under industrial conditions in a taut form reduces the amorphous content of synthetic fibres. So, there will be a decrease in iodine sorption and increase in critical dissolution value [57].

16.15 Determination of Biodegradability of Surfactants [58]

The efficiency of a sewage treatment is often expressed as the percentage removal of the BOD, less often in terms of COD removal. Dividing the percent removal of the surfactant by the percent removal of the BOD or COD gives the biodegradability index of the surfactant.

The procedure for alkylbenzenesulphonates (ABS) and linear alkylbenzenesulphonates given by the soap and detergent association involves both a presumptive and a confirmatory test.

In the presumptive test, a nutrient medium, to which 30 mg/l test surfactant has been added, is inoculated with micro-organisms in a culture flask and aerated by a reciprocating shaker at 128 two-four inch strokes / min at 25 ± 3°C. After two 72 h adaptive transfers, in which 1 ml of the 72 h culture is transferred to 100 ml of a fresh nutrient medium plus surfactant, samples are taken at zero time, i.e. immediately after inoculation and mixing and on 7th and 8th days. A blank under the same conditions but without the surfactant is carried out side by side. The samples are then tested for the active content by the Methylene Blue method. If analysis is not done immediately, 1 ml formaldehyde per 100 ml should be added as preservative. If the percent degradation is less than 80, the sample is non-biodegradable. If above 90, the sample is biodegradable and in this case no further test is necessary. A value of 80-90% indicates the necessity of carrying out a confirmatory test. Although presumptive test is simple and inexpensive it suffers from the disadvantage in that it takes 14 days in all and that it does not measure rate per day or per hour, but only total degradation in one week.

In the confirmatory test, activated sludge from a domestic sewage treatment plant, test surfactant (20 mg/l) and synthetic sewage of composition

Glucose	13.0 g
Neutrient	13.0 g
Beef extract	13.0 g
K_3HPO_4	13.0 g
$(NH_4)_2SO_4$	2.5 g
Tap water	1 litre

are mixed in a specially designed vessel, brought to a steady state and aerated for 23 h. After 1 h settling, supernatant liquid is withdrawn and the same amount is replenished with synthetic sewage containing 20 mg / l surfactant. This is repeated for a minimum of 15 days after which the active content is determined by Methylene Blue method. The confirmatory method suffers from the disadvantage that the testing time exceeds the normal retention time in an activated sludge system in sewage plants.

16.15.1 Methylene Blue method

A 10 ml aliquot of a solution containing 0.625 g of 100% active content in 500 ml is pipetted in a 100 ml graduated glass stoppered cylinder and 25 ml of aqueous methylene blue indicator (The indicator is prepared by pipetting 10 ml of 0.3% solution of methylene blue hydrochloride into 500 ml water, adding 12 g concentrated H_2SO_4 and 50 g Na_2SO_4 and then diluting to 1 litre) and 15 ml of chloroform added. The solution is then titrated with 0.004 M cetyl pyridinium bromide, shaking mixture vigorously for 3 min after each addition. As the titration continues there is a slow transfer of blue colour from chloroform to aqueous layer. When the colour of the two layers has equalised the end point is reached.

$$\text{Active ingredient, \%} = \frac{a \times b \times m \times 5}{w}$$

where, a = ml of titrant consumed,
b = molarity of above solution,
m = molecular weight of active ingredient, and
w = weight of sample in g.

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SUBJECT INDEX

Abaca, 2
Absorbancy, 452
Accelerated bleaching of blends, 167
Accelerated hypochlorite bleaching,
---, by steaming method, 167
---, conjunction with H_2O_2, 166
---, elevated temperature, 166
---, in danger zone, 166
---, in presence of additives, 167
Acetate fibres,
--, manufacturing of, 35
Acid hydrolysis of cotton, 346
Acrilan, 181
Acrylic fibres, 34
Action of acids, 350
---, on cotton, 345
Action of alkalies,
---, on cotton, 86, 346
---, -, nylon, 31
---, -, polyester, 357
---, -, silk, 86, 356
---, -, wool, 86, 355
Activated sludge plant, 385
Activators for,
--, chlorite bleaching, 183-185
--, H_2O_2 bleaching of silk, 179
--, ---, wool,174
--, peracetic acid, 189
Advantage of bleaching with,
----, chlorite, 187
----, hypochlorite, 167
----, peracetic acid, 191
----, peroxide, 181
Air pollution, 370
Air in kiers, 346, 348
Alkali cellulose, 285
Alkali earth metal, 88
Allwörden reaction, 463
Alpaca, 2
Amino acid content,
---, on silk, 12,15
---, -, wool, 12
Ammonia mercerization, 309
Amorphous region, 4
Amphoteric surfactants, 98
Amylase, 69,418,419
Amylopectin, 70
Analysis of non-cellulosic residues,
----, ash content, 443
----, calcium and magnesium, 444
----, iron and copper, 445
----, silicate and phosphate, 444
Analysis of water,
---, calcium hardness, 443
---, magnesium hardness, 443
---, suspended matter, 442
---, temporary and permanent hardness, 443
---, total hardness, 442
---, total soluble salt, 442
Animal fibres, 2
Anion active substances, 94
Anti-chlor treatment, 164, 166
Anti-redeposition agents,
---, CMC structure, 102

---, PVP structure, 103
AOX, 168, 372
Assistants, kier boiling, 134
Available chlorine, 165, 455
Auxiliary products in,
---, emulsifying bath, 101, 103, 106
---, mercerizing liquor, 250
---, kier boiling, 90, 91

Barium activity number, 466
Bast fibres, 16
Batch equipment,
--, cotton desizing, 79
--, -, scouring, 132
--, -, bleaching, 217
Battrice machine, 148
Becoflex roller, 255
Becco J- Box, 138, 224
Ben-bleach system, 230-232, 340
Beta-alkoxy reaction, 347
Bicomponent fibres, 43
Bio-degradation, 380, 384
Bilateral structure of,
---, cotton, 11
---, wool, 10
Bioplastic fibres, 43
Bio-polishing, 428
Bio-technology, 418
Bleaching agents,
--, chlorinated trisodium phosphate, 163
--, classification of, 161
--, emulsion, 178
--, oxidising, 161, 168, 188
--, lithium hypochlorite, 163
--, peroxygen derivatives, 196
--, reducing, 192
Bleaching of,
--, acetate, 180
--, acrylics, 180
--, blended fabrics, 203-299
--, cotton, 161, 168, 173, 183, 190
--, jute, 196-201
--, linen, 201, 202
--, nylon, 184, 195
--, polyester, 184
--, polyvinyl alcohol, 186
--, polyvinyl chloride, 185
--, regenerated fibres, 180
--, silk, 178
--, weft-knitted cotton, 193, 194, 209
--, wool, 192-194
Bleaching of blended fabrics,
----, acetate/cellulose, 208
----, acrylic/cellulose, 207
----, acrylic/wool, 206
----, nylon/ cellulose, 206, 207
----, nylon/wool, 207
----, polyester/cotton, 203-206
----, polyester/linen, 208
----, polyester/wool, 206
----, viscose/cotton, 209, 210
----, wool/viscose, 209
Bleaching of coloured woven goods, 166
Bleaching equipment, batch,
--, -, jiggers, 219
--, -, rope, 221

--, -, spiral jet, 222
--, -, winches, 220
Bleaching equipment, semi-continuous,
--, -, pad-batch, 222
--, -, pad-jig, 224
--, -, pad-roll, 223
Bleaching equipment, continuous rope,
--, --, 3-stage J-Box, 225
--, --, 2-stage J-Box, 226
--, --, DuBec system, 228
--, --, FMC Wet bottom, J-Box, 228
--, --, single stage plant, 226
Bleaching equipment, continuous open-width,
--, ---, Ben-bleach, 230
--, ---, combi-steamers, 236-237
--, ---, multilayer conveyer, 235
--, ---, PKS system, 238
--, ---, without plaited strorage, 233
--, ---, -, pre-steeping, 234
Bleaching, major break-throughs, 180
Bleaching powder,
--, action of acid, 162, 165
--, analysis of, 455
--, catalytic decomposition of, 165
--, chemical structure, 161
--, effect of pH & temp., 165
--, manufacture of, 162
--, rate of attack on cotton, 162,165
Blueing tints, 188
Boilers,
-, scaling, 362
-, water supply, 361
Brushing, 52
BOD, 372
Builders,
-, defination of, 93
-, effect on detergency, 93
Burrs, 107, 433

Cadoxen, 460,465,468
Calcium hypochlorite, 128
--, preparation of, 162
--, decomposition of, 162
Carbon fibres, 41
Carbonisation of wool, 355
---, enzymatic process, 113
---, rapid process, 111
Carbonising machineries, 150-152
Casein fibre, 27
Cannizaro intermediates, 349
Causticization, 287
Catalytic damage, 350, 354, 358
Cationic surfactants, 96
Cellobiose, 4
Cellulase treatment, 420
--, effect of temperature, 422
--, --, pH, 422
Cellulose,
-, chemical composition, 3
-, molecular weight, 4
-, morphology, 3
-, structure, 4
Cellulose I, II, 5, 24, 285, 286
Cellulose fibres,
--, continuous bleaching, 224-229
--, copper number, 352

--, fluidity, 458
--, man-nade, acetate, 25
--, --, cuprammonium rayon, 22
--, --, polynosic, 24
Chain mercerizing machine, 293
Chainless mercerizing machine, 294
Chelating agents, 91
Chemical structure of,
---, acetate fibres, 25
---, acrylics, 34
---,carbon fibres, 42
---, chloro fibres, 39
---, elastomeric fibres, 40
---, flax, 8
---, jute, 20
---, modified nylon, 33
---, -, polyester, 28-30
---, nylon, 30, 32
---, polyester, 28
---, polypropylene, 38
---, PTO fibres, 42
---, silk, 14-16
---, wool, 11
Chlorine dioxide, 182
Chlorite bleaching, 182
---, corrosion of, 186
Chlorous acid, 182
Cloud point, 98
Coagulation of impurities, 382
---, mechanism, 383
---, -, bridging, 383
---, -, charge patch, 383
Cold bleaching, 365, 369
Cold desizing, 78
Colour woven goods,
---, scouring of, 90, 94
---, kiering of, 133
---, bleaching of, 175
Combined processes,
--, scouring and bleaching, 180, 185, 210, 337, 339
--, ---, acetate fibres, 189
--, ---, knitted cotton, 210
--, ---, Polyester/cotton, 126,206
--, ---, silk, 180
--, scouring and desizing, 79, 84, 336
--, scouring and milling, 149
--, scouring and relaxation, 125
--, solvent assisted, 341
--, emulsified solvent, 337, 341
--, enzyme treatment, 342
--, desizing, scouring and bleaching, 82, 123
Combined processing equipment,
---, Ben-bleach, 340
---, C.R.C. process, 340
---, desizing / scouring/ bleaching, 399
---, Flex-nip, 340
---, Markal process, 340
---, mercerizing and bleaching, 305
---, mercerizing and desizing, 309
---, Reco-Yet, 340
---, solar system, 342
Combined plasma and enzyme treatment, 423, 434
Contact angle, 101
Cortex in wool, 10
Cotton fabric,

--, bleaching of, 85-120
--, boiling -off, 89
--, colouring matter, 166
--, desizing of, 69
--, scouring, 86
--, singeing, 55-65
--, mercerizing, 285
--, -, ammonia, 39
--, -, hot, 306
Crabbing of wool, 110,152
Critical micelle concentration, 94, 103
Corpping, 52
Cross-section of,
---, acrylics, 35
---, cotton, 4
---, flax, 17
---, hemp, 19
---, jute, 19
---, modacrylic, 36
---, nylon, 31, 34
---, plasma treated wool, 409
---, polyester, 29
---, polypropylene, 38
---, remie, 18
Cross-links in wool, 111
Crystallinity of,
--, cotton,
--, polyester, 28
--, silk, 15
--, wool, 13

Decatising apparatus 152-155
Dechlorinating agent, 204
Decomposition of H_2O_2, 77
Deconvolution count, 464
Degradation of cellulose, 344-355
---, during bleaching, 163, 166, 350
---, -, desizing, 344
---, -, scouring, 346-349
---, in hypochlorite, 350-353
---, -, hydrogen peroxide, 170, 173, 182, 353
---, -, alkali, 346
Degradation of,
--, flax, 203
--, jute, 197
--, silk, 179, 194, 356
Degradation of nylon,
---, during bleaching, 185
---, -, chlorite bleaching, 188
Degradation of polyester, 357
---, on exposure to γ-rays, 413
Deagradation of wool, 354-356
---, in acids and alkalies, 355
---, -, bleaching, 355
---, -, carbonising, 355
---, -, decatising, 355
Degreasing of wool by plasma, 407
Degree of polymerisation,
---, flax, 17
---, silk, 15
---, polypropylene, 37
Degumming of,
--, remie 118
--, silk, 114 -116
--, silk by plasma, 407
Degumming 351, 399, 409

-, and pH, 116
-, with alkali and acid, 116
-, -, enzymes, 117
-, -, foam, 117
-, -, soap, 116
-, -, synthetic detergent, 116
-, partial, 117
-, weight loss, 115
Delignification of flax, 203
Delustering of acetate fibres, 123
Demineralisation of cotton, 88
Desizing, 69-84
-, after-wash, 100
-, BOD, 377
-, mixture, 99
-, of blended fabrics, 78
-, -, cotton, 69
-, -, synthetic fabrics, 77
Desizing of starch,
---, acid application, 73
---, enzyme attack, 72 - 75
---, oxidation method, 75-77
---, peroxy compounds, 337
Desizing machineries, 79-84
--, batch process, 79
--, pad-batch, 80
--, pad-roll, 81
--, pad-steam, 337
--, pad-store, 338
--, continuous, 81
--, -, J-Box, 83
--, -, rope form, 80
--, -, solvent, 83
Desuinting, 230
Detergency, 44, 101, 103
-, detachment of oils, 101
-, effect of CMC, 344
-, effect of enzyme, 431
-, theory of soil removal, 102
Detergents,
-, anionic group, 118
-, interfacial tension, 101
-, cloud point, 88
-, concentration, 94
-, non-ionic structure, 97
-, soiling activity, 101
-, soil suspending, 101, 102
Dimensional stability, 270
Disadvantages of,
--, bleaching with peroxide, 181
--, --, bleaching powder, 167
--, --, sodium chlorite, 187
--, --, sulphur dioxide, 193
--, -, of jute, 199
Draves test, 452
Dolly machine, 149
Double bleach of silk, 195
Dynel, 39

Ecru silk, 115
Ecology, 372
Economy through,
--, process modification, 368
--, -, sequence, 369
Effluent problems in,
---, auxliliaries, 378

---, bleaching, 378
---, desizing, 376
---, scouring, 377
Effluent treatment,
--, and biotechnology, 435
Elastic recovery of Spandex, 41
Electrolyte effect during,
---, desizing, 95
---, mercerizing, 292
---, optical brightening, 325
Electrolytic method,
--, hypochlorite, 163
--, peroxide, 169
Emulsification of oil, 87, 88
Emulsified sovents, 105
Emulsion scouring, 337
--, mechanism of, 106
--, recipe, 106
Enzymes,
-, textile application, 418
-, chemistry of, 418
-, mechanism on textile, 418
-, heat protection, 14
-, pH response, 74
-, salt addition, 75
-, toxins, 422
Enzymatic degradation during,
---, bleaching of jute, 201
---, desizing, 345
---, bio-polishing, 428
Enzymatic processing,
--, advantages of, 424
--, disadvantages of, 425
--, of cotton, 425
--, -, silk, 428
--, -, wool, 432
Enzymatic,
-, bleaching of cotton, 428
-, --, wool, 432
-, carbonisation of wool, 433
-, degumming of silk, 426
-, desizing of cotton, 426
-, hand modification of wool, 435
-, mercerization, 426
-, shrink proofing of wool, 435
-, scouring of cotton, 426, 427
Enzyme effect on,
---, dyes, 429
---, mechanical agitation, 431
---, resins, 430
---, surfactants, 430
---, washing process, 431
Epicuticle, 10
Eumelanin, 173
Evaluation of,
--, lubricants, 446
--, saponification value, 447
--, unsaponified matter, 447
--, whitening efficiency, 468
--, wax content in cotton, 445

Fabrics,
-, blend mercerization of, 291
-, knitted mercerization of, 303
-, liquid ammonia treatment of, 309
Fatty acids, 131

--, in cotton wax, 7, 440
--, in wool, 14, 107
Fatty alcohols in cotton wax, 7
Fibril, 4
Fibrion,14
Fibre,
-, acetate, 25
-, cotton, 3
-, flax, 17
-, hemp, 19
-, jute, 19
-, rayon, 22
-, remie, 18
-, regenerated proteins, 26
-, synthetic, 27-54
-, viscose, 28
-, wool, 8
Fibre classification, 2
Fibre structure,
--, casein, 27
--, cotton, 2
--, linen, 4
--, protein fibres, 26
--, rayon, 22, 23
--, silk, 14, 15
--, synthetic fibres, 22-24
Fibrolane, 26
Flax,
-, bleaching of, 201, 202
-, removal of rust, 202
Flavone pigment, 180
Fleissner scouring bowl, 146
Flex-nip, 340
Flue gas, 382
Fluidity of cotton, 350, 458
Fluorescent brightening agents (FBA),
---, absorption and emission curves, 320
---, mechanism of, 323
---, photo-yellowing and tendering, 327
---, quanititative measurements of, 468
---, salt sensitivity, 325
---, solubility in bleach liquor, 326
---, temperature and exhaustion, 324
---, wet fastness, 327
FBA, application to,
-, --, acrylics, 330
-, --, blended fabrics, 322
-, --, cellulosic fibres, 326
-, --, CDPET fibres, 331
-, --, nylon, 329
-, --, polyester 328
-, --, polyvinyl chloride, 332
-, --, silk, 328
-, --, wool, 327

Gas singeing of,
---, blended fabrics, 57
---, cotton, 56
---, polyester, 57
---, regenerated fibres, 56
---, wool, 56
Gas singeing machines, 58-63
Galacturonic acid, 8
Gebauer kier, 135
Generic names of fibres, 3
Glass fibres, 43

Glass-transition temperature of,
----, acrylics, 36
----, olefin fibres, 37
----, polyester, 29
----, Spandex, 41
----, effect on singeing, 57
Glucose, 4, 449
Gluconates, 172
Glutamic acid, 12
Goldthwait test, 466
Glycerines, 12, 87

Hard water, 441
--, effect on cotton, 353
--, --, silk, 199
Harsh handle of,
---, silk, 179, 199
---, plasma treated wool, 410
Harrison test, 462
Heat-setting, 259-277
--, in autoclave, 261
--, bond rupture, 260
--, changes in dyeability, 271
--, --, structure, 272
--, by contact method, 261
--, by convection (tenter), 263
--, by infra-red, 266
--, of knitted fabrics, 265
--, of polyester,259
--, stages, 230
--, of texturised fabrics, 256
Heat-setting of blended fabrics,
-----, polyester/cotton, 271
-----, polyester/linen, 272
-----, polyester/silk, 272
-----, polyester/wool, 271
-----, polyvinyl chloride/cellulose, 272
Heat-setting degree, determination by,
---, --, assessment of handle,
---, --, crease recovery, 469
---, --, iodine absorption, 470
---, --, shrinkage test, 469
Hemi-cellulose, in
-, -, cotton, 8
-, -, flax, 17
-, -, hemp, 19
-, -, jute, 20, 21, 199
-, -, linen, 201
Hexa-methylene diamine, 30
High energy radiation,
---, bleaching of textiles, 413
---, degradation and cross-linking, 412
High pressure kier, 133
High wet modulus viscose, 23
Histidine, 12
Hydrocellulose, 182, 345
-, staining test, 461
Hydrosulphite,
-, in bleaching, 193
-, stabilised, 195
-, analysis of, 457
HLB system, 95
Hydrogen peroxide,
--, activation of, 170
--, analysis of, 456
--, bleaching action, 169

--, catalytic acceleration, 354
--, decomposition of, 169, 355, 356
--, expression of strength, 169
--, manufacture of, 166, 172
--, reaction with cellulose, 350
--, stabilisers, 170-173
--, reaction with wool, 355
Hydrogen peroxide bleaching of,
----, acetate, 180
----, acrylics, 180
----, cotton, 172
----, jute, 97
----, silk, 178
----, viscose, 180
----, wool, 173-178
Hydrogen peroxide, effect of,
--, --, concentration, 173
--, --, fluidity, 170
--, --, impurities, 169
--, --, metal ions, 353, 354
--, --, pH, 172
--, --, sodium silicate, 353
--, --, temperature, 172
--, --, time, 173
--, --, water, 171
Hyperfiltration, 388
(see reverse osmosis)
Hypochlorite bleaching, 162-168
Hot mercerization,
--, advantages of, 308
--, changes in properties, 307
--, comparison, 307
--, methods, 307
Husk in cotton, 88

Identification of starch, 450
Immature cotton, 210
Impurities in,
--, cotton, 5, 86
--, jute, 120
--, silk, 115
--, water, 361
--, wool, 13, 107
Impregnation,
-, Ben-impacta, 230
Inorganic salts in,
---, cotton, 7, 87
---, jute, 20
---, synthetic fibres, 120
---, wool, 126
Inspection of fabric,
---, burling, 50
---, by laser beams, 50
---, mending, 50
---, perching, 49
Interlock stitch, 51
Ion-exchange resin, 364

Jackson kier, 136
Jafferson Walker Kier, 134
J-Box,
--, Becco, 139, 229
--, bleaching range, 224-226
--, desizing, 83
--, Du Bec system, 228
--, Du Pont, 139, 229

--, FMC wet bottom, 227
--, material of construction, 224
--, preparation range, 126
Jet washer, 250
Jig,
-, process, 79
-, scouring, 137
J-piler, 224
Jute,
-, bleaching of, 196-198
-, chemical constitution of, 21
-, cottonisation of, 201
-, dimensions of, 20
-, drawback of, 129
-, lignin content, 19, 21
-, properties of, 21

KB value, 106
Kenaf, 2
Keratin, 11
Kinds of fibres, 1-47
Kier,
-, circulation, 33
-, high pressure, 133
-, horizontal, 135
-, Jackson, 138
-, low pressure, 132
-, open-width, 136
-, vertical, 133
-, Walsh's, 133
Kier boiling,
--, assistants, 134
--, coloured goods, 90
--, effect of air, 348
--, procedure, 134
--, yarn in hank, 109
Kitties, 447
Knitted fabrics,
--, bleaching equipment, 220, 227, 237
--, heat-setting of, 265
--, mercerization of, 304
--, opening of, 224
--, scouring of, 104
--, singeing of, 163
--, solvent scouring, 106
--, treatment with liquid ammonia, 311
--, wax content, 446

Lanolin, 18
Laminated structure of silk, 15
Lignin in,
--, coir, 21
--, flax, 21
--, jute, 19, 21, 199
--, -, action on bleaching, 197
--, -, removal of, 201
Lime-soda scouing, 89
Linen,
-, bleaching of, 201
-, -, loss in weight, 14, 201
-, reaction with chlorite, 202
-, --, hydrogen peroxide, 202
-, --, peracetic acid, 202
-, scouring of , 119
Lipases, 418
Liquid ammonia,

--, comparison, 312
--, effect of, 311
--, Prograde process, 310
--, properties of treated goods, 313-315
--, Sanfor-set process, 309
--, treated, test, 466
Lithium hypochlorite, 163
Lo-flo process, 142
Long vegetable fibres, 18
---, aspect ratio, 20
Loose wool scouring, 107
Lot number, 52
Low energy processes, 316, 317
Lubricants, 69, 103, 104, 446
-, for wool yarn, 109
-, for worsted, 110
-, removal of 110

Magnesium sulphate in bleaching, 171
Malt amylases, 73
Malt enzyme, 449
Maltose, 78, 89
Man-made fibres,
---, acrylics, 34
---, miscellaneous, 38
---, nylon, 29
---, olefin fibres, 37
---, polyester, 27
---, regenerated fibres, 22
Manufacturing process,
--, acetates, 25
--, acrylics, 35
--, nylon, 31
--, polyester, 28
--, rayon, 23
Markal process, 144
Maturity of cotton, 466
Mechanism of bleaching with,
----, chlorite, 182
----, hypochlorite, 162, 163
----, lithium hypochlorite 143
----, peracetic acid, 189, 190
----, peroxide, 170
----, peroxygen compounds 196
----, reductive agents, 176
----, TAED/H_2O_2, 190
Mechanism of reaction with,
----, alkali, 348
----, enzyme, 420
----, in wool scouring, 108
----, emulsion scouring, 106
Mechanical cleaning process,
---, brushing, 52
---, cropping, 52
---, shearing, 54
Mechanical removal of water, 345
Medulla in wool, 11
Melanine, 173
Mending, 50
Mercerization of,
-, blended fabrics, 291
-, cotton, 279-315
-, flax, 290
-, knit goods, 303
Mercerization of cotton,
---, adsorption of barium hydroxide, 460

---, --, caustic soda, 283
---, --, dyes, 289
---, --, water, 288
---, changes in properties, 280-290
---, in hank form, 302
Mercerization, effect of,
-, --, alkalies, 281, 282
-, --, fabric construction, 288
-, --, immature cotton, 290
-, --, lustre, 286
-, --, structural modification, 285
-, --, shrinkage, 285, 286
-, --, swelling, 281
-, --, temperature, 282
-, --, tension, 287
-, --, water during washing, 284
-, --, wetting agents, 280
Mercerization,
-, half mercerization, 289
-, hot, 306
-, liquid ammonia, 309
-, recovery of caustic soda, 387
-, strength, 288
-, theory, 283
Mercerizing efficiency, test by ,
--, --, barium activity number, 466
--, --, benzopurpurine, 465
--, --, deconvolution count, 464
--, --, Goldthwait method, 466
--, --, infra-red analysis, 468
--, --, lustre, 467
--, --, staining, 466
--, --, spotting, 465
--, --, swelling index, 465
--, --, X-ray analysis, 467
Mercerizing machines
--, causticizing, 298
--, chainless, 295, 297
--, clip-chain, 293
--, cloth (woven), 293
--, combined, 305
--, core, 300
--, Dimensa, 301
--, dual purpose, 301
--, Ecomerce, 296, 299
--, Flex-nip, 300
--, Goller perfecta, 301
--, hot, 301
--, knit goods, 304
--, liquid ammonia, 311
--, minimerce, 293
--, Prograde, 310
--, recuperator, 297
--, Sanforset range, 211
--, yarn, 302
Methods to generate plasma, 398
Methylene blue absorption, 352
Micellisation of surfactants, 100
Modacrylic fibre, 34, 36
Modified fibres,
--, acrylic, 36
--, nylon, 33
--, polyester, 30
Moisture sorption,
--, determination of, 447
--, of acetates, 26

--, -, acrylics, 35
--, -, cotton, 288
--, -, flax, 21
--, -, jute, 21
--, -, nylon, 32
--, -, PBI fibres, 34
--, -, polyester, 29
--, -, polypropylene, 38
--, -, viscose, 23

Molecular structure of,
---, acrylics, 34
---, cotton, 4
---, polyethylene, 37
---, polypropylene, 37, 38
---, polyvinyl alcohol, 40
Motes, 5, 14, 86
-, removal of, 453
Multi-layer stenter, 261

Natural fibres, impurities of,
--, --, cellulose and non-cellulosic, 6
--, --, cotton, 5
--, --, cotton wax, 7
--, --, flax, 21
--, --, silk, 21
--, --, wool, 13
Natural yellowish tint in,
----, cotton, 16
----, jute, 196
----, linen, 202
----, silk, 178
----, weft knitted cotton, 210
----, wool, 173
Nylon, 29-34
-, manufacturing of, 31
-, modified, 33
-, properties of, 32
Nylon, bleaching with,
-, --, peracetic acid, 190
-, --, peroxygen compounds, 196
-, --, reductive agents, 195
-, --, sodium chlorite, 184
Nylon, scouring of, 121
-, heat-setting of, 267

Olefin fibres, 37
Opener (fabric), 244
Open-width bleaching equipment,
----, bleaching, 281
----, desizing, 80
----, scouring, 138
----, washing, 247-255
Optical brightening agents,
---, chemical constitution of, 322
---, consumption of, 321
---, mechanism of, 325
---, application of, 325-337
Orlon, 42, 181
Oxon, 196
Oxidation of cellulose, 352, 358
---, with bromite, 345
Oxidative damage of cellulose, 348, 354
---, wool, 355
Oxycellulose, 89, 90, 346, 350
-, determination of, 455

Pad-steam process, 337
Pad-store process, 338
Paraffin wax, 88
Pectic substances, 5, 6, 88
Peracetic acid,
--, activators for, 189
--, bleaching of acetate, 191
--, --, acrylics, 191
--, --, jute, 198
--, --, nylon, 190
--, --, polyester/cotton, 205
--, manufacture of, 188
--, merits and demerits of, 191
--, properties of, 189
--, stability of, 189
--, in houshold detergents, 189
Perborates, 189
Perching, 49
Perfumed fibres, 43
Perhydroxyl ions, 179
Permanent hardness, 363
Permonosulphuric acid, 178
Permonosulphonate, 196
Peroxide,
-, advantage and disadvantages, 181
-, bleaching of cotton, 170
-, --, blended fabrics, 206
-, --, silk, 178
-, --, synthetic fibres, 180
-, --, wool, 174
-, volume defined, 169
Photo-bleaching of wool, 194
Photo-stability of bleached jute, 199, 200
Photo-yellowing of,
--, acrylics, 18
--, jute, 199
--, optical brighteners, 325
--, silk, 328
--, wool, 174, 327
Piler, 244
PKS unit, 238
Plasma,
-, concept to, 395
-, cold, 396
-, corona discharge, 396
-, generation, 397
-, glow-discharge, 396
-, interaction with substrate, 404
-, reaction, 405
-, -, initiation for grafting, 406
-, -, oxidation, 406
-, -, peroxide formation, 406
-, -, recombination, 405
Plasma generating equipment,
---, batch, 403
---, continuous, 404
---, corona reactor, 401
---, laboratory, 399
---, low pressure, 401
---, one atmosphere, 402
Plasma treatment for,
---, bleaching, 410
---, desizing, 410, 411
---, improved dye absorption, 407-409
---, mercerization, 410
---, soil repellency, 411

---, surface modification, 407
---, wettability and wetting, 410, 411
Prevention of corrosion,
---, in chlorite bleaching, 486
Prograde process, 309
Properties of fibres,
---, acetate, 26
---, acrylics, 35
---, cotton, 24
---, flax, 21
---, jute, 21
---, modacrylics, 36
---, nylon, 32
---, polyester, 29
---, viscose, 24
Protein in cotton, 5, 6, 88
Polyacrylate of sugar, 172
Polycarbonate fibre, 43
Polyethylene fibres, 37
Polyester, 27-29
Polynosic fibres, 23
Polypropylene fibre, 37
Polyvinyl chloride, 39
Pollution,
-, air and water, 372
-, loads of cotton, 374, 375
-, --, synthetic fibres, 373
-, --, wool, 378
-, assessment of parameters, 372
-, problems in textiles, 371
-, tolerance limit, 373
-, effluents from bleaching, 378
-, --, desizing, 376
-, --, scouring, 377
-, --, textile auxiliaries, 379
-, --, wool scouring, 378
-, from ozon depletion, 390
-, -, uv radiation, 390
-, -, -, absorption, 390
-, -, -, protection, 391
Pot eyes, 241
Potting of woollen fabrics, 110

Quality control, 404
Quina fibre, 34

Rayon,
-, cellulose acetate, 25
-, cuprammonium, 22
-, regenerated cellulose, 23
-, --, acetate, 25, 26
-, -, protein, 20
Reactivity of mercerized cotton, 290
Reco-yet, 348
Reductive bleaching of,
---, nylon, 195
---, silk, 194
---, wool, 192
---, -, with sodium bisulphite, 193
---, -, -, sodium hydrosulphite, 193
---, -, -, sulphur dioxide, 192
---, -, -, thio-urea dioxide, 194
Relaxation of,
--, textured nylon, 121
--, -, polyester, 124
--, acrylonitrile fibres, 122

--, wool, 110
Relaxing machines, 44
Remie, 18
-, degumming of, 116
Removal of impurities,
---, from cotton, 87, 88
Retting of,
--, flax, 17
--, remie, 19
--, jute, 19
Reverse osmosis, 386
Rope,
-, detwister, 245
-, expander, 245, 246
-, piler, 218, 244
-, squeezing, 244

Saran, 39
Sanforset, process, 309
-, range, 311
Saponification of wax, 39
Scouring of,
--, blended fabrics, 125
--, cotton, 89
--, coloured woven goods, 94
--, Jute, 120
--, linen, 119
--, raw wool, 107
--, synthetic fibres, 120
--, texturised fabrics, 123
--, wool yarn and fabric, 109
Scouring of blended fabrics,
----, acetate/wool, 128
----, acrylic/cellulose, 127
----, acrylic/wool, 127
----, containing casein, 129
----, -, viscose, 128
----, polyester/acrylic, 127
----, polyester/cotton, 125
----, polyester/silk, 129
----, polyester/wool, 126
Scouring of cotton with,
----, alkaline agents, 89-94
----, blended surfactants, 99
----, caustic soda boil, 89
----, emulsion process, 183
----, lime-soda boil, 89
----, mixed alkali, 90
----, soda-ash, 90
----, soap/soda boil, 90
Scouring efficiency, determination by,
--, --, Draves test, 452
--, --, wax contant, 452
--, --, weight loss, 452
Scouring machines,
--, batch, rope, 132
--, -, jig, 137
--, -, paddle, 125
--, -, rotary drum, 125
--, -, open-width, 135
--, semi-continuous, 138
--, continuous, 138
--, -, conveyer system, 142
--, -, J-Box, 138
--, -, steamer, 138
--, -, Vaporloc, 140

--, with relaxing, 142
--, in solvent, 144
Scouring of wool,
---, emulsion, 108
---, multi-stage, 108
---, raw, 107
---, refrigeration, 109
---, suint, 109
Scouring machine for wool,
----, fabric, 149
----, Fleissner, 146
----, hank, 147
----, jet, 146
----, Lo-flo, 147
----, raw wool, 145
Scrooping, 118
Scroll roller, 245
Scutcher, 245
Sericin, 14, 178
Semi-continuous bleaching equipment,
---, pad-batch, 222
---, pad-roll, 223
---, pad-jig, 224
Semi-continuous scouring equipment,
---, pad-roll, 128
---, -, perforated cylinder, 136
---, pad-steam-roll, 138
Semi-mercerization, 289
Setting of woollen fabric, 110
Sequestering agent,
--, chemical structures, 91
--, effect of pH, 92
--, mechanism of action, 95
--, organic, 92
--, organophosphates, 93
--, in scouring, 91
--, --, function of, 91
Sequential bleaching of,
---, jute, 198
---, wool, 126
Silk,
-, degumming, 115
-, gum content, 115
-, impurities, 115
-, photomicrograph of, 114
Silk bleaching with,
---, hydrogen peroxide, 178
---, --, process, 179
---, --, recipe, 179
---, --, stabilisers, 179
Silk deguming machines,
---, continuous, 157
---, piece goods, 157
---, star, 157
Singeing of fabrics,
---, blended, 67
---, knitted cotton, 63
---, polyester, 57
---, vegetable fibres, 56
---, wool, 56
Singeing machines,
--, gas, 56-60
--, gas range, 62
--, knitted fabrics, 64
--, plate, 57
--, position of burner, 61

--, rotary cylinders, 58
Silver nitrate test, 462
Sizes,
-, analysis of, 451
-, identification of, 449
-, for filament yarn, 448
-, -, spun yarn, 449
Soap, 96
Sodium bisulphite,
--, analysis of, 457
--, bleaching of wool, 193
Sodium chlorite bleaching,
---, acetate fibres, 185
---, acrylic fibres, 185
---, activation, 183-185
---, analysis of, 456
---, cotton, 183
---, damage of cotton, 182
---, jute, 198
---, mechanism of, 182
---, merits and demerits, 187
---, nylon, 184
---, polyester, 184
---, polyvinyl alcohol, 186
---, problems of corrosion, 186
Sodium hypochlorite bleaching
---, accelerated, 166
---, analysis of, 456
---, catalytic acceleration, 351
---, cotton, 165
---, decomposition of, 105, 163
---, factors effecting, 164
---, in danger zone, 166
---, -, conjuction with H_2O_2, 166
---, -, presence of additives, 167
---, -, steaming process, 167
---, merits and demerits of, 168
---, preparation of, 162
---, rate of attack, 350
---, reaction species, 352
---, -, with cellulose, 352, 353
Sodium silicate,
--, as stabiliser, 17
--, in kier boiling, 89
Soil repellency, 411
Solar heating, 342
Solvent,
-, booster, 106
-, difficulties, 107
-, detergents, 106
-, desizing machine, 83
-, scouring, 106, 108
-, -, machine, 144, 145
-, -, of wool, 109
-, -, with trichloroethylene, 127
Spin finishing agents, 104
Starch, 69, 70
-, liquifying enzymes, 73
Stabilisers,
-, analysis of, 457
-, bleaching silk, 179
-, -, wool, 174
-, for hydrogen peroxide, 169, 170, 172
-, -, sodium chlorite, 163
-, -, - -, analysis of, 468
-, as sequestrants, 171, 172

-, -, sodium silicate, 353
Stabilisation of wool, 40
Stabilised hydrosulphite, 192
--, analysis of, 457
Stain remover,
--, emulsion scouring, 105
--, emulsified solvents, 105
--, oxalic acid 106
Steamer, 82, 231, 236
Steam consumption, 365
Stenter, 260
Stero structure of polypropylene, 38
Stoving process, 192
--, disadvantage of, 193
Stone washing, 431
Structure of cotton, 4
--, silk, 14
--, wool, 11
Suint in wool,
---, constitution of, 13, 14, 107
---, scouring, 109
Sulphur dioxide,
--, bleaching of silk, 194
--, bleaching of wool, 192
Sulphurous acid, 193
Surface activity, in water, 100
Surface tension, 94, 100, 103
Surfactants,
-, amphoteric, 98
-, anionic, 95
-, blends, 99
-, cationic, 96
-, classification of, 95
-, cloud point , 98
-, HLB, 95
-, non-ionic, 97
-, as detergents, 101
-, -, emulsifier, 103
-, -, scouring agents, 101
-, -, wetting agents, 99
-, in synthetic fibre scouring, 95
-, -, wool scouring, 95

Tallow (Triglycerides), 87
-, evaluation of, 446
Tape scouring machine, 127
Tendering of cotton, 354
-, during bleaching with bromite, 345
-, ---, hydrogen peroxide, 353, 354
-, ---, hypochlorite, 350-352
-, --, wool, 355
-, during carbonising of wool, 355
-, -, desizing, 344
-, -, scouring, 94, 346, 350
Tendering of,
--, silk, 356
--, -, during degumming, 356
--, polyester, 357
--, wool, 354
--, -, assessment of, 463-464
--, --, microscopic test, 463
--, --, solubility test, 463
--, --, swelling test, 463
Tendering of cotton, determination of,
---, --, acidic group, 462
---, --, copper number, 460

---, --, fluidity, 458
---, --, methylene blue, absorption, 461
---, --, silver nitrate test, 462
Tentering, 260
Temporary hardness, 361
--, analysis of, 442
Textone, 182
Textured fabric,
--, heat-setting of, 260
--, relaxation of, 124
--, scouring of, 123
Textured yarns,
--, spin finishes, 124
--, --, removal of, 124
Thermosetting, 256
Thiourea
-, dioxide, 177, 192, 194
-, reductive bleaching, 176
Throwing of silk, 115
Triacetate, 25
Trichloroethylene, 106, 127
Trithiocyanuric acid, 177
Tussah silk, 178

Ultrafiltration method, 388
Ultramarine blue, 180, 320
Unsaponifiable matter,
---, analysis of, 447
uv radiation, 390
--, protection from, 391, 392
--, surface coating, 414

Vaporloc machine, 140
Vapour phase treatment, 414
Vegetable fibres, 16
--, chemical composition of, 16-21
Vicara, 22
Vinyon, 39
Viscose process, 39
Viscometer for fluidity, 459
Viscosity, 350

Washing of,
--, degummed silk, 118
--, scoured goods, 91
Washing machines,
--, rope, high speed, 241
--, -, slack, 242
--, -, square beater, 243
--, -, tight, 249
--, open-width, aquatex, 253
--, --, Becoflex, 253
--, --, Ben-extracta, 230
--, --, counter-current, 254
--, --, horizontal, 255
--, --, jet, 250
--, --, open soaper, 252
--, --, --, with beater, 252
--, --, roller conveyer, 251
--, --, Rotowa, 249
--, --, -, range, 250
--, --, spray drum, 250
--, --, suction drum, 247
--, --, --, ranges, 248
Waste water,
--, activated sludge, 385

--, assessment of, 372
--, incineration of, 390
--, pollution, 370
--, -, load, 374
--, management activity, 382
--, tolerance limit, 373
--, treatment plant, 380
Waste water pollution from,
----, auxiliary effluents, 379
----, bleaching effluents, 378
----, desizing effluents, 376
----, scouring effluents, 377
Waste water, recovery of,
--, --, caustic soda, 386
--, --, sizing agents, 386
--, --, size mixtures, 389
--, --, polyvinyl alcohol, 387
--, treatments, 380
--, -, tertiary, 385
--, -, by hyperfiltration, 386
--, -, -, precipitation and coagulation, 383
--, -, -, removal of inorganic matter, 386
---, -, --, organic matter, 386
---, plant, for wool scouring effluents, 384.
Water,
-, alkalinity, 361
-, analysis of, 435
-, consumption of, 249, 360
-, dissolved matter, 362
-, hardness, 436,362
-, turbidity of, 362
-, for boiler, 362
-, mangle, 246
-, metal content, 361
-, structure, 100
-, purification process,
-, --, base exchange, 364
-, --, lime-soda, 363
-, --, soda-alum, 363
Walsh's kier, 133
Wax/es,
-, acid value, 447
-, alcohol, 7
-, chemical nature, 13
-, content, evaluation of, 439-441
-, -, in cotton, 5, 6, 87, 88
-, -, --, composition of, 7
-, -, --, evaluation of, 445
-, -, in flax, 17
-, -, -, silk, 14
-, -, -, wool, 10, 13, 107
-, iodine value, 441
-, saponification value, 89
-, --, evaluation of, 449
-, unsaponified matter, 446
Weft knitted fabrics,
---, bleaching of, 209
---, mercerization of, 303
---, singeing of, 63
Wetting agents, 99
Wetting of textiles, 95, 100
Whitler rope regulator, 246
Wild silk,14
--, bleaching of, 179
Wool,
-, action of steam, 110

-, amino acid content of, 12
-, burrs, 107, 103, 104
-, carbonising, 110-113
-, chemical composition of, 12
-, cortex, 9, 10
-, crimp, 8
-, cuticle, 9
-, degradation, 44, 354
-, -, assessment of, 463, 464
-, disulphide exchange, 111, 112
-, -, rupture, 457
-, impurities, 13
-, process sequence, 47
-, pigmented, bleaching, 176
-, rapid carbonising, 113
-, structure, 11
-, yellowness, 11
Wool bleaching with,
---, acidic peroxide, 174
---, alkaline peroxide, 174
---, emulsified peroxide, 178
---, mordanting and peroxide, 175
---, Na_3 TTCA, 177
---, photobleaching, 194
---, sequential, 176
---, sodium hydrosulphite, 193
---, sulphur dioxide, 192
Wool scouring,
--, emulsion, 108
--, refrigeration, 109
--, solvent extraction, 109
--, suint, 109
--, systems, 107
--, yarn, 109
--, -, battrice machine, 148
--, -, tape machine, 148
--, fabric, 113
--, -, Dolly, 149
--, -, rapid, 150
Wool scouring machine,
---, conventional, 145
---, Fleissner, 146
---, jet, 146
---, Lo-flo, 147
--, treatment plant, 384
Woollen fabric,
--, carbonising range, 151
--, -, and washing, 151
--, -, in solvent, 152
--, crabbing of, 110
--, decatising, 155
--, -, machine, conticrabbing, 153
---, -, continuous multi-set, 153
--, -, -, kier decatising, 154
--, -, -, lustre decatising, 156
--, -, -, NR decatising, 154
--, -, -, permanent decatising, 156
--, singeing of, 56
--, potting of, 110, 112
Wool and Worsted fabrics,
----, burling, 49
----, mending, 50
----, perching, 49

Xanthation, 23
Xylanase, 201

Yarn,
-, liquid NH_3 treatment of, 310
-, mercerization, 302
-, -, with tension, 303
-, -, machine, 302
Yarn bleaching,
--, package form, 218
--, hank form, 192
Yellowness in,
--, acrylics, 35
--, cotton, 7, 8, 160
--, flax, 202
--, jute, 199
--, silk, 178
--, nylon, 31
--, wool, 174
Yellowness of fabrics, 174
---, during bleaching, 350
---, -, scouring, 348, 350
---, -, heat-setting, 184
---, -, optical whitening, 327
---, -, potting, 83