THE EFFECT OF PLASMA TREATMENT ON THE WOOL FIBRE SURFACE

by

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April 2000

A thesis submitted for the degree of Doctor of Philosophy of the Australian National University
STATEMENT OF ORIGINALITY

I hereby declare that this thesis is my own work, except where explicitly indicated.

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ACKNOWLEDGMENTS

Firstly, I would like to thank my supervisors for providing me with the opportunity to explore this fascinating topic and the Australian Wool Corporation and the DAAD for funding my research.

Secondly, I would like to thank everyone (around the world) who has helped me with advice, expertise, equipment, and encouragement.

Thirdly I would like to thank the ANU, CSIRO, DWI, RMIT and VUT for allowing me the use of their facilities during this project.

Finally, I would like to thank my wife and family for being there to the end, of what has been a long road.
DEDICATION

I would like to dedicate this thesis to:

"The Lorax and his Swomee Swans, Truffula Trees, Brown Bar-ba-loots, and Humming Fish" (Dr Seuss, 1972).

I would like to think I have done something to keep them alive and bring them back for my children and their children’s children.
PUBLICATIONS

JOURNAL PAPERS


CONFERENCE PAPERS


CONFERENCE POSTERS

ABSTRACT

Plasma treatment has become of special relevance, during this decade, to countries facing stringent environmental restrictions on the cleanliness of waste water, such as Germany. Plasma treatment of wool, which uses no water as part of its treatment process, is likely to become increasingly popular and therefore require detailed scientific understanding of its process of modification in order to bring it to full and effective utilisation.

Radio-frequency plasma modification of the wool fibre was investigated over a wide range of conditions, using a variety of surface analytical tools. The dominant reactive species modifying the wool was found to be atomic oxygen. Ozone, electrons and UV radiation were shown to have no significant effects. Based on these results a mechanism was developed to explain the different stages of plasma modification of the wool fibre.

The mechanism begins with an initial rapid oxidation of the wool surface, and then this proceeds to form a highly oxidised surface layer. Once the fully oxidised surface layer has formed on the lipid surface, etching starts to dominate the mechanism. The lipid layer is etched away to expose protein, and the protein then continues to be etched away. During the whole etching process a fully oxidised layer is maintained on the wool fibre surface.

Further studies of microwave and corona plasma treatment were performed at the Deutsches Wollforschungsinstitut (DWI), Germany. The mechanism was successfully extended to explain the results measured for these plasma treatments. Plasma treatment of industrial wet scoured wool was carried out and the mechanism was also successful in explaining these results.

The wide range of observations of the wool surface that were carried out revealed new information about the wool fibre surface. This information was synthesised with the current state of knowledge from the literature to derive a new “dynamic surface model”. In this model, the surface of the wool fibre is responsive to its molecular environment and will adjust its exposed surface in order to minimise its surface free energy.
Table of Contents

CONTENTS

CHAPTER 1

INTRODUCTION ........................................................................... 1
1.1 BACKGROUND ........................................................................ 1
1.2 THE STRUCTURE AND COMPOSITION OF THE WOOL FIBRE .......... 3
  1.2.1 The General Structure of Wool ........................................... 3
  1.2.2 The Chemical Structure of Wool ......................................... 4
  1.2.3 The Morphology of Wool .................................................. 8
  1.2.4 The Cortex ................................................................. 11
  1.2.5 The Cell Membrane Complex ........................................... 12
  1.2.6 The Cuticle .....................................................................
    1.2.6.1 The Endocuticle ....................................................... 14
    1.2.6.2 The Exocuticle ....................................................... 15
    1.2.6.3 The Epicuticle ....................................................... 15
  1.2.7 The Surface of the Wool Fibre ......................................... 16
1.3 PLASMA TREATMENT OF WOOL ........................................ 18
  1.3.1 Survey of Literature Up To 1990 ....................................... 19
  1.3.2 Survey of International Research in Progress in 1992 ............ 26
1.4 SIGNIFICANCE AND AIMS OF THIS PROJECT ....................... 28
1.5 LAYOUT OF THE THESIS .................................................... 29

CHAPTER 2

ANALYTICAL TECHNIQUES, APPARATUS AND METHODS ............ 31
2.1 MATERIALS ......................................................................... 31
  2.1.1 Wool Samples .................................................................. 31
  2.1.2 Chemicals ....................................................................... 32
  2.1.3 Gases ........................................................................... 32
2.2 PLASMA EQUIPMENT ........................................................... 32
  2.2.1 Radio-Frequency ............................................................ 33
  2.2.2 DWI Microwave ............................................................... 35
  2.2.3 DWI Corona ................................................................... 36
2.3 OTHER WOOL TREATMENTS USED AS 'MODELS' ................. 37
  2.3.1 Ultra-Violet Irradiation & Peroxide Bleaching ....................... 37
  2.3.2 Electron Beam Irradiation ................................................... 38
  2.3.3 Ozone Treatment of Wool ................................................... 38
  2.3.4 Chlorination of Wool ....................................................... 38
  2.3.4 Lipid Removal Techniques Using Hydrolysis ......................... 39
2.4 SURFACE CHARACTERISATION ............................................ 40
  2.4.1 Electron Microscopy ......................................................... 42
  2.4.2 X-ray Photoelectron Spectroscopy ....................................... 46
  2.4.3 Allwörden Membranes ..................................................... 52
  2.4.4 Wilhelmy Plate Measurement of Contact Angles ................... 52
# Table of Contents

2.5  TEXTILE PROPERTY TESTING .................................................. 59  
  2.5.1  Yarn Properties ......................................................... 59  
  2.5.2  Fabric Printing .......................................................... 59  
  2.5.3  Fabric Dyeing ............................................................ 60  
  2.5.4  Fabric Felting Shrinkage ............................................ 61  

CHAPTER 3  
ANALYSIS OF 'MODEL' TREATMENTS ........................................... 65  

3.1  INTRODUCTION ................................................................. 65  

3.2  OBSERVATIONS ................................................................. 66  
  3.2.1  FeSEM Appearance ...................................................... 66  
  3.2.2  Allwörden Sac Formation ............................................ 72  
  3.2.3  Surface Energy Changes .............................................. 73  
  3.2.4  Surface Chemistry (XPS) ............................................. 75  
  3.2.5  Textile Property Changes ............................................ 78  

3.3  DISCUSSION ........................................................................ 79  
  3.3.1  Soxhlet Extraction with Methylene Chloride .................... 79  
  3.3.2  Ultraviolet Irradiation .................................................. 80  
  3.3.3  Electron Beam Irradiation ............................................ 81  
  3.3.4  Ozone Treatment .......................................................... 82  
  3.3.5  Hydrogen Peroxide Treatment ....................................... 82  
  3.3.6  Ultraviolet Irradiation followed by Hydrogen Peroxide  
        Bleaching ................................................................. 83  
  3.3.7  DCCA Chlorination ...................................................... 83  
  3.3.8  Alcoholic Alkali Treatment ........................................... 84  

3.4  SUMMARY ........................................................................... 86  

CHAPTER 4  
RADIO FREQUENCY PLASMA TREATMENT ..................................... 89  

4.1  INTRODUCTION ................................................................... 89  

4.2  DETERMINATION OF THE IMPORTANT REACTIVE  
     SPECIES ........................................................................... 89  
  4.2.1  The Effect of Oxygen Plasma Treatment on Wool  
        Surface Energy ............................................................. 89  
  4.2.2  Using Baffles to Isolate Charged Particles and UV  
        Radiation ................................................................. 93  
  4.2.3  The Presence of Atomic Oxygen in Oxygen, Air and  
        Argon Plasmas ............................................................ 96  
  4.2.4  Definition of Atomic Oxygen Dose as a Measure of  
        Plasma Treatment ....................................................... 99  

4.3  OBSERVATIONS OF WOOL MODIFICATIONS AS A  
     FUNCTION OF ATOMIC OXYGEN FLUX .................................. 103  
  4.3.1  Field-emission Scanning Electron Microscope  
        Appearance ............................................................... 103  
  4.3.2  Transmission Electron Microscope Appearance ............... 106  
  4.3.3  Allwörden Sac Formation ............................................ 108  
  4.3.4  Surface Energy ........................................................... 108  
  4.3.5  Surface Chemistry (XPS) ............................................. 109  
  4.3.6  Textile Property Changes ............................................ 110  
  4.3.7  Aging Effects in Plasma Treatment ............................... 110
### Table of Contents

4.4 DISCUSSION ........................................................................ 119
- 4.4.1 Comparisons with 'Model' Treatments .............................. 119
- 4.4.1 Mechanism for Oxygen Plasma Treatment of Wool ............ 120
- 4.4.2 Extension of Mechanism to Glow Plasma Treatment with Other Gases .................................................. 123
- 4.4.3 Aging Effects on Plasma Treatment ................................ 125

4.5 DYNAMIC SURFACE MODEL FOR THE WOOL FIBRE .......... 126

4.6 SUMMARY ......................................................................... 132

CHAPTER 5 ·

MICROWAVE & CORONA PLASMA TREATMENT .................. 135

5.1 INTRODUCTION .............................................................. 135

5.2 OBSERVATIONS OF MICROWAVE PLASMA TREATMENT ........ 136
- 5.2.1 Observations of Wool Modifications as a Function of Treatment Time ............................................................ 136
- 5.2.2 FeSEM Appearance ..................................................... 136
- 5.2.3 TEM Appearance ....................................................... 137
- 5.2.4 Allwörden Sac Formation ............................................ 137
- 5.2.5 Surface Energy .......................................................... 137
- 5.2.6 Surface Chemistry (XPS) ............................................ 139
- 5.2.7 Textile Property Changes ............................................ 140
- 5.2.8 Aging Effects ............................................................ 140

5.3 DISCUSSION OF MICROWAVE PLASMA TREATMENT ........ 145
- 5.3.1 Mechanism for Oxygen Microwave Plasma Treatment of Wool ........................................................................ 145
- 5.3.2 Extension of Mechanism to Microwave Plasma Treatment with Nonreactive Gases ............................................ 148
- 5.3.3 Extension of Mechanism to Microwave Plasma Treatment with Reactive Gases .................................................... 150
- 5.3.4 Aging Effects on Microwave Plasma Treatment ................ 151
- 5.3.5 Model for the Surface of Wool - Dyeing Properties .......... 151

5.4 OBSERVATIONS OF CORONA PLASMA TREATMENT ....... 152
- 5.4.1 Observations of Wool Modification as a Function of Corona Dose ................................................................. 152
- 5.4.2 FeSEM Appearance ..................................................... 153
- 5.4.3 TEM Appearance ....................................................... 153
- 5.4.4 Allwörden Sac Formation ............................................ 153
- 5.4.5 Surface Energy .......................................................... 153
- 5.4.6 Surface Chemistry (XPS) ............................................ 154
- 5.4.7 Textile Property Changes ............................................ 155
- 5.4.8 Aging Effects ............................................................ 156

5.5 DISCUSSION OF CORONA PLASMA TREATMENT ............. 161
- 5.5.1 Mechanism for Double-sided Corona Plasma Treatment of Wool ................................................................. 161
- 5.5.2 Single-sided Versus Double-sided Corona Plasma Treatments ................................................................. 163
- 5.5.3 Aging Effects on Corona Plasma Treatment .................... 163
- 5.5.4 Different Electrode Types & Machines ............................ 164

5.6 SUMMARY ......................................................................... 164
CHAPTER 6

PLASMA TREATMENT OF INDUSTRIAL WOOL FABRIC.................. 167
6.1 INTRODUCTION.............................................................. 167
6.2 OBSERVATIONS.............................................................. 167
  6.2.1 FeSEM Appearance ................................................... 167
  6.2.2 Allwörden Sac Formation .......................................... 168
  6.2.3 Surface Energy ........................................................ 168
  6.2.4 Surface Chemistry (XPS) ........................................... 169
  6.2.5 Textile Property Changes ......................................... 170
6.3 DISCUSSION OF PLASMA TREATMENT OF INDUSTRIAL
  WOOL FABRICS .............................................................. 173
  6.3.1 Mechanism for Plasma Treatment of Industrial Wool
        Fabrics ................................................................... 173
6.4 SUMMARY .................................................................... 175

CHAPTER 7

CONCLUSIONS & SUGGESTED FURTHER WORK ....................... 177
  7.1 CONCLUSIONS ............................................................ 177
  7.2 SUGGESTIONS FOR FURTHER WORK ............................ 178

APPENDIX I

ANU RADIO FREQUENCY PLASMA DATA ............................... 181

BIBLIOGRAPHY ................................................................ 185
LIST OF FIGURES

Fig.1.1 Scanning electron micrograph of a clean merino wool fibre .................... 3
Fig.1.2 General formula of a L-α-amino acid (Rippon, 1992) ......................... 4
Fig.1.3 Schematic of a wool polypeptide (Rippon, 1992) ............................... 5
Fig.1.4 Schematic of different inter-chain bonds in wool (Rippon, 1992) ........ 5
Fig.1.5 Effect of pH on ionic bonds in wool .................................................. 8
Fig.1.6 An exploded diagram of the physical structure of the merino wool fibre .. 9
Fig.1.7 Schematic diagram of the cell structure of wool ................................... 10
Fig.1.8 Transmission electron micrograph of a cross-section of a fine wool fibre ................................................................. 11
Fig.1.9 Relationship between ortho/para division and fibre crimp (Rippon, 1992) ................................................................. 12
Fig.1.10 Schematic diagram of the wool cuticle (Rippon, 1992) ........................ 13
Fig.1.11 Wool fibre after the Allwörden reaction ........................................... 15
Fig.1.12 Formula of 18-methyleicosanoic acid ............................................. 16
Fig.1.13 Model for the epicuticle of keratin fibres (Negri et al., 1993) ............... 17
Fig.2.1 Schematic diagram of the radio-frequency apparatus .......................... 34
Fig.2.2 Schematic diagram of the microwave apparatus .................................. 35
Fig.2.3 Schematic diagram of the Corona Apparatus ...................................... 36
Fig.2.4 Schematic diagram of a basic SEM .................................................... 42
Fig.2.5 Schematic diagram of a basic TEM .................................................... 44
Fig.2.6 Schematic illustration of photo-electron and subsequent Auger electron excitation ................................................................. 47
Fig.2.7 Wide Scan Survey of Untreated Wool (ABUTC) with major elements identified .................................................................................. 48
Fig.2.8 XPS elemental spectra of wool before (solid line) and after (dotted line) 2% chlorination ................................................................. 50
Fig.2.9 a) A drop of liquid on a surface b) a solid immersed into a liquid ......... 53
Fig.2.10 A typical wetting force measurement recorded by the data collection program ...................................................................................... 57
Fig.3.1 FeSEM of Untreated Wool Fibre (ABUTC) ........................................... 67
List of Figures

Fig.3.2 Untreated Wool, Soxhlet Extracted with Methylene Chloride (ABUTC) ............. 68
Fig.3.3 Wool Fibre after 40 min. UV Treatment ......................................................... 68
Fig.3.4 Wool Fibre after 180 kV E-beam Treatment .................................................. 69
Fig.3.5 Wool Fibre after H₂O₂ Treatment ................................................................. 69
Fig.3.6 Wool Fibre after 1% DCCA Treatment .......................................................... 70
Fig.3.7 Wool Fibre after 3% DCCA Treatment .......................................................... 70
Fig.3.8 Wool Fibre after KOH/MeOH Treatment ....................................................... 71
Fig.3.9 Wool Fibre after t-BuOK/t-BuOH Treatment .................................................. 71
Fig.3.10 Allwörden Sac Formation on an Untreated Wool Fibre ABUTC ................. 72
Fig.3.11 No Allwörden Sac Formation on 3% DCCA Treated Wool Fibre .............. 72
Fig.3.12 Interaction Volume Simulation of E-beam Treated Wool Fibre
(from Veitch) ........................................................................................................... 81
Fig.4.1 The Effect of Treatment Time on Surface Energy (p = 0.03 mbar,
P = 100 W) ........................................................................................................... 90
Fig.4.2 The Effect of Treatment Power on a) Surface energy, b) N₁, and Tₑ, and........... 91
Fig.4.3 The Effect of Treatment Pressure on a) Surface energy, b) N₁, and Tₑ, c) N[O] and N[O₂*] .................................................. 92
Fig.4.4 The Effect of Pressure for Different Baffles on a) N[O] and b) N[O₂*] .......... 94
Fig.4.5 Surface Chemistry of Wool after Plasma Treatment (above Transition). ....... 97
Fig.4.6 The Effect of Pressure on a) N[O] and b) Surface Energy for Air & Oxygen .......... 99
Fig.4.7 Surface Energy of Wool after Plasma Treatment (using Water) ................. 100
Fig.4.8 Surface Energy After Oxygen Plasma Treatment (P=100 W,
p = 0.03 mbar) ....................................................................................................... 101
Fig.4.9 Possible Time-Dependent Profiles for N[O] Concentration in the Chamber ........................................................................................................... 102
Fig.4.10. FeSEM after Oxygen Plasma Treatments (p = 0.03 mbar, P = 100 W) ....... 104
Fig.4.11 TEM after Oxygen Plasma Treatments (p = 0.03 mbar, P = 100 W) .......... 107
Fig.4.12. Allwörden Sac Formation as a Function of Plasma Treatment ................. 112
Fig.4.13. Surface Energy as a Function of Oxygen Plasma Treatment ................... 112
Fig.4.14. Surface Energy as a Function of Air and Argon Plasma Treatment .......... 113
Fig.4.15. XPS Elements as a Function of Oxygen Plasma Treatment ...................... 113
List of Figures

Fig.4.16. Carbon Species as a Function of Oxygen Plasma Treatment ........................................ 114
Fig.4.17. Sulfur Species as a Function of Oxygen Plasma Treatment ........................................ 114
Fig.4.18. Wool Fabric Shrinkage as a Function of Plasma Treatment ........................................ 115
Fig.4.19. Wool Fabric Colour Depth as a Function of Plasma Treatment ................................. 115
Fig.4.20. Print Colour Yield as a Function of Plasma Treatment ............................................. 116
Fig.4.21. Yarn Tensile Properties as a Function of Plasma Treatment ...................................... 116
Fig.4.22 The Effect of Sample Age on Surface Energy Changes After .................................... 117
Fig.4.23 The Effect of Sample Age on Surface Chemistry Changes Produced by .................. 118
Fig.4.24. Schematic Diagram of the Oxygen Plasma Treatment of Wool ............................... 121
Fig.4.25. Process of Oxidation of the Surface Lipid of the Wool Fibre .................................. 122
Fig.4.26 FeSEM after Argon Plasma Treatment ($p = 0.1$ mbar, $P = 300$ W, $t = 600$ s) ............... 124
Fig.4.27. Development of the Exocuticle in the Follicle (from Jones et al., 1994) ................. 127
Fig.4.28. A Modified Model For The Surface Of Wool (from Phillips, 1995) ....................... 128
Fig.4.29 Schematic diagram of the wool cuticle cell envelope (Zahn et al, 1994) ...................... 130
Fig.4.30 Model of the fibre cuticle surface membrane (Jones et al, 1997) ............................... 130
Fig.4.31 Model of the possible surface of wool ................................................................. 131
Fig.4.32 Different Surface Structures Dependent on the Overlaying Material ...................... 132
Fig.5.1. Allwörden Sac Formation After Microwave Plasma Treatment ............................... 141
Fig.5.2. Surface Energy After Microwave Plasma Treatment .............................................. 141
Fig.5.3. Surface Energy After Microwave Plasma Treatment with Argon ........................... 142
Fig.5.4. XPS Elements as a Function of Oxygen Microwave Plasma Treatment ................... 142
Fig.5.5. Carbon Species as a Function of Oxygen Microwave Plasma Treatment ...................... 143
Fig.5.6. Sulfur Species as a Function of Oxygen Microwave Plasma Treatment ..................... 143
Fig.5.7. Wool Fabric Shrinkage as a Function of Microwave Plasma Treatment .................... 144
Fig.5.8. Wool Fabric Colour Depth as a Function of Microwave Plasma Treatment .................. 144
Fig.5.9. Wool Fabric Colour Depth as a Function of Introduced Chemical Groups ............. 145
List of Figures

Fig. 5.10. Schematic Diagram of the Oxygen Microwave Plasma Treatment of Wool ................................................................. 147

Fig. 5.11 Schematic Diagram of the Argon Microwave Plasma Treatment of Wool ................................................................. 149

Fig. 5.12. Allwörden Sac Formation After Double-sided Corona Treatment ......................................................... 156

Fig. 5.13. Surface Energy as a Function of Corona Treatment .......................................................... 157

Fig. 5.14. XPS Elements as a Function of Corona Treatment .......................................................... 157

Fig. 5.15 Carbon Species as a Function of Corona Treatment .......................................................... 158

Fig. 5.16 Sulfur Species as a Function of Corona Treatment .......................................................... 158

Fig. 5.17 Wool Fabric Shrinkage as a Function of Corona Treatment ......................................................... 159

Fig. 5.18 Wool Fabric Colour Depth as a Function of Corona Treatment ......................................................... 159

Fig. 5.19 Print Colour Yield as a Function of Corona Treatment ......................................................... 160

Fig. 5.20 Effect of Age on Surface Energy for Single-sided Corona Treatment ......................................................... 160

Fig. 5.21 Schematic Diagram of the Corona Plasma Treatment of Wool ......................................................... 162

Fig. 6.1. Allwörden Sac Formation for Industrial Wool Fabric after RF Oxygen Plasma Treatment ................................................................. 170

Fig. 6.2. Surface Energy of Industrial Wool after a) RF Plasma and b) Corona Plasma Treatment ................................................................. 171

Fig. 6.3 Industrial Wool Fabric Colour Depth after RF Plasma Treatment ................................................................. 172

Fig. 6.4. Schematic Diagram of the Plasma Treatment of Industrial Wool ................................................................. 174
LIST OF TABLES

Table 1.1 Structure and amount of amino acids in wool (Rippon, 1992) ......................... 7
Table 1.2 Amino acid composition of the wool cuticle (Rippon, 1992) ....................... 14
Table 1.3 Summary of Published Research into Glow Plasma Treatment pre-1990 .............. 21
Table 1.4 Summary of Published Research into Corona Plasma Treatment pre-1990 ........... 25
Table 2.1 Summary of Surface Characterisation Techniques ........................................ 41
Table 2.2 Carbon and sulphur functionalities observed in the wool fibre ...................... 49
Table 2.3 Surface energies of the test liquids ......................................................... 58
Table 3.1 Results for Allwörden Sac Formation with Model Treatments ..................... 73
Table 3.2 Surface Energy Values for Model Treatments (DW = \(\gamma_{d} \cos \theta_{l}\)) ............ 74
Table 3.3 Surface Chemistry (XPS) of Model Treatments (nm - not measured) .......... 75
Table 3.4 Textile Property Changes Relative to Untreated Wool (ABUT) ....................... 78
Table 4.1 The Effect of Baffles on Surface Energy after Oxygen Plasma Treatment .......... 95
Table 4.2 N[O] in Argon and Oxygen Plasma using Emission Spectroscopy ................. 98
Table 4.3 Wool Surface Energy (\(\gamma_{d} \) and polar \(\gamma_{p} \)) after Plasma Treatment ........ 108
Table 4.4 Wool Surface Chemistry (XPS) After Plasma Treatment ............................ 109
Table 5.1 Wool Surface Energy Components (\(\gamma_{d} \) and polar \(\gamma_{p} \)) after Microwave Plasma Treatment ......................................................... 138
Table 5.2 Wool Surface Chemistry (XPS) After Plasma Treatment ............................. 139
Table 5.3 Wool Surface Energy Components (\(\gamma_{d} \) and polar \(\gamma_{p} \)) after Corona Plasma Treatment ................................................................. 154
Table 5.4 Wool Surface Chemistry (XPS) After Corona Plasma Treatment ................. 155
Table 6.1 Wool Surface Energy Components (\(\gamma_{d} \) and polar \(\gamma_{p} \)) after Plasma Treatment ................................................................. 169
Table 6.2 Industrial Wool Surface Chemistry (XPS) After Plasma Treatment ............... 170
LIST OF SPECIAL NAMES AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ABUT</td>
<td>Untreated wool fabrics used for the majority of this research (see Chapter 2)</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ANU</td>
<td>Australian National University</td>
</tr>
<tr>
<td>AOX</td>
<td>Adsorbable Organic Halogen</td>
</tr>
<tr>
<td>ATR/FTIR</td>
<td>Attenuated Total Reflectance / Fourier Transform Infra-Red</td>
</tr>
<tr>
<td>C</td>
<td>when added to fabric designators it indicates that the fabric has been soxhlet extracted with methylene chloride e.g. ABUTC</td>
</tr>
<tr>
<td>CI</td>
<td>Colour Index</td>
</tr>
<tr>
<td>CMC</td>
<td>Cell Membrane Complex</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Research Organisation</td>
</tr>
<tr>
<td>DAAD</td>
<td>Deutscher Akademischer Austauschdienst e. V.</td>
</tr>
<tr>
<td>DCCA</td>
<td>Dichloroisocyanuric acid</td>
</tr>
<tr>
<td>DFE</td>
<td>Differential Friction Effect</td>
</tr>
<tr>
<td>DTNW</td>
<td>Deutsches Textilinstitut Nord West</td>
</tr>
<tr>
<td>DWI</td>
<td>Deutsches Wollforschungsinstitut (German Wool Research Institute)</td>
</tr>
<tr>
<td>DWT</td>
<td>Division of Wool Technology</td>
</tr>
<tr>
<td>E-beam</td>
<td>Electron beam</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>FeSEM</td>
<td>Field-emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FS&amp;F</td>
<td>Fibre Structure &amp; Function Group</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-Red</td>
</tr>
<tr>
<td>ITF</td>
<td>Institute Textile de France</td>
</tr>
<tr>
<td>IWS</td>
<td>International Wool Secretariat</td>
</tr>
<tr>
<td>JCUT</td>
<td>Untreated fabrics used for larger sample sizes, from Dr Jeff Church (see Chapter 2)</td>
</tr>
<tr>
<td>KMUT</td>
<td>Untreated fabrics used in initial printing experiments, from Dr. Keith Millington (see Chapter 2)</td>
</tr>
<tr>
<td>KOH/MeOH</td>
<td>Potassium Hydroxide in Methanol</td>
</tr>
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</table>
Special Names and Abbreviations

\n\mbox{\textbf{n}_e} & - \text{Electron density in a plasma which is usually assumed to be the same as the ion density (m}^{-3})\\
\textbf{na} & - \text{not applicable}\\
\textbf{nm} & - \text{not measured}\\
\% \text{o.m.f.} & - \text{Percentage on mass of fibre}\\
\% \text{o.w.f.} & - \text{Percentage on weight of fibre}\\
\textbf{PRL} & - \text{Plasma Research Laboratory}\\
\textbf{RF} & - \text{Radio-frequency}\\
\textbf{RSPhysSE} & - \text{Research School of Physical Sciences and Engineering}\\
\textbf{sccm} & - \text{standard cubic centimetres per minute}\\
\textbf{SEM} & - \text{Scanning Electron Microscopy}\\
\textbf{SFM} & - \text{Scanning Force Microscopy}\\
\textbf{T}_e & - \text{Electron temperature in a plasma}\\
\textbf{t-BuOK/t-BuOH} & - \text{Tertiary Butoxide in Tertiary Butanol}\\
\textbf{TEM} & - \text{Transmission Electron Microscopy}\\
\textbf{TI} & - \text{Textile Institute}\\
\textbf{TKUT} & - \text{Untreated fabrics used in Germany, from Thomas Klausen (see Chapter 2)}\\
\textbf{XPS} & - \text{X-Ray Photoelectron Spectroscopy}\\
\textbf{UV} & - \text{Ultra-Violet}\\
\textbf{VUV} & - \text{Vacuum Ultra-Violet}\\
\textbf{Wascator} & - \text{a washing machine specified in the standard IWS TM31 for use in fabric felting shrinkage tests}
CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Plasma is often recognised as the fourth state of matter and can be formed by heating a gas until ionisation occurs. Interest in electrical discharge theory began early in the 18th century with Michael Faraday, J. J. Thomson and J. S. E. Townsend laying the foundations of the field. The term plasma was first introduced by Langmuir in 1923, while working on electrical discharges, and its history since then has been interwoven with many disciplines (Chen, 1974).

A plasma is a complex mixture of many different particle types: ions, electrons, atoms, molecules, radicals, and emitted radiation. These exist in a state of electrical quasi-neutrality and the properties of the plasma depend on the collective behaviour of the particles, as distinct from the individual particles. The plasmas used in this research are classed as 'low temperature' discharges with electron temperature, $T_e$, of $10^4$ K and $10^{-5}\%$ ionisation. The low degree of ionisation, coupled with the large relative mass of the ions and atoms compared to the electrons, results in the overall temperature of the 'glow' plasma remaining at the ambient room temperature and thus eliminates heat damage as a problem. The individual electrons are heated to their elevated temperatures by the application of a high electric field under a vacuum and the collisions between the electrons and the other particles in the plasma generate reactive species and the emission of radiation. The plasma can then be used to modify the surface of materials, for example, its widespread use in modern microchip manufacture or on polymer sheeting for printing.

Plasma provides a means of modifying the outer surface of materials whilst not affecting the bulk properties. As the reactive particles are created and transported in the gas phase, only small amounts of input materials are used, and there is very little pollution created. The major expenses are the capital costs of purchasing equipment, as the running costs of electricity and gas are very low.

Textile processing of wool requires many stages to complete. Several of the processes are affected by the surface of the wool fibre e.g. spinning, printing, and dyeing. Other processing techniques set out to deliberately modify the surface of the wool fibre, for example, chlorination of wool to prevent shrinkage or for printing. The use of plasma treatment on wool has been studied as an alternative to traditional methods of wool...
processing during the past several decades. However, it has not found any widespread use due to the difficulty in handling textile structures using the available plasma technologies.

Chlorination is a traditional water-borne chemical technique that is used to process several million kg of wool each year. However in the past decade the recognition of the importance of environmental protection and the impact of pollutants has led to the price of water and effluent treatment increasing dramatically. This increase is still continuing and has led to a growing effort around the world to find alternative means of processing that use less water and produce less effluent.

The problem of Absorbable Organic Halogens (AOX) produced during industrial processes has been of particular concern in Europe (Müller, 1992). The regulations are becoming stricter and although the amounts of AOX can be reduced by more careful control of old techniques (Augustin et al., 1991), these reductions are not adequate for the future limits expected to be implemented by the European Community (EC).

The combined effects are particularly severe for the wool processing industry. A large amount of the processing of wool, from greasy raw wool through to finished fabric, uses large amounts of water as the carrier phase. This leads to the production of large amounts of polluted water that then require extensive treatment. This is exemplified in Germany which has recently introduced very stringent water pollution laws characterised by very low emission requirements.

As a consequence, alternative techniques such as plasma treatment have been subject to a serious re-examination in the 1990's. The availability of a greater variety of more sensitive surface analytical techniques has also been a major factor in heightening interests, by providing the potential for much new information to be discovered on how the plasma treatment of wool occurs. Carnaby, 1995 in his closing remarks at the 9th International Wool Textile Research Conference in Biella identified plasma technology as having 'come of age' and that it will be an important process in enabling the wool industry to meet the current environmental challenges.
1.2 THE STRUCTURE AND COMPOSITION OF THE WOOL FIBRE

All information presented in this section is based on the following texts: Makinson, 1979, Maclaren et al., 1981, Kroschwitz, 1990, Rivett, 1991 and Rippon, 1992. It represents the generally accepted state of knowledge in the field of wool research to this date. Any new information that has been published after Rippon, 1992 is individually referenced and could still be regarded as controversial by some researchers.

1.2.1 The General Structure of Wool

Sheep have been a domesticated animal since pre-historic times and wool fabrics are known to have been used in ancient Egypt several thousand years ago. Nowadays wool is produced by a large number of sheep breeds from around the world and is classified into types according to fibre diameter and length. The research in this thesis has been done on merino wool and the following descriptions will deal primarily with this type of wool and its properties. Australia is responsible for a large amount of the world production of fine merino wool which is used primarily for the apparel market (17-25 μm mean fibre length, 60-100 mm staple length).

Raw wool off the sheep's back contains 25-70% of impurities. Wool grease, perspiration products (suint) and dirt are removed by scouring, and vegetable matter is removed during later carbonising (woollen system) or carding and combing (worsted system). This clean wool (Fig.1.1) is then processed into the desired textile product.

![Fig.1.1 Scanning electron micrograph of a clean merino wool fibre.](image)

Wool is a protein fibre classified as belonging to a group of proteins known as keratins. Unstretched wool fibres show an X-ray diffraction pattern characteristic of α-keratin (helix structure). However, clean wool is a heterogenous material containing approximately 82% keratinous proteins (characterised by a high concentration of cystine), 17% nonkeratinous proteins (relatively low cystine content) and 1% nonproteinaceous materials. These molecules are not uniformly distributed throughout
the fibre, but are concentrated in specific regions of the structure and determine the behaviour of the different parts of the wool fibre.

1.2.2 The Chemical Structure of Wool

The major components of wool are proteins, which are natural polymers of high relative molecular mass. They are essential components of all animal and plant tissue and are made up of varying proportions of L-α-amino acids, which have the formula shown in Fig.1.2, where the side-chain R group determines the type of amino acid.

![Fig.1.2 General formula of a L-α-amino acid (Rippon, 1992)](image)

Proteins are formed by the condensation of L-α-amino acids via their carboxyl and amino groups. Two amino acids condense to form a dipeptide (equation 1.1) with further condensation by the same amino acid or a different amino acid producing a linear polymer. Such a compound can be regarded as a polyamide as each group is joined by an amide group (-RCONH-). However, for a protein the repeat unit is referred to as a peptide group (-NHCHRCONH-) and compounds containing multiples of this are known as polypeptides. The peptide group is also referred to as an 'amino acid residue', because it is the part of the amino acid remaining after the condensation reaction (Equation 1.1).

\[
\text{NH}_2\text{CHR}_1\text{COOH} + \text{NH}_2\text{CHR}_2\text{COOH} \rightarrow \text{NH}_2\text{CHR}_1\text{CONHCHR}_2\text{COOH} + \text{H}_2\text{O} \quad (1.1)
\]

The amino acid content of wool has been evaluated by many workers and considerable variation in the relative proportions occurs. This could be due to several factors: individual fibre and sheep variation due to genetic origin, physiological state, nutrition, and differential weathering along the length of the fibre. Also, the method of cleaning and the analysis technique can affect the results. The structure of the amino acids in wool and the amount from a typical analysis are shown in table 1.1.

The general structure of a wool polypeptide is shown in Fig.1.3 and a significant proportion of the polypeptide chains in wool are believed to be in the form of an α-helix.
The individual peptide chains in wool are held together by covalent crosslinks and noncovalent interactions: hydrogen bonds, ionic bonds and hydrophobic bonds. These bonds can be between separate chains (inter-chain) or between different parts of the same chain (intra-chain). Inter-chain bonds are more important when determining the properties of the wool fibre (Fig.1.4)
<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrocarbon side-chain</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Glycine             | -NH
|                     | CH
|                     | -CO     | 8.4 |
| Alanine             | -NH
|                     | CH-CH₃  | -CO     | 5.4 |
| Phenylalanine       | -NH
|                     | CH-CH₂-CH₃- | -CO     | 2.9 |
| Valine              | -NH
|                     | CH-CH  | -CO     | 5.6 |
| Leucine             | -NH
|                     | CH-CH  | -CO     | 7.7 |
| Isoleucine          | -NH
|                     | CH-CH₂-CH₃-CH₂ | -CO     | 3.1 |
| **Polar side-chain** |               |      |
| Serine              | -NH
|                     | CH-CH₂-CH  | -CO     | 10.4 |
| Threonine           | -NH
|                     | CH-CH  | OH-CH₃ | -CO     | 6.4 |
| Tyrosine            | -NH
|                     | CH-CH₂-CH-CH₂-OH | -CO     | 3.8 |
| **Acidic side-chain** |               |      |
| Aspartic Acid *     | -NH
|                     | CH-CH₂-CO₂H | -CO     | 6.5 |
| Glutamic Acid **    | -NH
<p>|                     | CH-CH₂-CH₂-CO₂H | -CO     | 11.9 |</p>
<table>
<thead>
<tr>
<th>Basic side-chain</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Histidine</td>
<td><img src="image" alt="Histidine structure" /></td>
<td>0.9</td>
</tr>
<tr>
<td>Arginine</td>
<td><img src="image" alt="Arginine structure" /></td>
<td>6.9</td>
</tr>
<tr>
<td>Lysine</td>
<td><img src="image" alt="Lysine structure" /></td>
<td>2.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulphur-containing side-chain</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methionine</td>
<td><img src="image" alt="Methionine structure" /></td>
<td>0.5</td>
</tr>
<tr>
<td>Cystine ***</td>
<td><img src="image" alt="Cystine structure" /></td>
<td>10.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heterocyclic side-chain</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tryptophan</td>
<td><img src="image" alt="Tryptophan structure" /></td>
<td>0.5</td>
</tr>
<tr>
<td>Proline</td>
<td><img src="image" alt="Proline structure" /></td>
<td>6.6</td>
</tr>
</tbody>
</table>

* Includes asparagine residues
** Includes glutamine residues
*** Includes oxidation by-product, cysteic acid

Table 1.1 Structure and amount of amino acids in wool (Rippon, 1992)
The disulphide crosslinks are comparable with the rungs in a ladder and are responsible for the greater stability and lower solubility of keratin, as compared to most proteins. Cleavage or rearrangement of the disulphide bonds in wool is a major part of important industrial processes such as shrinkproofing and setting.

Hydrogen bonds occur in large numbers between suitable donor and acceptor groups. Ionic bonds occur between the approximately equal numbers of basic amino and acidic carboxyl groups present in wool and are responsible for the amphoteric nature of wool and its ability to combine with large amounts of acids and bases. They are also referred to as 'salt linkages' and at neutrality both types of groups are fully ionised and the net electrical charge on the wool is zero (Fig.1.5)

$$H_3N^+\text{-wool-COOH} \longleftrightarrow H_3N^+\text{-wool-COO}^- \longleftrightarrow H_2N\text{-wool-COO}^-$$

<table>
<thead>
<tr>
<th>acidic</th>
<th>isoelectric</th>
<th>basic</th>
</tr>
</thead>
</table>

**Fig.1.5 Effect of pH on ionic bonds in wool**

Hydrogen bonds and salt linkages contribute significantly to the physical properties of dry wool and both are progressively disrupted by water adsorption. This is the reason that physical tests to determine the effects of chemical treatments on wool strength are usually carried out in the wet state so that the large contribution of salt linkages and hydrogen bonds to dry wool do not mask any damage that has occurred.

Hydrophobic bonds are formed by the approach of two nonpolar side-chains, with the consequent exclusion of nearby water molecules. This type of bonding is thought to contribute to the mechanical strength of keratin, particularly at high water contents.

Finally, wool is not chemically homogenous and contains an estimated 170 different types of protein molecule. These have been classified into three main groups: low-sulphur proteins, high-sulphur proteins, and high-glycine/high-tyrosine proteins. The different locations of these proteins is discussed in Section 1.2.3. Wool also contains about 1% by mass of lipid material. This material is believed to be concentrated in the intercellular regions of the fibre and is made up of sterols, polar lipids, fatty acids, and trace amounts of phospholipids.

### 1.2.3 The Morphology of Wool

The physical structure (Fig.1.6) of the wool fibre is a complex one, reflecting the chemical heterogeneity discussed above.
THE STRUCTURE OF A MERINO WOOL FIBRE

- High-S proteins
- High-tyr proteins
- Low-S proteins
- Microfibril (intermediate filament)
- Matrix
- Macrofibril
- Nuclear remnant
- Epicuticle
- Exocuticle
- Endocuticle
- Cuticle
- Root end
- Para-cortical cell
- Ortho-cortical cell
- Meso-cortical cell
- Cortex

Chapter 1. *Introduction*

The different components and their compositions have been determined by a complementary series of techniques:

a) chemical analysis of whole fibre digests

b) selective staining of specific chemical groups observed under the TEM

c) preferential separation or dissolution of components, followed by observation under the electron microscope and chemical analysis of the separate compounds.

Major advances have taken place over the past 50 years and continued research reveals more information every year.

Merino wool contains two types of cells (Fig.1.7). The cells of the cortex make up the internal part of the fibre (86.7% o.m.f.). The cells of the cuticle cover the surface of the wool (10% o.m.f.). Separating each cell from its neighbour is the cell membrane complex (3.3% o.m.f.). Each individual cuticle and cortical cell is surrounded by a thin, chemically resistant proteinaceous membrane, considered to be part of the cell membrane complex, or epicuticle on the fibre surface. Thus the wool fibre can be considered as a biological composite of the cuticle and cortical cells held together by the cell membrane complex.

Fig.1.7 Schematic diagram of the cell structure of wool

Direction of the fibre root in the sheepskin -->
1.2.4 The Cortex

The cortex comprises the majority of the cross-section of the wool fibre and is largely responsible for its mechanical behaviour. Each cortical cell is approximately 100 μm long and 3-6 μm wide. These are arranged in an overlapping and closely packed manner parallel to the fibre axis. Each cell is surrounded by the cell membrane complex, which is a continuous phase extending throughout the whole fibre.

Fine wools contain two types of cortical cells: orthocortical and paracortical (Fig.1.8). Sometimes a third type of cell, mesocortical, is present at the boundary between the orthocortex and paracortex. However, if present, it usually accounts for less than 4% of the whole fibre.

![Fig.1.8 Transmission electron micrograph of a cross-section of a fine wool fibre (orthocortex at top, paracortex at bottom left)](image-url)

For merino wools the cortex is bilaterally segmented with the orthocortex accounting for over 50% of the fibre cross-section. This produces the natural crimp of the wool
fibre with the orthocortex always oriented towards the outside radius of the crimp curl (Fig.1.9).

Fig.1.9 Relationship between ortho/para division and fibre crimp (Rippon, 1992)

The cortical cells are made up of rod-like elements of crystalline proteins (microfibrils) embedded in a relatively amorphous matrix. The microfibrils are sometimes known as 'intermediate filaments' and are approximately 7 nm in diameter with their length being uncertain but believed to be at least 1 µm. The microfibrils are relatively rich in the low-sulphur proteins which are dominated by the amino acids that favour $\alpha$-helix formation: lysine, aspartic acid, glutamic acid, and leucine. The matrix material is dominated by high-sulphur and high-glycine/high-tyrosine proteins.

Inside a cortical cell the microfibrils are grouped together in aggregates, known as macrofibrils. These are cylindrical units, 0.3 µm in diameter and having lengths ranging from 10 µm to the entire cortical cell. The cells of the cortex also contain around 13% of nonkeratinous proteins which consist of nuclear remnants and intermacrofibrillar material.

1.2.5 The Cell Membrane Complex

The cell membrane complex (CMC) is a continuous phase about 25 nm wide that provides adhesion between the cells of the wool fibre. The composition of the CMC is still being researched and is open to debate. However, there have been three major components identified: an easily swollen 'intercellular cement' consisting of lightly crosslinked nonkeratinous protein, a lipid component, and the chemically resistant proteinaceous membrane that surrounds each cortical and cuticle cell.

The CMC is known to have a large influence on the mechanical and chemical properties of the wool fibre. Its low mechanical strength controls abrasion resistance and it provides the pathway for the diffusion of dyes and reagents into the fibre.
1.2.6 The Cuticle

The cuticle cells comprise only 10% of a merino wool fibre. Yet as the outermost surface of the wool fibre they control the interaction of the wool fibre with its environment. They dominate many important properties including wettability, tactile properties and felting.

The cuticle cells, or scales, vary in thickness from 0.3 to 0.5 µm and are about 30 µm in length and 20 µm in width. They overlap like tiles on a roof with the amount of overlap being approximately 15% for fine wools and up to 15 layers in very coarse wools. Shoulders or 'false' scale edges also occur on a significant number of cells. The edges of the scales all point from the root to the tip of the fibre. This arrangement of the scales gives rise to the 'differential friction effect' (DFE). The coefficient of friction along the fibre is much larger in the tip to root direction than it is in the root to tip direction. It is the DFE that produces the ability of wool to felt when the fibre assembly is agitated, particularly in water. The fibres preferentially move in the direction of their roots and thus produce a smaller, denser fabric.

The cuticle has a higher cystine content than whole wool and contains a higher proportion of nonhelix-forming proteins. Thus, it is less extensible and is thought to be more amorphous in structure than the cortex. Under the transmission electron microscope the cuticle can be seen to be divided into several distinct layers as illustrated schematically in Fig.1.10.

![Schematic diagram of the wool cuticle](image)

Fig.1.10 Schematic diagram of the wool cuticle (Rippon, 1992)
Chapter 1. Introduction

The main distinguishing factor is the amount of cystine present in each layer (Table 1.2) The epicuticle is a very thin membrane covering the surface of the cuticle. Underneath are the two layers of the exocuticle (A and B layers) laid on top of the endocuticle.

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>Whole Wool</th>
<th>Cuticle</th>
<th>Exo-</th>
<th>Epi-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Whole</td>
<td>Endo-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alanine</td>
<td>5.4</td>
<td>5.8</td>
<td>6.7</td>
<td>6.4</td>
</tr>
<tr>
<td>Arginine</td>
<td>6.9</td>
<td>4.3</td>
<td>5.0</td>
<td>4.8</td>
</tr>
<tr>
<td>Aspartic Acid (1)</td>
<td>6.5</td>
<td>3.5</td>
<td>7.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Citrulline (2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1/2-Cystine (3)</td>
<td>10.3</td>
<td>15.6</td>
<td>3.1</td>
<td>19.9</td>
</tr>
<tr>
<td>Glutamic Acid (4)</td>
<td>11.9</td>
<td>8.7</td>
<td>10.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Glycine</td>
<td>8.4</td>
<td>8.2</td>
<td>8.2</td>
<td>-</td>
</tr>
<tr>
<td>Histidine</td>
<td>0.9</td>
<td>0.8</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>3.1</td>
<td>2.7</td>
<td>3.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Leucine</td>
<td>7.7</td>
<td>6.1</td>
<td>9.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Lysine</td>
<td>2.9</td>
<td>2.7</td>
<td>4.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Methionine</td>
<td>0.5</td>
<td>0.3</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>2.9</td>
<td>1.7</td>
<td>3.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Proline</td>
<td>6.6</td>
<td>10.5</td>
<td>8.9</td>
<td>12.3</td>
</tr>
<tr>
<td>Serine</td>
<td>10.4</td>
<td>14.3</td>
<td>10.7</td>
<td>11.9</td>
</tr>
<tr>
<td>Threonine</td>
<td>6.4</td>
<td>4.4</td>
<td>5.5</td>
<td>3.9</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>3.8</td>
<td>2.8</td>
<td>3.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Valine</td>
<td>5.6</td>
<td>7.5</td>
<td>7.5</td>
<td>8.2</td>
</tr>
</tbody>
</table>

(1) Includes asparagine residues
(2) Includes hydrolysis by-product, ornithine
(3) Includes oxidation by-product, cysteic acid
(4) Includes glutamine residues

Table 1.2 Amino acid composition of the wool cuticle (Rippon, 1992)

1.2.6.1 The Endocuticle

The endocuticle is a well defined layer about 0.2 µm thick and represents about 40% of the cuticle. It is bordered on the underside by the cell membrane complex which keeps
it separate from other cuticle cells and from the cortical cells. It has a low disulphide crosslink density which results in it being classified as a nonkeratinous component of the fibre. This results in the endocuticle being more susceptible to chemical attack and mechanically weaker than the exocuticle.

1.2.6.2 The Exocuticle

The exocuticle lies above the endocuticle, is about 0.3 µm thick, represents about 60% of the cuticle and may partially extend around the edge of the scale. The exocuticle contains the majority of the cystine in the cuticle, has double the disulphide crosslink density of whole wool and is classified as a keratinous protein. Under the transmission electron microscope it can be seen to be divided into two layers. The outer layer is known as the a-layer and is believed to account for 30-50% of the thickness of the exocuticle. The a-layer is denser and is believed to have a higher cystine content than the lower b-layer.

1.2.6.3 The Epicuticle

The thin membrane present on the surface of the cuticle cell is known as the epicuticle. It is resistant to acids, alkalis, oxidising agents, and enzymatic attack. It was first observed by Allwörden in 1916 and was defined as the membrane raised as bubbles or sacs along the fibre after immersion in chlorine water (Fig.1.11).

![Fig.1.11 Wool fibre after the Allwörden reaction](image)

This phenomenon is now known as the Allwörden reaction and is the result of the formation of osmotically active oxidation products derived from the protein material beneath the semipermeable epicuticle. Treatment of wool with chlorine results primarily in the oxidation of the disulphide bonds in cystine, to produce sulphonic acid residues, along with some cleavage of peptide bonds. These two reactions produce the soluble peptides responsible for the increase in osmotic pressure that stretches the epicuticle outwards. In order to generate sufficient sulphonic acid groups to produce Allwörden bubbles, a high concentration of cystine must be present beneath the epicuticle. The a-layer contains approximately 35% half-cystine which represents 1 in every 2.7 amino acid residues and is the highest level in the wool fibre. However, the
endocuticle and cortical cells contain much lower levels of half-cystine (Table 1.2) and do not exhibit Allwörden bubbles on isolated cells. The half-cystine levels are presumed to be too low to produce the increase in osmotic pressure required to raise the membrane.

Sacs are also produced on wool fibres by immersion in bromine water in the Herbig reaction. However, the bubbles produced are different from the Allwörden reaction with the surrounding membrane appearing thicker and including material from layers of the cuticle beneath the epicuticle.

Historically the epicuticle was thought to be an unique component of the wool fibre, but it is now known to be part of the resistant membrane system that surrounds all cuticle and cortical cells.

1.2.7 The Surface of the Wool Fibre

The surface of the wool fibre consists of the epicuticle and the small part of the CMC that extends to the fibre surface. This surface, once surface grease has been removed, has long been known to be hydrophobic, which was difficult to explain if the epicuticle was composed solely of protein.

Several different models had been proposed in the past (Makinson, 1979) but the latest model began when Leeder and Rippon, 1985 suggested that the surface of the wool fibre is covered with a very thin fatty layer, which they termed the F-layer, that is chemically bound to the epicuticle. Evans et al., 1985 confirmed the presence of bound fatty acids, with the major component being an unusual C$_{21}$ fatty acid containing a branched chain. They proposed that it was covalently bound to the surface of the epicuticle via an ester bond to a serine residue. Kalkbrenner et al., 1990 showed that the C$_{21}$ fatty acid is primarily located in the cuticle. TEM work by Negri et al., 1996 supported the proposal that the covalently bound fatty acids that completely surround the cuticle cells are an integral part of the cuticle cell membrane and are not part of the CMC in the cortex.

The C$_{21}$ fatty acid was since found to be present in the hair of other mammals and has been identified (Negri et al., 1991) as 18-methyleicosanoic acid (Fig. 1.12)

\[
\text{CH}_3\text{CH}_2\text{CH} (\text{CH}_2)_{16} \text{COOH}
\]

\[
\text{CH}_3
\]

Fig. 1.12 Formula of 18-methyleicosanoic acid

The next significant steps towards formulating a model for the wool fibre surface were taken by Negri et al., 1992, 1993, 1993. Their work suggested that the 18-
methyleicosanoic acid is bound to the protein of the epicuticle by a thioester bond to cysteine residues (also Evans & Lanczki, 1997). They found that there is sufficient bound 18-methyleicosanoic acid to form a hydrophobic layer on the exterior of each cuticle cell and that it appears to reside on the exterior of the fibre. Thus they proposed the following model (Fig.1.13).

![Diagram of the epicuticle model](image)

**Fig.1.13 Model for the epicuticle of keratin fibres (Negri et al., 1993)**

Negri *et al.*, 1992, 1993, 1993 view the epicuticle membrane as a protein heavily acylated with fatty acids, probably by means of cysteine residues. They imagine the protein would be folded in such a way as to present an abundance of cysteine residues at the protein surface. The estimated composition of the epicuticle is 25% lipid and 75% protein.

Support for their model is provided by published XPS results which have identified very high amounts of carbon in the outer 3 nm of the cuticle cells (Carr *et al.*, 1986, Dowling *et al.*, 1988, Körner *et al.*, 1990, Ward *et al.*, 1993, Brack *et al.*, 1996) and SIMS which has primarily yielded hydrocarbon fragments from the surface layer (Ward *et al.*, 1993, Brack *et al.*, 1996).

Ward *et al.*, 1993 used overlayer calculations on their XPS results to derive a lipid thickness over the wool surface of 0.9 nm. However, this result must be viewed with caution as the theory for overlayer calculations are derived for uniform thin flat surfaces (Briggs & Seah, 1990, Denning *et al.*, 1995), which is not the case for the
assembly of wool fibres in the wool fabric that was measured by Ward et al., 1993. Also the conformation of the lipid chains may differ between an anhydrous vacuum and normal biological conditions (Peet et al., 1995, Horr, 1997).

1.3 PLASMA TREATMENT OF WOOL

Plasma treatment of wool and other textile fibres has been reported in the literature since Kassenbeck, 1964. The plasma treatment of wool has been studied in two distinct phases of activity. There was initial interest in the 1970’s and 1980’s which concentrated on evaluating whether plasma treatment could be used successfully with wool. A number of different glow and corona apparatus were built and shown to produce useful modifications. A review of the earliest work is provided by Pavlath, 1974. Later work in this period also concentrated on trying to understand how the modifications were produced by the plasma. However, plasma treatment was not taken up by industry as the traditional wet chemical methods had lower capital costs and were more familiar to the textile industry.

In the early 1990’s, a second phase of research began. There was an upsurge in interest around the world as water, chemical, and pollution costs grew increasingly expensive, due to the rise in concern for environmental protection and consequent stricter legislative controls on effluent. This has meant that the older wet chemical methods now have much higher running costs than previously. As a result plasma treatment has become a more viable option. Dr. W. Rakowski received the Biella Wool Textile Award (Rakowski, 1992) for his comprehensive review of plasma treatment of wool and since then a number of pilot machines are believed to be undergoing testing with manufacturers in Europe and Japan (Byrne et al, 1994, 1995).

The research reported in this thesis was begun early in the second phase. Initially the research reported in the literature was confined mainly to Japan and Europe, up until 1995. At that time the 9th Quinquennial International Wool Textile Research Conference was held in Biella, Italy, where 14 papers on plasma treatment were presented. Since 1995 a small number of additional papers have been published.

This review of plasma treatment has been divided into two sections, based on these two phases. The first section summarises the state of knowledge at the beginning of this research. The second section reports on the meetings held with researchers in Europe in 1992. A six week visit to Europe had been undertaken, as the second phase of research was only just getting underway and hardly any reports had entered the literature. These discussions provided useful information on the directions being taken in current research and the initial findings of these groups.
Chapter 1. Introduction

The research is also divided into 2 parts: low pressure 'glow' plasma and atmospheric 'corona' plasma treatment. This is done because the mechanisms producing the modifications may be different and so the results should be interpreted separately.

1.3.1 Survey of Literature Up To 1990

Glow Plasma

Research into a wide variety of gases, textile properties, morphological changes, chemical changes, and analysis techniques had been undertaken in order to study the glow plasma modification of the wool fibre (Table 1.3). From this wide range of studies a number of key overall conclusions can be drawn:

1. For the majority of cases it has been found that plasmas involving oxygen react more rapidly and effectively than plasmas formed with other gases (Lee et al, 1974, 1975, 1976, Millard 1972, Pavlath et al, 1971, 1975, Gregorski et al, 1980, Rakowski et al, 1982, Ryu et al, 1987).

2. The frictional coefficients (wet and dry) of the wool fibre can be increased whilst the differential friction effect (DFE) is reduced. This change to the fibre surface friction produced significant improvements in yarn strength, abrasion resistance, and various other mechanical properties of wool top/yarn/fabric, as well as reducing felting (Section 1.2.6) shrinkage (Szklarek et al, 1986, Ryu et al, 1987, Rakowski, 1989).

3. The wool fibre surface is modified from hydrophobic to hydrophilic, so that it wets as easily as cotton (Rakowski et al, 1982, Yasuda et al, 1984). The changes to the surface also increase acid dye uptake/fastness (Pavlath et al, 1971), and fabric whiteness is improved (Gregorski et al, 1980, Rakowski, 1989).

4. Only the surface of the wool fibre is modified with no damage to the internal structure of the fibre. Plasma treatments of extremely long duration are required before physical modifications occurring to the surface of the wool fibre can be observed. These changes manifest as pits, longitudinal grooves, and cracks in the surface of the wool scales (Kassenbeck, 1964, Willard, 1975, Ward, 1975, Gregorski et al, 1980, Yasuda et al, 1984). No modification of the surface of the wool fibre can be observed using SEM (with metal coating) for 'normal' treatment levels (Pavlath et al, 1971, Lee 1976, Ryu et al, 1987).

5. The changes to the fibre surface chemistry measured by XPS show that the relative amount of oxygen and nitrogen on the surface of the wool fibre is increased with a concomitant decrease in carbon. The later more detailed XPS studies showed that
<table>
<thead>
<tr>
<th>Variables</th>
<th>Papers Investigating Glow Plasma Treatment of Wool up to 1990</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas Used</strong></td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>Pavlath* 1971; Rakowski* 1982</td>
</tr>
<tr>
<td>Helium</td>
<td>Pavlath* 1971; Yaseda* 1984; Rakowski* 1982</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Pavlath* 1971; Rakowski* 1982</td>
</tr>
<tr>
<td>Argon</td>
<td>Pavlath* 1971, 1975; Millard* 1972, 1972; Ward, 1975; Lee* 1976; Rakowski* 1982; Ryu* 1987</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Lee* 1974, 1975; Millard, 1975; Pavlath* 1975; Ward, 1975; Gregorski* 1980; Yasuda* 1984; Rakowski* 1982; Ryu* 1987</td>
</tr>
<tr>
<td>Tetrafluoromethane</td>
<td>Yasuda* 1984; Rakowski* 1982; Ryu* 1987</td>
</tr>
<tr>
<td>Tetramethylsilane</td>
<td>Ryu* 1987</td>
</tr>
<tr>
<td><strong>Textile Property Improvement</strong></td>
<td></td>
</tr>
<tr>
<td>Mechanical</td>
<td>Kassenbeck 1964; Pavlath* 1971; Lee* 1974, 1975; Gregorski* 1980; Rakowski* 1982; Yasuda* 1984; Szklarek* 1986; Rakowski 1989</td>
</tr>
<tr>
<td>Dyeing</td>
<td>Pavlath* 1971</td>
</tr>
<tr>
<td>Printing</td>
<td>Rakowski 1989</td>
</tr>
<tr>
<td>Surface Energy</td>
<td>Rakowski* 1982; Yasuda* 1984</td>
</tr>
<tr>
<td>Fibre Friction</td>
<td>Szklarek* 1986; Ryu* 1987; Rakowski 1989</td>
</tr>
<tr>
<td>Yellowness Index</td>
<td>Gregorski* 1980; Rakowski 1989</td>
</tr>
<tr>
<td>Oil Repellency</td>
<td>Millard* 1972; Lee* 1975</td>
</tr>
<tr>
<td>Morphological Modification</td>
<td>Kassenbeck 1964; Willard 1975; Ward, 1975; Gregorski* 1980; Yasuda* 1984</td>
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<td>----------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Surface Etching</td>
<td>Pavlath* 1971; Lee 1976; Ryu* 1987</td>
</tr>
<tr>
<td>No Surface Changes</td>
<td>Gregorski* 1980; Yasuda* 1984</td>
</tr>
<tr>
<td>Weight Loss</td>
<td></td>
</tr>
</tbody>
</table>

| Chemical Modification            | Millard 1975; Lee* 1976; Pavlath* 1976; Gregorski* 1980               |
| Surface Oxidation                | Millard 1975; Lee* 1976; Pavlath* 1976; Gregorski* 1980               |
| Higher N/C ratio                 | Millard 1975; Lee* 1976; Pavlath* 1976; Gregorski* 1980               |
| Carbon Oxidation                 | Millard 1975; Bradley* 1992                                          |
| Sulphur Oxidation                | Kassenbeck 1964; Millard 1972, 1972; Millard* 1972; Pavlath* 1976; Bradley* 1992 |
| No Fibre Damage                  | Kassenbeck 1964; Millard 1975; Lee 1976; Rakowski 1989               |
| Polymer Grafting                 | Millard* 1972, 1972; Lee* 1975; Pavlath* 1976; Yasuda* 1984           |
| Surface Lipid Removal            | Lee 1976                                                              |

<table>
<thead>
<tr>
<th>Analysis Technique Used</th>
<th>Kassenbeck 1964; Pavlath* 1971; Ward, 1975; Yasuda* 1984; Ryu* 1987</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Kassenbeck 1964</td>
</tr>
<tr>
<td>TEM</td>
<td>Kassenbeck 1964</td>
</tr>
<tr>
<td>X-Ray Diffraction</td>
<td>Lee 1976</td>
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<tr>
<td>Allwörden Sacs</td>
<td>Gregorski* 1980</td>
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<tr>
<th>Postulated Reaction Mechanism</th>
<th>Millard* 1972; Lee* 1974</th>
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<tbody>
<tr>
<td>UV</td>
<td>Millard* 1972; Lee* 1974, 1975; Pavlath* 1975</td>
</tr>
<tr>
<td>Electrons</td>
<td>Millard 1972; Millard* 1972; Lee* 1974, 1975, 1976; Pavlath* 1975</td>
</tr>
<tr>
<td>Reactive Species</td>
<td>Millard 1972; Millard* 1972; Lee* 1974, 1975, 1976; Pavlath* 1975</td>
</tr>
</tbody>
</table>


6. Plasma treatment is stable over time for several years (Gregorski et al., 1980).

7. When treatment variables such as power or time are increased, the modifications increase gradually or remain constant, depending on the apparatus used. No clear pattern to these observations was apparent. Extended treatments lead eventually to yellowing and then burning as too much energy is transported to the fibre surface (Gregorski et al., 1980, Yasuda et al., 1984). Prolonged plasma treatment was found to affect the lipid on the surface of the wool with the X-ray diffraction pattern being destroyed (Lee 1976).

8. Plasma effects are not produced by heat damage to the fibre (Lee, 1976). Plasma afterglow produces similar effects, although at a slower rate, to treatments performed inside the plasma (Lee et al., 1975, Pavlath et al., 1975). Studies showed that plasma polymerisation or non-volatile monomer grafting onto the wool surface is possible (Millard et al., 1972. Lee et al., 1975, Pavlath et al., 1976, Yasuda et al, 1984).

9. Electrons and other excited particles in the plasma were most commonly postulated as being responsible for producing the effects of plasma treatment. UV photons are also suggested as having a secondary effect in some gas plasmas. However, none of these possible reactants were directly measured in any of the plasma devices and no quantitative evidence has been published to support these theories (Millard et al., 1972, Lee et al., 1974, Pavlath et al., 1975).

10. Several different apparatus were built to treat wool in yarn and fabric form, with radio-frequency (RF) plasma generation being the most common form of plasma excitation (Kassenbeck 1964, Pavlath et al., 1971, 1976, Rakowski et al., 1982).

**Corona Plasma**

Corona plasma treatment has the economic advantage over glow plasma of taking place at atmospheric pressure and thus avoiding the expense of purchasing vacuum pumps. However, less control of the gas mixture is possible and it is more difficult to separate out individual reaction processes occurring in the corona, when compared to glow plasma. Thus, in the literature fewer gases, textile properties, morphological changes, chemical changes, and analysis techniques have been studied (Table 1.4) and the results are less clear-cut. The key overall results can be summarised as follows.

1. Air, with a small amount of chlorine gas and water vapour added, produced a much more rapid reaction than air, or any other gas, alone (Thorsen, 1968). However, in
Chapter 1. Introduction

another study it was the presence of oxygen that was determined to be the crucial ingredient for modifications to be observed (Benaissa et al, 1978). If the temperature of the corona cell was elevated to ~90 °C the levels of modification were also found to increase (Thorsen, 1968).

2. The frictional coefficients of the wool fibre are increased (Thorsen et al, 1966, 1971, Beljajew et al, 1975). Thus yarn strength, abrasion resistance, and other mechanical properties of wool top/fabric are increased and felting shrinkage reduced (Thorsen et al, 1966, 1970, Bateup et al, 1981, Bhalla et al, 1986). A harsher handle (the quality assessed by the reaction obtained from the sense of touch) is also produced, but the addition of softeners eliminated this problem (Thorsen, 1971).

3. The wool fibre is changed from hydrophobic to hydrophilic, and acid dye uptake is improved (Anderson et al, 1970, Belin et al, 1983). The surface was shown to be have become more polar, with an excess of negative groups, and shrinkresist polymers spread and adhered more easily after plasma treatment (Bateup et al, 1981). Increases in the wool fibre's yellowness after treatment could be eliminated by scouring or solvent treatment (Wakelyn et al, 1972).

4. The plasma modifications are limited to the cuticle, with no damage to the fibre bulk properties. Corona treatments of extremely long duration are required before physical modifications can be observed on the surface of the wool fibre. Severe etching and damage is caused by the extremely long treatments. The epicuticle was observed to remain intact after 'typical' corona treatments. No modification of the surface of the wool fibre can be observed by SEM (using metal coating) for 'normal' treatment levels (Thorsen et al, 1966, Wakelyn et al, 1972, Belin et al, 1983).

5. The XPS measurements of changes in surface chemistry showed that the relative amount of oxygen and nitrogen on the surface of the wool fibre is increased, with a concomitant decrease in carbon, and sulphur groups on the surface are oxidised (Pavlath et al, 1976, Benaissa et al, 1978).

6. Corona was found by Thorsen, 1971 to produce a large initial increase in fibre friction, that decreased over a period of one month, to a stable moderate increase. Yet Belin, 1971 using a different apparatus observed modifications to be stable in long term storage.

7. Increasing power or time of the treatments tended to increase the modifications, until a maximum was reached, but this depended on the apparatus used and none of the studies investigated these variables in a systematic manner (Thorsen et al, 1972, 1966, 1970, Belin, 1971, Benaissa et al, 1978).
<table>
<thead>
<tr>
<th>Variables</th>
<th>Papers Investigating Corona Plasma Treatment of Wool up to 1990</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas Used</strong></td>
<td></td>
</tr>
<tr>
<td>Air + chlorine + water</td>
<td>Thorsen 1968</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Thorsen* 1966; Thorsen 1968; Belin, 1971; Benaissa* 1978</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Thorsen* 1966; Thorsen 1968; Belin, 1971</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>Thorsen 1968; Benaissa* 1978</td>
</tr>
<tr>
<td>Argon</td>
<td>Belin, 1971</td>
</tr>
<tr>
<td>Bromine</td>
<td>Thorsen 1968</td>
</tr>
<tr>
<td><strong>Textile Property Improvement</strong></td>
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</tr>
<tr>
<td>Dyeing</td>
<td>Thorsen* 1966; Beljajew* 1975; Belin* 1983</td>
</tr>
<tr>
<td>Printing</td>
<td></td>
</tr>
<tr>
<td>Surface Energy</td>
<td>Anderson* 1970; Thorsen 1971; Bateup* 1981; Belin* 1983</td>
</tr>
<tr>
<td>Fibre Friction</td>
<td>Thorsen* 1966; Thorsen, 1971; Beljajew* 1975</td>
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<tr>
<td>Yellowness Index</td>
<td>Wakelyn* 1972</td>
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<tr>
<td>Oil Repellency</td>
<td></td>
</tr>
<tr>
<td>Morphological Modification</td>
<td>Benaissa* 1978; Belin* 1983</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Surface Etching</td>
<td></td>
</tr>
<tr>
<td>No Surface Changes</td>
<td></td>
</tr>
<tr>
<td>Weight Loss</td>
<td></td>
</tr>
<tr>
<td>Chemical Modification</td>
<td>Pavlath* 1976</td>
</tr>
<tr>
<td>Surface Oxidation</td>
<td></td>
</tr>
<tr>
<td>Higher N/C ratio</td>
<td>Pavlath* 1976</td>
</tr>
<tr>
<td>Carbon Oxidation</td>
<td></td>
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<tr>
<td>Sulphur Oxidation</td>
<td>Millard 1972; Pavlath* 1976; Benaissa* 1978</td>
</tr>
<tr>
<td>No Fibre Damage</td>
<td>Thorsen* 1966</td>
</tr>
<tr>
<td>Cuticle Modification</td>
<td>Wakelyn* 1972; Wakelyn 1972, 1972; Belin, 1971; Beljajew* 1975</td>
</tr>
<tr>
<td>Surface Polarity</td>
<td>Thorsen* 1966; Thorsen 1968, 1971; Landwehr 1969; Belin, 1971</td>
</tr>
<tr>
<td>Analysis Technique Used</td>
<td>Anderson* 1970; Benaissa* 1978; Belin* 1983</td>
</tr>
<tr>
<td>SEM</td>
<td>Millard 1972; Pavlath* 1976</td>
</tr>
<tr>
<td>XPS</td>
<td>Benaissa* 1978</td>
</tr>
<tr>
<td>FTIR</td>
<td>Beljajew* 1975</td>
</tr>
<tr>
<td>Protein Analysis</td>
<td>Wakelyn 1972, 1972</td>
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<td>Allwörden Sacs</td>
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<td>Postulated Reaction Mechanism</td>
<td>Belin, 1971</td>
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<td>UV</td>
<td>Millard 1972; Benaissa* 1978</td>
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<td>Electrons</td>
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<td>Reactive Species</td>
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</table>
10. Several different apparatuses were built to treat wool in top and fabric form, including a pilot plant by Thorsen et al., 1970. The use of dielectric coverings over the metal plates and small air gaps at low relative humidities produced the most stable coronas (Belin et al., 1983).

1.3.2 Survey of International Research in Progress in 1992

This project was begun at the same time as the resurgence of interest in plasma treatment of wool, that was taking place around the world in 1992. Thus new research was currently underway and had not been published in the general literature. In order to update the level of knowledge a six week visit was undertaken to the institutions and companies in Europe involved in the new research. This was done in order to ensure that there was no unnecessary duplication of work currently under way and to establish links. Results could then be discussed informally to stay abreast of developments.

Discussions were held with scientists located at the International Wool Secretariat (IWS) in Ilkley, the Deutsches Wollforschungsinstitut (DWI) in Aachen, Softal in Hamburg (manufacturers of industrial corona machines), Centexbel in Verviers, the Institut Textil de France (ITF) in Lyon, and the Textile Institute (TI) in Lódz. New information that was provided to us at this time is summarised by topic below. The summary represents a picture of the state of plasma research on wool during early 1992.

An IWS survey of Europe had found that the running costs for water and effluent for industry were increasing markedly above the inflation rate. Also, the European Community was likely to introduce the stricter German pollution standards over the next decade. It was considered that an alternative to current methods needed to be found, but glow plasma technology was too expensive, and only corona plasma technology could currently compete on a cost basis. In addition plasma polymerisation would be of interest in the future to replace current methods of adding polymers to wool, which also have effluent problems.

IWS had held talks with a Russian group that had had several industrial batch glow machines running for at least two years. They did not need to scour the fabrics before treatment and produced good dyeing behaviour and improvements in shrinkresistance, but were still not up to IWS standards. They suggested that ionic bombardment is the reaction mechanism and have an agreement with a German company, Klockner-Moeller, to market their machines in the West.

Dr. Rakowski at the TI in Lódz also has a fully working and characterised glow plasma machine for continuously treating several wool tops at a time. He considers that controlling gas flow was important to prevent yellowing of the wool fibres. Centexbel
have had access to an industrial installation for continuous glow plasma treatments and
found that continuous and batch plasma processes give very similar modifications.
They noticed little difference when using different gases and consider that oxygen is
always present from the wool and the residual air in the apparatus.

The French have used a microwave plasma system for their research which is
concentrates on plasma polymerisation of fluorinated carbon monomers onto textiles in
order to get a high quality, washable finish for stain resistance. Argon is used with
\( \text{C}_2\text{H}_2\text{F}_2 \) because they consider that Ar 'activates' the surface by creating radicals.
\( \text{NH}_2/\text{NH}_3 \) plasma is used for nitrating the surface of aramids (fully aromatic
polyamides e.g. Nomex, Kevlar) for improving adhesion in composites. When plasma
polymerisation takes place, the chamber gets very "dirty" and an air or oxygen plasma
has to be used to clean it.

IWS has found that there was no significant difference in print yield (Section 2.5.2)
between glow and corona treatment, although print yield is very dye specific. Also,
Basolan SW is the only shrinkresist polymer that will work with corona treatment.
However, there is no clear understanding of how shrink-resist polymers adhere to wool,
only that the more cationic a polymer, the more effective.

DWI has found that corona and glow treatment give faster dye uptake, as well as
shorter dye saturation times, and are more level than untreated wool fabrics. Preliminary results indicate that the amount of 18-methyleicosanoic acid does not
change after glow plasma treatment. TEM shows modifications to the a-layer only and
the same effects occur regardless of what gas is used. Using XPS they observe that
carbon decreases and oxygen, nitrogen, and sulphur levels increase. Oxygen is the best
oxidising plasma followed by nitrogen, argon, and hydrogen. They suggest that
treatment levels could be controlled by using different plasma gases.

Corona plasma treatment at DWI does not produce soluble proteins on the surface of
the wool fibre as occurs for chlorination. Ammonia extraction returns the XPS of
corona treated wool back towards that of untreated wool. SEM shows no damage in
corona treatment, except at high levels.

Softal produces corona devices that they attempt to optimise for each particular
customer. Their designs are based on empirical formulas as the current theories are too
difficult and unnecessary for their work. They consider that corona is made up of "soft
sparks" (plasma discharges of 10 - 20 ns duration) and use metal-metal, metal-
dielectric, and dielectric-dielectric electrodes on their machines. They suggested that
there may be fibre 'shading' of neutral and charged particles in the fabric which could
cause uneven modifications. In their experience if there are lubricants or additives on
Chapter 1. Introduction

the material being treated, this means that the treatment has to be longer in order to get rid of the covering layer of contaminant. Corona treatment has to be applied just prior to the printing station or coater in order to get the maximum effect.

1.4 SIGNIFICANCE AND AIMS OF THIS PROJECT

One of the key points to come out of the survey of the literature was that all the work on plasma treatment of textiles had been performed by scientists with little familiarity with the fundamental physics and chemistry of how a plasma works. This meant that previous studies had been primarily empirical in nature with little understanding of how the settings on the various plasma devices correlated with the reactive species that could be present in the plasma. The literature also showed that any attempts at fundamental chemical and physical studies have been limited by the lack of suitably sensitive techniques for examining the surfaces of fine textile fibres.

At the same time as this project was begun, the Australian National University (ANU) Plasma Research Laboratory (PRL) in the Research School of Physical Sciences and Engineering (RSPhysSE) began to undertake research into the question of which active species in the plasma were responsible for the plasma treatment of wool. The PRL provided the expertise and knowledge of how a plasma works and the measurement of active species in the plasma. They built a plasma treatment chamber to allow the isolation and measurement of the reactive products present in the plasma whilst the Commonwealth Scientific and Research Organisation (CSIRO) Division of Wool Technology (DWT) provided access to facilities for measuring the modifications occurring to the surface of the wool fibre.

Using all of the information reviewed in this chapter it was decided that the primary objective of this thesis should be determining the main reaction mechanisms and effects on the wool fibre due to plasma treatment. This would be done by applying well known surface analytical techniques to the plasma modified wool. The results would be correlated with changes in the textile properties produced by the plasma treatments and the measurements of the reactive particles present in the plasma performed at the PRL. At the same time, the surface analytical techniques would also be applied to a range of wool treatments that would either model the effects of particular individual reactive species in the plasma or were well documented chemical treatments of the wool fibre that produce similar effects to plasma treatment.

Having surveyed the available surface analytical techniques, it was found that whilst there were a number of techniques available for the measurement of surface morphology and chemistry, the analysis of the surface energy of wool fibres had not
been studied in any great depth. As one of the main features of the plasma treatment of wool is the dramatic change in water wettability, it was necessary to develop a methodology for the analysis of changes to the surface energy of wool after plasma treatment.

Thus, a secondary objective was the review of current surface energy theories and an assessment of their usefulness for understanding the surface energy changes of textile fibres. At the same time a simple reproducible method for the measurement of the surface energy of wool fibres needed to be developed.

1.5 LAYOUT OF THE THESIS

This thesis is organised as follows. Chapter 2 reviews the analytical techniques used and details the apparatus and methods utilised throughout the thesis. Chapter 3 presents the experimental results for the surface analysis of the model treatments used for comparisons with plasma treatment. A summary of the different reaction paths and effects of each treatment is presented so that easy comparisons with plasma treatment can be made in later chapters.

Chapter 4 deals with the experimental results for wool treated by radio-frequency plasma at the ANU PRL and the correlation of these results with the measurements of reactive species present in the plasma. Based on these observations a mechanism for the plasma treatment of wool is proposed. Chapter 5 presents the results for research performed at the DWI in Germany, during a 3 month visit, where studies of microwave plasma and corona treated wool were performed. The mechanism developed in chapter 4 is expanded in order to provide a full explanation of these results. Chapter 6 presents an evaluation of the plasma treatment of industrial wool fabric and the applicability of the plasma treatment mechanism to an industrial situation.

Finally, in Chapter 7 the conclusions from this project are presented. Suggestions for further work and the implications of the present results for the commercial plasma treatment of wool are also discussed.
2.1 MATERIALS

2.1.1 Wool Samples

A number of different fabrics were used in this study and a system of four letter identifier codes as shown below has been used to identify each wool fabric in the results section e.g. ABUT - Andrew Bean UnTreated wool fabric (see next paragraph).

The wool used in the majority of this research was a plain weave lightweight fabric (155 g.m⁻²) made from 20 µm Australian merino wool (ABUT). The fabric was wet scoured before treatment.

For the early printing results a plain weave, lightweight (130 g.m⁻²) 100% wool challis fabric, typical of that widely used for commercial wool prints was provided by Dr. Keith Millington (KMUT). The fabric was open-width scoured and blown before treatment.

Later in the research when larger samples of fabric were required a fabric provided by Dr. Jeff Church was used. This fabric had been used for the model treatments performed by other scientists in the CSIRO FS&F group and allowed for comparisons with plasma treatment. This fabric was a plain weave lightweight fabric (155 g.m⁻²) made from 21 µm Merino wool (JCU T). This fabric has been given minimal finishing before it was used in research. The finishing consisted of decatising ("greasy blow"), followed by scouring, then hydroextraction, and finished with drying in a stentor.

Whilst in Germany some samples were studied from treatments done on fabric provided by the IWS. This was a plain weave lightweight (100 g.m⁻²) 100% wool fabric (TKUT).

For fabric felting measurements a standard shrinkage fabric produced by the CSIRO was used. This is a plain weave lightweight (150 g.m⁻²) worsted wool fabric designed to have a very open structure that was particularly prone to felting (Fabric A from Guise et al, 1989).

Prior to the majority of the treatments, the fabrics were cleaned by soxhlet extraction in methylene chloride for 2 hours in order to remove any residual chemicals or lipids on the fabric (The fabrics which were not cleaned using this method are discussed in...
Chapter 2. Analytical Techniques, Apparatus and Methods

Chapter 6. The specimen fabrics were placed into an extraction thimble in a Soxhlet extractor barrel and the apparatus was assembled in a fume cupboard. Methylene chloride was poured into the extractor until the siphon operated and then a further 20 ml was added and the condensor fitted to the assembly. The Soxhlet flask was then heated so that a siphoning rate of 10-12/hour was achieved and the apparatus was left for 2 hours. After 2 hours the solvent was poured off and the fabrics were left to air dry in the fume cupboard. The fabrics were then stored in polyethylene bags until use (C designator is added to the end of the identifier code e.g. ABUTC). From this stage onwards handling of the fabrics was performed using tweezers that had been cleaned with ethanol.

The determination of the solvent extractable matter from a sample fabric was performed according to AS 2001.3.4 (Test A) using methylene chloride.

2.1.2 Chemicals

The water used was from a 0.22 µm filter Millipore system using distilled water. The diiodomethane (methylene iodide) was 99% purity from Aldrich. The n-Decane was 99% from BDH.

For bleaching treatments commercial grade hydrogen peroxide (50%, Interox), tetrasodium pyrophosphate and sodium bisulphite were used in wet treatments.

2.1.3 Gases

The gases used in the ANU plasma treatment were supplied by BOC. They were industrial oxygen (99.5%), dry air, industrial argon (99.99%), or industrial hydrogen (99.9%).

2.2 PLASMA EQUIPMENT

The majority of the research in this thesis was performed on wool plasma treated at the ANU PRL by X. J. Dai using the radio-frequency (RF) apparatus. Her PhD thesis (Dai, 1995) contains a complete description of the apparatus and the measurement techniques used on the plasma.

Once the mechanism of plasma treatment had been developed using the RF plasma a three month research visit to DWI in Aachen, Germany, funded by the DAAD, was undertaken in 1994. At DWI plasma treatment of wool samples were studied using their microwave glow apparatus and a lab scale corona apparatus they had obtained from Softal.
Prior to all glow plasma treatments the wool fabrics were stored in a vacuum desiccator for a minimum of 24 hours. Fabrics for corona treatment were stored under ambient laboratory conditions.

2.2.1 Radio-Frequency

The RF plasma equipment utilised in this research was specifically designed and built at the ANU PRL for this project (Fig.2.1). It is made up of a glass cylinder, 150 mm diameter and 300 mm long, mounted vertically above a continuously pumped reaction chamber. The working gas is introduced at the top of the apparatus via a flow controller. The gas flows at 6.0 and 12.0 sccm to provide a pressure range in the chamber between \(10^{-3}\) and \(10^{-1}\) mbar, as measured by a capacitance manometer. An electrodeless discharge is produced in the glass cylinder by current supplied from an industrial RF generator (at 12.56 MHz). The current is coupled via a matching network into a close-fitting coil/antenna wrapped around the glass cylinder. Power to the source is supplied in the range 25 to 300 W either continuously or in single pulses of duration between 0.1 and 10 seconds.

Plasma products generated in the source diffuse into the stainless steel reaction chamber, which is 650 mm long with a 320 mm diameter. At one end of the chamber is a hinged door fitted with a 250 mm diameter glass viewing window. The door provides access for samples which are located 16 cm below the source on a stainless steel platform in the chamber. The size of the samples for surface energy measurements are normally 140 mm x 40 mm. For printing, dyeing, and felting experiments the samples were much larger at 200 mm x 300 mm.

Six ports in the other end plate and one in the base of the chamber provide access for Langmuir probes to measure the spatial profile of the plasma parameters. Two opposing ports in the side of the cylindrical chamber provide optical access for vacuum ultra-violet measurements of the neutral species concentrations. The whole system is evacuated by an oil diffusion pump to a base pressure of \(10^{-6}\) mbar.

The separation of the reaction chamber from the source was designed in this manner as it allows the sample to interact with high concentrations of reactive species without the presence of high electro-magnetic fields. Also baffles can be interposed between the plasma source and the reaction chamber in order to control the flux of charged particles and UV radiation into the chamber without seriously affecting the flux of neutral particles.

Two types of baffles were used. The first was a fine stainless steel wire mesh inserted between the source and the chamber. The grid size (30 µm x 30 µm) of the mesh was chosen to be smaller than the Debye length of the plasma in the source (~200 µm), and
its transmissivity was about 55%. The second used a loose-fitting glass plate, supported by the mesh, to block out both the charged particles and UV radiation.

Fig. 2.1 Schematic diagram of the radio-frequency apparatus.

(a) Side view section. (b) End view section, showing the optical arrangement for VUV absorption measurements. (1) working gas, (2) flow controller, (3) plasma source, (4) RF matching box, (5) RF generator, (6) RF antenna, (7) location of baffles when used, (8) MgF₂ window, (9) access ports for Langmuir probes, (10) vacuum system, (11) viewing window and sample access, (12) reaction chamber (13) sample location, (14) VUV light source, (15) MgF₂ lens, (16) VUV monochromator and its detection system.
2.2.2 DWI Microwave

At the DWI in Aachen there is a lab scale "Hexagon" microwave plasma device obtained from Fa. Technics Plasma, Kirchheim b. München (Fig.2.2). It uses a magnetron YJ 1530 from Firma Valvo. The apparatus has a single chamber where the plasma is formed and the sample is treated.

The working gas is introduced via a flow controller at between 14 and 20 sccm to produce a pressure of $10^{-1}$ mbar. An electrodeless discharge is produced in the chamber by the magnetron which supplies 2.45 GHz microwaves through the wave guide. Power to the source is supplied continuously at 300 W. The whole system is evacuated by a diffusion pump to a base pressure of $10^{-5}$ mbar.

The wool fabric sample sizes are the same as used in the RF apparatus (see 2.2.1). The position of the samples in the plasma could be varied by using a glass frame to raise the sample into the centre of the plasma. Otherwise the sample would rest on the base of the chamber.

Fig.2.2 Schematic diagram of the microwave apparatus.

(1) microwave generator, (2) waveguide, (3) reaction chamber, (4) vacuum pump, (5) pressure gauge, (6) mass flow controller.
2.2.3 DWI Corona

The corona equipment used at the DWI is a lab-scale apparatus "Linear Simulator" obtained from Fa. SOFTAL GmbH, Hamburg (Fig. 2.3). The base is a bi-directional moving plate on which the sample is fixed by tape at the edges. This plate is 210 mm wide and 280 mm long and passes under a stationary upper electrode (0.3 m wide), MMD-Keramikelectrode CEE 24-0-1MD. The speed of the plate can be varied between 0.5 - 50 m/min. The corona generator was a Model 3050 MFG. The corona dose, $e$ (kJ/m$^2$) is determined using the formula

$$e = \frac{P \times n}{v \times w}$$

(2.1)

Where $P$ = power (W), $n$ = number of passes, $v$ = velocity (m/s), and $w$ = width of the electrode (0.3 m). All wool treatments were performed at room temperature and pressure in an unconditioned room.

Treatments of the sample fabrics were classified as single-sided or double-sided. Single-sided treatments only treated one side of the fabric, which was passed under the electrode at a given dose level. Thus potentially the back side of the fabric may have received a lower level of dose than the top side. Double-sided treatments had two sets of passes under the electrode for each dose level, so that both sides of the fabric received the same dose level.

Fig. 2.3 Schematic diagram of the Corona Apparatus

(1) table on which sample is placed (counter-electrode), (2) electrode, (3) sample, (4) motor for table movement, (5) direction change roller, (6) drive belt, (7) guide rail
2.3 OTHER WOOL TREATMENTS USED AS 'MODELS'

A number of possible explanations forwarded by previous researchers have tried to explain plasma treatment by postulating that only one of the reactive species present in the plasma was responsible for the modifications observed. It was planned to test these theories by isolating the reactive species in the RF plasma (section 2.2.1). As well various model treatments were chosen to be compared with the plasma treatments. These model treatments have been described in great detail in the literature and the reaction paths are well known.

The model treatments fall into two groups. The first represents reaction paths that may be occurring in the plasma: ultra-violet irradiation, electron beam irradiation, and ozone treatment. It should be possible to evaluate their contribution to the overall plasma effect by comparing the results obtained from these treatments that 'model' the effect of individual components in the plasma.

The second group of treatments are well known from the literature for removing the surface lipid layers and/or oxidising the wool surface. They have been described in the literature for several decades and provide chemical models for the possible final state of the wool fibre surface after treatment.

Where possible samples were obtained for the majority of the different treatments from colleagues and then evaluated with the analysis equipment used in this thesis. This data is also correlated in later chapters with the literature results available. For a limited number of the treatments no samples could be obtained, or some of the analysis techniques were no longer available, and thus only literature results were available and these were used for comparison purposes.

2.3.1 Ultra-Violet Irradiation & Peroxide Bleaching

The model treatment used here is the "Siroflash" process developed by Dr. Keith Millington at CSIRO. "Siroflash" uses continuous UV irradiation of dry wool fabric followed by a conventional peroxide bleach. This method gives excellent whiteness, high colour yields, and low fibre damage (Millington, 1995). In this thesis UV treated, peroxide bleached, and "Siroflash" samples were studied and all samples were provided by Dr. Keith Millington.

The UV treatment used static UV exposure with Phillips TUV low-pressure mercury arcs (0.3 W/m), either individually or in a bank of eight tubes. These tubes produce a high fraction of 252.7 nm radiation (90%). Samples were wrapped tightly around single...
tubes during irradiation, or placed flat 1-2 cm below the array, for times of 5 or 40 minutes.

Hydrogen peroxide bleaching was carried out for 1 hour at 60°C, using 0.75% w/v peroxide solution stabilised using tetrasodium pyrophosphate (6g/l). After bleaching the fabric was rinsed with water containing a small amount of sodium bisulphite (1g/l) to strip soluble protein from the wool.

The "Siroflash" treatment used continuous UV exposure on two IST Strahlentechnick systems equipped with medium-pressure mercury arcs (type CK lamps) operating at 120 W/cm with a transport speed of 2-3 m/min. This was followed by the hydrogen peroxide bleach described above. The medium pressure arcs produce a lower fraction of UV-C (~12%) than the low-pressure arcs used for the static UV exposure.

2.3.2 Electron Beam Irradiation

Electron beam treated fabrics were obtained from Herr Bert Gilleßen. Electron-beam irradiation of fabric samples (Gilleßen et al, 1995) was performed in an industrial scale electron accelerator, manufactured by Dürr, Stuttgart, Germany with an acceleration unit from Polymer-Physik, Tübingen, Germany. All fabrics were transported through the irradiation chamber by means of a conveyer belt at a speed of 10m/min and were irradiated at an acceleration voltage of 180 kV. The radiation dose was varied between 10 and 150 kGray. The irradiation chamber was continuously flushed with nitrogen.

2.3.3 Ozone Treatment of Wool

Ozone treated samples were not available for examination during this research. Comparisons are made in later chapters based on references in the literature (Thorsen, 1965, Thorsen & Kodani, 1967, Thorsen & Landwehr, 1975, Bradley et al, 1995, Shao et al, 1997) which are cited in the appropriate sections.

2.3.4 Chlorination of Wool

Chlorination was performed using dichloroisocyanuric acid (Basolan DCCA) in a lab-scale apparatus. The recipe used was:

Leophan M 1% o.w.f. (on weight of fibre)
Sodium Acetate 2% o.w.f.
Acetic Acid 2% o.w.f.
Basolan DCCA x%, o.w.f. (Where x = 1, 2, 3, Saturated)
Water
Chapter 2. Analytical Techniques, Apparatus and Methods

The Basolan was added and run for 120 minutes at 30°C (exhaustion was checked with Starch/Iodide paper). At the end of this period the bath was dumped and the samples were rinsed with water. Then the bath was refilled and bisulphite and Uniperol added:

Bisulphite 2% o.w.f.
Uniperol 1% o.w.f.

The fabrics were then gently agitated for another 20 minutes.

Leophan M is an aliphatic sulfonate wetting agent manufactured by BASF.

2.3.5 Lipid Removal Techniques Using Hydrolysis

The treated fabrics were provided by Mr. Miklos Lanczki and Dr. Don Rivett. They used the methods of Negri et al., 1991. For potassium hydroxide in methanol (KOH/MeOH) treatments the wool was soaked in 0.1M KOH in MeOH at room temperature for various times and rinsed twice with water. For tertiary butoxide in anhydrous tertiary butanol (t-BuOK/t-BuOH) treatments the dried wool (vacuum oven 40°C, 24 h) was treated with 0.1 M potassium t-butoxide in t-butanol for 2 h at 40°C.
2.4 SURFACE CHARACTERISATION

In the past decade a wide range of powerful and sensitive techniques have become available for the surface analysis of wool and other polymers (Höcker, 1992). Previously techniques were developed using conducting metals or other robust surfaces and when these older techniques were applied to wool they often damaged the area being studied. They did not have adequate sensitivity and showed only gross changes to the wool surface.

It is necessary to use complementary techniques when studying wool as its surface cuticle layer is made up of a complicated series of differing layers (Section 2.2). Each technique differs in the depth of information and the quantitative and qualitative information it provides (Table 2.1).

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Principle of Technique</th>
<th>Depth of Analysis</th>
<th>Type of Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angle</td>
<td>Interactions between the atoms/molecules in the surface of the material and the covering liquid determine the wettability of the surface and depend on the polar and dispersion components of the surface energies</td>
<td>One surface layer</td>
<td>Quantitative surface energy and information about the relative polarity of the surface</td>
</tr>
<tr>
<td>XPS</td>
<td>A beam of X-rays incident on the surface of the material results in the ejection of photo-electrons with energies characteristic of the emitting atom</td>
<td>3 - 8 nm</td>
<td>Quantitative elemental composition and some chemical bond information</td>
</tr>
<tr>
<td>FeSEM</td>
<td>A low voltage, high brightness electron beam is scanned over the surface and the secondary electrons ejected from the surface are detected and used to form an image</td>
<td>1-10 nm</td>
<td>Topography</td>
</tr>
<tr>
<td>TEM</td>
<td>An electron beam is shone onto a thin slice of material and the transmitted electrons are used to produce a density dependent image of the cross-section</td>
<td>resolution = 0.2 nm</td>
<td>Morphology of cross-section and some atom distribution information</td>
</tr>
<tr>
<td>Allwörden Membranes</td>
<td>Wool fibres are immersed in chlorine water which causes the epicuticle to form swollen raised membranes</td>
<td>3 - 6 nm</td>
<td>Degree of disruption/damage to the surface layers of the wool surface</td>
</tr>
</tbody>
</table>
2.4.1 Electron Microscopy

Scanning Electron Microscope (SEM)

Scanning Electron Microscopy (SEM) has been available since the 1960s and was quickly adopted for imaging the surface of wool fibres. An electron beam is focussed onto the surface of the wool fibre and then rastered across it. Secondary electrons are emitted from the surface and detected to form an image on a cathode-ray tube (Fig.2.4).

The secondary electrons are low energy electrons formed due to the excitation of loosely bound atomic electrons by the high energy primary beam through inelastic scattering. Therefore they can only escape from a very thin layer of the surface (1-10 nm) and are very dependent on the angle of incidence. This gives image contrast that is very sensitive to geometrical configuration. The sample has to be measured under vacuum due to the short path length of electrons in air.

![Schematic diagram of a basic SEM](image)

Fig. 2.4 Schematic diagram of a basic SEM.

(D) deflection coil, (A) aperture, (S. G.) scan generator, (CRT) cathode-ray tube, and (AMP) amplifier.
In the past an accelerating voltage between 10 - 20 kV was typical for wool measurements. Due to wool's insulating nature a conductive metal coating (usually 10 nm of gold) had to be sputtered onto the sample in order to limit surface charging that would distort the image. Both of these factors limited image resolution.

In this research the newly developed Field-emission SEM (FeSEM) was used. The FeSEM differs from traditional SEM's by using a field emission gun as its electron source to give a very bright focussed electron beam that can achieve satisfactory image quality at low beam energies (~1 kV gives ~10 nm beam diameter). This is achieved by having the electrons drawn away from a hard metal tip by an electric field and then accelerated towards the sample at the chosen voltage.

The FeSEM has great advantages when working with biological materials as the low accelerating voltage still provides high resolution images, whilst reducing sample charging problems. At 1 kV wool fibres do not charge significantly and it is possible to observe them without a metal coating. Surface features are enhanced as the electrons do not penetrate as far into the sample and less specimen damage is produced by the electron beam. It is also possible to enhance the visible surface structure by limiting the penetration of electrons even further by coating the specimen with a fine layer (2 - 4 nm) of chromium or carbon. These thin coatings produce a negligible loss in resolution when compared to the gain in visible surface structure, unlike the earlier 10 nm gold coatings.

The SEM used was a Hitachi S4100 FeSEM. For imaging the beam energy was 1 keV, working distance of 5 mm, beam current around 2.5 pA, an emission current of 10 µA, and an aperture of 20 µm.

Transmission Electron Microscope (TEM)

The use of TEM on wool fibres was first described in Wool Sci. Rev., 1948 and since then has been used to a great extent to image cross-sections of the wool fibre. This has permitted the study of both fine structure (Jones et al, 1994, Negri et al, 1996) and the reaction pathways of various wool processes (Leeder et al, 1985). A beam of electrons is focussed onto a thin slice of fibre cross-section and the transmitted electrons produce a magnified image on a fluorescent screen (Fig.2.5).

The short wavelength of the electrons allows an image resolution ~0.2 nm and the image contrast is determined by the interaction of the electron beam with the sample. Electrons in the beam are elastically scattered by atomic nuclei and the number of electrons deflected increases with atomic number and thickness of the sample. Thus a density-dependent image is formed. The sample has to be measured under vacuum due to the short path length of electrons in air.
Wool is a biological material and there are problems with contrast due to its component atoms being of similar small atomic numbers. Thus typically the wool fibres are stained with a heavy element and fixed in resin. Careful selection of the staining agent allows different atoms to be highlighted in the cross-section due to the differing affinities of the stain for particular atoms or molecular bonds. After curing the resin is sliced by a microtome into 50 - 100 nm thick cross-sections that are floated onto a conducting grid which is placed into the TEM for imaging.

A limited amount of TEM was undertaken at DWI, Aachen using an EM 109 from Firma Zeiss, Oberkochem with a beam energy of 50 kV. Wool yarns were removed from the fabric samples and stained with ammoniacal 0.1 M silver nitrate solution, by shaking for 3 days with air excluded. The silver ions are specifically attracted to sulphur groups with concentrations of silver in the wool of 3 M Ag/Mol cysteine and 6 M Ag/Mol cystine (Klausen, 1995). This sensitivity to sulphur makes the silver ion particularly suited to the study of the cuticle layers in the surface of wool.

Fig.2.5 Schematic diagram of a basic TEM
After staining the samples were washed with distilled water and then dried in a vacuum desiccator wrapped in foil to exclude light. The dried yarns were stretched onto a specially prepared wooden carrier and then embedded in an acrylic resin inside gelatin capsules. The gelatin capsules were kept in an oven at 50 °C for 24 hours to allow the polymerisation of the resin to take place.

The acrylic resin was made up of:

- 5.25 ml n-butylmethacrylate
- 0.5 ml methylmethacrylate
- 1.0 g benzoylperoxide
- 13 ml 2-hydroxyethylmethacrylate

The capsules were then sliced into 100 nm thick sections using an ultramicrotome and examined in the EM 109.
2.4.2 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) was first observed at the beginning of this century by researchers working on the photoelectric effect. However it was not until the 1950's that XPS came into its own as a tool for the investigation of the elemental and chemical structure of the surface of materials (another name used for XPS is Electron Spectroscopy for Chemical Analysis (ESCA)). With this technique the sample is irradiated with a beam of monochromatic X-rays which cause photoemission of electrons from atoms in the samples. The kinetic energy, $E_k$, of the ejected electrons is measured and used to determine the original binding energy, $E_b$, of the atomic orbital the electron was ejected from, by the equation

$$E_k = h\nu - E_b - \phi$$  \hspace{1cm} (2.2)

where $h\nu$ is the characteristic energy of the incident X-rays and $\phi$ is the "work function" of the spectrometer (which is a constant for any given machine). In addition to the photoelectrons there is also the emission of Auger electrons due to relaxation of the excited ions left after the original photoemission. The newly created hole in the inner atomic orbital of the ion is filled via a transition from an outer atomic orbital. The difference in energy between the atomic orbitals becomes available as excess kinetic energy and it is possible for this energy to excite an electron in the same outer level (Fig 2.6), or in a more shallow level, whereupon the electron is ejected.

The electrons leaving the specimen are detected by an electron analyser which measures their kinetic energy. As the sample is losing electrons charging can become a problem with non-conducting insulators such as polymers. The most common solution in this case is to use the aliphatic carbon peak as a binding energy reference and set it to 285.0 eV.

The incident X-rays excite atoms up to a depth of 10 µm but the excited electrons will suffer inelastic scattering inside the solid. This scattering will change the energy of the electrons and destroy the information they carry, producing a background noise signal. Only the photoelectrons which can escape from the specimen without scattering are useful and as the inelastic mean free path of electrons in a solid is only ~3 monolayers this results in XPS being a very surface sensitive technique.
Chapter 2. *Analytical Techniques, Apparatus and Methods*

![Diagram of X-ray photon, photoelectron, and Auger electron](image)

**Fig. 2.6** Schematic illustration of photo-electron and subsequent Auger electron excitation

The signal intensity drops off exponentially with distance from the surface and the sampling depth in XPS is defined as that thickness from which 95% of the signal is derived, which is given by

\[ d = 3 \lambda \sin \alpha \]  

(2.3)

where \( \lambda \) = attenuation length of the electron and \( \alpha \) = angle of emission relative to the surface. As we are dealing with a rough organic surface when measuring wool there are extra considerations to be taken into account when using this equation. Firstly, \( \lambda \) is dependent on the kinetic energy of the electron and the nature of the matrix through which it passes [Seah & Dench, 1979]. The value for \( \lambda \) in an organic matrix is controversial and can vary from 1.2 - 2.6 nm [Briggs & Seah 1990, Ward *et al* 1993]. Secondly, \( \alpha \) can vary over the entire range from 0 - 90 degrees for each emitted electron. This leads to a range of sampling depths from which information is gained, with a maximum depth of 7.8 nm with 66% of the information coming from depths of less than 2.6 nm. These depths cover the epicuticle and some penetration into the a-layer of the exocuticle (See Section 2.2).

Each element has a unique spectrum of binding energies so that when the analyser performs a wide scan survey the display will show peaks characteristic of the particular elements present in the sample (Fig.2.7).
Chemical information can also be obtained from XPS spectra. The XPS peak for an element will occur at slightly different positions depending on the environment of the atom. This 'chemical shift' is affected by any parameter which affects the electron density about the atom, such as oxidation state and coordination. The limiting factor on this functional group analysis is the resolution, as peak widths are generally 1.6 - 2.0 eV in width whilst peak shifts are in the range of 1 - 10 eV.

In the case of wool, carbon and sulphur functionalities are easily identified when they occur and are shown in Table 2.2.
Chapter 2. *Analytical Techniques, Apparatus and Methods*

<table>
<thead>
<tr>
<th>Chemical Group</th>
<th>Binding Energy (eV)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, C 1s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C / C-H</td>
<td>285.0</td>
<td>Carbon bound to itself and/or hydrogen, regardless of hybridisation</td>
</tr>
<tr>
<td>C-O</td>
<td>286.5</td>
<td>Oxygen induces shifts to higher binding energies by 1.5 eV per oxygen bonded</td>
</tr>
<tr>
<td>O-C-O / C=O</td>
<td>288.0</td>
<td></td>
</tr>
<tr>
<td>Sulphur, S 2p</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-S</td>
<td>164.0</td>
<td>Sulphur bound to sulphur</td>
</tr>
<tr>
<td>S-SO₂⁻ / SO₂H</td>
<td>166.2</td>
<td>Disulfide monoxide and/or sulfinic acid</td>
</tr>
<tr>
<td>S-SO₂H / R-SO₃H</td>
<td>168.0</td>
<td>Disulfide dioxide and/or sulfonic acid</td>
</tr>
<tr>
<td>S-SO₃H</td>
<td>169.0</td>
<td>Bunte Salt</td>
</tr>
</tbody>
</table>

Table 2.2 Carbon and sulphur functionalities observed in the wool fibre

Unfortunately both oxygen and nitrogen have most of their functionalities falling within a narrow range of ~ 2 eV around their main peak. So that for wool there is no additional chemical information to be gained from these peaks. An example of this is the chlorination of wool which is known to remove part of the wool surface and oxidise the revealed surface (Fig.2.8). Changes in the total level of oxygen and nitrogen are clearly visible, but only carbon and sulphur show clear chemical shifts. The effect of charging can also be seen as all the peaks are shifted by 22.0 eV.

Quantitative analysis is achieved with XPS by using the relative intensities of the elemental peaks. Empirical sensitivity factors are assigned to the most prominent peaks for each element and the atomic fractional concentration \( C_i \) of element \( i \) is calculated by

\[
C_i = \frac{A_i / S_i}{\sum (A_j / S_j)}
\]

(2.4)

where \( A_i \) is the normalised area under the specific peak from element \( i \), \( S_i \) the sensitivity factor for this peak, and the denominator is the sum over all elements \( j \) included in the calculation.
Fig.2.8 XPS elemental spectra of wool before (solid line) and after (dotted line) 2% chlorination
Ion beam sputtering has been used with XPS to provide depth profiles of elemental composition and chemical state in various materials. However when this is done with polymers there is extensive surface damage, preferential removal of oxygen and possibly other elements as well as decomposition of carbon groups to aliphatic carbon. Thus any results obtained using depth profiling with XPS on wool should be treated with caution.

Any carbon contamination and residual free lipids present on the wool surface were removed prior to treatment by soxhlet extraction with methylene chloride (Section 2.1.1). After this cleaning had been performed handling of the fabrics occurred only by tweezers cleaned in ethanol. The treated fabrics were stored using specially designed frames that kept a pristine untouched surface available for XPS measurement. Carbon contamination however is still a potential concern and must be considered when discussing any measurements.

Several XPS machines located at different facilities were used during this research. The two machines used primarily were:

University of South Australia which has a PHI Model 5100 spectrometer, with a Mg Kα X-ray source operating at 300 W and with an analyser pass energy of 35 eV. The vacuum in the analysis chamber was always < 10^-8 mbar during analysis with the sample cooled by a liquid nitrogen cold finger. The energy scale was calibrated using the Fermi edge and the Ag 3d5/2 line (binding energy 367.9 eV)., whilst the retardation voltage was calibrated noting the position of the Cu 2p3/2 (binding energy 932.67 eV) and Cu 3p3/2 (binding energy 75.13 eV) peaks.

DWI has a X-Probe Spectrometer, Model 206 from Surface Science Instruments (SSI) with an Al Kα X-ray source operating at 175 W.

Three more machines were used to study 6 samples as part of a pre-purchase evaluation carried out by CSIRO. There was not much detailed information provided by the companies involved. Thus the results were only used to confirm measurements made with the above two machines. They did in fact give very similar results with the differences being well within error. This enhanced the level of confidence in the XPS results that had been obtained. The companies involved were:

Perkin Elmer, Physical Electronics Division, Analytical Laboratory, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344, USA. They used a PHI 5600 spectrometer, with an Al source operating at 200 W with an analyser pass energy of 22.5 eV.

Fisons Instruments / VG Scientific, Birches Industrial Estate, Imberhorne Lane, East Grinstead, West Sussex, RH19 1UB, UK. They used an Escalab 220i fitted with the XL
lens system, co-axial charge compensation and a microfocussed (1mm) Al Kα X-ray source with an analyser pass energy of 20 eV.

Kratos Analytical used a Kratos Maxim spectrometer with monochromatic X-radiation (excitation parameters of 15 kV and 20 mA) and standard charge neutralisation conditions. The analyser pass energy was 40 eV.

2.4.3 Allwörden Membranes

When wool fibres are immersed in chlorine water a thin surface membrane is observed to be raised as bubbles or sacs along the fibre (Allwörden, 1916, Truter & Wakelyn, 1973). This phenomenon is now known as the Allwörden reaction and the thin Allwörden membranes present on the surface of the cuticle cell are known as the epicuticle. It is resistant to acids, alkalis, oxidising agents, and enzymatic attack. However physical or chemical damage to the surface of the wool fibre has been observed to produce a reduction or elimination of the formation of Allwörden membranes. In this thesis the percentage of fibres producing Allwörden membranes after an experimental treatment has been used to indicate the degree of damage to the epicuticle produced by the treatment.

Chlorine water was produced using the method of Vogel, 1948 and stored overnight in a refrigerator if necessary. Wool fibres were isolated from treated fabrics by cutting a section of yarn from the fabric and then teasing this apart with tweezers. The fibres were placed on a microscope slide and covered with a glass cover slip. The slide was placed onto the stage of a Leitz microscope, and observed at 500x magnification. Drops of chlorine-water were then added at the side of the cover slip until enough was present to fully surround the fibres. The fibres were then observed for up to 5 minutes and the percentage of Allwörden membranes determined by counting the number of fibres on the slide which formed Allwörden membranes after 1 minute. This number was then compared to the total number of fibres under the slide (at least 20 fibres were observed in any sample).

2.4.4 Wilhelmy Plate Measurement of Contact Angles

The surface energy of a solid controls the interaction of the solid with liquids that come into contact with it. If a liquid is brought into contact with a surface then the shape of the interface between the liquid and the surface (Fig.2.9) is given by Young's equation:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta_{sl}$$  (2.5)
Chapter 2. Analytical Techniques, Apparatus and Methods

Fig. 2.9 a) A drop of liquid on a surface b) a solid immersed into a liquid

where $\gamma_{SV} = \text{surface energy of the solid surrounded by the liquid's vapour (mJ/m}^2\text{)}, \gamma_{SI} = \text{surface energy of the solid covered by the liquid (mJ/m}^2\text{)}, \gamma_{LV} = \text{surface tension of the liquid surrounded by its vapour (mN/m)}, \text{and } \theta_{SI} = \text{contact angle between the liquid and solid interface (N.B. mJ/m}^2\text{ are identical units to mN/m, but by convention the surface energy of a solid is expressed as an energy per unit area and the surface energy of a liquid is expressed as a surface tension in units of force per unit length).}$

Thermodynamic analysis shows that in order to calculate the value of $\gamma_{SI}$ the Dupre equation must be used:

\[ \gamma_{SI} = \gamma_S + \gamma_L - W_{SI} \tag{2.6} \]

where $\gamma_{SI} = \text{surface energy of the solid covered by the liquid (mJ/m}^2\text{)}, \gamma_S = \text{surface energy of the solid}, \gamma_L = \text{surface tension of the liquid (mN/m)}, W_{SI} = \text{work of adhesion between the solid and the liquid (J)}.$

By combining equations 2.5 and 2.6 the Young-Dupre equation can be obtained:

\[ W_{SI} = \gamma_L (1 + \cos \theta_{SI}) + (\gamma_S - \gamma_{SV}) \tag{2.7} \]

since $\gamma_L = \gamma_{LV}.$ The term $(\gamma_S - \gamma_{SV})$ is defined as the equilibrium spreading pressure $\pi_e$ and represents the decrease of surface energy due to vapour absorption. Absorption will occur when the condensed vapour has a surface tension similar to or lower than that of the solid, or in other words when the liquid has a low contact angle on the substrate (less than 10°). $\pi_e$ can be measured by vapour absorption using the following relationship:

\[ \pi_e = \int_{p_0}^{p_0} \Gamma d\mu = RT \int_{p_0}^{p_0} \Gamma d(ln p) \tag{2.8} \]

where $p_0$ is the saturated vapour pressure, $\Gamma$ is the number of moles of the vapour adsorbed on a unit area of the substrate, $\mu$ the chemical potential of the vapour, and $p$
the vapour pressure. \( \pi_v \) is only of importance for \( \theta < 10^2 \) and for simplicity of further analysis it is generally assumed by workers in this field that, as a first approximation, \( \pi_v = 0 \). Therefore the Young-Dupre equation can be well represented by

\[
W_{sl} = \gamma_1 (1 + \cos \theta_{sl}) = \gamma_s + \gamma_1 - \gamma_{sl}
\]  

(2.9)

Equations 2.5 - 2.7 show that \( \theta_{sl} \) or \( W_{sl} \) appears in explicit or implicit form in any equation for interfacial energy. Therefore, in order to solve equations for interfacial energy it is necessary to express \( \cos \theta_{sl} \) or \( W_{sl} \) in terms of thermodynamic parameters describing the surface properties of the interacting phases, for instance their surface energies \( \gamma_s \) and \( \gamma_1 \). A relationship of the form

\[
\gamma_{sl} = f(\gamma_s, \gamma_1)
\]  

(2.10)

must be found.

The search for such a relation remains subject to fierce debate by many researchers. There are several concepts regarding estimation of surface energies of solids that do not yet provide an unequivocal solution to the problem. The most commonly accepted procedure is based on the additivity approach (Wu, 1982, Israelachvili, 1985, Good et al, 1990, Gutowski, 1990, van Oss, 1993). According to the additivity approach the total thermodynamic work of adhesion between two substances in contact comprises contributions arising from various types of interactions, i.e.

\[
W_A = W_A^d + W_A^{n-d}
\]  

(2.11)

where \( W_A^d \) is the dispersion term of the work of adhesion \( W_A \), while \( W_A^{n-d} \) refers to the non-dispersion interactions, e.g. dipole-dipole, dipole-induced dipole, and acid-base, including hydrogen-bond interactions.

Fowkes derived the additivity approach when he studied the standard theory of intermolecular force across an interface (London Debye Keesom (LDK) theory) and was led to hypothesise that the surface energy of a liquid or solid could be subdivided into components due to the London dispersion force \( \gamma^d \), Debye induction force \( \gamma^i \) and the Keesom dipole-dipole force \( \gamma^p \). Fowkes also included a component due to hydrogen bonding, \( \gamma^h \). For phase \( i \),

\[
\gamma_i = \gamma_i^d + \gamma_i^i + \gamma_i^p + \gamma_i^h
\]  

(2.12)

This was further simplified by combining the non-dispersion interactions into a single term \( \gamma^{n-d} \) so that:

\[
\gamma_{total} = \gamma^d + \gamma^{n-d}
\]  

(2.13)
Chapter 2. Analytical Techniques, Apparatus and Methods

Fowkes showed that the dispersion component of the work of adhesion $W_A^d$ across an interface between two materials (1 and 2) is well predicted by

$$W_A^d = 2\sqrt{\gamma_1^d \gamma_2^d} \quad (2.14)$$

Successful use of this equation led many researchers to suggest that the non-dispersion interactions can also be quantified by this geometric-mean expression

$$W_A^{n-d} = 2\sqrt{\gamma_1^{n-d} \gamma_2^{n-d}} \quad (2.15)$$

Using the Dupre equation 2.6 this yields:

$$\gamma_{12}^d = \left[\left(\gamma_1^d\right)^{1/2} - \left(\gamma_2^d\right)^{1/2}\right]^2 \quad (2.16)$$

and the same logic applies for the non-dispersion components so that:

$$\gamma_{12} = \left[\left(\gamma_1^{n-d}\right)^{1/2} - \left(\gamma_2^{n-d}\right)^{1/2}\right]^2 + \left[\left(\gamma_1^{n-d}\right)^{1/2} - \left(\gamma_2^{n-d}\right)^{1/2}\right]^2 \quad (2.17)$$

This theory was completed by 1970 and although its assumptions can be seriously criticised, a large body of data has been collected using this technique over the past 20 years. These results have provided theoretical and experimental verification of this approach and can be helpful in the analysis of surface phenomena.

Wu, 1971 & 1982 found that Fowkes extended equation (2.17), using a geometric mean, gave large errors when applied to polar/polar polymer/liquid systems, as opposed to the non-polar systems Fowkes had originally tested to produce equation 2.14. Wu, 1971 showed that when the polarisabilities of the two phases are not too significantly different, then a reciprocal mean dispersion term is as appropriate as the geometric mean approximation. Wu then showed empirically that if the reciprocal mean approximation is also applied to the non-dispersion term then the predictions of the new equation (2.18) more closely match the experimentally measured interfacial tensions as opposed to the predictions given by the geometric mean approximation of Fowkes (which had errors of 50 - 100%).

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^{n-d} \gamma_2^{n-d}}{\gamma_1^{n-d} + \gamma_2^{n-d}} \quad (2.18)$$

Brookes & Rahman, 1986 compared the Fowkes and Wu equations on single wool fibres using methylene iodide (a highly dispersive liquid) and water (a highly polar liquid) and concluded that Wu's equation gave more useful results. Their conclusion, in combination with the extensive results of Wu, 1982 led to the decision in this thesis to
use Wu’s reciprocal mean approximation for determining the dispersion and non-dispersion components of the surface energy of the treated wool. When equation 2.18 is combined with equation 2.9 for the case of a liquid \( (\gamma_i = \gamma_i^d + \gamma_i^p) \) on a solid \( (\gamma_s = \gamma_s^d + \gamma_s^p) \), the following equation is produced:

\[
W_A = \gamma_i (1 + \cos \theta) = \frac{4 \gamma_s^d \gamma_i^d}{\gamma_s^d + \gamma_i^d} + \frac{4 \gamma_s^p \gamma_i^p}{\gamma_s^p + \gamma_i^p}
\]

(2.19)

where \( \gamma_i^p \equiv \gamma_i^{n-d} \). The use of \( p \) (short for polar) to represent the non-dispersion component of energy is introduced here in order to conform with the accepted usage of current literature. From equation 2.19 we can see that if the \( \gamma_i^d \) and \( \gamma_i^p \) values are known for two different test liquids and then the contact angle between the solid and the two test liquids is measured, then it is possible to solve two simultaneous equations and evaluate \( \gamma_s^d \) and \( \gamma_s^p \) for the solid being examined. In this thesis the method of Saito & Yabe, 1983 for solving equation 2.19 simultaneously, using values measured with two test liquids, was combined with a spreadsheet program to allow the quick and easy calculation of wool surface energy values. The calculated values are not strictly valid but the technique is still a useful guide to relative measurements and allows changes to the wool surface to be monitored and compared.

The measurements of the contact angle between the wool fibre and the different test liquids were performed on fabric strips using the Wilhelmy Plate method. This method was fully described in Hsich et al, 1992, where it was demonstrated that the wetting force measurements for a fabric strip gave the same contact angles, with less error, as the measurement of individual fibre wetting forces. In this method a fabric strip is lowered into contact with a test liquid and the liquid will rise along the vertical side of the fabric producing a wetting force. The vertical component of this force, \( F_w \), is given by:

\[
F_w = \gamma_l \text{P} \cos \theta_a
\]

(2.20)

where \( \gamma_l \) = surface tension of the test liquid (mN/m), \( \text{P} \) = perimeter of the liquid/solid interface (m), and \( \theta_a \) = advancing contact angle between the liquid and solid interface. \( \text{P} \) is determined by using a liquid of known small surface energy that will fully wet the surface of the fibres and thus give a contact angle of zero. Once \( \text{P} \) is known, the contact angle between the fabric and the test liquids of interest can be determined. This method was preferred in contrast to performing contact angle measurements on individual wool fibres for the following reasons. It would require large amounts of time to prepare each fibre for measurement, require very sensitive equipment (µg measurements), is prone to large errors, and requires a large number of fibres to be measured in order to be statistically significant. The fabric strip used in the Wilhelmy Plate method contains
several thousand fibres and circumvents the other problems of individual fibre measurement by taking less than 3 minutes to measure a sample.

For each experiment a rectangle of fabric measuring at least 6 cm x 1 cm was cut out parallel to the warp direction using new scissors cleaned with ethanol and at least 5 fabric strips were tested for each treatment level. This strip was mounted underneath an electronic balance. A 6 cm diameter petri dish filled with the measuring liquid was raised up towards the 1 cm edge, using a hand wound laboratory stand, until contact was made. A desktop PC running a simple data collection program was used to collect the weight data from the balance and once the advancing steady state was achieved, the petri dish was lowered until the fabric-liquid interface separated. The measured increase in weight was equal to $F_w$ plus the weight of any fluid that had risen into the fabric structure due to capillary rise, $W_i$ (Fig 2.10). Following separation of the fabric-liquid interface $W_i$ was measured and subtracted from the maximum weight value recorded in order to give the value of $F_w$.

![Diagram](image)

**Time, s**

Fig.2.10 A typical wetting force measurement recorded by the data collection program

The liquid-fabric interface, $P$, was measured using n-decane (following the work of Brooks & Rahman, 1986). The surface energy changes were evaluated using Millipore water and 99% methylene iodide (Table 2.3), to measure the dispersion and polar characteristics of the wool surface [Van Oss, 1993]. Between measurements the fabrics were dried in ambient laboratory conditions of 20 °C and 65% RH. The 12% increase in diameter of the individual wool fibres, due to swelling when immersed in water [Alexander *et al*, 1963, Brooks & Rahman, 1986], was factored into the n-decane measured interface, $P$, before evaluation of the water measurements.
The test liquid surface energies were measured using the maximum pull on a 6.01 mm radius rod [Padday et al, 1975]. This was done before and after the fabric strip measurements to confirm there was no contamination of the test liquids by the samples. If contamination did occur (as shown by a reduction in the liquid’s surface tension) then the liquid was replaced and the measurement was repeated.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface Tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma^d$</td>
</tr>
<tr>
<td>n-decane</td>
<td>23.9</td>
</tr>
<tr>
<td>methylene iodide</td>
<td>44.1</td>
</tr>
<tr>
<td>water</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Table 2.2 Surface energies of the test liquids

The 6 cm length of the test fabric strips meant that contact angles greater than 90° could not be measured due to fabric bending and so the published 96° ± 2° contact angle of water on untreated wool is taken from the Brooks & Rahman, 1986, single fibre measurements.

In the course of this thesis it was found that a simpler calculation provided an easier way to track the changes that were occurring to the surface energy of the plasma treated wool fabric. In order to assess the extent of the increase in surface energy of the wool surface, equation 2.21 was derived directly from equations 2.5 and 2.20.

$$\Delta W = F_w / P = \gamma^d \cos \theta_a = \gamma_{SV} - \gamma_{SL}$$  \hspace{1cm} (2.21)

$\Delta W$ represents the decrease in surface energy when the solid surface is covered by a test liquid. $\gamma^d$ is the surface tension of the liquid in mN/m, $\theta_a$ is the advancing contact angle of the liquid on the solid and $\gamma_{SV}$ and $\gamma_{SL}$ are the surface energies in mJ/m$^2$ of the solid-vapour interface and solid-liquid interface respectively. $\Delta W$ for methylene iodide (a highly dispersive liquid) correlated closely with the values calculated for the dispersion component of the wool surface energy and $\Delta W$ for water (a highly polar liquid) correlated closely with the values calculated for the polar component.

$\Delta W$ values are used in the graphs in this thesis to monitor the increasing levels of dispersion and polar components of the wool surface energy after plasma treatment. Surface energy values, with the dispersion and polar components, have been calculated for the treated wool fibres for comparison purposes with the model treatments and the literature.
2.5 TEXTILE PROPERTY TESTING

2.5.1 Yarn Properties

A major factor influencing the mechanical properties of yarns is the interfibre friction between the individual fibres making up the yarn (Makinson, 1979). By measuring the effect of plasma treatments on yarn mechanical properties it should be possible to compare the degree of modification of the frictional properties of the surface of the wool fibres.

Two different methods were used to evaluate the changes in yarn tensile properties. The first method used an Uster Tensorapid 3 to measure the %elongation of a yarn with a twist factor of $\alpha=144$. Individual hanks of 60 m were wound off and then plasma treated. The hanks were then rewound onto cones and the changes in yarn properties were measured on the Uster Tensorapid 3 under standard testing conditions of 20°C and 65% RH. Fifty measurements were made on 0.5 m lengths. At the same time untreated yarns were also measured to provide a baseline for comparison.

The second method used an Instron to measure the strain and load at breaking point of yarns. The yarns used for this method had been isolated from a treated square of ABUTC fabric using tweezers. The yarns were measured using gauge lengths of 200 mm (30 samples) and 10 mm (22 samples) for both untreated and treated fabrics. All changes observed were significant at a t-test level of 99%. The 200 mm gauge length samples were used to indicate changes in the frictional properties of the wool fibres and are reported in later chapters.

The 10 mm gauge length was used to confirm that no changes had occurred to the bulk properties of the fibres in the yarn. This is because such a short gauge length produces results dependent only on the fibre bulk properties. No change from untreated yarns was detected for this 10 mm gauge length, regardless of the degree of treatment.

The %elongation, strain at break, and load at break values reported in this thesis have been reported as a percentage improvement over untreated wool (untreated wool = 0%).

2.5.2 Fabric Printing

Wool printing is highly sensitive to the level of pretreatment that has taken place (Bell, 92). Efficient preparation of the wool goods prior to printing is required for full colour yields, levelness and brightness to be achieved. Traditionally wool is oxidised prior to printing, using chlorination, in order to allow adequate wetting of the fibres by the print paste and dye uptake into the wool fibres during steaming.
The printing of fabrics was performed by Dr. Keith Millington as described in Millington, 1995. Printing was done using simple pastes of the following composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indalca PA3, (10% w/v stock solution)</td>
<td>50%</td>
</tr>
<tr>
<td>Urea</td>
<td>10%</td>
</tr>
<tr>
<td>Water</td>
<td>38%</td>
</tr>
<tr>
<td>Dye</td>
<td>2%</td>
</tr>
</tbody>
</table>

The following reactive dyes were used:

- Lanasol Black R (CI Reactive Black 43)
- Lanasol Blue 3R (CI Reactive Blue 50)
- Cibacron Turquoise Blue GR (CI Reactive Blue 72)

The majority of the work was performed using the reactive dye Cibacron Turquoise Blue GR. This is a copper phthalocyanine complex with a high molecular weight, and gives a very wide range in colour yields from untreated wool to conventionally chlorinated wool using DCCA.

Rectangular blocks (75 x 50 mm) were printed onto fabric using flat screens on a Johannes Zimmer Sample Printing Machine, type MDK, using two passes of a magnetic squeegee bar (electromagnet setting level 3). After printing the fabric was dried at room temperature, steamed at 100°C for 30 minutes in an Andrew Autosetter autoclave, washed off in dilute ammonia, acid scoured with dilute acetic acid, dried and pressed.

Reflectance spectra of printed samples were measured using a Spectrogard instrument. Colour yield (K/S) values, which relate to the concentration of the dye on the fabric surface, were recorded at the centre of the strongest absorption band for each dye. A mean of three K/S readings was recorded. The colour yield values reported in this thesis have been normalised against a 4% DCCA chlorination treatment, which was set equal to 100%. The colour yield values are used in this thesis to indicate how similar the experimental treatments are to chlorination in their effect on the wool fibre surface.

### 2.5.3 Fabric Dyeing

When wool is dyed the process is characterised by a surface barrier effect that influences the rate of dyeing (Pailthorpe, 1992, Rippon, 1992). This effect is thought to be due to the complex surface structure of the wool fibre (Section 1.2). During dyeing, wool dyes appear to diffuse through the intercuticular regions first and then into the
nonkeratinous regions of the endocuticle, the intercellular cement and the intermacrofibrillar cement.

Competition dyeing provides an easy method to compare the dyeing rates of wool fabrics that have undergone different treatments and thus the effect of the treatments on the surface barrier of the wool. Equal masses of identical (except for the treatment type) fabric are introduced into a single dye bath and the dyeing process is allowed to proceed to exhaustion. Treatments that reduce the surface barrier to dyeing will dye more rapidly and thus achieve a greater dye colour depth than untreated wool. Untreated wool was included in every dye bath to provide a standard.

Competition dyeing was performed using an AHIBA 1000 Turbomat laboratory dyeing system. The samples were cut into circular (4 sample comparisons) or half-circles (8 sample comparisons) that would fit into the bottom of the AHIBA dyeing basket. The solution used was:

Lanasol Blue 8G 1% o.w.f.
Water 200 ml

The wool in the dyeing baskets was added to the solution which was then heated to 50°C. The solution was then acidified using acetic acid to pH 4.5. It was then heated at a rate of 1°C/min to 98°C and kept at this temperature for 1 hour. This resulted in complete exhaustion of the dye onto the fabrics. Lanasol Blue 8G (CI Acid Blue 185) was chosen as it is a phthalo-cyanine derivative and is very bulky with 3 or 4 SO₂ groups.

The colour depth was measured using CIE Lab values, under D65 illumination, obtained from a Datacolour 3890 spectrophotometer. The colour depth values reported in this thesis were normalised -ΔL values, with the value for untreated wool being set equal to 1. ΔL represents the lightness/darkness of the fabric under illumination, as compared to a standard white tile. Thus the more negative a ΔL value the darker the fabric and so the greater the colour depth achieved by the blue dye.

2.5.4 Fabric Felting Shrinkage

Wool fabrics are prone to dramatic felting shrinkage when washed mechanically. This is thought to be due to the "differential friction effect" (DFE) which is caused by the shape of the wool fibre scales (Section 1.2.6). Oxidation of the wool surface by chlorination or removal of surface lipids by hydrolysis is known to reduce this effect (Makinson, 1979, Leeder & Rippon, 1985). It has been suggested that chlorination works by removing the scale structure and eliminating the DFE. However, other methods, including removing surface lipids by hydrolysis, do not alter the scale
structure. It has been suggested that these methods may work by increasing the frictional coefficients of the scales, in both directions, to a high enough level as to prevent any fibre movement at all during washing (Makinson, 1979).

CSIRO standard shrinkage fabric (Fabric A from Guise et al., 1989, see Section 2.1.1) was plasma treated and then tested using IWS test method TM31. A single ISO 7A wash cycle was carried out to relax the fabric, followed by multiple ISO 5A wash cycles to evaluate shrinkage, in a Wascator (a washing machine specified in the standard IWS TM31).

For the fabric relaxation stage, the fabric specimens were conditioned for several days, then placed in the Wascator and ballast was added to to give a total load of 1 kg. The detergent was dissolved in water and added during the first water fill. Then a single 7A wash cycle was carried out. The fabric was dried and then conditioned for at least 24 hours in a standard testing atmosphere of 65 ± 2% relative humidity and temperature of 20 ± 2 °C. The relaxed fabric measurements were then carried out.

This was followed by the shrinkage evaluation stage. The fabrics were placed in the Wascator and ballast was added to give a total load of 1 kg. The detergent was dissolved in water and added during the first water fill. Then a single 5A wash cycle was carried out. The fabric was dried and then conditioned for at least 24 hours in a standard testing atmosphere of 65 ± 2% relative humidity and temperature of 20 ± 2 °C. The felting shrinkage fabric measurements for one 5A cycle were then measured. This process was repeated for a total of five 5A cycles. The area shrinkage for each cycle was calculated using the method specified by IWS test method TM31.

The fabric area shrinkage values reported in this thesis are compared to the shrinkage of the untreated wool fabric after a single 5A cycle and then after a total of five 5A cycles. The single 5A cycle indicates the ability of the fabric to resist felting for a limited number of home washings. The five 5A cycles represent how the fabric would stand up to a long lifetime of multiple home washes. A fabric shrinkage of greater than 5% is generally considered to be commercially unacceptable.
CHAPTER 5 ANALYSIS OF MODEL TREATMENTS

INTRODUCTION

The plasma treatment is a useful pretreatment method for modifying the surface of the coated form. By re-combining the coating polymers affected by plasma treatment with other coated treatments in order to find optimal conditions, the separate reactions mechanisms occurring in plasma treatment are presented separately so that they can be compared with the plasma treatments presented in Chapter 4.

The 'model' treatments studied can be divided into two groups. The first set of treatments was investigated in order to determine whether the polymer films formed in the plasma treatment are the same, and if not, how much of the coating that had been applied is still present in the plasma treatment. This was determined by comparing the substrates of various plasma treatments and the effects of plasma. U.V. reactor treatment alone and plasma treatment were investigated in order to find the degree of cure of the surface treated. This was then compared with the effect of the plasma treatment.

The second set of treatments involved four different substrates. These were coated with plasma and exposed to different conditions in order to determine the effect of various plasma treatments and the effect of the plasma treatment on the resulting substrates. The substrates were exposed to different plasma treatments: sensitivity testing, sensitization testing, and sensitization testing using u.v. (365 nm) light. This was followed by examining the results of the plasma treatments and comparing them with the results of the other treatments. The results of the plasma treatments were then compared with the results of the other treatments.
CHAPTER 3: ANALYSIS OF 'MODEL' TREATMENTS

3.1 INTRODUCTION

The plasma treatment of wool represents a new method for modifying the surface of the wool fibre. By comparing the modifications produced by plasma treatment with other model treatments it may be possible to distinguish the separate reaction mechanisms occurring in plasma treatment. The experiments were carried out in parallel to the plasma research but the results and analysis for the model treatments are presented separately so that they can be compared and contrasted with the plasma treatments presented in Chapters 4 - 6.

The 'model' treatments studied can be divided into two groups. The first set of treatments was investigated in order to determine whether the proposals put forward in the past literature were correct. Reactive species that had been suggested, yet not formally investigated, were ultraviolet (UV) radiation, electrons, or unspecified other reactive particles (see Tables 1.3 - 1.4). To investigate if these claims could explain the effects of plasma, UV irradiation, electron beam, and ozone treatments were investigated. An alternative outcome from these studies was that it may be possible to distinguish a partial contribution of the individual effects to the overall effect of plasma treatment.

The second set of treatments have been studied extensively for several decades and were well documented in the literature. They all produce oxidation of the wool fibre, but differ in their reaction pathways, depth of penetration into the wool fibres, and the chemical groups attacked. The reaction paths and the effects the treatments have on the wool fibre were well known and generally agreed on by the research community. By finding the similarities and differences between plasma treatment and these techniques the possibilities for the reaction mechanisms of plasma treatment can be narrowed down. The treatments investigated were hydrogen peroxide bleaching (H$_2$O$_2$), chlorination using "Basolan" dichloroisocyanuric acid (DCCA), alcoholic (using methanol) potassium hydroxide (KOH/MeOH) and tertiary butoxide in anhydrous alcoholic (using tertiary butanol) conditions (t-BuOK/t-BuOH).

The results from the techniques used to study the model treatments are presented in section 3.2. In section 3.3 each model treatment is discussed separately and a mechanism for its reaction with the wool fibre is suggested based on the results.
observed and the literature. Where data for these treatments has been obtained from the literature it is individually referenced in the accompanying tables and graphs.

3.2 OBSERVATIONS

The surface analysis associated with these treatments has been discussed in the literature but for completeness an analysis has been made using the techniques used in this thesis. Where possible samples were obtained for the majority of the different treatments from colleagues (Section 2.3). For a limited number of the treatments no samples could be obtained, or some of the analysis techniques were no longer available, and thus only literature results were available and were used for comparison purposes.

Undertaking this analysis fulfilled two functions. It allowed comparison of the results with the documented results in the literature and ensured that the technique was being reproduced properly. Also, by using the more modern equipment and/or newer techniques available, it was possible to study whether the heightened sensitivity shed any new light on the treatment process that had not been observed previously. All the results presented here have used the measurements of ABUTC samples as the base-line for comparison between the different treatments.

3.2.1 FeSEM Appearance

Observation of the uncoated samples at low voltage allowed fine surface details to be compared between the samples. Due to the newly developed status of the FeSEM no papers have been published of FeSEM studies on the model treatments studied in this chapter. Previous work reported in the literature used SEM's that had a much higher accelerating voltages and required a conductive metal coating (see section 2.4.1). The resultant charging and thick coatings will have obscured fine detail in the surface and often this meant that extreme conditions of treatment had to be investigated before any changes to the surface were observed (e.g. Hepworth et al, 1969). For this reason previous papers have not been discussed in this section.

Untreated wet scoured wool (Fig.3.1) shows a smooth surface with a pattern of slight ridging on the top surface of the scales. The face of the scales shows a slight scalloping along a line midway up the edge. These features were slightly more accentuated after the wool fibre has been soxhlet extracted with methylene chloride (Fig.3.2). The methylene chloride soxhlet extraction removes 0.6% o.m.f. (on mass of fibre) of grease (AS 2001.3.4 Test A) and this leads to an improvement in the visibility and definition of the scale edges. However, the two images do not differ greatly.
Chapter 3. Analysis of Model Treatments

The first group of treatments (Fig.3.3, 3.4) have little effect on the appearance of the surface of wool. UV radiation and electron beam leave the surface appearing identical to the untreated wool. No samples were available for ozone treated wool (Section 2.3.3).

The second group of treatments have a much wider range of effects. The H2O2 bleach (Fig.3.5) leaves the surface unchanged. The chlorination treatments (Fig.3.6, 3.7) clearly damage the fibre surface. 1% DCCA produces pronounced ridging on the scale surface. The damage appears to have occurred to the material under the scale surface, causing the surface layer to subside. 3% DCCA removed the scale structure almost entirely, leaving a fairly flat surface covered with pinholes.

KOH/MeOH and t-BuOK/t-BuOH treatments (Fig.3.8, 3.9) attack the bound lipids of the wool fibre. Although these processes are known to break the bonds of the lipids bound to the wool surface, neither produce any change to the surface features.

Fig.3.1 FeSEM of Untreated Wool Fibre (ABUT)
Chapter 3. Analysis of Model Treatments

Fig. 3.2 Untreated Wool, Soxhlet Extracted with Methylene Chloride (ABUTC)

Fig. 3.3 Wool Fibre after 40 min. UV Treatment
Chapter 3. *Analysis of Model Treatments*

Fig. 3.4 Wool Fibre after 150 kGray E-beam Treatment

Fig. 3.5 Wool Fibre after H$_2$O$_2$ Treatment
Chapter 3. Analysis of Model Treatments

Fig. 3.6 Wool Fibre after 1% DCCA Treatment

Fig. 3.7 Wool Fibre after 3% DCCA Treatment
Fig. 3.8 Wool Fibre after KOH/MeOH Treatment

Fig. 3.9 Wool Fibre after t-BuOK/t-BuOH Treatment
3.2.2 Allwörden Sac Formation

Allwörden Sac formation was used to monitor the degree of damage to the epicuticle of the wool fibre surface. An untreated wool fibre (Fig. 3.10) gives a normal Allwörden reaction with bubbles or sacs being clearly visible on both sides of the wool fibre. Chlorination is known to damage the surface scale structure of wool, as seen in Fig. 3.7, and thus 3% DCCA treatment results in no Allwörden sac formation (Fig. 3.11). The results for all the treatments are shown in Table 3.1 (No results were available for ozone or H2O2+UV, due to lack of samples).

![Fig. 3.10 Allwörden Sac Formation on an Untreated Wool Fibre ABUTC](image)

![Fig. 3.11 No Allwörden Sac Formation on 3% DCCA Treated Wool Fibre](image)

In the first group of treatments only UV produced a change in Allwörden sac formation, with a drop to 30%.

All of the second group of treatments have an effect on Allwörden sac formation. The H2O2 bleach does a small amount of damage to the wool surface. The damage caused to the scale structure by the chlorination treatments produces a rapid decrease in sac formation with no more sacs being formed from levels of 2% upwards. This correlates well with the FeSEM results. The disulphide and peptide bonds, prone to reaction with chlorine to form Allwörden sacs, are already destroyed by the DCCA treatment.

The KOH/MeOH treatment does not lead to the formation of Allwörden sacs whilst the t-BuOK/t-BuOH leaves a small number of fibres to produce sacs. These results agree well with Negri et al 1992, who studied the Allwörden sac formation of these
treatments in great detail. The KOH/MeOH penetrates throughout the fibre and ruptures the bonds required for Allwörden sac formation. The t-BuOK/t-BuOH treatment is performed under anhydrous conditions to restrict the swelling of the wool and, in combination with the bulky reagents, limits its reaction to the surface of the wool. Thus some of the bonds required for the Allwörden reaction survive inside the fibre surface and produce a small amount of sac formation.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>% Fibres with Allworden Sacs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABUT</td>
<td>(± 10%)</td>
</tr>
<tr>
<td>ABUTC</td>
<td>100%</td>
</tr>
<tr>
<td>UV 5 min.</td>
<td>30%</td>
</tr>
<tr>
<td>UV 40 min.</td>
<td>35%</td>
</tr>
<tr>
<td>E-beam 150 kGray</td>
<td>100%</td>
</tr>
<tr>
<td>Ozone</td>
<td>nm</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>90%</td>
</tr>
<tr>
<td>H₂O₂ + UV</td>
<td>nm</td>
</tr>
<tr>
<td>1% DCCA</td>
<td>30%</td>
</tr>
<tr>
<td>2% DCCA</td>
<td>0%</td>
</tr>
<tr>
<td>3% DCCA</td>
<td>0%</td>
</tr>
<tr>
<td>Saturated DCCA</td>
<td>0%</td>
</tr>
<tr>
<td>KOH/MeOH, 60 min</td>
<td>0%</td>
</tr>
<tr>
<td>t-BuOK/t-BuOH</td>
<td>20%</td>
</tr>
</tbody>
</table>

Table 3.1 Results for Allwörden Sac Formation with Model Treatments

(nm - not measured, see Section 2.3)

3.2.3 Surface Energy Changes

Plasma treatment produces a large increase in the surface energy of the wool fibre. Thus for any of these model treatments to prove useful as a comparison they would also have to produce dramatic changes in wool's surface energy (Table 3.2 [ozone samples were not available for surface energy analysis])

The results show that UV and e-beam treatments have very little effect on the wool fibre's surface energy. Small increases in surface energy occur for the dispersion component, but these are within the same range as wool after it has been soxhlet extracted with methylene chloride (ABUTC) to give a clean, grease-free surface. Neither treatment will allow water to wet the wool fibre. Shao et al, 1997 found that
ozone eventually produced decreased wetting times after long exposures of 5 - 10 minutes.

All of the oxidising treatments produce significant changes in wool’s surface energy. H2O2 primarily increases the polar component. But when UV treatment is combined with H2O2 there are significant increases in dispersion and polar components.

Chlorination produces a large increase in the dispersion component but a smaller increase in the polar component. This correlates well with the damage shown in the FeSEM and Allwörden results, as it is clear that chlorination strips off the surface layers of the wool. It is interesting that the increasing levels of chlorination produce decreasing values for the polar component. This may be related to the depth of penetration of the treatment and thus the modified surface layer (exocuticle, endocuticle or cuticle) of wool left on the surface.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>ΔW (mJ/m²)</th>
<th>Surface Energy (mJ/m²)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>methylene iodide</td>
<td>water</td>
<td>$\gamma_s^d$</td>
<td>$\gamma_s^P$</td>
</tr>
<tr>
<td>ABUT</td>
<td>16.9±1.2</td>
<td>[-7.6]</td>
<td>[20.1]</td>
<td>[5.8]</td>
</tr>
<tr>
<td>ABUTC</td>
<td>27.5±1.3</td>
<td>[-7.6]</td>
<td>[28.9]</td>
<td>[3.1]</td>
</tr>
<tr>
<td>UV 5 min.</td>
<td>20.3±1.2</td>
<td>&lt; 0</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>UV 40 min.</td>
<td>24.3±0.9</td>
<td>&lt; 0</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>E-beam 150 kGray</td>
<td>22.6±2.0</td>
<td>&lt; 0</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ozone</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O2</td>
<td>21.3±2.9</td>
<td>35.8±1.5</td>
<td>22.3±2.0</td>
<td>21.0±1.5</td>
</tr>
<tr>
<td>H2O2 + UV</td>
<td>34.5±3.1</td>
<td>46.5±4.1</td>
<td>30.3±2.1</td>
<td>20.6±1.4</td>
</tr>
<tr>
<td>1% DCCA</td>
<td>38.4±1.8</td>
<td>43.0±1.7</td>
<td>45.0±2.0</td>
<td>10.7±0.9</td>
</tr>
<tr>
<td>2% DCCA</td>
<td>38.2±2.9</td>
<td>45.0±1.4</td>
<td>43.3±2.1</td>
<td>13.2±0.6</td>
</tr>
<tr>
<td>3% DCCA</td>
<td>40.9±2.1</td>
<td>39.4±1.2</td>
<td>47.1±1.9</td>
<td>7.8±0.4</td>
</tr>
<tr>
<td>Saturated DCCA</td>
<td>37.0±1.7</td>
<td>37.0±1.3</td>
<td>44.0±1.9</td>
<td>8.1±0.6</td>
</tr>
<tr>
<td>KOH/MeOH 60 min</td>
<td>43.3±1.5</td>
<td>51.6±1.9</td>
<td>36.4±1.2</td>
<td>22.7±1.2</td>
</tr>
<tr>
<td>t-BuOK/t-BuOH</td>
<td>45.3±1.5</td>
<td>40.8±2.5</td>
<td>38.8±1.2</td>
<td>14.4±2.0</td>
</tr>
</tbody>
</table>

Table 3.2 Surface Energy Values for Model Treatments ($\Delta W = \gamma_1 \cos \theta_a$).
[Values in square brackets were derived using Brooks et al 1986 water $\theta_a = 96 \pm 2^\circ$]

{Surface energy components based on methylene iodide and water; na - not applicable (cannot be calculated without a $\Delta W$ value for water (Section 2.4.4))}
The KOH/MeOH produces a large change in both the polar and dispersion components. The t-BuOK/t-BuOH has a similar increase in the dispersion component but a smaller increase in the polar component which leads to a total surface energy similar to chlorinated wool.

### 3.2.4 Surface Chemistry (XPS)

XPS measurements (Table 3.3) show how the model treatments changed the surface chemistry of the wool fibre (e-beam and ozone samples were not available for XPS analysis). The ratio of an element to nitrogen indicates how close the surface is to being a protein layer (Ward et al., 1993) and the %oxidised is useful for indicating the change from untreated wool.

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>Atomic%</th>
<th>Elemental Ratio</th>
<th>% Oxidised</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>ABUT</td>
<td>75.1</td>
<td>12.6</td>
<td>8.5</td>
</tr>
<tr>
<td>ABUTC</td>
<td>70.4</td>
<td>15.6</td>
<td>11.0</td>
</tr>
<tr>
<td>UV 40 min.</td>
<td>73.4</td>
<td>16.9</td>
<td>8.2</td>
</tr>
<tr>
<td>E-beam 150 kGray</td>
<td>(70.5)</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td>Ozone</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
</tr>
<tr>
<td>H_2O_2</td>
<td>74.2</td>
<td>16.1</td>
<td>7.9</td>
</tr>
<tr>
<td>H_2O_2 + UV</td>
<td>73.2</td>
<td>15.9</td>
<td>7.8</td>
</tr>
<tr>
<td>1% DCCA</td>
<td>66.2</td>
<td>19.7</td>
<td>7.7</td>
</tr>
<tr>
<td>2% DCCA</td>
<td>59.4</td>
<td>21.6</td>
<td>13.0</td>
</tr>
<tr>
<td>3% DCCA</td>
<td>62.1</td>
<td>21.2</td>
<td>11.2</td>
</tr>
<tr>
<td>Saturated DCCA</td>
<td>64.2</td>
<td>19.1</td>
<td>13.1</td>
</tr>
<tr>
<td>KOH/MeOH 60 min</td>
<td>50.7</td>
<td>27.2</td>
<td>9.7</td>
</tr>
<tr>
<td>t-BuOK/t-BuOH</td>
<td>51.7</td>
<td>29.1</td>
<td>7.9</td>
</tr>
</tbody>
</table>

| Protein (Albumin) ratio’s from Ward et al., 1993 | 4.3 | 1.25 | 0.05 | nm | nm |

Table 3.3 Surface Chemistry (XPS) of Model Treatments.
(Values in brackets for the e-beam are from Gilleßen et al., 1995)
(nm - not measured and there are no values given in the literature)
[Error in all values is ± 10% of the value]

The carbon figures have to be treated with caution due to the potential for free lipid contamination, despite the extreme care that was taken. It is also necessary to remember that the information has been measured from a wide range of sample depths due to the random configurations and individual heterogeneity of the wool fibres in the sample.

The untreated wool fibre (ABUT) still has residual grease present (0.6 % o.m.f., Section 2.1.1) after aqueous scouring. This is removed by the methylene chloride soxhlet extraction (ABUTC) which produces a slight decrease in carbon and an increase in the oxygen and nitrogen as the surface layer of grease is removed, revealing the actual wool surface. The extracted grease has a higher level of oxidation than the wool surface underneath, presumably due to weathering and the effects of processing, as seen in the decrease in the oxidised carbon ratio. The wool surface contains less oxidised lipid and with the concealing layer of grease removed, a small amount of oxidised sulfur was observed within the surface.

UV slightly increases the carbon and oxygen, whilst decreasing the nitrogen and sulphur on the surface. This suggests that oxidised material has been introduced onto the surface as a covering layer. This is supported by the observed increase in the relative amount of oxidised sulfur, while the proportion of oxidised carbon does not change.

E-beam treatment does not change the carbon or sulfur signal at all from ABUTC. However, the proportions of oxidised carbon and sulfur both increase indicating that some oxidised sulfur and carbon is being formed in the surface (Gilleßen et al, 1995).

Ozone treatment increases the carbon and sulfur oxidation levels above untreated wool, with the sulfur appearing to become nearly 100% oxidised after ozone treatment (Bradley et al, 1995, Shao et al, 1997).

H2O2 produces a similar effect to UV except that the oxidised carbon ratio decreases slightly and the oxidised sulfur ratio increases even more. When UV treatment is combined with H2O2 there is an even greater increase in the amount of oxidised sulfur to three-quarters of the sulfur present on the surface. However these treatments cause a small decrease in oxidation of the surface carbon and combined with the decrease in surface nitrogen indicates the presence of an oxidised layer on top of the surface.

Chlorination has a dramatic effect on all the elements present in the surface. The low level 1% DCCA treatment produces decreases in carbon and nitrogen while increasing the oxygen. The high oxidation levels of the carbon and sulfur suggests a layer of oxidised material has been built up on the surface, covering the nitrogen signal and diluting the carbon signal. The increasing amounts of nitrogen present on the surface as
the treatment level increases indicates that the treatment is penetrating deeper and deeper into the surface and revealing changing protein layers. As each new layer of protein was revealed, all of the surface sulfur was oxidised and there were even larger increases in the relative amount of oxidised carbon.

The KOH/MeOH and t-BuOK/t-BuOH both produce the largest drop in carbon which is matched by the largest increase in surface oxygen. The relative amounts of oxidised carbon and oxidised sulfur are higher than untreated, although not as dramatic as for chlorination. The lower levels of nitrogen indicate an overlayer of oxidised material containing much higher levels of oxygen than the previous treatments had produced.
3.2.5 Textile Property Changes

It was not the intention of this research to evaluate the changes in all the textile properties of the model treatments as these were not the focus of this thesis. However, it was thought useful to review the available literature and try to draw general trends for the other properties for comparison with the plasma treatments. These trends have only been evaluated in very simple terms as either showing: no change, an increase or a decrease. No attempt has been made to quantify the changes as the varying experimental conditions and wool samples used would mean that any quantitative conclusions would be highly questionable. However, it was possible to investigate the dye colour depth (section 2.5.3) in competition dyeing experiments performed during this research, except for ozone for which no samples were available (Table 3.4).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Fabric Shrinkage</th>
<th>Dye Colour Depth (±0.02)</th>
<th>Print Colour Yield</th>
<th>Yarn / Fabric Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABUTC</td>
<td>na</td>
<td>1.00</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>UV</td>
<td>no change</td>
<td>1.39</td>
<td>Improve</td>
<td>Decrease</td>
</tr>
<tr>
<td>E-beam 150 kGray</td>
<td>Improve</td>
<td>1.18</td>
<td>Improve</td>
<td>no change</td>
</tr>
<tr>
<td>Ozone</td>
<td>Improve</td>
<td>Improve</td>
<td>Improve</td>
<td>no change</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>no change</td>
<td>0.80</td>
<td>Improve</td>
<td>no change</td>
</tr>
<tr>
<td>H$_2$O$_2$ + UV</td>
<td>Improve</td>
<td>1.55</td>
<td>Improve</td>
<td>Decrease</td>
</tr>
<tr>
<td>1% DCCA</td>
<td>Improve</td>
<td>2.00</td>
<td>Improve</td>
<td>Decrease</td>
</tr>
<tr>
<td>2% DCCA</td>
<td>Improve</td>
<td>2.15</td>
<td>Improve</td>
<td>Decrease</td>
</tr>
<tr>
<td>3% DCCA</td>
<td>Improve</td>
<td>2.63</td>
<td>Improve</td>
<td>nm</td>
</tr>
<tr>
<td>Saturated DCCA</td>
<td>Improve</td>
<td>1.21</td>
<td>Improve</td>
<td>Improve</td>
</tr>
<tr>
<td>KOH/MeOH 60 min</td>
<td>Improve</td>
<td>1.78</td>
<td>Improve</td>
<td>Improve</td>
</tr>
<tr>
<td>t-BuOK/t-BuOH</td>
<td>Improve</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4 Textile Property Changes Relative to Untreated Wool (ABUT). Dye Colour Depth was measured by experiment, text entries are based on the literature (na - not applicable as untreated wool is the base-line for comparison).

UV treatments have been reported as having no effect on wool fabric shrinkage. However UV radiation has been observed to lead to an increase in print colour yield and a decrease in yarn/fabric strength (Makinson, 1979, Milligan, 1980, Nicholls, 1980, Maclaren et al, 1981, Carr & Lewis, 1993, Körner et al, 1995, Goddinger et al, 1995, Millington, 1995).
Very little has been reported in the literature on e-beam treatment of wool. Nothing has been reported about the effect of e-beam treatment on wool fabric shrinkage or print colour yield. E-beam treatment has been reported to have no effect on yarn/fabric strength (Needles, 1978, Herrling et al, 1995, Gilleßen et al, 1995).

Ozone treatment has been reported as improving wool fabric shrinkage, dye colour depth, and print colour yields. No measurements have been reported on the effect of ozone on wool fabric/yarn strength (Thorsen, 1965, Thorsen & Kodani, 1967, Thorsen & Landwehr, 1975, Bradley et al, 1995, Shao et al, 1997).

Hydrogen peroxide bleaching alone has been reported to have no effect on wool fabric shrinkage or yarn/fabric strength. A small improvement has been reported for print colour yield (Makinson, 1979, Maclaren et al, 1981).

Hydrogen peroxide combined with UV treatment is a new treatment developed by CSIRO and has been reported to increase dye colour depth and print colour yield, but to have no effect on yarn/fabric strength. No results for wool fabric shrinkage have been reported (Millington, 1995).

Chlorination by DCCA is well documented in the literature for improving wool fabric shrinkage and print colour yield, but decreasing yarn/fabric strength (Makinson, 1979, Maclaren et al, 1981, Millington, 1995).

Alcoholic alkali treatments have been documented as improving wool fabric shrinkage and print colour yield. However only tertiary butoxide in tertiary butanol (t-BuOK/t-BuOH) has been reported as improving yarn/fabric strength (Leeder & Bradbury, 1971, Makinson, 1979, Maclaren et al, 1981, Leeder & Rippon, 1985, Leeder et al, 1985, Negri et al, 1993)

3.3 DISCUSSION

3.3.1 Soxhlet Extraction with Methylene Chloride

The soxhlet extraction with methylene chloride was undertaken to remove any loosely bound surface grease and contaminants that were not removed by aqueous scouring of the raw wool or that may have been applied during the processing stages. It was also done in order to ensure that the wool treatments studied during this research were performed on similar surfaces and could be compared properly. Although it only removed the small amount of 0.6% o.m.f., this was concentrated on the wool surface as a thin layer, and thus had a significant effect on the wool fibre surface.

The FeSEM showed that removal of this material leads to improvement in the visibility and definition of surface features. However, no major surface features change. This is
also confirmed by the Allwörden sac formation of 100% which shows that there is no
damage to the wool epicuticle after this treatment.

The removal of the surface contaminants increased the surface energy of the wool, yet
not enough to allow water to wet the surface. XPS shows that the material removed was
higher in carbon than the actual wool surface, which would be expected if it is
predominantly grease. This carbon material was more highly oxidised than the wool
surface and its removal exposed some oxidised sulfur on the wool surface. The
oxidation levels present are probably due to damage by weathering of the wool fibres
on the sheep's back.

This cleaning method does not lead to any significant changes in the shrink-resistance,
dyeing, printing or strength properties of the wool.

3.3.2 Ultraviolet Irradiation

UV treatment had no visible effect on the surface of the wool as observed using the
FeSEM. However it did produce a drop in the Allwörden sac formation to 30%. There
was also a slight decrease in surface energy back towards the untreated wool value
(ABUT). XPS shows some changes in the surface chemistry from the soxhlet extracted
wool fibre (ABUTC). The amount of nitrogen and sulfur decreases and the level of
oxidised sulfur increases. This suggests that some of the disulfide bonds on the surface
are being broken by the UV, producing a slightly oxidised layer on the surface. There is
no reported effect on fabric shrinkage but UV does lead to an improvement in dyeing
and printing, along with a decrease in strength properties.

These changes can be explained by the attack of UV radiation (~4.9 eV) on the
disulphide (~2.6 eV) and peptide (~3.0 eV) bonds in the surface of the wool fibre. The
rupture of the bonds by the UV radiation prevents the chlorine from reacting with the
surface of the wool fibre to produce the Allwörden effect. The oxidised surface also
allows greater colour depth in the wool fibres after printing and dyeing as the oxidation
partially removes the 'barrier' effect of the wool surface layers.

However, UV radiation is a line-of-sight dose effect that penetrates deeply into the
wool fibre. Thus, it has only a small effect on the wool surface and the UV is absorbed
by the first fibres it encounters, which will produce a shadowing effect. Thus any fibres
hidden under the first fibre will not be affected by the UV and are still capable of
producing the Allwörden effect even after long treatment times.

The values for untreated wool are thought to be influenced by weathering (sunlight
exposure) on the sheep's back (Maclaren & Milligan, 1981). UV mimics the effect of
natural weathering and thus produces no dramatic changes from the surface of untreated wool.

### 3.3.3 Electron Beam Irradiation

The electron beam produced no change to the fibre surface as viewed by the FeSEM. Allwörden sac formation, surface energy of the wool fibre surface or total carbon and sulfur results (XPS from Gilleßen et al, 1995). The carbon and sulfur did show a higher level of oxidation than the untreated.

There are no reports in the literature (Gilleßen et al, 1995) of electron beam treatment having an effect on wool shrinkage and printing properties and there was no measured significant change in fibre strength. Dye colour depth does improve after electron beam treatment (Table 3.4).

The electron beam accelerated at 180 keV has a penetration depth of greater than 350 µm (Fig.3.12), which is much greater than the thickness of the fibre. It appears the electrons, on passing through the surface, produce a low level of surface oxidation on the soxhlet cleaned fibres similar to the weathering present on ABUT fibres, as shown by the carbon oxidation ratio. Herrling et al, 1995 found that even TEM could only observe slight changes to the surface of the exocuticle for e-beam treatment that were attributed to oxidation of the surface.

![Interaction Volume Simulation](image)

**Fig.3.12 Interaction Volume Simulation of E-beam Treated Wool Fibre (from Veitch)**

The observed oxidation could be caused by collisions between the electrons and molecules in the wool fibre leading to broken bonds that are then free to react with...
residual oxygen. As the electrons penetrate into the fibre they similarly oxidise some of the disulfide bonds, increasing the oxidised sulfur ratio. This oxidation produces a slight increase in fibre surface energy and the damaged regions of oxidised material open up the surface to easier penetration by dye molecules. However, the electrons pass easily through the fibre, due to their high energies, and thus do not cause many reactions in any given fibre.

3.3.4 Ozone Treatment

There has been no report of ozone having any effect on the surface structure of the wool fibre or Allwörden sac formation in the literature.

Bradley et al, 1995 and Shao et al, 1997 showed that UV/ozone treatment led to an increase in carbon oxidation levels and nearly all of the sulphur was oxidised. As well they showed that ozone would improve the shrinkage, dyeing, printing and wetting properties of wool fabrics. There has been no report of any effect on yarn/fabric tensile properties.

Shao et al, 1997 claimed the UV/ozone is a photosensitised oxidation process where the surface molecules are excited and/or dissociated by the UV and react with atomic oxygen (created by ozone reacting with the UV to make atomic oxygen). This would then lead to an oxidised surface layer being formed over the surface of the wool fibre.

3.3.5 Hydrogen Peroxide Treatment

Hydrogen peroxide (H₂O₂) bleaching of wool left the surface appearance unchanged and only slightly decreased the Allwörden sac formation to 90%. It had little effect on the dispersive component of wool fibre surface energy but greatly increased the polar component and thus the total surface energy. XPS shows the carbon and oxygen levels as similar to ABUTC wool, but the nitrogen and sulfur levels decrease. The level of carbon oxidation is similar to ABUTC but the sulfur oxidation is very high.

Dye colour depth decreases after H₂O₂ treatment but the H₂O₂ treatment has no effect on wool shrinkage or tensile properties. Millington, 1995 has reported a small increase in print colour yield.

These results can be explained by the H₂O₂ oxidising a large number of the sulfur groups in or near the surface. This increases the polar component of the surface energy while producing a layer of oxidised groups near the surface that cover and reduce the total nitrogen and sulfur signals. The dye colour depth decreases due to the whiter ground of the bleached fabric combining with the dye, to produce a lighter colour than for the yellowed untreated wool fibre. The print colour yield is partly improved by the
increased surface energy and by the presence of oxidised sulfur groups that improve the uptake of dye in the fibre.

3.3.6 Ultraviolet Irradiation followed by Hydrogen Peroxide Bleaching

No FESEM and Allwörden results were available, but both components of the surface energy increase when UV and H₂O₂ are combined. The XPS for the atomic% and the carbon oxidation ratio is very similar to H₂O₂ treatment but the amount of sulphur oxidised increases dramatically to nearly 75% of total sulphur.

The combined treatment improves dyeing and printing properties and has no effect on yarn/fabric strength. The effect on shrinkage has not been evaluated.

These results can be explained by the UV damaging the surface protective layer which then allows the H₂O₂ easier access into the surface protein, through the damaged regions, where it oxidises more sulfur then if it were acting alone. The H₂O₂ increases the polar component and the UV increases the dispersion component of the surface energy. The UV effects and the H₂O₂ effects combine in a positive way to give a considerably more oxidised sulfur surface.

3.3.7 DCCA Chlorination

Chlorination clearly damages the surface of the wool as shown by FeSEM, with 1% DCCA appearing to undermine the surface and causing it to subside. Higher levels remove the surface altogether leaving a slightly pitted or ridged, but predominantly smooth surface. The Allwörden results closely parallel the FeSEM results with no sac formation from 2% DCCA and higher.

Chlorination dramatically increases surface energy, although most of the increase is in the dispersion component with only smaller levels for the polar component. This differs from Brooks et al 1986, who found a greater increase in the polar component than for the dispersion. However, their sample was made up of individual Lincoln fibres which had been chlorinated to a level of 0.5% and so represent a lower level of treatment on a different type of wool fibre.

XPS shows a large decrease in carbon and a large increase in oxygen atomic concentration, while the nitrogen level depends on the degree of treatment. The carbon oxidation ratio increases dramatically while all of the available sulfur in the surface is oxidised.

Chlorination is well known in the literature (Makinson, 1979, Maclaren & Milligan, 1981, Bell, 1992, Byrne, 1995) for improving fabric shrinkage, printing and dyeing
properties whilst damaging the fibre, so that there is a decrease in strength properties. It
gave the greatest increase in colour depth in the competition dyeing experiments.

These results suggest that increasing levels of chlorination etch into the wool fibre to
greater and greater depths. The low level of 1% DCCA attacks the original surface,
oxidising both disulfide and peptide bonds and producing a layer of oxidised groups on
the surface that mask the nitrogen signal. There is not enough chlorine present to
oxidise every sulfur and peptide bond available to the chlorine, thus some Allwörden
sacs still form and the scale structure is still recognisable.

Higher levels than 1% DCCA oxidise all the sulfur and peptide bonds available for
reaction in the surface, which causes the surface of the wool fibre to be destroyed and
dissolved away. More and more of the surface material is removed to greater and
greater depths as the amount of chlorine increases. This explains the changing surface
energy components and different levels of carbon, nitrogen and sulfur as new protein
layers of the exocuticle and then endocuticle are revealed. The surface that is left is
covered with a layer of partially oxidised carbon and wholly oxidised sulfur. No
Allwörden sacs form as there is no longer any non-reactive membrane on the wool
surface as it has been removed when the outer layers of protein are dissolved.

Wool shrinkage improves as the scale structure is removed. Also, the high surface
energy of the new surfaces increases the friction between the chlorinated wool fibres to
such an extent that the differential friction effect no longer occurs (Makinson, 1979).
The damage to the fibre surface opens up easy access routes for dye molecules, thus
improving the dyeing and printing properties. The negative side of this damage is that it
occurs throughout the fibre and so reduces fibre strength significantly.

3.3.8 Alcoholic Alkali Treatment

Neither of the KOH/MeOH or the t-BuOK/t-BuOH has any effect on the surface
appearance of the wool fibre under FeSEM. However, they both reduce the Allwörden
sac formation. The KOH/MeOH produces no sacs whilst the t-BuOK/t-BuOH still
allows 20% of sacs to form. They also produce the greatest change in wool surface
energy with both the polar and dispersion components increasing dramatically.

XPS shows they both have the largest drop in carbon content and the largest increases
in oxygen levels. KOH/MeOH has slightly less oxygen and more nitrogen at the surface
whilst the effect of t-BuOK/t-BuOH is vice versa. KOH/MeOH has an equally high
level of carbon and sulfur oxidation while the t-BuOK/t-BuOH has increased carbon
oxidation but with an even more increased level of sulfur oxidation.
Both techniques are known to improve fabric shrinkage and printing properties. Only t-BuOK/t-BuOH has received any mention in improving strength properties. Both improve the dyeing properties of wool with KOH/MeOH producing a small increase and the t-BuOK/t-BuOH producing a very large increase.

Both methods attack the bound lipids in the wool fibre and break these bonds by hydrolysis. KOH/MeOH swells the wool fibre and reacts throughout the fibre. The t-BuOK/t-BuOH, however, is performed under anhydrous conditions so that no fibre swelling occurs and the reaction is confined to the surface. Because both methods only attack the bonds between lipids and proteins there is no observable fibre damage, as the proportion of this type of bond is very small compared to the number of protein-protein bonds (Rivett, 1991).

The bound lipid methyleicosanoic acid (C21) is believed to be an integral component of the protective membrane surrounding the cuticle (the epicuticle) that produces the Allwörden membranes, and so the removal of this bound lipid by the alcoholic alkali stops the formation of Allwörden sacs. The fact that KOH/MeOH destroys all the membranes whilst the t-BuOK/t-BuOH still allows a small amount of Allwörden sac formation demonstrates that the C21 is not just restricted to the surface.

The KOH/MeOH appears to hydrolyse equally the carbon and sulfur linkages present and thus produces substantial increases in both the polar and dispersion components of surface energy. As it reacts throughout the whole fibre there is not as large an increase in the XPS oxygen signal or decrease in the nitrogen signal. Thus, while there is an oxidised layer formed at the surface, it is not as dense as for the t-BuOK/t-BuOH.

The t-BuOK/t-BuOH is restricted to the wool fibre surface and forms an oxidised layer on top of the surface. This is confirmed by the highest observed oxygen signal and the reduction in the nitrogen signal. This treatment also produces more oxidised sulfur groups than carbon groups which agrees with the results suggesting that the C21 lipid is bound to the wool protein through a thioester linkage (Negri et al, 1992, 1993, 1996, Evans et al, 1985, 1997). As the proportion of sulfur oxidised is greater than the proportion of carbon, the increase in the dispersion component of surface energy is greater than the increase in the polar component, as was observed with chlorination. The improvement in dyeing properties is greater as there is a larger concentration of oxidised groups at the surface which reduces the dye barrier.

Fabric shrinkage and printing improve for both treatments due to the oxidised layer present and the increase in surface energy. The t-BuOK/t-BuOH produces an increase in yarn/fabric strength properties due to the concentrated oxidation layer present at the
surface improving the surface friction of the fibres, while the KOH/MeOH has no record in the literature of improving strength properties.

3.4 SUMMARY

The different model treatments have been characterised in this chapter using the experimental techniques available for this research or the available literature, where possible. They have been shown to produce different and distinctive modifications to the wool fibre. Mechanisms explaining how these treatments produce the modifications have been presented. These are summarised below for the two different groups of treatments.

The first group of model treatments (UV, electrons, and ozone) only produce small changes to the wool fibre surface, with ozone being the most significant. UV radiation breaks molecular bonds in the fibre surface, producing an oxidised and damaged surface layer. Electron beam irradiation causes minor amounts of oxidation of the surface. Ozone produces an oxidised layer over the surface of the wool fibre.

The second set of model treatments (H$_2$O$_2$, UV/H$_2$O$_2$, chlorination, and alcoholic alkali) are capable of producing much more dramatic changes to the surface of the wool fibre. H$_2$O$_2$ appears to be limited to the wool surface and produces only minor oxidation of the wool surface. UV followed by H$_2$O$_2$ synergise to produce dramatic changes in the properties evaluated. The UV damages the surface which allows the H$_2$O$_2$ greater access into the fibre where more oxidation takes place than for each treatment individually. DCCA chlorination produces a highly oxidised surface and removes significant layers of protein from the cuticle, depending on the level of treatment. The alcoholic alkali treatments produce the greatest increase in the surface energy of wool with a high level of carbon and sulfur oxidation of the surface of wool. KOH/MeOH reacts throughout the bulk of the wool fibre and therefore does not produce as great a surface modification as the t-BuOK/t-BuOH which is limited to the surface.

The results and discussion of the model treatments in this chapter will be used as a basis for comparison with the observations and analysis of the plasma treatment of wool presented in chapters 4 - 6.
CHAPTER 4: RADIO FREQUENCY PLASMA TREATMENT

4.1 INTRODUCTION

Radio frequency (RF) plasma generation using primarily oxygen, as well as air and argon, was performed under a variety of conditions. These treatments were performed to identify whether the observed reactive species present were responsible for the observed modifications (Chap. 4.2). Once the reactive species had been identified, further treatments were performed to study the mechanism by which the wood fiber was modified by the plasma technique. The effects under range of feasible properties were measured and correlated with the observed plasma-induced chemical changes (section 4.2). The plasma mechanism by plasma treatment on the wood fiber is presented in section 4.4. The observed effects were used to develop a more detailed model for the wood surface (section 4.3).

The measurements of friction, contact angle and optical density were conducted on the chapter, which were carried out at the Plasma Research Laboratory by R. I. The tests are described in detail in their 1984 thesis (Clark 1984). The results for these treatments are shown in section 4.2.1. are then given for the chapter. The data in the table are used as part of the examination of the effects of plasma treatments for the wood (Clark’s data) presented in Appendix 1.

4.2 DETERMINATION OF THE IMPORTANT REACTIVE SPECIES

4.2.1 The Effect of Oxygen Plasma Treatment on Wood Surface Energy

Plasma treatments have been well documented in the literature in improving many changes in the surface energy of wood fibers. Thus this property was monitored for examining the effects of plasma treatments (Figs. 4.10), power (Fig. 4.11), and pressure (Fig. 4.12) on the change in the surface energy of wood.

It was observed that as the plasma treatment time increased (increasing time of power) there is a rapid improvement in a considerably lower level of surface energy at around 4 s (Fig. 4.1) or 100 W (Fig. 4.2) so that the original level of property remained unchanged for the next several orders of magnitude. These observations explain why the majority of the reports in the literature have observed a significant increase in surface energy on matter how they vary their treatments. That is, because the plasma treatments used have always contained HF as a reactant gas (Y core 1982, Y Research, 1992). That
vertical recovery for the brine streams of the foam tank. The KCl/MgCl₂ was passed through a 10% KOH solution to simulate the quench process. The residue in the foam tank was discarded.

The contents of the incinerator were analyzed for all the major elements and volatile species. The analysis was performed using a combination of atomic emission spectrometry and gas chromatography. The results showed that the major species were chlorine, carbon, and hydrogen. The chlorine content was the highest, followed by carbon and hydrogen.

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CHAPTER 4: RADIO FREQUENCY PLASMA TREATMENT

4.1 INTRODUCTION

Radio frequency (r.f.) plasma treatment using primarily oxygen, as well as air and argon, was performed under a wide range of conditions. These treatments were performed to identify which of the possible reactive species present was responsible for the observed modifications (section 4.2). Once the reactive species had been identified, further treatments were performed to clarify the mechanisms by which the wool fibre was modified by the active species and the effects on a range of textile properties were measured and correlated with the observed physical and chemical changes (section 4.3). The proposed mechanism for plasma treatment of the wool fibre is presented in section 4.4. The observed effects were also used to postulate a more detailed model for the wool surface (section 4.5).

The measurements of electron temperature and neutral particle concentrations presented in this chapter were carried out at the Plasma Research Laboratory by X.J. Dai and are described in detail in her PhD thesis (Dai, 1995). The results for these parameters shown in section 4.2.1 are taken from her work and are used in the later sections as part of the examination of the effects of plasma treatment on the wool fibre's properties (see Appendix I).

4.2 DETERMINATION OF THE IMPORTANT REACTIVE SPECIES

4.2.1 The Effect of Oxygen Plasma Treatment on Wool Surface Energy

Plasma treatment has been well documented in the literature as producing major changes in the surface energy of wool fibres. Thus this inquiry commenced by examining the effect of changing time (Fig.4.1), power (Fig.4.2 a)), and pressure (Fig.4.3 a)) on the changes to the surface energy of wool.

It was observed that as the "intensity" of the treatment increases (increasing time or power) there is a rapid approach to a maximum level of surface energy at around 1 s (Fig.4.1) or 100 W (Fig.4.2a)). This maximum level then remains unchanged for the next several orders of magnitude. These results demonstrate why the majority of the reports in the literature have observed a constant, large increase in surface energy, no matter how they vary their treatments. This is because the minimum treatments used have always exceeded 10 seconds and/or 100 W (Pavlath, 1974, Rakowski, 1992). Thus
they have remained above the level necessary to observe this transition to maximum surface energy.

Once it was recognised that saturation occurred at low levels of treatment, the research was concentrated on studying treatments performed in this transition region. Measurements of surface energy were compared with measurements of plasma species over a range of r.f. power (Fig.4.2) and gas filling pressures (Fig.4.3). The ion density, \( N_i \), electron temperature, \( T_e \), and concentration of possible reactive species (atomic oxygen, \( \text{N}[\text{O}] \), and singlet (excited) molecular oxygen, \( \text{N}[\text{O}_2^*] \)) in the reaction chamber depends on both power and pressure in the chamber. Electron density can be assumed to be equal to ion density for a quasi-neutral plasma (Chen, 1974).

In Fig.4.2 the only plasma variable that shows similar behaviour to the surface energy is \( \text{N}[\text{O}] \), with an increase around 100 W to a steady maximum. As usual in such low-pressure glow discharges, the electron temperature \( T_e \) is little changed as the exciting power is increased, while the ionisation, \( N_i \), increases monotonically. \( \text{N}[\text{O}_2^*] \) shows a peak at 100 W and then a steady decline, which is not observed for the surface energy. As the power is increased above 100 W the increased electron density causes more and more of the \( \text{N}[\text{O}_2^*] \) to dissociate into atomic oxygen or make the transition back to the ground state (Dai, 1995).

The variation of surface energy with pressure in Fig.4.3 shows a similar relationship to that of \( \text{N}[\text{O}] \). Both rise to a peak in the region between 0.03 - 0.08 mbar followed by a drop to a lower level. \( T_e \) continually decreases from a maximum value at the lowest pressure. \( N_i \) also shows a decrease as pressure increases, whilst \( \text{N}[\text{O}_2^*] \) steadily increases with pressure.

![Fig.4.1 The Effect of Treatment Time on Surface Energy (p = 0.03 mbar, P = 100 W)](attachment:image)
Fig. 4.2 The Effect of Treatment Power on a) Surface energy, b) $N_i$ and $T_e$, and c) $N[O]$ and $N[O_2^+]$ for Oxygen Plasma
Fig. 4.3 The Effect of Treatment Pressure on a) Surface energy, b) $N_i$ and $T_e$, c) $N[O]$ and $N[O_2^+]$.
From these results it appears that atomic oxygen is the dominant reactive species. There is a clear correlation for dependencies on both power and pressure between the concentration of atomic oxygen, N[O], and the changes in surface energy. None of the other species present (ions, electrons, and singlet molecular oxygen) show similar correlations in their dependencies.

However, the correlation is not exact and it is possible the other species or ultra-violet radiation emitted by the plasma could contribute to the modifications as well. This is explored in more detail in the following sections.

4.2.2 Using Baffles to Isolate Charged Particles and UV Radiation

The plasma chamber was specifically designed so that the plasma source would be separate from the reaction chamber where the wool samples were located. This allowed the possibility of introducing baffles of differing properties between the plasma and the wool samples in order to screen out the effects of different possible reactants. The first baffle was a fine metal mesh (see Section 2.2.1) which would prevent any charged particles from entering the reaction chamber. For the second baffle the mesh was used to support a loose-fitting glass plate directly above the wool samples so that UV photons of wavelength below about 400 nm from the plasma would not be incident on the wool.

The effect of interposing the baffles between the source and the reaction chamber varied depending on the plasma species measured. As expected the charged particle density in the chamber, \( N_i \), was reduced below the equipment’s detection level (< \( 10^8 \) cm\(^{-3} \)). However, the neutral particle densities were reduced only slightly (Fig.4.4), with the behaviour of the N[O] and N[O\(_2^*\)] dependent on the pressure in the chamber.

The reduction of the N[O] was caused mainly by the mesh reducing the flow of energetic electrons into the chamber so that little or no collisional dissociation occurred locally, as well as some of the atomic oxygen being lost by recombination on the mesh. Thus, the addition of the glass produced no change from the reduction already caused by the mesh. The increased reduction of the N[O\(_2^*\)] at higher pressures can be explained by O\(_2^*\) de-exciting on the surface of the baffles (Dai, 1995).
Chapter 4. Radio Frequency Plasma Treatment

The change in surface energy of the wool fibre when the baffles are in place depends on the level of treatment (Table 4.1). Above the saturation point the baffles had no effect with the same maximum change in surface energy always occurring, no matter what pressure, power and time combination was explored.
Table 4.1 The Effect of Baffles on Surface Energy after Oxygen Plasma Treatment

<table>
<thead>
<tr>
<th>Plasma Treatment</th>
<th>Baffles</th>
<th>ΔW (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p = 0.005 \text{ mbar}, P = 200 \text{ W}, t = 60 \text{ s} ) (past transition point)</td>
<td>none</td>
<td>53.1 ± 4.0</td>
</tr>
<tr>
<td></td>
<td>mesh+glass</td>
<td>53.5 ± 4.0</td>
</tr>
<tr>
<td>( p = 0.08 \text{ mbar}, P = 100 \text{ W}, t = 0.8 \text{ s} ) (within transition region)</td>
<td>none</td>
<td>56.8 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>mesh</td>
<td>56.2 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>mesh+glass</td>
<td>3.7 ± 1.9</td>
</tr>
</tbody>
</table>

Below the saturation point the mesh made no significant difference (Table 4.1). This is despite the dramatic drop in charged particle concentration or the decrease in reactive neutral particle concentrations that occurs for \( p = 0.08 \) mbar (Fig.4.4). These results demonstrate that the charged particles make little or no contribution to the modification of the wool fibre’s surface energy.

The combination of the mesh + glass reduces the modification very significantly below the transition point (Table 4.1). This is in contrast to the negligible changes in steady state neutral particle concentration that occurs when the glass is added to the mesh (Fig 4.4). These results indicate two possibilities. One is that the short times (< 1 s) required to achieve 'below-transition' treatments do not allow enough time for the neutral particles to diffuse past the mesh + glass and achieve their steady concentrations, thus limiting the amount of reaction possible with the wool fibre. The second possibility is that UV from the plasma does make some contribution to the treatment and this effect is significant only at low levels, below the transition point. Above the transition region the effect of atomic oxygen dominates the modifications that occur.

Dai, 1995 performed Electron Paramagnetic Resonance (EPR) spectroscopy on wool samples that had been placed in EPR sample quartz glass tubes and vacuum sealed, then placed in the plasma treatment chamber with the plasma switched on for 30 minutes. This ensured the wool was only exposed to UV radiation from the plasma at wavelengths to which the quartz is transparent (\( \lambda \geq 200 \text{ nm} \)). The untreated wool showed no detectable signal, but after exposure to plasma UV there was a broad and intense signal with some fine structure. This signal indicated the presence of a large number of free radicals present on the wool surface which were shown to be relatively stable to exposure to air, even after one hour.

This observation suggested that UV radiation may be one of the primary mechanisms for the formation of free radicals on the wool surface by plasma. The presence of these
free radicals could speed up the oxidation reactions by atomic oxygen on wool surfaces at low plasma doses (Dai, 1995).

To summarise, this work with baffles has demonstrated that charged particles have no significant involvement on the wool surface. UV produced by the plasma may have a significant effect below the saturation region. However, once higher levels of plasma treatment are used no effect due to the UV can be distinguished from the effects due to atomic oxygen.

4.2.3 The Presence of Atomic Oxygen in Oxygen, Air and Argon Plasmas

Conclusive proof for atomic oxygen being the dominant reactive species was provided by comparing results for treatments using discharges in oxygen, air and argon. The neutral species concentrations and changes to the surface energy and chemistry (XPS) for the three different filling gases are shown below.

The initial measurements of surface energy changes for air and argon plasmas showed the same general trends as occurred for oxygen plasma (see Fig.4.1). The main difference was that it took longer for the saturation point to be reached, for a given combination of pressure and power. Comparisons showed that oxygen takes roughly 2 seconds, air 4 seconds, and argon 30 seconds to achieve a stable maximum surface energy \( (p = 0.033 \text{ mbar}, P = 100 \text{ W}) \).

When the surface chemistry of wool after plasma treatment was measured for the different plasmas (Fig 4.5), they were all shown to have produced a decrease in carbon and an increase in the oxygen level of between 5 - 10%. No other new elements were introduced into the surface by the plasmas. These results indicate that the addition of oxygen to the surface is responsible for the observed changes, regardless of the plasma gas used.

The differences in treatment time required to reach saturation can be explained by studying the different levels of oxygen species concentration present in the different plasmas. The first observation was that the presence of singlet (excited) molecular oxygen could not be measured in the air and argon plasmas at all. Its density was below the detection limits of the system.

However, atomic oxygen could be detected in all three plasmas. By studying the variation of \( \text{N}[O] \) with pressure for oxygen and air (Fig.4.6) it can be observed that plasma formed in a discharge in air has roughly half the atomic oxygen concentration compared with a plasma formed in a discharge of oxygen at the same pressure. As air only contains 20% molecular oxygen this means that nearly 50% of its oxygen is dissociated (Dai, 1995) compared to 20% dissociation for oxygen plasma.
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.5 Surface Chemistry of Wool after Plasma Treatment (above Transition)

[Oxygen = 0.03 mbar, 2 s, 100 W; Air = 0.1 mbar, 5 s, 200 W; Argon = 0.001 mbar, 60 s, 200 W; Oxygen Soak = 0.03 mbar, 600 s]

[Error in all values is ± 10% of the value]

One possible explanation is that the presence of nitrogen has been shown to increase oxygen dissociation in plasmas by reducing wall diffusion losses (De Souza, 1993). It has been shown that the surface energy changes (below transition) as a function of pressure, follow similar trends as the atomic oxygen concentration for both oxygen and air plasma (Fig. 4.6). This leads to the conclusion that atomic oxygen is the dominant reactant for air plasma.

For argon plasma the concentration of the atomic oxygen is much lower and could only be measured by studying the atomic oxygen line emission at 130 nm. This was calibrated against the atomic absorption results at low concentrations where self absorption was shown to be unimportant (Dai, 1995). Table 4.2 presents two important results. Firstly, atomic oxygen is present in low concentrations (< 5%) in the nominally argon plasma itself even in the absence of wool arising from contamination of the
chamber walls and/or impurities in the gas. Moreover, when a wool sample is present in the chamber the N[O] increases threefold, probably arising from dissociation of residual water outgassed from the sample (despite its previous drying and storage in a vacuum desiccator). These results strongly suggest that plasma treatment of wool, regardless of the gas used or care taken in cleaning and handling, will inevitably involve atomic oxygen present at low levels as a contaminant.

<table>
<thead>
<tr>
<th>Plasma (p = 0.03 mbar, P = 200 W)</th>
<th>Atomic Oxygen Emission at 130 nm (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon (no wool present)</td>
<td>0.3</td>
</tr>
<tr>
<td>Argon (with wool)</td>
<td>1</td>
</tr>
<tr>
<td>Oxygen (with wool)</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 4.2 N[O] in Argon and Oxygen Plasma using Emission Spectroscopy
4.2.4 Definition of Atomic Oxygen Dose as a Measure of Plasma Treatment

The results shown earlier in this chapter have indicated that the dominant reactive particle in oxygen, air or argon plasmas is atomic oxygen. Taking this result one step further we compared the surface energy changes with the total number of oxygen atoms reaching a unit area of the wool surface. This is proportional (assuming constant gas temperature) to the atomic oxygen concentration \( N[O] \) measured at the sample position (cm\(^{-3}\)) and the time (s) of exposure to the plasma. It is convenient to define an arbitrary effective 'dose unit' as:

\[
1 \text{ dose unit} = 10^{14} \text{ cm}^{-3}.s
\]
Consequently all of the measurements for all three gases could be represented on a single graph (Fig. 4.7). This plot includes results for the entire range of plasma conditions examined \( (50 < P < 300 \text{ W}, 0.005 < p < 0.1 \text{ mbar}, 0.1 < t < 600 \text{ s}) \) and covers several orders of magnitude of treatment levels. For convenience in the logarithmic graphs it has been assumed that a treatment of 0.1 dose units (which is too small to be measured) does not differ from the measurement for untreated wool.

Once this relationship had become clear it was explored in greater detail to determine how reliable the relationship was in the transition region. A series of oxygen plasma treatments were performed with steadily increasing 'dose'. By using a constant combination of power and pressure, a very clear reaction line can be drawn using the normal continuous treatments (Fig. 4.8). Strikingly, this reaction line is the same as the general reaction line drawn by fitting a line of best fit to the whole range of conditions observed (Fig. 4.7).

![Fig. 4.7 Surface Energy (using Water) of Wool After a Wide Range of Plasma Treatments \( (50 < P < 300 \text{ W}, 0.005 < p < 0.1 \text{ mbar}, 0.1 < t < 600 \text{ s}) \)
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.8 Surface Energy After Oxygen Plasma Treatment (P=100 W, p = 0.03 mbar)

Now that the reaction line had been observed it was decided to clarify how sensitive the treatment was to the short time duration necessary to produce observations within the transition region. The concentrations of atomic oxygen measured and used in the x-axis of these graphs are taken from vuv absorption measurements performed without wool being present in the chamber and are measured over a period of time much longer than (10-100 x) the treatment times used here (0.1 - 2 s) (Dai, 1995). Thus it is possible that the establishment times taken for steady equilibrium concentrations of N[O] to develop are longer than the treatment times used, which for short treatments could lead to substantial errors in correlating the results.

This question was examined by using a pulsed treatment technique. The plasma equipment was set to switch on for only 0.1 s. Then, to get higher levels of treatment, a sample was exposed to several pulses with sufficient time between pulses to allow any N[O] present to be removed from the chamber by the vacuum pump. This allowed an examination of whether the amount of N[O] present for the continuous treatments could be treated as a square pulse or had substantial establishment or dwell times (Fig.4.9).
When the results for the pulsed technique are compared to the normal continuous treatments there is very close agreement. Thus the N[O] must establish its steady-state concentration within a very short time and the N[O] profile can be treated as a square pulse, even for very short durations of treatment. Therefore the correlation between the measured N[O] and the dose of treatment for the wool should be exact, with minimal errors.

Now that the establishment time for N[O] has been shown to be negligible it is possible to state that UV from the plasma makes a significant contribution to the observed modifications, below the saturation region (as discussed in section 4.2.2).
4.3 OBSERVATIONS OF WOOL MODIFICATIONS AS A FUNCTION OF ATOMIC OXYGEN FLUX

In the previous section a detailed study of the correlation between different plasma variables and the changes to the surface energy of the wool fibre has shown that the flux of atomic oxygen to the surface dominates the reaction. Using this information the modification of the wool fibre by plasma could be studied using other techniques. Correlating these results with the atomic oxygen flux will allow a model for the plasma treatment of wool fibres to be deduced. The majority of the results presented here are for oxygen plasma with other gases specified when they appear. All of the plasma treatments were carried out on ABUTC fabric.

4.3.1 Field-emission Scanning Electron Microscope Appearance

Previous studies of plasma treated wool (Chapter 1) have shown that extremely long times and/or high levels of treatment were required before any modifications to the surface of the wool fibre could be observed using SEM. This observation is also true for the plasma treatment performed in this study. Even with the higher sensitivity of the FeSEM, the plasma treatments showed no changes occurring until extremely long treatment times/large doses were studied (Fig.4.10). After 5 minutes (~1500 du) of oxygen plasma treatment the surface is still very similar to the untreated methylene chloride cleaned surface (Fig.3.2).

It is only after 10 minutes (~2700 du) that the surface starts to show features resulting from the plasma treatment. This includes minor etching, which appears as parallel troughs, and at the centre of each scale edge a row of pits parallel to the edge is evident. Although these structures are present in a minor way in the untreated wool ABUTC (Fig.3.2), the extended oxygen plasma treatment has clearly etched further into them. It has removed material to show the structures in greater depth and clarity than was evident prior to plasma treatment. The results do not resemble any of the model treatments from Chapter 3.
Fig. 4.10. FeSEM after Oxygen Plasma Treatments ($p = 0.03$ mbar, $P = 100$ W)
(a) Wool fibre surface after a treatment time of 5 minutes using two different magnifications as indicated
Fig. 4.10. FeSEM after Oxygen Plasma Treatments ($p = 0.03$ mbar, $P = 100$ W)
(b) Wool fibre surface after a treatment time of 10 minutes using two different magnifications as indicated (arrows indicate rows of pits)
Chapter 4. Radio Frequency Plasma Treatment

4.3.2 Transmission Electron Microscope Appearance

TEM can be used to observe modifications to the wool surface at a higher level of resolution than is possible with the FeSEM. Oxygen plasma treated wool showed no change in the surface of the wool fibre after 5 seconds (~20 du) of treatment, (Fig.4.11). However, after only 30 seconds (~140 du), small changes, undetected by the FeSEM, appear. The a-layer shows some minor pitting and the epicuticle appears to have become more diffuse in some, and fully removed from other, parts of the surface.

(a) Untreated Wool Fibre (ABUTC)
Fig. 4.11 TEM after Oxygen Plasma Treatments ($p = 0.03 \text{ mbar}, P = 100 \text{ W}$)

(a) 5 seconds (~20 du)

(b) 30 seconds (~140 du)
4.3.3 Allwörden Sac Formation

There is no change in Allwörden sac formation from untreated wool until after 50 dose units. The level steadily decreases from 100% of fibres on the slide to a plateau of 67% for levels of treatment greater than 200 dose units (Fig. 4.12). This pattern also holds true for air and argon plasma treatments. The results do not resemble any of the model treatments.

4.3.4 Surface Energy

The dispersive character (ΔW - methylene iodide) of the wool fibre surface energy increases from 27 to 42 mJ/m² for low levels of oxygen plasma treatment, and then stabilises from 1 dose unit onwards (Fig. 4.13). The polar character (ΔW - water) shows a small jump to 3 mJ/m² for very small levels of treatment and then a rapid increase to ~58 mJ/m² between 1 and 5 dose units. Air and argon plasma results also show this pattern (Fig. 4.14). This is reflected in the rapid increase of the total surface energy $\gamma_s$ of the treated wool fibre, as well as the polar $\gamma_s^p$ and dispersion $\gamma_s^d$ components, for all plasma treatments (Table 4.3).

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>N(O) x Time (dose units)</th>
<th>Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\gamma_s^d$</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.1</td>
<td>28.4 ± 1.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.5</td>
<td>37.4 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>38.2 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>42.2 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>481</td>
<td>36.4 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>5213</td>
<td>35.5 ± 1.4</td>
</tr>
<tr>
<td>Air</td>
<td>0.6</td>
<td>40.8 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>41.3 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>43.0 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>156</td>
<td>42.9 ± 1.3</td>
</tr>
<tr>
<td>Argon</td>
<td>3.8</td>
<td>39.1 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>37.7 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>35.4 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>1171</td>
<td>35.6 ± 1.5</td>
</tr>
</tbody>
</table>

Table 4.3 Wool Surface Energy (dispersion $\gamma_s^d$ and polar $\gamma_s^p$) after Plasma Treatment
Chapter 4. Radio Frequency Plasma Treatment

The change in dispersive character is similar to the lipid removal technique of KOH/MeOH and t-BuOK/t-BuOH. However, the increase in polar character is greater than even these techniques achieved.

4.3.5 Surface Chemistry (XPS)

The chemical changes to the surface (Fig 4.15) are linked to the changes in surface energy. The proportion of carbon remained constant at 70% for low levels, decreased between 1 and 20 dose units, and then stabilised at 60%. Oxygen showed a steady increase from 15% to 22% up to 20 dose units and then remained constant. Nitrogen began at 11% and increased to 14% at 100 dose units. Sulfur dropped to 2.4% from 2.8% initially, then increased to 4% after 100 dose units.

This is reflected by the corresponding data for the oxidised/unoxidised carbon and sulfur species. Unoxidised carbon (Fig.4.16) begins at 56% and then drops to 26% between 1 and 10 dose units. There is a complementary rise in oxidised carbon from an initial value of 15% to a plateau of 33% from 10 dose units onwards. Unoxidised sulfur (SII) (Fig.4.17) begins at 2.4%, increases slightly to 2.6% at 20 dose units, and then drops steadily to 1.9% at 1000 dose units. Oxidised sulfur (SVI) initially remains constant at 0.4%, then between 1 to 100 dose units rises steadily to a plateau of 1.5%.

The changes in the XPS nitrogen and oxidation ratios (Table 4.4) show that similar trends are occurring for air and argon plasmas. Only one model treatment, 2% DCCA, shows any similarity to plasma treatment (Table 3.3). However, this is only true for moderate treatment levels ~32 dose units and the sulfur oxidation ratio is not comparable. The early transition region and the very high levels of treatment do not match with any model treatments.

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>N[O]xTime (dose units)</th>
<th>Atomic%</th>
<th>Elemental Ratios</th>
<th>% Oxidised</th>
<th>C/N</th>
<th>O/N</th>
<th>S/N</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.1</td>
<td>70.4</td>
<td>15.6</td>
<td>11.0</td>
<td>2.8</td>
<td>0.2</td>
<td></td>
<td>6.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.5</td>
<td>70.6</td>
<td>15.7</td>
<td>9.5</td>
<td>2.5</td>
<td>0.4</td>
<td></td>
<td>7.4</td>
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<td>5.5</td>
<td>65.1</td>
<td>20.4</td>
<td>10.9</td>
<td>3.4</td>
<td>0.2</td>
<td></td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>59.6</td>
<td>22.2</td>
<td>13.2</td>
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<td></td>
<td>481</td>
<td>58.1</td>
<td>23.5</td>
<td>14.4</td>
<td>3.2</td>
<td>0.8</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>Air</td>
<td>24</td>
<td>60.9</td>
<td>25.5</td>
<td>10.5</td>
<td>3.1</td>
<td>0.0</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>Argon</td>
<td>18</td>
<td>71.1</td>
<td>18.7</td>
<td>9.2</td>
<td>0.8</td>
<td>0.2</td>
<td></td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table 4.4 Wool Surface Chemistry (XPS) After Plasma Treatment

[Error in all values is ± 10% of the value]

-109-
4.3.6 Textile Property Changes

The felting shrinkage of plasma treated wool fabric showed a small reduction in shrinkage at low treatment levels, with a dramatic drop occurring around 20 dose units to stable values of maximum shrinkage (Fig.4.18). The values observed were 8% after one standard 5A wash cycle and 32% after five 5A cycles. Air plasma treatment lies on the same trend line as the oxygen plasma treatment.

Plasma treatment has little effect on the colour depth of wool fabrics after dyeing with CI Acid Blue 185 until 10 dose units is reached (Fig.4.19). Between 10 and 200 dose units there is a dramatic increase in colour depth until a plateau is reached equal to a 48% increase over the untreated wool. Again, air plasma treatment exhibits the same results as oxygen plasma treatment.

Print colour yield (Fig.4.20) appears to reach a steady uptake level after 50 dose units. The level of improvement achieved depends on the colourant used, but they all show similar trends. Cibacron Turquoise-Blue appears to show a sharper transition around 20 dose units with air plasma lying on the same trend line as oxygen plasma treatment.

The effect of plasma treatment on the tensile properties of wool yarn (Fig.4.21) follows similar trends to the print colour yield. Strain and load at break both show a transition occurring around 20 dose units to a stable maximum level of improvement at 100 dose units. %Elongation showed a steady climb, that may level off after 100 dose units. However, this is not clear and needs to be investigated further. Oxygen, air and argon plasma results all lie on the same trend line for %Elongation.

The only model treatments that improve all four textile properties are the alcoholic alkali treatments. However, the improvement in dye colour depth after plasma treatment actually lies between the results of KOH/MeOH and t-BuOK/t-BuOH and so they cannot be said to have produced the same modifications.

4.3.7 Aging Effects in Plasma Treatment

The surface energy changes produced by plasma treatment were measured after two weeks and four weeks, using different samples for each data point (Fig.4.22). For oxygen plasma treatment there appears to be a slight difference with older samples having the transition region shifted 2 - 3 dose units higher. However, this shift is only slightly greater than the experimental uncertainty of the atomic oxygen dose and may not be significant. When air plasma treatment was evaluated a clear shift to the right of 10 dose units was observed.
Unpublished work by Ward et al also examined the effect of aging on the XPS measurements of the wool surface after RF oxygen plasma treatment in a simple labbench apparatus. They observed changes in the elemental ratios over a period of 18 days (Fig.4.23). After 5 days the samples appeared to have reached steady values. Similar patterns were observed for solvent-extracted wool (equivalent to ABUTC) and wet-scoured wool (equivalent to ABUT), although the changes in the carbon and oxygen values were more dramatic for the wet-scoured wool.

Samples of plasma treated ABUT and ABUTC that had been stored for up to three years in polyethylene bags were also measured and no changes in the surface energy values were observed for plasma treatments greater than 50 dose units.
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.12. Allwörden Sac Formation as a Function of Plasma Treatment

Fig. 4.13. Surface Energy as a Function of Oxygen Plasma Treatment
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.14. Surface Energy as a Function of Air and Argon Plasma Treatment

Fig. 4.15. XPS Elements as a Function of Oxygen Plasma Treatment
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.16. Carbon Species as a Function of Oxygen Plasma Treatment

Fig. 4.17. Sulfur Species as a Function of Oxygen Plasma Treatment

-114-
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.18. Wool Fabric Shrinkage as a Function of Plasma Treatment

Fig. 4.19. Wool Fabric Colour Depth as a Function of Plasma Treatment
Chapter 4. Radio Frequency Plasma Treatment

Fig. 4.20. Print Colour Yield as a Function of Plasma Treatment

Fig. 4.21. Yarn Tensile Properties as a Function of Plasma Treatment
Fig. 4.22 The Effect of Sample Age on Surface Energy Changes After Plasma Treatment with a) Air and b) Oxygen
Fig. 4.23 The Effect of Sample Age on Surface Chemistry Changes Produced by Oxygen Plasma for a) Solvent Extracted Wool and b) Wet Scoured Wool (taken from Ward, unpublished, p = 0.1 torr, P = 20 W, t = 60 s)
Chapter 4. Radio Frequency Plasma Treatment

4.4 DISCUSSION

4.4.1 Comparisons with 'Model' Treatments

Many of the papers published about glow plasma treatment (Millard, 1972, Millard et al, 1972, Lee et al, 1974, 1975, 1976, Pavlath, et al, 1975) have suggested that the modifications could be due to a single species e.g. electrons or UV, or that the treatment follows a similar path to other well-known chemical treatments of wool. However, these proposals have never been thoroughly investigated before.

The FeSEM of glow plasma treated wool showed that over very long treatment times (i.e. with extremely large doses) etching produced an accentuation of the pits and striations already visible on the untreated wool fibre (ABUTC). However, no effect was visible in the 10 - 200 dose unit range where the observed changes in other properties occurred (Fig.4.12 - 4.21). TEM showed that etching of the epicuticle and top of the a-layer of the exocuticle was in fact occurring, in this 10 - 200 range, even though it was too small to be observed by the FeSEM. This etching process was not observed in any of the 'model' treatments studied here. The Allwörden sac formation stays at 100% until 50 dose units are reached and then drops to a steady level of 67% after 200 dose units. These levels do not show any similarity with the 'model' treatments.

At intermediate plasma treatment levels of 20 - 50 dose units, the surface energy results show some similarity in the dispersion component between 2% DCCA and plasma treatment. At higher levels (> 200 dose units), the plasma treatment dispersion component decreases and becomes more similar to the lipid removal oxidation techniques of KOH/MeOH and t-BuOK/t-BuOH. Plasma treatment shows a much greater increase in the polar component than any of the 'model' treatments. The XPS results do not show any similarity between low levels of plasma treatment (< 20 dose units) and any of the 'model' treatments. However, at higher levels of plasma treatment the atomic percentages of carbon, oxygen, nitrogen, and sulfur appear similar to 2% DCCA. This similarity holds true for the nitrogen ratios and the oxidised carbon ratio, but the oxidised sulfur ratio is very different for plasma treatment (29% vs. 100%).

Plasma treatment produces an improvement in fabric shrinkage, dye colour depth, print colour yield and yarn strength. The only 'model' treatment that also produces improvements in all four of these properties is t-BuOK/t-BuOH. However, its improvement in dye colour depth ($\Delta L = 1.78$) is much greater than plasma treatment ($\Delta L = 1.50$).

These comparisons have produced two important conclusions. The first conclusion is that none of the single species suggested so far in the literature have been shown to
produce the effects manifested by plasma treatment. Electrons, UV, and ozone do modify wool in different ways, but cannot produce the wide range of effects possible with plasma treatment.

The second conclusion follows from the fact that plasma treatment has some chemical similarities to three of the chemical oxidation and hydrolysis treatments investigated: 2% DCCA, KOH/McOH, and t-BuOK/t-BuOH. However, there are major physical differences in the way the effects are manifested on the wool fibre surface. This leads to the conclusion that plasma treatment represents a new type of oxidation pathway, different to those previously applied to wool.

4.4.1 Mechanism for Oxygen Plasma Treatment of Wool

The results presented in this chapter so far have shown that all the different plasma modifications to the wool fibre that have been measured can be linked to the flux of atomic oxygen to the fibre surface. Most of the detailed research was carried out with oxygen plasma as this provides the simplest set of reactive combinations with which to deal. A mechanism will now be proposed to explain the oxygen plasma treatment of wool. In this mechanism oxygen glow plasma treatment progressively changes the characteristics of the outer surface of the wool fibre. Oxidation of the surface takes place, followed by a slow etching process that removes the epicuticle and exposes the underlying protein.

The results reported in section 4.3 can be understood in terms of a sequence of reactions of atomic oxygen with the outer layers of the fibre surface. These stages (shown schematically in Fig.4.24) take place as the integrated flux of atomic oxygen from the plasma to the surface of the wool fibre increases over several orders of magnitude.

Initially there is a rapid partial oxidation of the wool surface. The initial surface energy change at 0.2 dose units is explained by the increased concentration of oxidised groups in an already partially oxidised surface. Ulman et al, 1992 has studied contact angle variation on self-assembled alkane thiol monolayers containing mixtures of OH and CH₃ groups at the air-monolayer interface. These surfaces can be assumed to approximately model the oxidised lipid surface produced by the oxygen plasma in the first stages of this mechanism, where increasing numbers of CH₃ terminal groups are oxidised by the atomic oxygen (Fig.4.25). Their results indicate that it is not until ~25% OH groups are present on a hydrocarbon surface that advancing water contact angles become less than 90° i.e. \( \Delta W = \gamma_{lv} \cos \theta_a > 0 \).
Surface Onset of Wettability

Maximum change in surface energy

Formation of oxidised surface groups

Maximum change in printing, shrinkage and tensile properties

Maximum change in dyeing, and Allworden reaction

Fully oxidised layer present on the surface

Protein exposed

Etching into protein

Lipid layer removed

Lipid layer present on the surface

Etching of lipid layer

Oxidation of surface lipid layer

Protein

N[O] x time (dose units)

Fig.4.24. Schematic Diagram of the Oxygen Plasma Treatment of Wool
The surface energy data (Table 4.3) suggest that the untreated wool fibre surface initially contains a low level of oxidised groups, presumably due to UV weathering on the sheep's back. This level is \( \leq 20\% \) OH (similar to Horr, 1997) and thus only a small amount of initial oxidation, less than 1 dose unit, is required to produce a hydrophilic surface with a contact angle less than 90 degrees (~25% OH). The subsequent steady increase in oxidation up to 8 dose units (Fig.4.16) produces a high level of carbon oxidation, corresponding to ~80% OH groups on the lipid surface (based on Ulman et al 1992). This high oxidation level of the lipid produces the saturation in surface energy (Fig.4.13).

Once the lipid is fully oxidised, breakage and removal of the lipid/protein chains begins to dominate and some etching of the surface results. The atomic oxygen has 4.2 eV of available energy to break the C-C (3.5 eV) and C-H (4 eV) bonds of the lipid. The broken bonds will react with the various constituents of the plasma and the XPS results indicate that most of the new groups formed contain oxygen. The surface remains covered with the maximum amount of oxidised carbon groups maintaining complete oxidation on the surface (Fig.4.16). However, some penetration through the lipid to reveal the underlying protein is required before saturation of the levels of oxygen (Fig.4.15), oxidised sulfur (Fig.4.17), shrink-resistance (Fig.4.18), print colour yield (Fig.4.20), and yarn tensile properties (Fig.4.21) are observed after 20 dose units.

Between 8 and 100 dose units the lipid layer is etched away and the underlying protein of the exocuticle a-layer is exposed. After 100 dose units the lipid of the epicuticle has been fully removed and the surface is now the protein of the exocuticle, as observed by TEM (Fig.4.10). The exocuticle continues to be oxidised and etched with similar reaction processes to those described with the lipid layer. Now that the protein is exposed, Allwörden sac formation decreases (Fig.4.12) and saturation of the level of nitrogen (Fig.4.15) and colour depth (Fig.4.19) occurs. Eventually, at much higher levels (~2700 dose units), pitting on the fibre surface is observed by FeSEM (Fig.4.10). This pitting was already observed at lower levels by the higher resolution of the TEM.
Chapter 4. Radio Frequency Plasma Treatment

(Fig.4.11). The FeSEM results confirm that the etching remains concentrated at weak points in the surface, rather than being a uniform layer by layer removal.

This process of etching while maintaining a complete oxidised layer on the surface presumably continues as treatment levels increase. The decrease in unoxidised sulfur levels (Fig.4.17) indicates the removal of protein, as the top of the a-layer is oxidised and then etched away exposing deeper, less sulfur-rich, regions. [Klausen, 1995, Klausen et al, 1995 and Phillips, 1995 observed very similar effects on microwave plasma treated wool at their very high treatment levels. Their results are discussed, in more detail in terms of this mechanism in Chapter 7, in combination with the microwave plasma treatments carried out at DWI for this thesis.]

4.4.2 Extension of Mechanism to Glow Plasma Treatment with Other Gases

The results presented in section 4.3 provide further confirmation for atomic oxygen being the dominant reactive species in the plasma treatment of wool for oxygen, air and argon plasmas. These results show that air and argon plasmas lie on a similar trend line to oxygen plasma when atomic oxygen dose is used as the x-axis. This is true for every measurement evaluated: Allwörden sac formation (Fig.4.12), surface energy (Fig.4.14 & Table 4.3), surface chemistry (Table 4.4), shrinkage (Fig.4.18), dye colour depth (Fig.4.19), print colour yield (Fig.4.20), and tensile properties (Fig.4.21). FeSEM of argon plasma (Fig.4.26) showed pitting and striations, similar to that observed for oxygen plasma, and only appearing after extremely high levels of treatment.

These results suggest that the mechanism proposed here (Fig.4.24) will be applicable in a modified form to all types of plasma treatment of wool. This is because oxygen will be present in all cases, at some level, due to contamination of the plasma by water released from the wool, low levels of impurities present in the gas or on the surfaces of the plasma chamber, and from dissociation of oxygen-containing molecules in the plasma.
Reports in the literature of plasma treatment of wool (see Rakowski, 1992 for a comprehensive review) can be analysed in terms of the amount of oxygen that may be present using the mechanism described here. The time taken for the effects to be observed will be determined by the concentration of atomic oxygen formed in the plasma. This depends in a complex way on the configuration of the apparatus and other chemical species present in the gas. For example, nitrogen has been shown to increase oxygen dissociation by reducing wall diffusion losses (De Souza et al, 1993). Also many previous plasma treatments have been performed with the samples located inside the discharge region itself, which would produce much greater fluxes of atomic oxygen. Without measurements of the amounts of atomic oxygen present in the plasmas it is only possible to make qualitative comparisons.

Pavlath and Slater, 1971 used a variety of gases in their glow plasma. However, their continuous yarn treatment system would have allowed air to enter the plasma with the yarn. They found very little difference in their area shrinkage results with gas type and explained this by suggesting that electrons in the plasma control the reactions. This hypothesis was shown to be invalid during the mesh baffle experiments described in section 4.2.2. The present mechanism suggests that their results are due to the oxygen introduced by the unavoidable air input with the wool yarn. Pavlath and Slater also observed increased yarn strength, dye fastness and no surface modification, which would indicate that they had oxidised/etched down to the exocuticle a-layer protein, but had not penetrated very deeply.
Chapter 4. Radio Frequency Plasma Treatment

The reported results of glow air plasma treatment of wool top performed in Poland (Byrne et al, 1995, Rakowski et al, 1982, Rakowski, 1989, 1992, 1997) are also explained by the present mechanism. These researchers also attributed the changes observed to electrons in the plasma. However, the increases in wettability, dye fastness and dye exhaustion, mechanical processing efficiency, printing, and shrink-resistance, together with absence of damage to the wool fibre, are similar to the results reported here and can be explained by the atomic oxygen present in the air plasma.

Herrling et al, 1995 studied the effects of glow plasma treatment on the fibre surface with a variety of gases using TEM. The modifications they observed were independent of gas type and mainly dependent on time of exposure, as the present mechanism predicts. They observed initial modifications to the a-layer followed by pitting and then formation of grooves in the a-layer, similar to the observations with FeSEM in section 4.3.1. Even more extensive treatments led to removal of the a-layer and sputtering of the underlying exo- and endocuticle, with extremely long treatments finally removing the cuticle and leading to modification of the cortex. At the same time they could detect no modification due to UV radiation in the cell membrane complex or cortex which supports atomic oxygen being the dominant reactive particle.

Klausen et al, 1995 used SEM, Atomic Force Microscopy (AFM), and XPS to study a wide range of oxygen plasma treatment times in the same plasma device as Herrling et al, 1995. Their results are similar to those presented here, with the AFM detecting modifications to the surface at low doses, while the SEM showed no changes. At higher levels pronounced etching was observed with both techniques. The XPS results showed a decrease in unoxidised aliphatic carbon and increases in oxidised carbon, total sulfur, and oxidised sulfur (S\textsuperscript{VI}), as the mechanism would predict.

From the above analysis of the literature it can be seen that the proposed mechanism successfully explains a wide range of published plasma treatments, using a wide variety of machines and gases, performed by different researchers.

4.4.3 Aging Effects on Plasma Treatment

Previous studies on corona treatment had raised the question of the stability of plasma treatment effects over time. Thorsen, 1971 found that a large initial increase in fibre friction decreased over a period of one month to a stable moderate increase. However, Belin, 1971 observed modifications to be stable in long term storage.

The majority of sample measurements in this thesis were performed 2 weeks after plasma treatment to allow for transfer from the ANU to the different laboratories used for testing. The choice of a standard 2 week period ensured that the XPS and surface energy measurements could be correlated.
Chapter 4. Radio Frequency Plasma Treatment

The results (Fig. 4.22) show that once the lipid layer was fully oxidised and some of the protein had been exposed by etching (> 50 dose units) no aging effect occurred for the surface energy. Ward et al. (unpublished) showed that aging was occurring within the first five days for their oxygen plasma treatment (Fig. 4.23). However, measurements on the plasma treatments in this thesis were not performed until 14 days had passed. Their stable XPS results (after 5 days) agreed with the XPS values observed for oxygen plasma treated wool after two weeks. It would appear that enough delay had been introduced into the measurements for this thesis to ensure that the treatment levels were stable from then on.

For plasma treatments lower than the saturation region, a shift in the position of the transition region was observed. For oxygen plasma this shift was minor but for air plasma it was significant. The aging effect in the transition region is more distinct in air plasma due to the lower levels of atomic oxygen present and thus the longer times of treatment necessary to get a particular level of oxidation on the surface. Treatments that have only oxidised the top layer of lipid may be more prone to reorientation of the lipid over time. The polar end groups could be redirected into the fibre with untreated lipid end groups reorienting outwards to replace the polar groups on the surface.

Ward et al. (unpublished) also performed SIMS analysis that suggested reorientation of the wool protein was occurring for their solvent extracted sample. For the wet scoured sample they suggested that migration of free internal lipids to the surface could be occurring in addition to the reorientation.

4.5 Dynamic Surface Model for the Wool Fibre

The detailed study of the wool surface that was undertaken during this research has led to questions about the current understanding and models of the structure of the wool surface. The current state of knowledge at 1993 suggested a uniform monolayer of bound lipid covering a layer of highly crosslinked protein. The lipid was covalently linked to the protein via a thioester linkage and together they formed the 'epicuticle' layer responsible for the Allwörden sacs (section 2.2.7).

In contrast, the etching observed in the plasma treatments seems to favour specific features on the fibre surface which may be linked to the underlying structure inside the cuticle. The parallel structures (Fig. 4.10) had an average separation ~ 200 nm. This etching indicates a substructure below the surface of the lipid layer consisting of parallel structures of two different materials. One is more resistant and less easily etched than the other.

This hypothesis agrees with Jones et al., 1994 who used TEM to study the developing wool fibre in the follicle. They observed closely packed plates of highly crosslinked...
protein spaced 100 - 200 nm apart (Fig.4.27) in the developing exocuticle (the dark bands in the fibre cuticle (FC) region). The boundaries between the plates were no longer observed after the fibre separated from the follicle wall. Instead, the normal appearance of the a-layer of the exocuticle was observed. It was suggested that this was due to the packing of the plates becoming too dense and the subsequent heavy staining obscuring the fine detail.

Fig.4.27. Development of the Exocuticle in the Follicle (from Jones et al, 1994, Fig. 4. The cleavage between fibre cuticle (FC) and inner root sheath cuticle cells (IRSC) is indicated by a white band (arrowed) appearing at the central region of intercellular laminae. Bar equals 0.1 µm)

Phillips, 1995 studied the surface of untreated and chemically modified wool fibres with AFM/SFM and FeSEM and found surface structure very similar to the plasma results reported here. From her results, Phillips proposed that the plates observed by Jones et al, 1994 were closely packed rods of crosslinked proteinaceous material running longitudinally along the scale in the a-layer of the exocuticle, separated by water soluble protein (Fig.4.28).

The results reported here indicate that the crosslinked protein is also more resistant to plasma etching and so the protein between the rods is preferentially etched away by the plasma. Similar etching results have been observed for microwave glow plasma treatment (Phillips, 1995, Klausen, 1995 and Klausen et al, 1995). This model could also explain the longitudinally rippled structure observed for chlorinated 1% DCCA wool (Fig.3.7). The chlorine attacks much more deeply into the exocuticle, resulting in greater subsidence into the crevices that are formed under the surface.
Fig 4.23 A modified model for the surface of wool, proposed to explain the SFM, FeSEM and other research. (a) transverse section through model wool fibre (b) longitudinal section through model wool fibre (c) high magnification look at boundary area between rods of material in the exocuticle (exaggerated in x-direction)
All of these results confirm that the structure observed by Jones et al, 1994 persists beyond the follicle and needs to be taken into account when analysing modifications to the surface of the wool fibre. This model would indicate that at lower levels of treatment (~ 100 du) etching has begun but is so superficial that no change to the surface can be observed by FeSEM, until over 2000 du is reached. This correlates with the TEM observations in section 4.3.2 and those of Klausen, 1995.

During the time period of this thesis there has been debate in the literature about the nature of the surface of the wool fibre. This has concentrated on the distribution of the lipid with respect to the protein, the relative configurations of the molecules and whether the epicuticle is actually a distinct separate layer.

German researchers at DWI have suggested that the epicuticle does not exist as a separate layer (Zahn, et al, 1994, Phan et al, 1995). They support the concept of Leeder's F-layer (Leeder & Rippon, 1985) attached to a cuticle cell envelope (the a-layer of the exocuticle). Zahn explains Ward's 0.9 nm thickness result for the lipid layer (Ward et al, 1993) by suggesting that the surface fatty acids are folded back in analogy to cycloalkanes (Fig.4.29). However, Denning et al, 1995 object that the folding of the lipid chains in half has no precedent in fatty acid surface chemistry.

The results in this chapter have shown that a distinct layer of predominantly hydrocarbon material surrounds the surface of the wool fibre (Fig.4.15 & 4.16), which has been identified as a separate lipid layer (Fig.4.24). This layer has to be etched away before significant changes are observed in Allwörden sac formation, dyeing, printing, yarn tensile properties, nitrogen, sulfur and sulfur oxidation levels to occur. This etching takes ~200 dose units, which is ~45 s in the RF apparatus, and thus represents an appreciable thickness.

Jones et al, 1996, and Jones & Rivett, 1997 studied the developing fibre cuticle surface membranes in human hair naturally deficient in 18-methyleicosanoic acid. Based on these studies they suggest that the 18-methyleicosanoic acid does not surround the entire fibre cuticle boundary, but rather covers only the upper surface, with approximately 30% of the covalently bound lipid being trapped within the protein layer of the epicuticle (Fig.4.30). The epicuticle is thought to consist of an inert protein matrix containing isopeptide crosslinks. Their model is consistent with the results observed in this thesis.

Finally, there is debate over whether the surface is a chemically homogeneous layer of hydrocarbon lipid. Brooks & Rahman, 1986 studied contact angle measurements on individual wool fibres and found receding contact angle measurements gave much greater polar components than were present for advancing contact angles. They suggest
that this is due to re-orientation of molecular groups on the surface - particularly polar groups towards water. Horr, 1997 studied contact angle data using the Israelachvili-Gee equation and suggests that the surface of wool has a likely composition of 70% methyl-like and 30% hydrophilic groups or possibly a 65% methyl-like, 10% methylene-like, and 25% hydrophilic surface. These proposals were also supported by the pH-dependent surface charge of the wool/water interface (Rippon, 1992).

Fig.4.29 Schematic diagram of the wool cuticle cell envelope (Zahn et al, 1994)

Fig.4.30 Model of the fibre cuticle surface membrane (Jones et al, 1997)
Chapter 4. Radio Frequency Plasma Treatment

The results presented in this chapter also support the idea of hydrophillic groups being present on the surface of untreated wool rather than a uniform layer of hydrocarbon lipid as suggested by the bulk chemical analysis methods used previously. The surface chemistry and energy results in this chapter suggest that the wool surface is already partially oxidised (≤ 20% OH), or else has enough exposed protein on the surface to give an effect equivalent to ≤ 20% OH being present. However, the Allwörden effect requires that any exposed protein patches are too small to allow dissolved protein fragments, produced by the chlorine reaction, to exit via these holes. Thus, it is possible that the untreated wool fibre is made up of a combination of lipid with patches of partially oxidised lipid and exposed protein (Fig.4.31).

![Lipid Chains](image)

**Fig.4.31 Model of the possible surface of wool**

The re-orientation of bonds suggested by Brooks & Rahman, 1986 can be explained by having a dynamic surface model where the surface of the wool fibre responds to its molecular environment. Thus we can combine the surface in Fig.4.31 with the Jones et al., 1997 model (Fig.4.30) and have the reorientation of the covalently bound lipid trapped within the protein depend on the external molecular environment of the fibre. If the surface is covered with water then some of the lipid will reorient so that the hydrocarbon moves within the fibre surface exposing more protein and/or oxidised lipid. This process will be assisted by the diameter swelling of the wool fibre in an aqueous environment. If the surface is covered with an oil layer then the process reverses and the lipid reorients outwards and the protein and oxidised lipid is covered by more exposed lipid (Fig.4.32). It should be noted that the natural state of the wool fibre surface on the sheep’s back is to be covered with a layer of wool grease (loosely bound lipids).

The previously reported results have not addressed this possibility because they have used techniques that could not focus on all the possible surface states available to the wool fibre. This is because they were either chemical treatments that dissolve lipid...
Chapter 4. Radio Frequency Plasma Treatment

from a large number of fibres (e.g. lipid analysis by Leeder & Rippon, 1985, or Negri et al, 1993) or were done with single fibres fixed in a single unnatural state with no water present (e.g. TEM by Jones et al, 1997 or Phan et al, 1995).

Exposed

Fig.4.32 Different surface structures dependent on the overlaying material
a) covered with water (polar liquids) b) covered with oil (non-polar liquids)

4.6 SUMMARY

Atomic oxygen has been found to be the dominant reactive species in oxygen, air, and argon plasmas. The degree of treatment in these plasmas has been shown to depend on the flux of atomic oxygen to the surface of the wool fibre. Comparisons of the plasma treatment with the 'model' treatments from Chapter 3 have shown that plasma treatment appears similar only to the oxidation/hydrolysis reactions, but clearly follows a different oxidation route.

A mechanism has been proposed to explain the process of plasma treatment. Oxidation of the surface takes place followed by a slow etching process that removes the lipid layer and exposes the underlying protein. Throughout the whole process a fully oxidised surface is maintained. This mechanism was successfully extended to explain plasma treatment by other gases due to the presence of residual oxygen through contamination from the gas, plasma chamber and/or wool sample.

Aging effects were shown to be insignificant once a minimum level of treatment had been reached or once 5 days had passed after the treatment.

A model for the surface structure of wool has been proposed incorporating current ideas in the literature as its basis and then extending this to a new dynamic surface model based on the results presented in this chapter. It suggests that the surface is made up of
a patchwork of different materials, which can undergo molecular reorientation, dependent on the molecular environment covering the surface.
SUMMARY

A mechanism has been proposed to explain the process of plasma treatment. Observations of the surface under plasma showed that energetic particles cause bond breaking in the surface of the wood. The mechanism was successfully expanded to explain plasma treatment of other materials and the presence of residual oxygen during the process was confirmed in a wood sample.

A model for the surface structure of wood has been employed incorporating different ideas in the literature. It was based on an existing model and was extended into a new dynamic surface model based on the results presented in this chapter.
CHAPTER 5: MICROWAVE & CORONA PLASMA TREATMENT

5.1 INTRODUCTION

The Deutsches Wollforschungs Institut (DWI) in Aachen, Germany has been carrying out research into plasma treatment since 1990. Researchers have concentrated on studying the chemical modifications to the wool fibre using a microwave plasma device, a lab-scale corona device and the plasma chamber at the Wool Research Institute, Lodz, Poland. In 1995 a Deutscher Akademischer Austauschdienst (DAAD) scholarship, to go to DWI for 3 months, was awarded to allow the extension of the studies on the modification to the wool fibre caused by radio-frequency plasma treatment to include comparison with microwave plasma and corona plasma treatments.

This opportunity was used to compare the observations of RF plasma treatment with microwave plasma and corona plasma treatments as well as to access the research expertise and equipment at DWI. It allowed the evaluation of how these other plasma treatments would fit in with the developing ideas about the mechanism for plasma treatment of the wool fibre by RF plasma.

In addition a particular goal was to investigate whether the observed changes to the wool fibres could imply that atomic oxygen was also appearing to dominate in these other plasma treatments. No studies have been performed on the reactive species present in the DWI microwave plasma or corona and as a result the conclusions in this chapter were based on the observed effects on the wool fibres.

In section 5.2 the results from the techniques used to evaluate the microwave plasma treatment of wool are presented. These results are then used to formulate a mechanism for microwave plasma treatment of wool in section 5.3. The different effects possible from using different gases in the plasma, the effect of aging, and the cuticle's role in dyeing wool with acid dyes are also discussed in section 5.3.

Section 5.4 presents the results observed for corona plasma treatment. A mechanism for corona plasma treatment is formulated in section 5.5. The differences between single-sided and double-sided treatments, aging effects, and different electrodes and machines are also discussed in section 5.5.
5.2 OBSERVATIONS OF MICROWAVE PLASMA TREATMENT

5.2.1 Observations of Wool Modifications as a Function of Treatment Time

No studies have been published about the plasma constituents and their concentrations in the DWI microwave plasma device. This meant that it was not possible to use the 'dose units' of N[O] as the horizontal axis, as had been done in chapter 4. However, the microwave plasma treatments were always performed at the same pressure of 0.3 ± 0.2 mbar and power of 300 W. Consequently, the concentration of atomic oxygen, N[O], present in the DWI plasma would be at a constant level, within a particular gas. This assumption was based on the studies by Dai, 1995 of the ANU RF plasma which showed N[O] will vary with pressure and with power, but time does not affect the concentration (see section 4.2). Thus, the treatment level in the DWI plasma should simply be proportional to the time of treatment. Therefore, time has been used as the horizontal axis for the data presented in this section and, for convenience, the measurements for untreated wool have been assigned a time of 0.1 s.

The other significant factor is that the DWI plasma treatments have always been carried out inside the plasma itself, unlike the RF treatments where the samples were separate from the plasma. This suggested that the treatment could be much more rapid and harsh than occurred for the RF plasma, which relies on the diffusion of active particles into the sample chamber. By comparison with Chapter 4 the results suggest that 1 second of DWI microwave plasma treatment corresponds to 10 ± 4 du in the ANU RF plasma. But without a reliable measurement of the conditions in the microwave plasma it was felt preferable to measure the changes as a function of time, i.e. increasing fluence. The trends with increasing fluence can be compared with those for increasing fluence given for the RF plasma in the previous chapter. Where results in this section could not be obtained by direct experimental measurement, relevant results from the literature have been presented and discussed.

5.2.2 FeSEM Appearance

There was no opportunity to use the FeSEM to study the samples that were treated at DWI. Thus this section draws on research where scanning electron microscopy has been used to study the DWI plasma treated wool. Klausen et al, 1995, used SEM and found that etching could only be observed after 600 s in oxygen plasma. Studies of sample treated for 10 s or 60 s did not show any changes to the surface. However, Klausen, 1995, also had the opportunity to use a FeSEM and, with its greater sensitivity, was able to detect slight modifications after 10 s in oxygen plasma.

Phillips, 1995 used the FeSEM to show that short treatment times of 10 s or 60 s only modified the cuticle faces and surfaces of the wool fibre while the upper edge of the
cuticle surface remained relatively unchanged. For longer treatment times of 600 s, heavy striations were observed which were similar to those observed for high levels of RF plasma treatment. Phillips also used a Scanning Force Microscope to show that surface roughness increased with increased times of treatment in oxygen plasma. This was observed even at the lowest treatment levels of 10 s (also see Klausen et al., 1995; Höcker, 1995).

5.2.3 TEM Appearance

Klausen, 1995 used TEM on oxygen plasma treated samples and found that etching of pits into the a-layer of the exocuticle could be observed after treatments of 60 s in oxygen. This pitting was similar to that observed for RF plasma treatment in this thesis (section 4.3), except that it was even more accentuated. After 600 s in oxygen, the entire cuticle had been removed and the cortex was revealed on the surface of the modified wool fibres.

Herrling et al., 1995 used TEM and found that modifications to the wool surface were fairly independent of gas type and mainly dependent on exposure time for oxygen, nitrogen, hydrogen, argon and ammonia. In the first 10 - 60 s modifications to the a-layer were observed with pitting and grooves being formed. Treatments of 300 s removed parts of the a-layer of the exocuticle and 600 s removed surface layers down to the endocuticle. Treatments of 1800 s led to removal of the entire cuticle and the cortex started to be modified and etched away. In addition, no evidence was detected for UV modification of the wool protein.

These results are also confirmed by Hesse, 1994 who used TEM to observe that a 300 s treatment in oxygen plasma removed the a-layer completely.

5.2.4 Allwörden Sac Formation

Allwörden sac formation (Fig.5.1) remains unchanged from untreated wool until 100 s is reached. Then there is a steep drop from 100 - 300 s to 0% sac formation. All of the gases lie on a similar reaction line. This trend line is very similar to that observed for RF plasma (see Fig.4.12).

5.2.5 Surface Energy

The dispersive character of the wool fibre surface energy increases from 27 to 45 mJ/m² for low levels of treatment and then remains stable from 1 s onwards (Fig.5.2), exactly as occurred for RF plasma (Chapter 4). However, after 200 s it appears to start dropping. The polar character increases to 58 mJ/m² fairly rapidly where it remains unchanged for all longer times of treatment, exactly as occurred for RF plasma.
Different gases produce different results for the polar component, but not the dispersive component.

Oxygen plasma shows an almost immediate jump in the polar component at 1 s, whereas the argon and sulfur dioxide gases show a transition region between 5 - 10 s. Nitrogen and ammonia show the same changes as the other gases for the higher levels of treatment at which they were measured. At high levels of treatment the same surface energies are produced, regardless of the gas used, and these match those achieved for RF plasma treatment (Table 5.1).

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>Time (s)</th>
<th>Surface Energy</th>
<th>Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \gamma_s^d )</td>
<td>( \gamma_s^p )</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.1</td>
<td>28.4 ± 1.8</td>
<td>2.7 ± 0.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.0</td>
<td>47.2 ± 1.5</td>
<td>23.6 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>43.5 ± 1.3</td>
<td>19.4 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>47.4 ± 1.4</td>
<td>22.4 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>43.3 ± 1.3</td>
<td>23.0 ± 0.7</td>
</tr>
<tr>
<td>Argon</td>
<td>1.0</td>
<td>28.1 ± 0.6</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>49.1 ± 1.5</td>
<td>6.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>43.5 ± 1.3</td>
<td>22.8 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>47.3 ± 1.5</td>
<td>23.6 ± 0.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>5.0</td>
<td>47.7 ± 1.4</td>
<td>20.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>43.5 ± 4.4</td>
<td>24.6 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>47.6 ± 1.4</td>
<td>23.4 ± 1.0</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>1.0</td>
<td>28.1 ± 0.6</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>43.5 ± 1.3</td>
<td>19.4 ± 1.1</td>
</tr>
<tr>
<td>Ammonia</td>
<td>50</td>
<td>43.5 ± 1.3</td>
<td>25.3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>41.5 ± 1.3</td>
<td>22.7 ± 1.2</td>
</tr>
</tbody>
</table>

Table 5.1 Wool Surface Energy Components (dispersion \( \gamma_s^d \) and polar \( \gamma_s^p \))

The effect of varying the position of the sample and the use of a metal mesh baffle in the plasma was also investigated. This was done by placing the sample on the bottom of the chamber, rather than on the glass spacer that was normally used to keep the sample in the middle of the plasma. The second possibility investigated was using a metal mesh buffer (the same as used for the RF investigations) to cover the sample on the bottom of
the plasma chamber. The mesh was placed in contact with the metal walls of the chamber in order to electrically isolate the sample from the plasma.

When these experiments were evaluated (Fig. 5.3) no difference in the modifications for oxygen plasma occurred. However, for argon in the base + mesh configuration there was a slight shift in the transition region to higher times.

5.2.6 Surface Chemistry (XPS)

The surface chemistry changes for oxygen plasma treatment (Fig. 5.4) reflect the changes in surface energy. The proportion of carbon dropped to 60% at 1 s and then decreased to 52% at 300 s. Oxygen jumped to 21% at 1 s and then remained constant. Nitrogen began at 11% and increased to 18% at 300 s. Sulfur remained constant at 4% until 300 s when it increased slightly to 4.3%.

This is reflected by the corresponding data for the oxidised/unoxidised carbon and sulfur species. Unoxidised carbon (Fig. 5.5) begins at 43% and drops to 29% at 1 s, then decreases to 23% at 300 s. There is a complementary small jump in oxidised carbon from an initial value of 28% to a plateau of 31% from 1 s onwards. Unoxidised sulfur (S\text{II}) (Fig. 5.6) begins at 4%, drops to 2.6% at 1 s and then decreases slightly to 2.3% at 300 s. Oxidised sulfur (S\text{VI}) jumps from 0% to 1.3% at 1 s, remains constant and then jumps again to 2.1% at 300 s.

<table>
<thead>
<tr>
<th>Plasma Gas</th>
<th>Time (s)</th>
<th>Atomic%</th>
<th>Elemental Ratio</th>
<th>% Oxidised</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.1</td>
<td>70.4</td>
<td>15.6</td>
<td>11.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.0</td>
<td>60.8</td>
<td>21.0</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>58.5</td>
<td>21.7</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>53.1</td>
<td>24.2</td>
<td>17.1</td>
</tr>
<tr>
<td>Argon</td>
<td>255</td>
<td>57.6</td>
<td>22.3</td>
<td>15.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>255</td>
<td>59.9</td>
<td>21.4</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Table 5.2 Wool Surface Chemistry (XPS) After Plasma Treatment

[Error in all values is ± 10% of the value]

The changes in the XPS nitrogen and oxidation ratios (Table 5.2) are very similar to RF plasma treatment for 1 s and 10 s. But the very high treatment at 255 s shows an increase in nitrogen accompanied by another drop in carbon and an increase in oxygen levels. The surface chemistry changes produced by argon and nitrogen plasmas at 255 s
are not quite as extreme as oxygen plasma, but are still beyond the low levels of oxygen plasma treatment, showing more similarity with a 10 s treatment than a 1 s treatment.

5.2.7 Textile Property Changes

The felting shrinkage shows a large reduction after 10 s of treatment with oxygen or nitrogen plasma (Fig.5.7). Then it declines steadily for higher levels of treatment. The argon plasma treatment follows a pattern similar to the RF plasma with only a slight reduction at 10 s followed by a rapid drop to levels similar to the nitrogen and oxygen plasma treatments. The final values achieved were better than RF plasma with 5% shrinkage after one standard 5A wash cycle and 16% after five 5A cycles.

Competition dyeing with CI Acid Blue 185 showed that the dye colour depth increases steadily with treatment time and does not reach a maximum value. All the gases studied produce results that lie on the same reaction line (Fig.5.8).

A separate study was done using gases that are known to introduce chemical groups onto the surface of the wool fibre (Denda, et al, 1995). This showed that differences can occur dependent on the gas used (Fig.5.9). Oxygen produced the greatest increase in dye colour depth, with ammonia results being very similar to oxygen. Sulfur dioxide produced comparatively small increases which were more similar to those produced by RF treatment.

No printing or yarn properties were evaluated or have been published for the DWI microwave plasma treatments.

5.2.8 Aging Effects

No aging effects between two and four weeks were observed for the surface energy changes produced by oxygen plasma treatment. Samples that had been stored for up to 3 years in polyethylene bags were also measured and no changes were observed in the surface energy values for any of the plasma treatments.
Chapter 5. Microwave & Corona Plasma Treatment

Fig. 5.1. Allwörden Sac Formation After Microwave Plasma Treatment

Fig. 5.2. Surface Energy After Microwave Plasma Treatment
Fig. 5.3. Surface Energy After Microwave Plasma Treatment with Argon and at Different Sample Positions

Fig. 5.4. XPS Elements as a Function of Oxygen Microwave Plasma Treatment
Chapter 5. *Microwave & Corona Plasma Treatment*

Fig. 5.5. Carbon Species as a Function of Oxygen Microwave Plasma Treatment

![Graph of carbon species as a function of time.](image)

Fig. 5.6. Sulfur Species as a Function of Oxygen Microwave Plasma Treatment

![Graph of sulfur species as a function of time.](image)
Chapter 5. Microwave & Corona Plasma Treatment

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**Fig. 5.7.** Wool Fabric Shrinkage as a Function of Microwave Plasma Treatment

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**Fig. 5.8.** Wool Fabric Colour Depth as a Function of Microwave Plasma Treatment
Chapter 5. Microwave & Corona Plasma Treatment

5.3 DISCUSSION OF MICROWAVE PLASMA TREATMENT

5.3.1 Mechanism for Oxygen Microwave Plasma Treatment of Wool

The results presented in section 5.2 have shown that if treatment time is used on a logarithmic horizontal axis very similar behaviour for microwave plasma compared to RF plasma was observed. The values measured for surface energy changes are almost identical, and the surface chemistry is very similar for treatment times less than 100 s.

The FeSEM, TEM, Allwörden sac formation, felting shrinkage, and competition dyeing results all show similar trends to RF oxygen plasma treatment. The main difference is that they occur in much shorter time spans than for the RF results.

These results combine to suggest that an almost identical mechanism is occurring for microwave plasma treatment as for RF plasma treatment (see Fig.4.24). The only difference is that the process occurs more rapidly (Fig.5.10). Thus, the first stages occur almost instantly (< 1s) and produce a fully oxidised lipid surface. As a result, dramatic felting shrinkage and surface energy changes occur immediately. Etching into the surface also starts occurring immediately and the lipid layer is completely removed within the first few seconds. This produces the increase in dye colour depth and
observed changes in surface chemistry. From then on the etching continues into the protein, while maintaining a fully oxidised surface layer.

After longer treatment times of several minutes (~ 255 - 300 s), the microwave plasma appears to have etched through the a-layer of the exocuticle and exposed the next layer of protein to oxidation. This is supported by the FeSEM and TEM observations of etching and the drop in the dispersive component of surface energy that begins to occur around those times. In addition, the dye colour depth has been shown to increase continuously with time. At this treatment level it has almost reached the same intensity as saturated DCCA, which was shown to act by a combination of oxidation and protein layer removal (Chapter 3).

The surface energy modification does not change if the sample is moved to the edge of the microwave plasma. This indicates that the active species is well distributed throughout the plasma. Electrically isolating the sample using the metal mesh baffle made no difference to the observed results, which shows that electrons are not the active species.

The results discussed above, combined with the similarity to RF plasma treatment of all the results for all the analysis techniques used, strongly suggest that atomic oxygen, or some oxygen containing species producing an identical effect, is responsible for the modifications observed in an oxygen microwave plasma.
Chapter 5. Microwave & Corona Plasma Treatment

5.3.2 Extension of Mechanism to Microwave Plasma Treatment with Nonreactive Gases

Microwave plasma treatment of wool using argon or nitrogen gas produced the same results and trend lines as were observed for oxygen gas for all the analyses performed. This was true for Allwörden sac formation, TEM, surface energy, XPS, felting shrinkage, and dye colour depth. The only difference observed was for argon gas which required an extra ~8 seconds of treatment time to produce the observed improvements in surface energy and shrinkage.

The presence of the wool samples inside the plasma and the consequently more rapid etching appear to combine so that there are significant amounts of atomic oxygen (or active species) generated in the plasma during treatment. This occurs regardless of the primary gas used and is likely to be due to oxygen in the wool being released by outgassing and bond breakage (see section 4.2.3).

The results for argon gas have a delay ~8 s which would indicate that the amount of oxygen recombining with the surface is smaller for other gases than in an oxygen plasma. However, the results for nitrogen produce the same results as oxygen. This can be explained by the results of De Souza, 1993 who found that when nitrogen is present in a plasma it will produce an increase in oxygen dissociation by reducing wall dissociation losses. Thus, nitrogen effectively produces additional atomic oxygen to react with the wool.

It would appear that argon plasma represents the minimum amount of atomic oxygen available to produce the wool modification. As a result, there is a delay in improvements for surface energy and felting shrinkage, which are dependent on the formation of an oxidised layer on the surface of the wool. However, argon shows no difference from oxygen for dye colour depth improvement. The results presented in Chapter 4 showed that dye colour depth improvement required etching into the protein layers of the surface. Thus, this result for argon indicates that etching is occurring rapidly inside the plasma and protein is being exposed before the establishment of a fully oxidised layer.
Formation of oxidised surface groups

Onset of Wettability

Maximum change in surface energy

Maximum change in shrinkage

Maximum change in Allworden reaction

Protein
Lipid
Surface

Oxidation of surface lipid

Oxidation of lipid layer

Lipid layer removed

Protein exposed

Etching into protein

Fig. 5.11 Schematic Diagram of the Argon Microwave Plasma Treatment of Wool
As a consequence the mechanism for microwave plasma treatment with nonreactive gases will be slightly different from that for microwave oxygen plasma, depending on the gas used. If the gas used in the plasma does not provide an extra source of oxygen (e.g. argon) then the etching effect dominates the results (Fig.5.11). The surface protein layers are revealed before a fully oxidised surface layer is formed. However, the surface energy results indicate that a fully oxidised surface layer is formed on the protein, after it is exposed, and the fully oxidised layer is maintained as the protein is etched away. Microwave plasma treatment with gases that can provide an extra source of oxygen (e.g. nitrogen) will follow the same mechanism as occurs for oxygen microwave plasma treatment (Fig.5.10).

5.3.3 Extension of Mechanism to Microwave Plasma Treatment with Reactive Gases

Plasma treatment with ammonia and sulfur dioxide was studied and compared to oxygen plasma. No differences were found between the results or trend lines for TEM, Allwörden sac formation, and surface energy. However, dye colour depth produced different results, with the different gases showing different trend lines (Fig.5.9).

Denda et al, 1997 have shown that plasma treatment with ammonia introduced amine groups onto the surface of wool, and that plasma treatment with sulfur dioxide introduced oxidised sulfur groups onto the surface. They used this difference in surface chemistry to explain the differences in dye colour depth that are observed when dyeing with Lanasol Blue 8G.

The results for ammonia and sulfur dioxide presented in this chapter show that these gases produce the same surface energy and etching results as oxygen. This indicates that there must also be significant amounts of atomic oxygen present in these plasmas, as was discussed above in section 5.3.2. The presence of significant amounts of atomic oxygen in the sulfur dioxide plasma may be due to dissociation of the sulfur dioxide molecule, which provides an additional source of oxygen. For the ammonia gas there would be dissociated nitrogen present in the plasma, which has been shown to increase oxygen dissociation in plasmas by reducing wall dissociation losses (De Souza, 1993). Thus both of these gases could provide additional atomic oxygen to react with the wool.

However, there were significant differences in dye behaviour. The improvement in dye colour depth for ammonia was almost as dramatic as for oxygen, but sulfur dioxide showed a much smaller improvement. Denda et al, 1997 explained their results by suggesting the cationic amine groups introduced by the ammonia plasma would attract more of the acid dye molecules to the surface than would occur for the anionic sulfur groups introduced by the sulfur dioxide plasma. However, oxygen produces an even
more dramatic improvement, almost as great as saturated DCCA (see chapter 3). This may be due to the introduced oxygen groups also being cationic. Alternatively, oxygen plasma may have a slightly higher rate of etching, since both sulfur dioxide and ammonia are reacting with, and forming new molecular groups onto, the surface, and this could result in a reduction of the etching rate for these gases.

Despite the difference in dyeing, the other results for ammonia and sulfur dioxide conform to the other plasma results and so the mechanism for oxygen microwave plasma treatment will still hold (Fig.5.10). The results indicate that the same oxidation/etching process is occurring, but it is necessary to factor in the reactivity of the gas and any possible new groups that may be forming on the surface, in addition to the oxygen containing groups.

5.3.4 Aging Effects on Microwave Plasma Treatment

No aging effects were observed for oxygen microwave plasma treatment. This is as expected because the lowest level of treatment studied (1 s) produces saturation of the surface energy changes. Thus, the lipid is already partially removed and protein has been revealed, which, combined with the fully oxidised surface layer, would mean that the non-wetting state cannot be re-established by bond reorientation.

5.3.5 Model for the Surface of Wool - Dyeing Properties

The results for dye colour depth modifications after microwave plasma treatment have been shown to keep on improving with increasing treatment time, as more and more of the cuticle is removed. These results indicate that the dyeing process is affected by the thickness of the cuticle present.

If the improvements in dye colour depth were only due to 1) a layer of oxidised groups producing a reservoir of the dye on the surface; or 2) dyeing depending only on diffusion through the cell membrane complex, between the cuticle scales; or 3) the presence of a single specific barrier layer on the surface of wool, then a saturation level of dye colour depth should have been observed once either the oxidised layer had formed or the lipid had been etched away. However, this was not the case. As more and more of the protein was removed, e.g. the a-layer after 300 s, the dye colour depth level continued to increase. These effects were similar to the effects observed with chlorinated wool (see chapter 3).

This continuing increase in dye colour depth indicates that dye diffusion through the protein layers of the cuticle is important in determining the outcome of dyeing processes, at least for acid dyes. The cuticle layers provide a physical barrier to
diffusion of the dye into the fibre that is steadily reduced as more and more of the cuticle is removed.

5.4 OBSERVATIONS OF CORONA PLASMA TREATMENT

Researchers at the DWI have also been active in studying the corona treatment of wool fibres at atmospheric pressure. They have a lab-scale apparatus purchased from Softal GmBH which was used to study this type of treatment. As well, Softal GmBH had been kind enough to perform corona treatments at their factory using different electrode types and it was desirable to compare these with DWI treatments to investigate if electrode material made any differences. Corona treatment is of particular interest from an industrial point of view. It is performed at atmospheric pressure and thus is less expensive than glow plasma treatment, due to the savings in vacuum equipment and chamber housing. Its disadvantage is that since it is performed in the open air, the only reactive gas is air and care must be taken that unexpected organic fumes/contaminants are not introduced into the plasma and possibly polymerised onto the wool. Japanese researchers (Wakida et al., 1993) have experimented with surrounding the corona with a chamber and then filling this chamber with particular combinations of gases in order to try and control the reactions to produce a desired effect. However, this type of study was not possible at DWI.

At DWI the studies were restricted to treatment in air, with a view to determining how corona plasma treatment would integrate with the developing atomic oxygen model for RF plasma treatment.

5.4.1 Observations of Wool Modification as a Function of Corona Dose

Corona treatment of plastics has been taking place in the plastics industry for several decades, and Softal GmBH have been supplying machines for corona treatment for most of this time. Softal base their treatment levels on the amount of energy supplied to a given area and have defined a 'Corona Dose' in J/m² (see section 2.2.3). No studies on the constituents in the Softal corona plasma have been published and Softal GmBH suggest in their brochures (Softal, 1992) that electrons impacting on the surface are the active species. They suggest the electrons modify the surface by producing broken bonds on the surface.

In the corona plasma, pressure is held constant at atmospheric pressure. Dai, 1995 observed for the RF plasma that N[O] is constant for constant pressure and increases with power. Corona dose is a linear function of power and time (see equation 3.1). Thus, it is likely that if atomic oxygen is present in the corona plasma then the corona
dose should correspond to the 'dose units' of N[O]. Based on this assumption the corona
dose has been used as the horizontal axis for the data presented in this section. For
convenience, the measurements for untreated wool have been assigned to a corona dose
of 10 J/m\(^2\).

For the corona plasma treatments the wool passes through the actual plasma itself.
Thus, it is possible that the treatment could be much more rapid and harsh than
occurred for the RF plasma, which relies on the diffusion of active particles down into
the sample chamber. Alternatively, the corona plasma may not be able to penetrate fully
through the wool fabric to modify all fibres evenly. This was explored by using single-
and double-sided treatments. By comparison with Chapter 4, the results suggest
that 100 J/m\(^2\) of Softal corona plasma treatment corresponds to 2.2 ± 0.8 du (in the
ANU RF plasma) for double-sided treatments, and 0.5 ± 0.2 du for single-sided
treatments. But without a reliable measurement of the conditions in the corona plasma,
it was felt preferable to measure the changes as a function of corona dose, i.e.
increasing fluence. The trends with increasing fluence can be compared with those for
increasing fluence given for the RF plasma in Chapter 4. Where results could not be
obtained by direct experimental measurement, relevant results from the literature have
been presented and discussed below.

5.4.2 FeSEM Appearance

The FeSEM was used to study a wide range of corona dose levels up to 5333 J/m\(^2\). No
changes from untreated wool were observed on the surface of the treated fibres.

5.4.3 TEM Appearance

Thomas et al, 1992 used TEM to study corona treatments for levels up to 800 J/m\(^2\).
They found very little difference from untreated wool, with only a slight swelling or
diffuseness of the a-layer being observable.

5.4.4 Allwörden Sac Formation

Allwörden sac formation remained unchanged from untreated wool until 1000 J/m\(^2\) was
reached (Fig.5.12). After this point it fell significantly towards zero between 1000-6000
J/m\(^2\).

5.4.5 Surface Energy

Corona treatment shows identical behaviour to microwave and RF plasma treatment
(Fig.5.13). The dispersive character increases rapidly to 45 mJ/m\(^2\) and remains steady
from this point. The polar character shows a transition region between 100 - 400 J/m\(^2\)
and then achieves a stable value of 58 mJ/m\(^2\).
Chapter 5. Microwave & Corona Plasma Treatment

There is no significant difference between the results from Softal and DWI machines. However, the changes to the polar component for single-sided treatments require an additional 200 J/m² in order to achieve the same levels as double-sided treatments. This effect can also be observed in the polar component of surface energy (Table 5.3). The surface energy results are very similar to those for RF and microwave plasma treatments.

<table>
<thead>
<tr>
<th>Plasma Treatment</th>
<th>Corona Dose (J/m²)</th>
<th>Surface Energy $\gamma_s^d$</th>
<th>$\gamma_s^p$</th>
<th>$\gamma_s$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>10.0</td>
<td>27.5 ± 1.8</td>
<td>2.7 ± 0.8</td>
<td>31.1 ± 2.6</td>
</tr>
<tr>
<td>Single-Sided</td>
<td>167</td>
<td>43.6 ± 1.3</td>
<td>3.2 ± 0.4</td>
<td>46.8 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>667</td>
<td>43.5 ± 1.3</td>
<td>14.1 ± 1.0</td>
<td>57.6 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>43.5 ± 1.3</td>
<td>18.9 ± 2.8</td>
<td>62.4 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>43.5 ± 1.3</td>
<td>25.5 ± 0.8</td>
<td>69.0 ± 2.1</td>
</tr>
<tr>
<td>Double-Sided</td>
<td>167</td>
<td>43.5 ± 1.3</td>
<td>8.1 ± 0.4</td>
<td>51.6 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>667</td>
<td>42.1 ± 1.3</td>
<td>26.7 ± 0.8</td>
<td>68.8 ± 2.1</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>43.5 ± 1.3</td>
<td>26.7 ± 1.5</td>
<td>70.2 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>43.0 ± 1.4</td>
<td>24.7 ± 1.0</td>
<td>67.6 ± 2.0</td>
</tr>
</tbody>
</table>

Table 5.3 Wool Surface Energy Components (polar $\gamma_s^p$ and dispersion $\gamma_s^d$) after Corona Plasma Treatment

5.4.6 Surface Chemistry (XPS)

The surface chemistry changes of the treated sides match the changes to surface energy (Fig.5.14). There is no difference between single-sided and double-sided treatments. This is not unexpected since XPS is very surface specific. The modified surface of a single-sided treatment should be identical to the modified surface for a double-sided treatment as both were produced by being passed face up through the corona plasma.

The changes to the surface chemistry have already occurred at the minimum corona dose observed (200 J/m²) and then remain unchanged. Carbon drops to 58%, oxygen increases to 23%, nitrogen jumps to 13%, while sulfur increases to 4%. The nitrogen ratios and the oxidised percentages remain the same regardless of the level of treatment (Table 5.4). These results are at a level that matches RF plasma treatment for intermediate doses (~32 du).

The carbon and sulfur species data confirmed this similarity with RF plasma (Fig.5.15, 5.16). The level of oxidised carbon jumps above that of unoxidised carbon while the
oxidised sulfur ($S^{VI}$) increases and the unoxidised sulfur ($S^{II}$) decreases. The results then remain constant up to 600 J/m$^2$.

<table>
<thead>
<tr>
<th>Corona Treatment</th>
<th>Dose (J/m$^2$)</th>
<th>Atomic%</th>
<th>Elemental Ratio</th>
<th>% Oxidised</th>
<th>$S_{ox}/S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td>Untreated</td>
<td>10.0</td>
<td>70.4</td>
<td>15.6</td>
<td>11.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Single-sided</td>
<td>200</td>
<td>58.6</td>
<td>23.1</td>
<td>13.0</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>57.6</td>
<td>22.8</td>
<td>13.9</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>60.2</td>
<td>21.8</td>
<td>12.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Double-sided</td>
<td>200</td>
<td>58.7</td>
<td>23.0</td>
<td>12.9</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>58.3</td>
<td>22.3</td>
<td>13.8</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>55.8</td>
<td>23.4</td>
<td>13.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 5.4 Wool Surface Chemistry (XPS) After Corona Plasma Treatment

[Error in all values is ± 10% of the value]

5.4.7 Textile Property Changes

The felting shrinkage of corona treated wool shows a steady reduction as corona dose increases (Fig. 5.17). The level reached at high corona doses, 6% for one 5A cycle and 38% for five 5A cycles, is very similar to RF plasma treatment. There is a fairly constant difference between single-sided and double-sided treatments (~8%), until treatments above 2000 J/m$^2$ are reached, when the difference reduces to insignificant levels.

Corona treatment produced almost no effect on the colour depth after dyeing with CI Acid Blue 185 (Fig. 5.18). There is a small increase ~10% up to 3000 J/m$^2$ and then an increase up to 30% over untreated at 7000 J/m$^2$. Double-sided treatment showed a slight increase over single-sided for the dark side, but the difference is barely significant. The difference in dye colour depth is much more significant for the light side.

Print colour yield (Fig. 5.19) shows an increase over untreated wool using Cibacron Turquoise Blue, similar to RF plasma. Single-sided treatments required a higher corona dose (~ 500 J/m$^2$) to achieve the same effect as double-sided. The Softal treatments achieved saturation at a lower level (~600 J/m$^2$) than the DWI treatments.
5.4.8 Aging Effects

Aging effects can only be observed for single-sided treatments (Fig. 5.20). For treatments measured after 4 or 16 weeks, the transition region for the polar component of surface energy can be seen to shift to higher dose levels by an order of magnitude. Once saturation is achieved there is no effect due to aging. Even after 3 years the improvement in surface energy remains once the saturation level has been reached.

![Graph showing percentage of fibres showing Allwörden Sac formation after double-sided corona treatment](image)

*Fig. 5.12. Allwörden Sac Formation After Double-sided Corona Treatment*
Chapter 5. Microwave & Corona Plasma Treatment

**Fig. 5.13.** Surface Energy as a Function of Corona Treatment

**Fig. 5.14.** XPS Elements as a Function of Corona Treatment
Fig. 5.15 Carbon Species as a Function of Corona Treatment

Fig. 5.16 Sulfur Species as a Function of Corona Treatment
Chapter 5. Microwave & Corona Plasma Treatment

Fig. 5.17 Wool Fabric Shrinkage as a Function of Corona Treatment

Fig. 5.18 Wool Fabric Colour Depth as a Function of Corona Treatment
Chapter 5. Microwave & Corona Plasma Treatment

Fig. 5.19 Print Colour Yield as a Function of Corona Treatment

Fig. 5.20 Effect of Age on Surface Energy for Single-sided Corona Treatment
5.5 DISCUSSION OF CORONA PLASMA TREATMENT

5.5.1 Mechanism for Double-sided Corona Plasma Treatment of Wool

The results presented in section 5.4 have shown that if corona dose is used on a logarithmic horizontal axis, very similar behaviour to RF and microwave plasma treatment can be observed. The values measured for surface energy changes are almost identical and the surface chemistry is similar to intermediate levels of plasma treatment above saturation of the surface energy.

The FeSEM showed no changes while TEM showed slight modifications to the α-layer of the exocuticle. Allwörden sac formation, felting shrinkage, and dye colour depth all show similar trends to RF plasma treatment. The main difference is that the results are distributed over an order of magnitude and require relatively high levels of treatment to manifest significant improvements.

These results combine to suggest that the same mechanism is occurring as for RF plasma treatment, with the difference that for corona treatment the process occurs more slowly than for RF plasma treatment (Fig.5.21). The initial oxidation has already occurred by a level of 200 J/m\(^2\). This is reflected by the saturation of the surface energy, surface chemistry, and printing results. Between 200 - 1000 J/m\(^2\), a fully oxidised surface layer is formed while the lipid is etched away, which is reflected in the fabric shrinkage improvement and TEM results.

From 1000 J/m\(^2\) onwards etching into the protein begins, while the fully oxidised surface layer is maintained. As a result, Allwörden sac formation starts to decrease and dye colour depth begins to improve.
It is not possible to any draw definite conclusions about the active species in corona plasma treatment. It is possible to speculate that atomic oxygen (or some other oxygen species) could be producing the observed modifications, or possibly electrons are breaking bonds in the wool fibre which react with oxygen present in the corona. However, it can be concluded that the effect of corona treatment follows the same mechanism as occurs for atomic oxygen modification in RF oxygen plasma. The etching rate appears to be significantly slower for corona plasma treatment and may not penetrate into the protein layers until such high corona dose levels are reached as to be impractical for industrial use.

5.5.2 Single-sided Versus Double-sided Corona Plasma Treatments

In corona plasma treatment the wool fabric passes through the vertical sheet of corona between the two electrodes. Thus, there was some interest in the level of uniformity of the corona's ability to diffuse through the fabric as it passes rapidly between the electrodes.

The results in section 5.4 show that there is a difference between single-sided and double-sided treatments in the transition region 200-1000 J/m². The single-sided treatments require ~600 J/m² more than double-sided treatments in order to achieve the same improvements in surface energy, area shrinkage, dye colour depth, and printing. Once 1000 J/m² has been reached the single-sided and double-sided results converge and there are no significant differences between them. This is true for all but dye colour depth, where the untreated side of the single-sided treatment still shows significantly less improvement.

The surface chemistry results show that the treated side of the single-sided treatments is identical to the double-sided treatments. However, the difference in behaviour between 200 - 1000 J/m² indicates that the corona plasma does not fully penetrate through to the other side of the fabric. As a result, there appears to be a minimum corona dose required to allow full penetration of the fabric by a single-sided treatment. Even then the modification level appears to be dependent on the depth within the fabric as the dyeing results still show the untreated side of the single-sided treatment producing less improvement than the treated side and double-sided treatments. At these levels an oxidised surface appears to have formed throughout the fabric, but the protein removal due to etching is slower on the untreated side as only a limited quantity of active species can penetrate through the fabric.

5.5.3 Aging Effects on Corona Plasma Treatment

Only single-sided corona plasma treatments show aging effects. The observed aging behaviour is identical to that observed for RF air plasma. In the transition region a shift
to higher corona dose levels is observed as the time after treatment increases. Once saturation of the surface energy is reached after 1000 J/m² and protein has been exposed by etching, no aging effects are observed.

Double-sided treatment does not show aging effects as the surface energy changes have already reached saturation within 200 J/m² and enough lipid has been removed that reorientation will not bring back the non-wetting surface.

5.5.4 Different Electrode Types & Machines

The surface energy changes for fabrics treated at Softal with two different electrodes and on the DWI lab-scale machine were compared and no differences were observed for the three different configurations. However, the Softal treatments produced a more rapid improvement for print colour yield than the DWI treatments. Thus, it is possible that different electrode configurations may make a difference to the intensity of the corona plasma treatment. Further investigation would be required to confirm this.

Wakida et al, 1993 in two sequential papers investigated surrounding the corona with a chamber and then filling this chamber with particular combinations of gases at 1 atmosphere. They hoped to control the reactions taking place by varying the relative gas proportions to produce a desired effect. Although they used helium/argon and acetone/argon gas mixtures the reported results for SEM, XPS, wettability and acid dyeing properties followed a very similar pattern to the DWI and Softal corona results presented in this chapter. The increase in oxygen levels measured by the XPS indicate that the mechanism discussed in section 5.5.1 can be used to explain the observed changes.

Despite Wakida et al, 1993 using a different machine from the Softal and DWI machines it is possible to use the same mechanism (section 5.5.1) to explain the observed results. This suggests that the mechanism has the potential to be of general utility for explaining the corona treatment of wool. However further research is required to investigate how great an effect the different machine configurations may have on altering the different stages of the mechanism for each individual machine.

5.6 SUMMARY

The results have shown that microwave plasma treatment follows the same mechanism as RF plasma, as was presented in Chapter 4. The main difference is that the modifications occurred more rapidly, as the plasma treatment had been performed inside the plasma. The mechanism can be used for any of the gases studied, once all possible sources of atomic oxygen have been accounted for. If reactive gases are used
the mechanism will still apply, but allowance has to be made for any new groups that may be formed on the surface.

For corona treatment the same basic mechanism for modification of the wool fibre also applies. However, for corona the modifications occur more slowly than for RF plasma. Although it is not possible to conclude what the reactive particle(s) is, the final result is an oxidised wool surface that is then etched away. There may be some differences in the modification levels for different corona electrodes, but the different stages of the mechanism still hold true. However this will require further investigation.

The intensity of the modifications depends on the thickness of the fabric with single-sided treatments clearly being less effective in the transition region. Once saturation of the surface energy is reached then the results for single-sided converge to that of double-sided. However, effects that rely on the etching of protein are still prone to being less effective for single-sided treatments (e.g. dye colour depth) which demonstrates that the etching decays in intensity as the corona plasma penetrates through the fabric.
CHAPTER 6: PLASMA TREATMENT OF INDUSTRIAL WOOL FABRIC

6.1 INTRODUCTION

This thesis has concentrated on studying the plasma treatment of wool from a scientific point of view. Thus, the majority of the plasma treatment has been performed on as clean a wool surface as possible (ABUTC), in order that the modifications would occur to as consistent a surface structure as possible. However, if plasma treatment is to be utilised in the wool industry, it would have to be applicable to the lower standard level of cleanliness found in industry for wool fabrics.

Thus the final research done was to study the plasma treatment of industrially wet scoured wool fabrics (ABUT). This fabric had been processed from the raw greasy wool fleece in the industrial-scale mill at CSIRO DWT. The final stage the fabric roll underwent in its processing was a wet scour and it was used in the 'as received' state for the research in this chapter, with no further cleaning. This meant that there was still some residual grease present (0.6 % o.m.f).

The results from this fabric should be a useful indicator of the potential of plasma treatment in an industrial situation. RF plasma treatment was used primarily, because of the detailed work and modeling that had already been done for the RF plasma treatment (Chapter 4). Corona treatment was also studied because it represents the cheapest and easiest option for introducing plasma treatment into the wool industry.

The results from the techniques used to study the two plasma treatments on industrially wet scoured wool are presented in Section 6.2. In Section 6.3 the results are discussed in terms of the proposed mechanism for plasma treatment and its ability to be applied to industrial wet scoured wool fabrics.

6.2 OBSERVATIONS

6.2.1 FeSEM Appearance

No changes from the untreated wool surface were observed for RF plasma treatment on ABUT, up to 1800 dose units, or for corona treatment up to 5333 J/m² on ABUT.
6.2.2 Allwörden Sac Formation

Allwörden sac formation remains unchanged for ABUT until 100 dose units is reached after which it starts to drop towards zero (Fig.6.1). This trend is very similar to RF plasma treatment of ABUTC wool.

6.2.3 Surface Energy

The initial values of the surface energy for industrial wet scoured wool are lower than for ABUTC wool. The dispersive character of the industrial wool’s surface energy steadily increases from 17 up to 45 mJ/m² after 100 dose units (Fig.6.2a). The polar character jumps from -15 mJ/m² to a slightly positive value after 1 dose unit and then jumps again to 52 mJ/m², between 50 - 100 dose units. The same trend line holds true for oxygen, air, or argon plasma treatment. This behaviour is similar to the RF plasma treatment of ABUTC (see section 6.3), except that it takes an additional order of magnitude of dose units for the changes to surface energy to reach saturation.

Corona plasma treatment of industrial wool fabric also shows similar behaviour to ABUTC corona treatment. The dispersive character has reached its steady value of 45 mJ/m² after 333 J/m² (Fig.6.2b)). The polar character reaches a maximum value of 54 mJ/m² after 5000 J/m². Up to this point the polar character shows a steady increase, with the double-sided treatment increasing more rapidly than the single-sided treatment. This behaviour matches what was observed for ABUTC fabric in Chapter 5, except that it requires roughly an order of magnitude greater corona dose to achieve the saturation values.

The surface energy values (Table 6.1) above saturation are the same for RF oxygen plasma treatment of ABUT or ABUTC wool. However, the corona treatment surface energies are only the same for the dispersion component. The polar component ~20.5 mJ/m² is still below the saturation value for ABUTC ~ 25 mJ/m².
Chapter 6. Plasma Treatment of Industrial Wool Fabric

### Plasma Treatment of Industrial Wool Fabric

#### Plasma Treatment of Industrial Wool Fabric

<table>
<thead>
<tr>
<th>Plasma Treatment</th>
<th>Dose Units or Corona Dose</th>
<th>Surface Energy Components (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.1 or 10 J/m²</td>
<td>( \gamma_s^d ) 24.5 ± 1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \gamma_s^p ) 1.8 ± 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \gamma_s ) 26.3 ± 2.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.25 J/m²</td>
<td>39.8 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>32.0 J/m²</td>
<td>36.2 ± 1.8</td>
</tr>
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<td></td>
<td>128 J/m²</td>
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</tr>
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<td></td>
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<td>Argon</td>
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<td>42.5 ± 1.4</td>
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</tr>
</tbody>
</table>

Table 6.1 Wool Surface Energy Components (polar \( \gamma_s^p \) and dispersion \( \gamma_s^d \)) after Plasma Treatment

#### 6.2.4 Surface Chemistry (XPS)

The surface of ABUT wool (Table 6.2) has more carbon, less oxygen and less nitrogen than ABUTC wool (see Table 5.2). RF oxygen plasma treatment produces a very different result from what was observed for ABUTC wool. The carbon level remains very high, while the nitrogen and sulfur levels drop dramatically. The oxygen increases by the same amount as observed for ABUTC wool. This is reflected in the nitrogen ratios. The change in the carbon oxidation ratio remains the same as was observed for plasma treatment of ABUTC wool, but the oxidised sulfur ratio is much smaller.

After corona treatment of ABUT (Table 6.2) the surface chemistry is similar to corona treatment of ABUTC (see Table 5.4). The C/N and O/N ratios are higher than observed previously, but conversely the oxidation ratios are slightly lower than before (see section 5.4.6).
Chapter 6. Plasma Treatment of Industrial Wool Fabric

<table>
<thead>
<tr>
<th>RF Plasma or Corona</th>
<th>Dose</th>
<th>Atomic%</th>
<th>Elemental Ratio</th>
<th>% Oxidised</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
<td>N</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.1 / 10</td>
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Table 6.2 Industrial Wool Surface Chemistry (XPS) After Plasma Treatment

6.2.5 Textile Property Changes

Competition dyeing with CI Acid Blue 185 on ABUT showed only a slight improvement after 30 dose units (Fig. 6.3) and then remained steady at a level of 15% improvement. Both sides of the fabric gave similar results.

Fig.6.1. Allwörden Sac Formation for Industrial Wool Fabric after RF Oxygen Plasma Treatment
Chapter 6. Plasma Treatment of Industrial Wool Fabric

Fig. 6.2. Surface Energy of Industrial Wool after a) RF Plasma and b) Corona Plasma Treatment
Chapter 6. Plasma Treatment of Industrial Wool Fabric

Fig. 6.3 Industrial Wool Fabric Colour Depth after RF Plasma Treatment
6.3 DISCUSSION OF PLASMA TREATMENT OF INDUSTRIAL WOOL FABRICS

6.3.1 Mechanism for Plasma Treatment of Industrial Wool Fabrics

The results presented in Section 6.2 have shown some basic similarities with plasma treatment of clean wool surfaces. However, there were significant differences in the surface chemistry.

The FeSEM and Allwörden sac formation trends are typical of what has been observed previously for plasma and corona treatment. The changes in surface energy followed the same trends as before, except that an extra order of magnitude of treatment level was required to achieve the saturation region. Also, corona treatment appears to produce a slightly lower value for the final polar component of the surface energy.

The surface chemistry values produced by RF plasma treatment of ABUT wool are very different. The values suggest that the surface layer of initially partially oxidised wool grease is oxidised by the plasma treatment. This produces a new layer of highly oxidised grease on top of the remaining grease. Hence, the carbon levels remain high, the oxygen levels increase, and the nitrogen and sulfur levels drop as the protein is buried even deeper within the grease layers. Some etching is occurring, as after 192 dose units the oxidised sulfur ratio increases, which indicates that some protein has been exposed, or at least come closer to the surface. However, the carbon oxidation remains constant, indicating that the surface oxidation layer is retained throughout the etching.

The surface chemistry of the corona treated ABUT shows more similarity to the corona treated ABUTC surface chemistry than occurred after RF plasma treatment. The oxidation ratios are slightly lower, but that is the only significant difference. These observations indicate that corona treatment for ABUT and ABUTC wool are following similar processes.

The slight improvement in dye colour depth results for ABUT suggests that the improvement will increase but at a much slower rate than observed previously for RF plasma (Section 4.3). In the literature Byrne et al, 1995 and Bona et al, 1995, have observed improvements in shrinkage and yarn tensile properties for both corona treatment and glow plasma treatment of industrial wool fabrics.
Protein

Onset of Wettability

Maximum change in surface energy

Maximum change in Allwörden reaction

Surface
Formation of oxidised surface groups
Fully oxidised layer present on the surface

Lipid
Oxidation/etching of lipid layer
Lipid layer removed

Surface Grease

Protein
Protein exposed
Etching into protein

N[O] x time (dose units)
All of these results combined suggest that in the main the same mechanism would be operating for plasma treatment of industrial wet scoured wool with the exception that for ABUT wool the extra layer of grease on the surface must be factored in (Fig.6.4). The layer of grease clearly oxidised quickly, as shown by the XPS. However, it appears that the removal of this grease layer takes a significant amount of time and delays the onset of the usually observed improvements by an order of magnitude. Presumably, the etching into the protein will follow once the grease layer has been removed. However, this would require further investigation to confirm.

6.4 SUMMARY

An initial exploration into the plasma treatment of industrial wet scoured wool has shown that similar behaviour was observed for the analytical techniques used, as had been observed for laboratory cleaned wool. The observations are consistent with the presence of an extra grease layer on the surface which must first be oxidised. After this has occurred the changes for industrial wet scoured wool are similar to that of laboratory cleaned wool. There is thus a delay for the onset of observed improvements and the total treatment level required is increased by an order of magnitude. With this interpretation it is clear that this delay needs to be factored into any industrial scale plasma treatment, but does not present any serious difficulty.
7.1 CONCLUSIONS

The plasma treatment of the wool fibre has been evaluated in this thesis using a wide range of conditions and surface analytical techniques. From this work the plasma treatments were shown to bear no significant resemblance to any of the model treatments evaluated in Chapter 3. In particular ozone, electrons and UV have been proven to make no significant contribution to the effects produced by plasma treatment.

In Chapter 4 the radio-frequency plasma treatments were shown to depend predominantly on the flux of atomic oxygen to the surface. This information was used to develop a new and original mechanism to account for the plasma treatment of the wool fibre. This mechanism was able to explain the results in this thesis and previous reports of plasma treatment of wool from the literature.

The mechanism proposed to describe plasma treatment is that atomic oxygen interacts with the surface of the wool fibre. The atomic oxygen causes an initial oxidation of the surface which then continues until a fully oxidised surface layer is formed. Once this has occurred, etching begins to dominate the effect, with the lipid being removed, and then etching into the protein of the cuticle occurring. Whilst the etching is occurring, the surface maintains a state of full oxidation.

The microwave plasma treatment of wool was examined and the same mechanism for RF plasma was shown to give a good explanation of the observed results. The additional factors that needed to be taken into account were other possible sources of atomic oxygen in the gases used and any other reactions of molecular groups onto the wool surface that may occur for reactive gases. The oxidation also occurred much more rapidly because the wool had been placed within the plasma.

Corona atmospheric plasma treatment can also be explained using this mechanism. For corona plasma, the mechanism occurred more slowly because the penetration of the etching effect through the fabric was less effective at atmospheric pressures.

Finally, the mechanism was able to explain the results observed for the plasma treatment of industrial wet-scoured wool fabric. The residual layer of surface grease present on the surface represents an extra barrier that has to be oxidised and etched away, which results in higher treatment levels being required before most of the expected improvements are observed.
The work performed in this research has also led to the conclusion that the current static models of the wool surface were not adequate to explain the observed results. A new dynamic surface model has been proposed, whereby the wool surface is made up of a patchwork of lipid, oxidised lipid, and protein. This surface can reorient, to produce different surfaces, dependent on the molecular environment surrounding the wool surface.

As well, the observed behaviour for wool dyeing with acid dyes, after microwave plasma treatment, has led to the conclusion that the whole of the cuticle represents a barrier to dyeing, rather than there being a particular barrier layer within or on top of the cuticle. As more and more of the cuticle is removed the dye colour depth continues to increase without coming to a maximum value.

7.2 SUGGESTIONS FOR FURTHER WORK

The continuing increases in the costs of water and the treating of polluted water from traditional chemical treatments of wool implies a bright future for plasma treatment in the textile industry.

The RF plasma chamber built for this research represents an excellent resource to extend the results presented here. The plasma treatment of wool with other gases could be investigated to confirm that the mechanism will still hold, for other non-reactive gases and reactive gases. Of even greater interest for the future is the ability of plasma treatment to circumvent the normal rules of chemical reaction through plasma polymerisation of specific finishes onto the wool fibre, for example to produce stain repellency, or flame-proofing, or improved shrink-resistance.

The 3 months spent at DWI was sufficient for an initial investigation of the microwave and corona plasma treatments, in terms of the mechanism that has been proposed. However, further confirmation of the behaviour of plasma treated wool from these different reactors, in terms of the mechanism presented here, would be useful.

Finally, the model for the surface of the wool fibre is in need of further investigation and plasma treatment of wool represents a fruitful method for probing the state and behaviour of the wool surface and its underlying layers.
APPENDIX B: ULTRA HIGH FREQUENCY AND RADIO FREQUENCY PLASMA DATA

All the plasma measurements were performed in the A21-U by J.J. Del and E. Tangen of the Plasma Research Laboratory and are described in detail in their PhD thesis (Del, 1983). This appendix contains a summary of all plasma data that was used in Chapter 8, and it includes the majority of the original data. 1979 is also incorporated as a useful starting point for understanding the plasma phenomena.
7.2 CONCLUSIONS FOR FURTHER WORK

The following sections of the point of view and the working of pinhole data have been thoroughly investigated. The definition of what is meant by the term 'pinhole' has been discussed in detail.

The pinhole character itself for the pinhole is a very interesting phenomenon. The physical characteristics of a pinhole with different sizes could be investigated in practice. But the mechanism will still need further investigation. All opens greater names for the future in the ability of physics continuous development and related areas of chemical reaction through process optimization and design. The future is here with the unique in principle state of analytical equipment and software that allow further development.

The specific topic of this investigation was the initial evaluation of the prospective and complex phenomena. The understanding of the basic principles and the development of the techniques of various treatments with the aid of our own detectors, more advanced detectors, should be considered.

Finally, the study of the mechanism of the quantum and power transmission, the application and potential of our understanding of the quantum and power transmission the state and behavior of the material will in turn lead to new directions.
APPENDIX I: ANU RADIO FREQUENCY PLASMA DATA

All the plasma measurements were performed at the ANU by X-J. Dai and colleagues in the Plasma Research Laboratory and are described in detail in her PhD thesis (Dai, 1995). This appendix contains a summary of the plasma data that was used in Chapter 4 and 6 to create the majority of the figures. Chen, 1974 is also recommended as a useful starting point for understanding plasma dynamics.
### Plasma Statistics from X-J Dal

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#### Atomic Oxygen Emission at 130 nm

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  - 100 W
  - 200 W

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**N.B.** Can't do absorption measurements with Argon as the concentrations are too low.

---

* Te is not really correct as the distribution of electrons is not Maxwellian.
* ** All values above are 10% error at least.
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BIBLIOGRAPHY


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