

**An Investigation of the Performance of Photochromic Dyes  
and their Application to Polyester and Cotton Fabrics**

Being a Thesis presented by

**MOHANAD ALDIB**

In application for

**THE DEGREE OF DOCTOR OF PHILOSOPHY**

HERIOT-WATT UNIVERSITY

Scottish Borders Campus

School of Textiles and Design

April 2013

*"The copyright in this thesis is owned by the author. Any quotation from the thesis or use of any of the information contained in it must acknowledge this thesis as the source of the quotation or information."*

## ABSTRACT

Six commercial photochromic dyes were applied to polyester and, to a lesser extent, cotton fabrics by different dyeing and printing methods. The photochromic performance of the dyed and printed fabrics was investigated in terms of the degree of photocolouration, background colour, fading characteristics, fatigue resistance and storage stability. A traditional aqueous-based disperse dyeing method was used to apply the photochromic dyes to polyester fabric. Solvent-based dyeing methods also were investigated for application of the photochromic dyes to polyester fabric. Solvent-based inks were formulated and applied to polyester and cotton fabrics by digital inkjet printing. The photochromic performance and colour fastness to light and washing of the photochromic fabrics were evaluated and comparison made. UV/visible spectra of the commercial photochromic dyes in a range of solvents were obtained and interpreted in terms of solvent polarity. On the basis of this study, the photochromic performance of the fabrics was improved by selecting the appropriate application solvents which transferred minimum background colours onto the fabrics. A new method of evaluating lightfastness of photochromic fabrics was established, aimed at replacing the conventional method by an instrumental method. This method was based on comparing the decrease in the degree of photocolouration of photochromic fabrics after light exposure with measured values of the colour differences of the blue wool references after fixed periods of light exposure. Two photochromic dyes were synthesized by azo coupling of a spironaphtho[2,1-*b*]oxazine with diazonium salts obtained from *p*-nitroaniline, and *m*-nitroaniline. Molecular modeling of the new photochromic systems, which are referred to as azospirooxazine dyes, showed that the dyes were predicted to have the potential to show photochromism. Thus, the photochromism of the azospirooxazine dyes in a range of solvents was investigated. The investigations showed that the dyes performed differently in different solvents in terms of the hue, the rate of the photochromic colour change and the colour reversibility.

## **DEDICATION**

### **To my soul mate ... RAMIA**

Who has been patient, contented and giving me pure love

### **To my joy in life .... Leen and Heba**

Who have missed me and kept asking me 'Daddy stay at home today'

### **To my parents**

Who have been ready to do everything to see me happy

### **To my home country.... Syria**

Greatest love and gratitude

## **Acknowledgement**

I would like to thank my PhD supervisor, Professor Robert Christie, who has been supporting, understanding, giving honest advice and ready to help with all issues.

*My great respect and gratitude*

ACADEMIC REGISTRY  
**Research Thesis Submission**



|   |                               |   |                |
|---|-------------------------------|---|----------------|
| Name:   | MOHANAD ALDIB                 |   |                |
| School/PGI:                                       | School of Textiles and Design |   |                |
| Version: <i>(i.e. First, Resubmission, Final)</i> | Final                         | Degree Sought<br>(Award <b>and</b><br>Subject area) | PhD (Textiles) |

**Declaration**

In accordance with the appropriate regulations I hereby submit my thesis and I declare that:

- 1) the thesis embodies the results of my own work and has been composed by myself
- 2) where appropriate, I have made acknowledgement of the work of others and have made reference to work carried out in collaboration with other persons
- 3) the thesis is the correct version of the thesis for submission and is the same version as any electronic versions submitted\*.
- 4) my thesis for the award referred to, deposited in the Heriot-Watt University Library, should be made available for loan or photocopying and be available via the Institutional Repository, subject to such conditions as the Librarian may require
- 5) I understand that as a student of the University I am required to abide by the Regulations of the University and to conform to its discipline.

\* *Please note that it is the responsibility of the candidate to ensure that the correct version of the thesis is submitted.*

|                         |  |       |  |
|-------------------------|--|-------|--|
| Signature of Candidate: |  | Date: |  |
|-------------------------|--|-------|--|

**Submission**

|  |               |
|--|---------------|
| Submitted By <i>(name in capitals)</i> : | MOHANAD ALDIB |
| Signature of Individual Submitting:      |               |
| Date Submitted:                          |               |

**For Completion in the Student Service Centre (SSC)**

|  |  |       |  |
|--|--|-------|--|
| Received in the SSC by <i>(name in capitals)</i> :   |  |       |  |
| <i>Method of Submission</i><br><i>(Handed in to SSC; posted through internal/external mail):</i> |  |       |  |
| <b><i>E-thesis Submitted (mandatory for final theses)</i></b>                                    |  |       |  |
| Signature:   |  | Date: |  |

## Contents

|   |    |
|---|----|
| <b>List of Publications</b> .....   | xi |
| Chapter 1 – Introduction .....  | 1  |
| 1.1. Background .....   | 1  |
| 1.2. Aims and Objectives .....  | 2  |
| 1.3. Structure of the Thesis .....  | 3  |
| Chapter 2 - Literature Review .....   | 5  |
| 2.1. Historical Perspective.....  | 5  |
| 2.2. Chromic Phenomena .....  | 6  |
| 2.3. Photochromic Systems .....   | 14 |
| 2.4. Applications of Photochromic Compounds .....   | 19 |
| 2.5. Photodegradation of Textile Dyes.....  | 25 |
| 2.6. Dyeing Mechanisms of Textile Fibres .....  | 27 |
| 2.7. Polyester Dyeing Technology .....  | 28 |
| 2.8. Cotton Dyeing Technology .....   | 34 |
| 2.9. The Use of Solvents in Textile Dyeing.....   | 38 |
| 2.10. Dry heat-fixation .....   | 44 |
| 2.11. Textile Printing .....  | 44 |
| 2.12. Inkjet Printing .....   | 45 |
| 2.13. Colour Measurement.....   | 54 |
| Chapter 3 - The Application of Photochromic Dyes to Polyester as Disperse Dyes by an Exhaustion Method.....   | 65 |
| 3.1. Introduction .....   | 65 |
| 3.2. Experimental .....   | 67 |
| 3.3. Results and Discussion.....  | 72 |
| 3.3. Dyeing at a temperature of 120°C; dyeing time of 45 minutes .....  | 72 |
| 3.3.2. Dyeing at neutral conditions pH~7, temperature 120°C and time 45 minutes - Conditions D.....   | 74 |
| 3.3.3. Investigation of dyeing conditions.....  | 75 |
| 3.3.4. Optimisation of UV light irradiation time .....  | 76 |
| 3.3.5. Degree of photocolouration and background colours of all dyes applied to polyester fabric by an exhaustion method at different dyeing concentrations ..... | 77 |
| 3.3.6. Fading time of polyester fabric dyed with all dyes applied by the exhaustion method .....  | 83 |
| 3.3.7. Fatigue resistance of polyester fabric dyed with all dyes by an exhaustion method .....  | 85 |
| 3.3.8. Storage stability of polyester fabric dyed with all dyes by an exhaustion method .....   | 85 |

|  |     |
|--|-----|
| 3.3.9. Colour fastness to light of polyester fabric dyed with photochromic dyes by an exhaustion method .....  | 86  |
| 3.3.10. Using additives in an attempt to improve lightfastness .....   | 89  |
| 3.3.11. Colour fastness to washing of polyester fabric dyed with photochromic dyes by an exhaustion method .....   | 106 |
| 3.3.12. Carrier dyeing of polyester with photochromic dyes.....  | 109 |
| 3.4. Conclusions .....   | 112 |
| Chapter 4 -The Application of Photochromic Dyes To Polyester Fabric by a Solvent-Based Pad Dry-Heat Dyeing Method.....   | 114 |
| 4.1. Introduction .....  | 114 |
| 4.2. Experimental .....  | 115 |
| 4.2.1. Colour measurement methodology and conditions .....   | 115 |
| 4.2.2. Materials .....   | 115 |
| 4.2.3. Variations in dye concentrations.....   | 116 |
| 4.2.4. Solvent-based pad dry-heat dyeing of polyester fabric with photochromic dyes.....   | 116 |
| 4.2.5. Fading characteristics, fatigue resistance and shelf life.....  | 116 |
| 4.2.6. Colour fastness to light of polyester fabrics dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method.....  | 117 |
| 4.2.7. Using additives in an attempt to improve lightfastness of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method.....                              | 117 |
| 4.2.8. Colour fastness to washing of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method.....   | 117 |
| 4.3. Results and Discussion.....   | 117 |
| 4.3.1. Dyeing polyester fabric with photochromic dyes by a solvent-based pad dry-heat dyeing method.....   | 117 |
| 4.3.2. Degree of photocoloration and background colours of polyester fabric dyed with photochromic dyes at different dyeing concentrations by a solvent-based pad dry-heat dyeing method ..... | 123 |
| 4.3.3. Fading time of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method .....  | 130 |
| 4.3.4. Fatigue resistance of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method .....   | 135 |
| 4.3.5. Storage stability of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method .....  | 137 |
| 4.3.6. Colour fastness to light of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method .....  | 140 |
| 4.3.7. Additives used in an attempt to improve lightfastness of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method.....                               | 142 |

|  |     |
|--|-----|
| 4.3.8. Colour fastness to washing of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method.....                             | 147 |
| 4.4. Conclusions .....   | 148 |
| Chapter 5 - Digital Inkjet Printing of Polyester Fabric with Photochromic Dyes ....  | 152 |
| 5.1. Introduction .....  | 152 |
| 5.2. Experimental .....  | 154 |
| 5.2.1. Colour measurement methodology and conditions .....   | 154 |
| 5.2.2. Materials .....   | 154 |
| 5.2.3. Ink formulation .....   | 154 |
| 5.2.4. Digital inkjet printing of polyester fabric with photochromic dyes.....   | 155 |
| 5.2.5. Fading characteristics, fatigue resistance and shelf life.....  | 156 |
| 5.2.6. Colour fastness to light of polyester fabric inkjet printed with photochromic dyes .....  | 156 |
| 5.2.7. Colour fastness to washing of polyester fabric inkjet printed with photochromic dyes.....   | 156 |
| 5.3. Results and Discussion.....   | 156 |
| 5.3.1. The application of photochromic dyes to polyester fabric by an inkjet printing method.....  | 156 |
| 5.3.2. Degree of photocoloration and background colours of polyester fabric inkjet printed with photochromic dyes with different numbers of printing passes..... | 162 |
| 5.3.3. Fading time of photochromic dyes applied to polyester fabric by an inkjet printing method.....  | 165 |
| 5.3.4. Fatigue resistance of photochromic dyes applied to polyester fabric by an inkjet printing method.....   | 168 |
| 5.3.5. Storage stability of photochromic dyes applied to polyester fabric by an inkjet printing method.....  | 170 |
| 5.3.6. Colour fastness to light of polyester fabric inkjet printed with photochromic dyes .....  | 172 |
| 5.3.7. Colour fastness to washing of polyester fabric inkjet printed with photochromic dyes.....   | 174 |
| 5.4. Conclusions .....   | 176 |
| Chapter 6 - The Application of Photochromic Dyes to Cotton Fabric by a Solvent-Based Direct Dyeing Method.....   | 178 |
| 6.1. Introduction .....  | 178 |
| 6.2. Experimental .....  | 179 |
| 6.2.1. Materials .....   | 179 |
| 6.2.2. Solvent-based direct dyeing of cotton fabric with photochromic dyes .....   | 179 |
| 6.2.3. Colour measurement methodology and conditions .....   | 180 |



|   |     |
|---|-----|
| 6.2.4. Fading characteristics, fatigue resistance and storage stability of dyed fabrics .....   | 180 |
| 6.3. Results and Discussion.....  | 180 |
| 6.3.1. The application process of photochromic dyes 1-6 to cotton fabric by a solvent-based direct dyeing method .....                                  | 180 |
| 6.3.2. The degree of photocolouration and background colours of photochromic dyes applied to cotton fabric .....  | 183 |
| 6.3.3. Fading time of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method .....  | 184 |
| 6.3.4. Fatigue resistance of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method .....                                   | 187 |
| 6.3.5. Storage stabilities of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method .....                                  | 188 |
| 6.4. Conclusions .....  | 189 |
| Chapter 7 - Photochromism and Absorption Spectra of Photochromic Dyes in Different Solvents .....   | 190 |
| 7.1. Introduction .....   | 190 |
| 7.2. Experimental .....   | 191 |
| 7.2.1. Colour measurements of dye solutions .....   | 191 |
| 7.2.2. Materials .....  | 192 |
| 7.2.3. Application of photochromic dyes to polyester fabric from different solvents by the Solvent-based pad dry-heat dyeing method.....                | 192 |
| 7.2.4. Colour measurements of polyester fabric dyed with photochromic dyes by the solvent-based pad dry-heat dyeing method from different solvents..... | 192 |
| 7.3. Results and Discussion.....  | 192 |
| 7.4. Conclusions .....  | 198 |
| Chapter 8 – An Investigation of an Instrumental-Based Method for Assessment of Colour Fastness to Light of Textiles .....                               | 200 |
| 8.1. Introduction .....   | 200 |
| 8.2. Experimental .....   | 201 |
| 8.2.1. Materials .....  | 201 |
| 8.2.2. Instrumental methods.....  | 201 |
| 8.3. Results and Discussion.....  | 202 |
| 8.3.1. Principles of the instrumental-based method of lightfastness measurement.....  | 202 |
| 8.3.2. Assessment of colour fastness to light of polyester fabric dyed with photochromic dyes by the exhaust dyeing method.....                         | 207 |
| 8.4. Conclusions .....  | 208 |
| Chapter 9 - Development of New Photochromic Systems for Evaluation in Textile Applications .....  | 210 |

|   |                                     |
|---|-------------------------------------|
| 9.1. Introduction .....   | 210                                 |
| 9.2. Experimental .....   | 211                                 |
| 9.2.1. Starting materials .....   | 211                                 |
| 9.2.2. Instrumental methods.....  | 211                                 |
| 9.2.3. Synthesis of azospirooxazine dyes .....  | 211                                 |
| 9.2.4. Molecular modelling of spirooxazine 1 and azospirooxazine dyes 2 and 3   | 217                                 |
| 9.2.5. Photochromism of spirooxazine 1 and azospirooxazine dyes 2 and 3 in<br>different solvents.....                 | 217                                 |
| 9.3. Results and Discussion.....  | 217                                 |
| 9.3.1. Investigations of Photochromism of spirooxazine 1 in different solvents...                                     | 219                                 |
| 9.3.2. Investigation of the photochromism of azospirooxazine dye 2 .....  | 227                                 |
| 9.3.3. Investigation of photochromism of azospirooxazine dye 3 .....  | 247                                 |
| 9.3.4. Investigation of photochromism of the ortho-derivative of azospirooxazine<br>dyes (azospirooxazine dye 4)..... | 258                                 |
| 9.4. Conclusions .....  | 261                                 |
| Chapter 10 – Conclusions .....  | 263                                 |
| 10.1. General Conclusions .....   | 263                                 |
| 10.2. Future Work .....   | 266                                 |
| Appendix .....  | 268                                 |
| Published Papers .....  | <b>Error! Bookmark not defined.</b> |
| Chapter 11 - References .....   | 269                                 |

## Publications

### A. Published Papers

1. Mohanad Aldib and Robert M Christie, *Textile applications of photochromic dyes. Part 4: Application of commercial photochromic dyes as disperse dyes to polyester by exhaust dyeing*, *Coloration Technology*, **127**, 5, 282-287 (2011).
2. Mohanad Aldib and Robert M Christie, *Textile applications of photochromic dyes. Part 5: Application of commercial photochromic dyes to polyester fabric by a solvent-based dyeing method*, *Coloration Technology*, **129**, 2, 131–143 (2013)
3. Robert M. Christie, Keith M Morgan, Ayesha Rasheed, Mohanad Aldib, Georgina Rosair, *The molecular design, synthesis and photochromic properties of spirooxazines containing a permanent azo (hydrazone) chromophore*, *Dyes and Pigments*, **98**, 1, 263-272, (2013)

### B. Conferences

1. **5<sup>th</sup> Annual Heriot-Watt Postgraduate Conference**. Poster has been presented, *Evaluation of the application of photochromic dyes to polyester fabric by an aqueous disperse dyeing method*’ **03 June 2010**
2. **KT Conference, Heriot-Watt University**. Poster accepted and presented. *Evaluation of the application of photochromic dyes to polyester fabric by an aqueous dyeing method*. **23 April 2010**

## **Chapter 1 – Introduction**

### **1.1. Background**

Textile materials are essential for various applications in our daily life, such as clothing and furnishing and there are also technical uses such as protective clothing, medical textiles and geotextiles. Imparting colours into textiles has opened the door for creative ideas and has extended the application fields of these materials. The pleasure delivered by colours may have been behind the thinking of ancient Egyptians who applied colour to their clothing as long ago as 2500 BC, and the consequent development of colorants from natural dyes derived mainly from plants through to the modern synthetic dyes that are used for introduction of different colours on various textile materials. The introduction of colours to textiles nowadays is a well established technology. The main recent research on textiles coloration has focused on improving dye uptake by textiles, producing new colours, improving process economics, enhancing environmental performance and improving the quality of colorants in terms of colour fastness, such as to light, wash and rubbing.

Some colour changeable materials have common uses, such as the colourless spectacles which turn to grey in sunshine to become sunglasses; however, the development of colour changeable textiles has not led to significant industrial production, mainly due to technical difficulties in the application of the dyes and their performance. The concept involved in the development of colour changeable textiles is based on applying special colorants to textile materials. These particular colorants possess the ability to undergo reversible colour change under the influence of external stimuli such as light, heat or chemical processes. As an example of the colour changeable materials, photochromic colorants are a class of unusual colorants which undergo reversible colour change stimulated by applying light of different wavelengths. Incorporation of these dyes into textiles may potentially lead to the production of photochromic fabrics which would offer colour changeable backgrounds and UV sensitive fabrics which may, for example, be used as a visual alarm signal indicating high levels of UV light in specific areas.

The development of photochromic fabrics by optimization of a range of methods of application of commercial photochromic dyes to textiles and also the synthesis of some new photochromic systems for evaluation in textile applications are the main subjects of investigation in this thesis.

## **1.2. Aims and Objectives**

The general aim of the research described in this thesis is the establishment of optimized technical methods for producing photochromic fabrics by incorporating photochromic dyes into textiles. The photochromic fabrics produced may then have the potential to be useful in different applications.

This research aims at achieving its objectives in two related directions. The first direction involves the investigation of the application of commercial photochromic dyes to textiles and an optimization of the application methods. This was carried out in an attempt to produce photochromic textiles which may have the potential to meet the requirements of design concepts in different fields where colour changeable backgrounds are essential or desirable for their creative potential. Another proposed application of these materials is in UV light sensitive fabrics which would alert workers in some areas to high levels of UV light in the work environment and so enable them to avoid exposure to the dangers of this radiation. With regard to this first research direction, several different application methods for a series of commercial photochromic dyes applied to polyester and cotton fabrics were investigated. The application methods investigated were aqueous-based disperse dyeing, solvent-based dyeing and digital inkjet printing.

Following the success of the optimization of methods for application of commercial photochromic dyes to textiles, the second direction focused on an investigation of the photochromic performance of new photochromic systems. It was envisaged that the unique chemical structures of the dyes and synthesis methods developed might open the door for production of photochromic dyes of various colours for textile applications. Thus, the second direction of the research was the synthesis of spirooxazine-based dyes containing an azo (hydrazone) group and an investigation of their photochromic properties. The synthesis process is based on connecting a photochromic compound capable of acting as a coupling component by azo coupling with diazotized nitroaniline derivatives. It was anticipated that the synthesised dyes, which are referred to in this thesis as azospirooxazine dyes, would undergo photochromic colour changes due to the presence of the photochromic spirooxazine moiety in the dye molecule. In addition, the presence of the azo (hydrazone) group in the azospirooxazine dye molecule was expected to provide the synthesised dyes, in principle, with the possibility of a wide range of permanent colours. It was envisaged that the dyes might provide unusual photochromic colour change effects with potential possibilities for textile applications.

### **1.3. Structure of the Thesis**

The stages that were followed to achieve the aims of this research are described in separate chapters in this thesis as follows.

Chapter 2 contains a review of literature that is relevant to the research contained in the thesis. It encompasses the classification of chromic phenomena, photochromic systems, applications of photochromic systems, the dyeing and printing technologies used for polyester and cotton and an overview of the principles of colour measurement.

Chapter 3 describes the application of six commercial photochromic dyes to polyester fabric as disperse dyes by an aqueous-based exhaust dyeing method. Optimization of the dyeing process, photochromism of the dyed fabrics and their colour fastness to light and washing were investigated.

Chapter 4 describes the application of the same series of commercial photochromic dyes to polyester fabric by a solvent-based pad dry-heat dyeing method. The dyeing method and the properties of the dyed fabrics were investigated.

Chapter 5 describes the application of the commercial photochromic dyes to polyester fabric by a digital inkjet printing method. Solvent-based photochromic inks were formulated, the printing method was optimized and the printed fabrics were compared with the same fabrics dyed according to the methods described in chapters 3 and 4 in terms of their photochromic properties and colour fastness to light and washing.

Chapter 6 describes the application of the commercial photochromic dyes to cotton fabric by a solvent-based direct dyeing method. The dyeing procedure was optimised and photochromic properties of the dyed fabrics were investigated.

Chapter 7: On the basis of the results discussed in preceding chapters with regard to the differences in photochromic performance of fabrics dyed or printed from different media, the photochromism of the commercial dyes in various solvents with different polarities was investigated. This investigation was carried out in an attempt to select appropriate solvents for textile applications of the photochromic dyes by minimizing the background colours of photochromic fabrics.

Chapter 8 describes the establishment of a new method for assessment of lightfastness of photochromic fabrics based on an instrumental measurement of the decrease in the degree of photocolouration of photochromic fabrics as a result of light exposure and

comparing the measured values to instrumentally measured values of the colour difference between exposed and unexposed parts of the blue wool references.

Chapter 9 describes the synthesis of new photochromic dyes by azo coupling of a spirooxazine compound with diazotized nitroaniline derivatives. The photochromic properties of the synthesized azospirooxazine dyes were investigated in different solvents.

Chapter 10 is the final chapter which describes general conclusions from the research and suggests potential for future work.

Chapter 11 provides a list of the literature referred to in this thesis.

## Chapter 2 - Literature Review

### 2.1. Historical Perspective

The applications of colour changes in an object can be observed frequently in our daily life. These changes may take place either from colourless to coloured or from one colour to another. Colour change phenomena have been applied to develop useful devices capable of transferring information to an observer. When these colour changes are reversible and brought about by external stimuli, many applications may be proposed. Compounds that undergo a reversible colour change upon the application of external stimuli have been investigated intensively by researchers in attempts to widen their range of applications.

Photochromism may be characterised as a reversible colour change involving a particular chemical compound. The forward change is stimulated by UV light, and the change in the other direction takes place after removing the UV light source, and is induced either thermally when the light source is removed (T-type), or on irradiation with a different wavelength of light (P-type). The forward colour change of a photochromic compound is usually bathochromic, i. e. from shorter to longer absorption wavelengths. [1] The reasons for the bathochromic change are related to the mechanism of the colour change process; more details about this process are given in section 2.3. Photochromism may be defined as a reversible phenomenon initiated by light, involving a colour change of a photosensitive compound due to formation of an isomer exhibiting a different absorption spectrum in the visible region. [2-5]

The first example of photochromism was reported in 1867 when Fritzsche observed that the orange colour of tetracene in solution was bleached in daylight and regenerated in the dark. [6] The discovery of the phenomenon of photochromism was first reported in 1876 when Meer discovered that the solid potassium salt of dinitroethane was red in daylight and yellow in the dark. [7] This phenomenon was described initially by the terms 'phototropy' or 'phototropism', but subsequently these terms have been used largely for biological systems. [8]

Interest in the photochromism of organic materials began to increase around 1940. The term 'photochromism' was originally suggested by Hirshberg in 1950. The study of the excited states derived from the photochromic response and the transient species involved in the photoreactivity of photochromic molecules was facilitated by the development of techniques such as flash spectroscopy and laser photophysical methods.[3]



The interest in the applications of photochromic systems increased in the 1980s when the obstacle of the low fatigue resistance of photochromic compounds was overcome by synthesizing stable organic photochromic compounds, such as spirooxazine and naphthopyran derivatives. Since then, commercial applications of photochromism, such as the plastic photochromic ophthalmic lenses, have become widespread. [3, 8]

## **2.2. Chromic Phenomena**

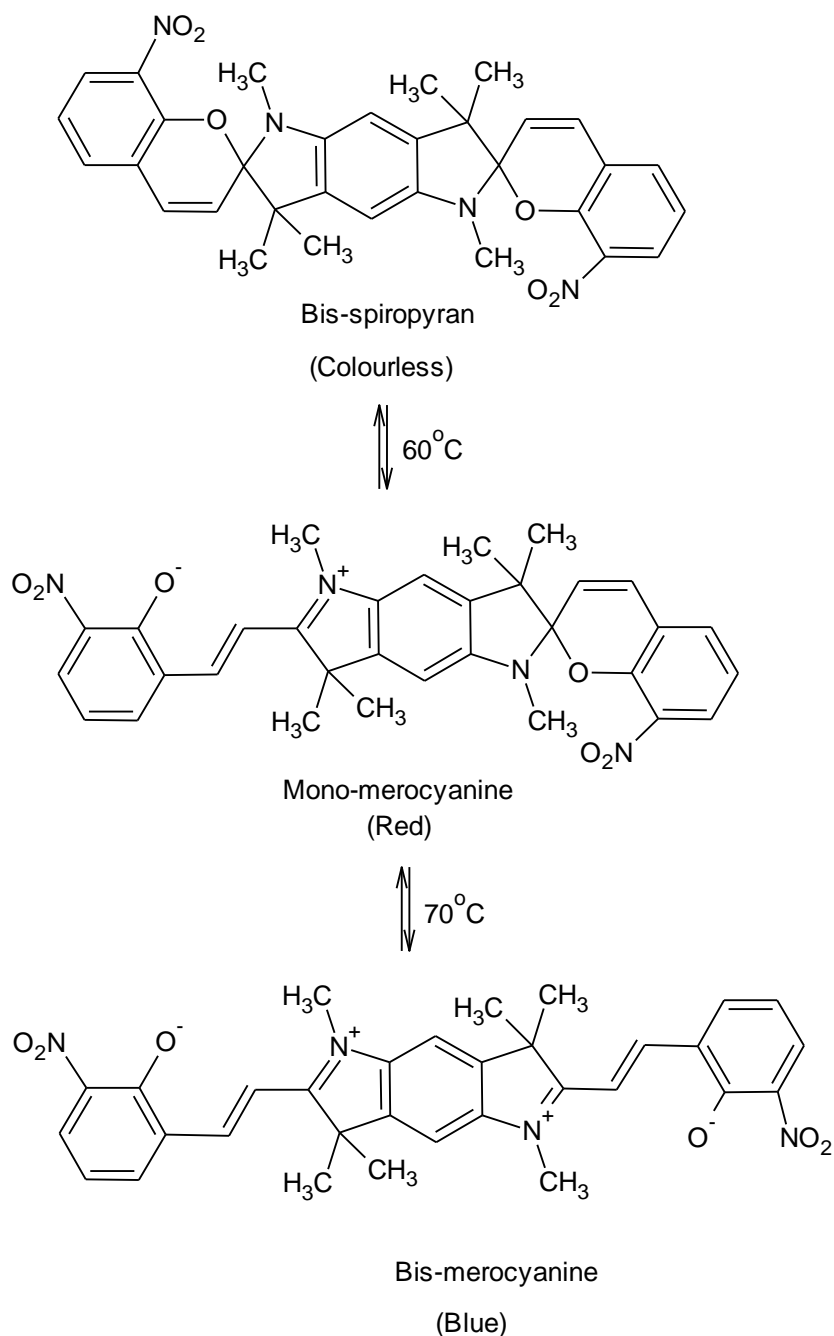
The colour change of chromic materials brought about by an external stimulus is referred to as chromic colour change. The chromic phenomena are classified according to the nature of the stimulus of the colour change. This stimulus is normally UV light in the case of photochromism, while it is electrical potential or current flow that brings about the reversible colour change, as a result of an oxidation or reduction reaction, in the case of electrochromism. Thermochromism, solvatochromism and ionochromism are chromic phenomena stimulated by heat, solvents and ions respectively. [1]

### ***2.2.1. Photochromism***

Photochromism is discussed in detail in section 2.3. The general structure and mechanism of photochromism of spirooxazines, a commercially important class of photochromic dyes, are shown in Scheme 2.10, which is given in that section. The colourless state of the photochromic dye is referred to as the ring-closed form, while the coloured state is referred to as the ring-opened form or the photomerocyanine (PMC).

### ***2.2.2. Thermochromism***

Thermochromic systems are divided into ‘intrinsic’ systems, where heat is the sole stimulus of the colour change, and ‘indirect’ systems, where the colour change is stimulated by the environment change around the system brought about by the heat. [9] Although they are better known for their photochromism, spiropyrans and spirooxazines may also exhibit thermochromism. [1]



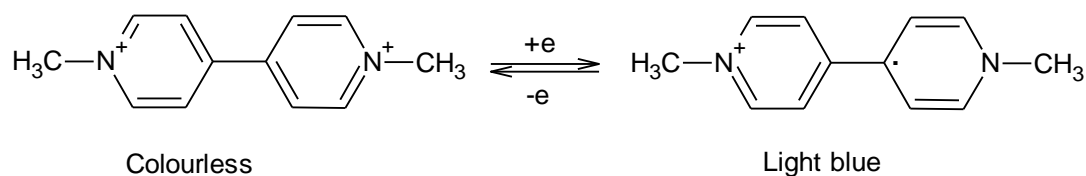
**Scheme 2.1** Sequential thermochromism of a bis-spiropyran

Scheme 2.1 shows the sequential thermochromic colour change of a bis-spiropyran, which is a reversible intrinsically thermochromic system. Heating to 60°C of the colourless bis-spiropyran in *n*-propanol changes its colour to red, which is the colour of the mono-merocyanine. Continuous heating to 70°C converts the red mono-merocyanine to the blue bis-merocyanine. [1]

### 2.2.3. Electrochromism

Electrochromism is the reversible colour change of an electroactive species brought about by electron transfer or an oxidation/reduction process involving this species. [1]

The most widely investigated electrochromic compound in solution is methyl viologen, as shown in Scheme 2.2, which undergoes a reversible electron transfer between two states showing different colours. [10] This type of electrochromic material has been applied in car anti-dazzle, and rear view mirrors.



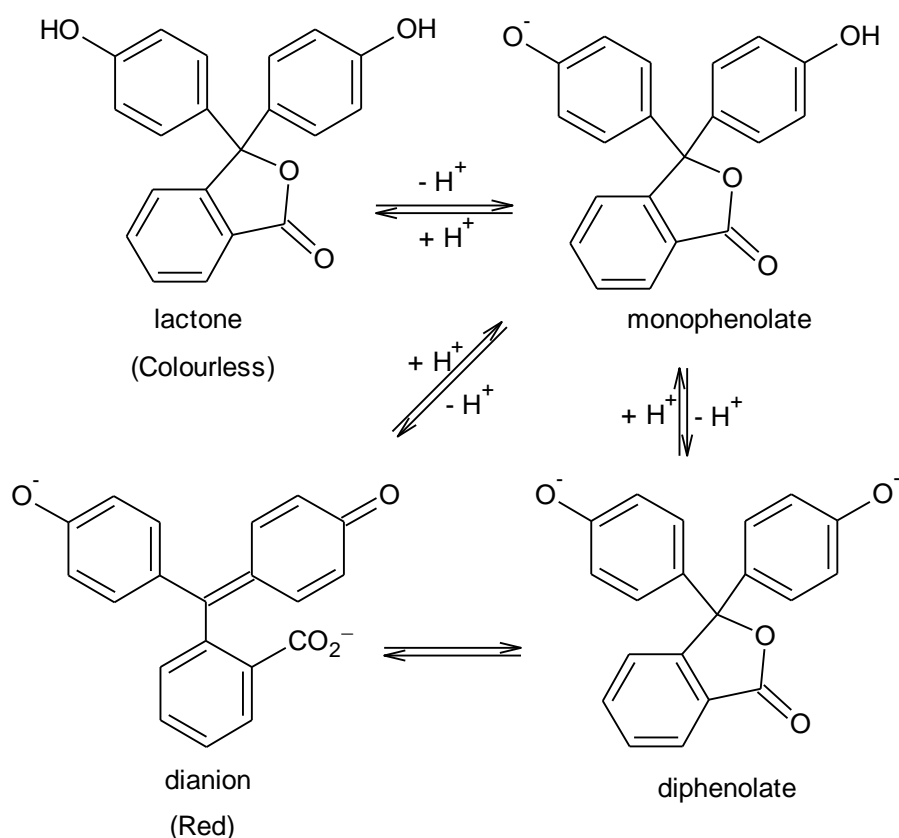
**Scheme 2.2** Electrochromism of methyl viologen

#### 2.2.4. Solvatochromism

Solvatochromism is a phenomenon which involves a change in colour of a compound when it is dissolved in different solvents. The interest in solvatochromism has increased since the 1980s due to their important commercial applications in optical probes and sensors. [1]

#### 2.2.5. Ionochromism

Ionochromism refers to a reversible colour change phenomenon brought about by the interaction of compounds with an ionic species. The terms halochromic, acidochromic or pH sensitive are often used to describe ionochromism when the solvated hydrogen ion is the ionic species involved in the colour change of the compound. Phthalides, triarylmethanes and fluorans are the main classes of commercial importance as pH sensitive dyes. The mechanism of ionochromism of a dihydroxy derivative of the phthaleins, which is a well known class of pH-sensitive dyes having the phthalide structure and referred to as phenolphthalein, is shown in Scheme 2.3.



**Scheme 2.3** Ionochromism of phenolphthalein

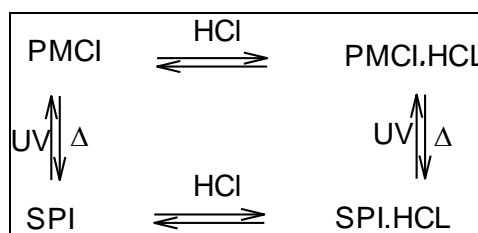
The colourless lactone is converted into the mono and then the diphenolate ion, when alkali is added progressively. The diphenolate, then, rearranges via ring opening of the lactone to give the red planar dianion. This reversible process provides an easy method for indicating the pH change in the range 8.5 – 9.0. [1]

### 2.2.6. Unusual chromic systems

In recent years, there has been interest in developing chromic systems which exhibit more than one chromic phenomenon and also in combining chromic systems with other functionalities.

#### a) Photochromism and acidochromism

When a neutral alcoholic spirooxazine solution is made acidic by addition of hydrochloric acid, the absorption, luminescence and photochromic characteristics are changed. This phenomenon is an example of acidochromism.



**Scheme 2.4** Acidochromism and photochromism of spiro(1,3,3-trimethylindolo-2,3'-naphth-1,4-oxazine)

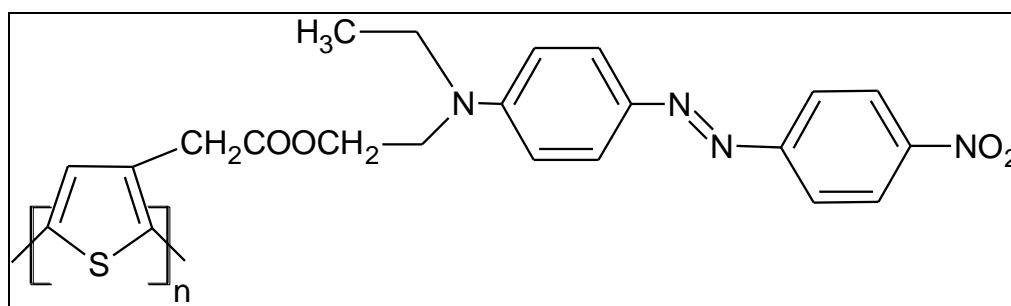
PMCI + HCl: Photomerocyanine generated upon UV excitation of SPI + HCl

A model for the acidichromic and photochromic processes of the spiro(1,3,3-trimethylindolo-2,3'-naphth-1,4-oxazine) has been proposed, as shown in Scheme 2.4.

The merocyanine (PMCI) which is the ring-open form generated by UV irradiation of the ring-closed spiroxazine (SPI) compound, exists as a planar and fully conjugated system. When hydrochloric acid complexes with the conjugated system (PMCI), the donor-acceptor system is destroyed through the formation of an internal salt. The loss of the donor-acceptor system is associated with reduced  $\pi$ -system delocalization and leads to a hypsochromic shift in the absorption spectrum of the internal salt with respect to the merocyanine form. [11]

*b) Thermochromism, solvatochromism and acidochromism*

It is reported that conjugated polymers showing chromic effects have been synthesized and characterized aiming towards possible applications in the areas of sensors, diagnostics and drug screening. [12-15]

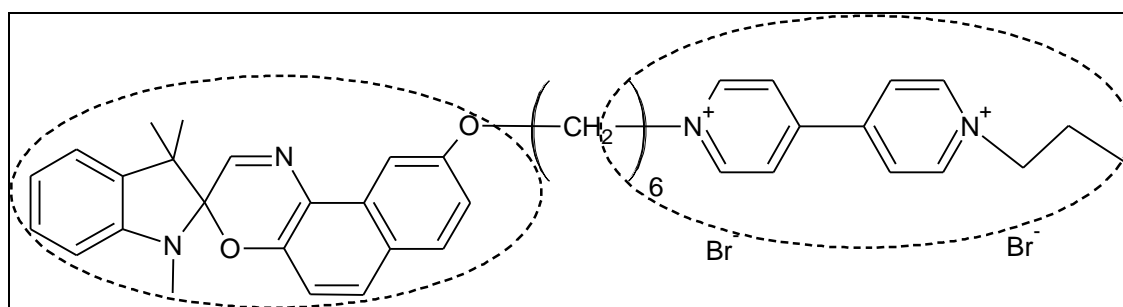


**Figure 2.1** Chemical structure of a polyazothiophene

An example of this type of polymer is polyazothiophene, as shown in Figure 2.1, a polythiophene derivative with azobenzene side-groups, which shows multi-chromic

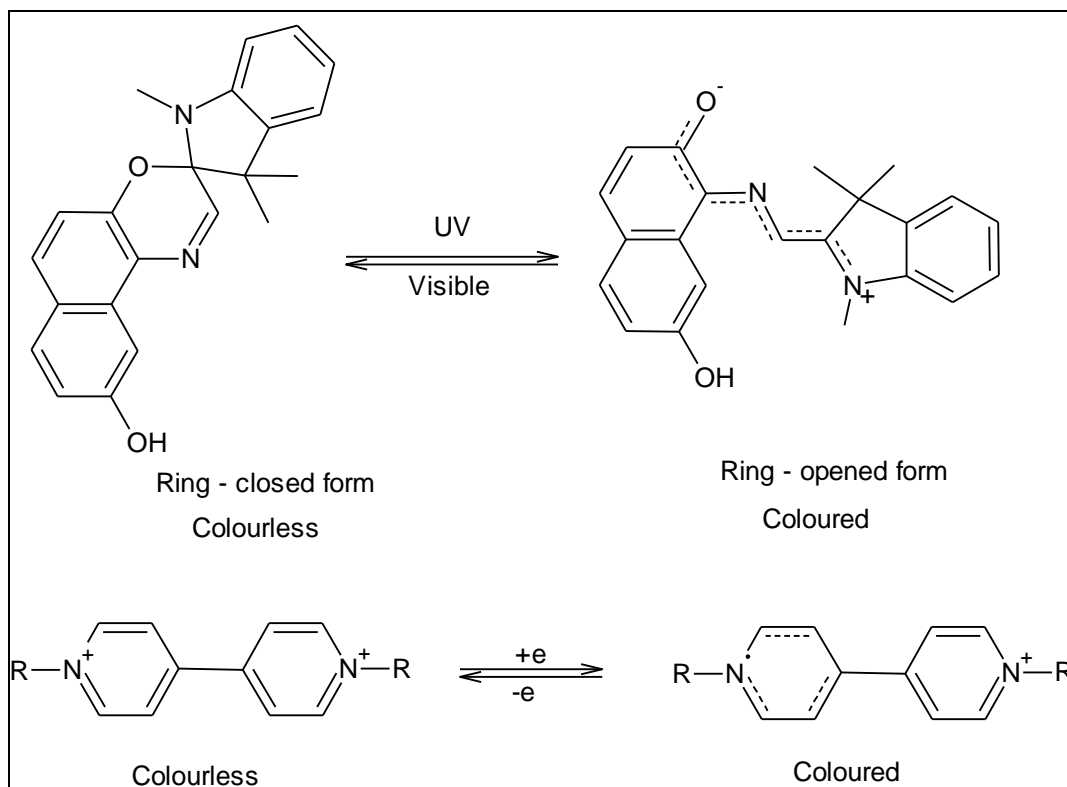
properties. Solutions of the polyazothiophene in different solvents showed a reversible colour change when they were subjected to a heating-cooling cycle between 10°C -70°C. The reversible thermochromism was observed for polythiophenes with different side-chain groups, and therefore it was evident that the thermochromic effect of the polyazothiophene is attributed to the polythiophene backbone of the polymer. The thermochromic behaviour of polythiophenes is brought about by changes in the conformation of transitional isomers during the structural changes of the polymeric chains which lead from planar (highly conjugated) to non-planar (less conjugated) as a result of temperature increase. This explanation was supported by the observation of a hypsochromic shift of polyazothiophene solutions upon heating, which is an expected result of the decrease in the effective conjugation length of the polymer chain which is associated with the transition from the planar to the non-planar structure. Acidochromism was observed when a mineral acid was added to the polymer solution. It was confirmed that this effect is due to the protonation of the azobenzene group in the side chain and also the protonation in the main chain. Solvatochromism of solutions of polyazothiophene was also observed with increasing the solvent polarity. However, it was not possible to explain the solvatochromic effect in this case simply on the basis of the solvent polarity. [12]

c) *Photochromism and electrochromism*



**Figure 2.2** Hetero-bi-functional chromic dye

An example of a multifunctional chromic system was reported in 2007, as shown in Figure 2.2. [16] A hetero-bi-functional dye showing both photochromism and electrochromism at the same time was synthesized and characterized in terms of its optical properties. The spirooxazine, the photochromic part, and the viologen, the electrochromic part, were combined together in the same molecule to provide multifunctional chromic effects

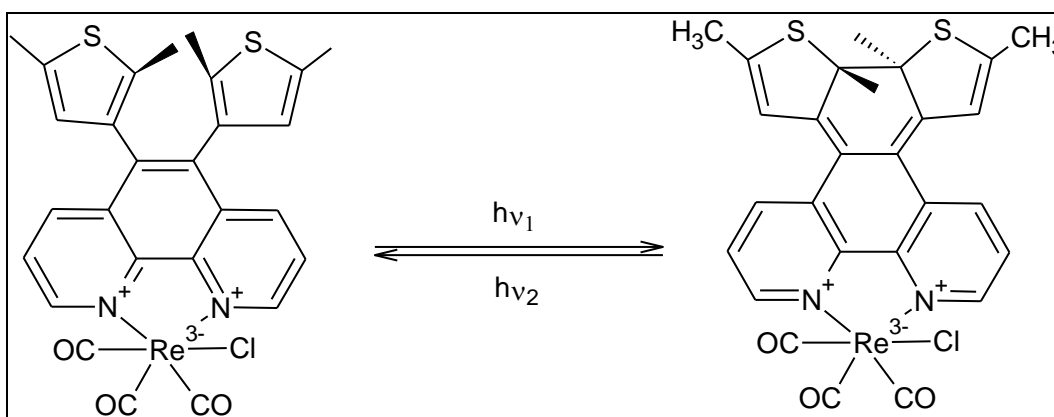


**Scheme 2.5** Photochromism of spirooxazine and electrochromism of Viologen

The hetero-bifunctional dye showed both photochromism and electrochromism when subjected to UV irradiation, and electric energy was applied to the dye solution in DMSO. The photochromic colour change is brought about by the reversible heterolytic cleavage of the C (spiro)-O bond on irradiation with UV light. The viologen undergoes one-electron reduction to provide a coloured radical cation, as shown in Scheme 2.5. [17]

*d) Functionalized photochromic systems*

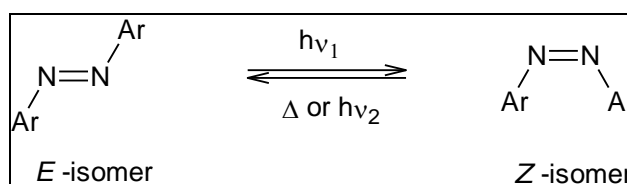
Sophisticated chromic systems were synthesized by combining photochromic systems with organometallic fragments which lead to functionalization of the attached photochromic system due to the redox-active nature of the metal species. [18-20]



**Scheme 2.6** Photochromism of a diarylethene-containing rhenium complex

An example of such a sophisticated photochromic system was synthesized and characterized. This system is a rhenium complex of a diarylethene derivative; its chemical structure and photochromism are illustrated in Scheme 2.6. It is well known that diarylethenes show photochromism by photocyclization of their ring-open forms to their ring-closed form upon irradiation with UV light. More details about the photochromism of diarylethenes are given in section 2.3.4. The UV exposure of a solution in benzene of the rhenium complex of diarylethene derivative showed a bathochromic shift of the absorption spectrum to the visible region compared to the absorption spectrum of the diarylethene derivative which is located in the UV region. Thus, this extension of photochromism to the visible region may be attributed to the perturbation of the transitions by the metal centre in the metal complex. [20]

e) *The photochromic isomerisation of azoaromatic dyes*



**Scheme 2.7** Photochromism of azoaromatic dyes

The photo-induced reversible isomerisation process of azoaromatic dyes about the azo bond involving interconversion between the E- and Z- isomers is one of the longest established chromic phenomena. This reversible phenomenon has attracted attention due to the application of these compounds when they are incorporated in compatible matrices, such as liquid crystals and sol-gel systems. The E- and Z- isomers exhibit different absorption spectra, and therefore they have different colours. The intense



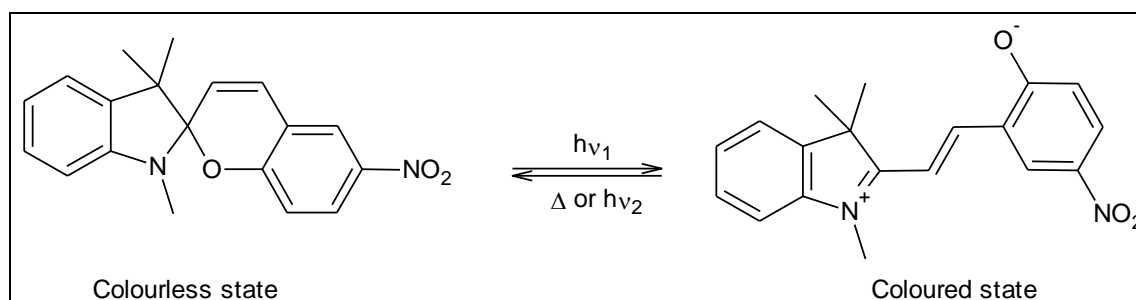
colour of the thermally stable E-isomer is attributed to the extended  $\pi$ -conjugation in the structure of this isomer. Continuous irradiation with visible light gives rise to conversion to the weakly coloured, or non-coloured, and non-planar Z-isomer. When the light source is removed, the Z-isomer reverts thermally, or photochemically, to the highly-coloured E-isomer, as shown in Scheme 2.7. [21]

### 2.3. Photochromic Systems

The most important photochromic systems can be classified as follows: [3]

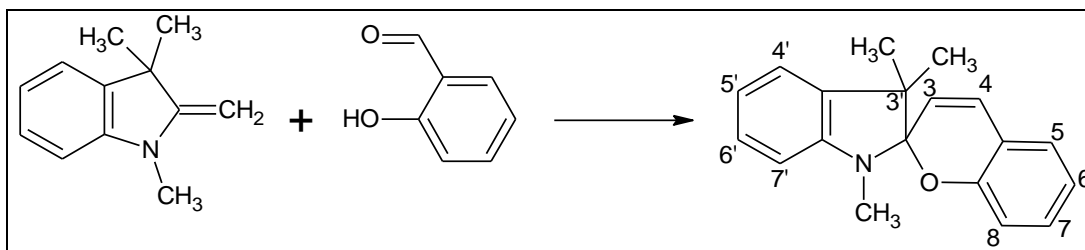
- Spiropyrans.
- Spirooxazines. This family of compounds is characterized by their resistance to photodegradation due to the photochemical stability of the oxazine molecular framework in the ring-closed form as well as in the ring-opened form.
- Diarylethenes, with heterocyclic rings, which are useful for information storage.
- Benzo- and naphtha- pyrans.
- Fulgides and fulgimides. The most popular application is information storage in erasable optical disks.
- Spirodihydroindolizines.

#### 2.3.1. Spiropyrans



**Scheme 2.8** Photochromism of spiropyrans

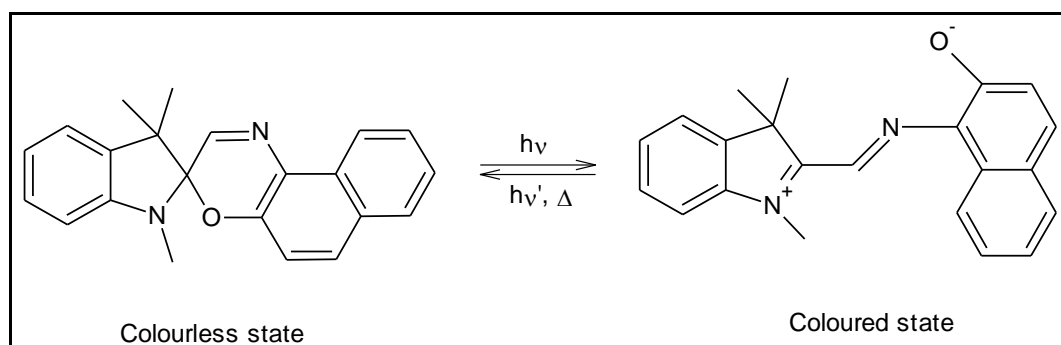
Spiropyrans represent the most intensively investigated families of photochromic compounds especially in the early years of their development. Scheme 2.8 shows the general chemical structure and mechanism of photochromic colour change of indolinospiropyrans. [3] The reversible colour change of spiropyrans is attributed to the reversible cleavage of the  $C_{\text{spiro}}\text{-O}$  bond in the 2H-chromene ring. [3, 22] The photochromic behavior of spiropyrans is observed due to the different UV/Visible absorption spectra of the colourless, or weakly coloured, ring-opened form (SP) and the intensely coloured, ring-opened, merocyanine form (MC). [23]



**Scheme 2.9** Synthesis of 1',3',-dihydrospiro(2H-1-benzopyran-2-2'-(2H)-indole)

The most common method of synthesizing spiroyrans is exemplified in Scheme 2.9. The condensation of a 2-alkyl heterocyclic quaternary salt or the corresponding methylene base with 2-hydroxy unsaturated aldehyde grouping leads to the formation of the spiroyrans referred to as 1',3'-dihydrospiro(2*H*-1-benzopyran-2-2'-(2*H*)-indole). [3]

### 2.3.2. Spirooxazines

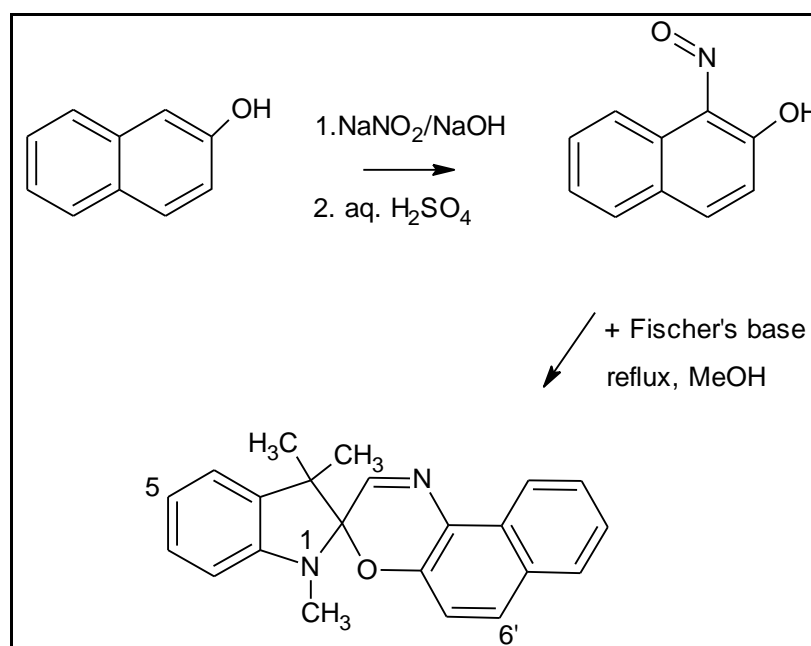


**Scheme 2.10** Photochromism of spirooxazines

Scheme 2.10 shows the general structure and mechanism of the photochromic reaction of spirooxazines. [24] The photochromism of spirooxazines is attributable to the photochemical cleavage of the spiro C- O bond in the ring-closed colourless form, which results in the extension of  $\pi$  - conjugation in the ring-opened coloured form, which is referred to as the photomerocyanine, and thus shifts the absorption in the visible region. [25, 26] The photochromism of spirooxazines can be observed when their colourless, or only weakly coloured, solutions become intensely coloured after irradiation with UV light. The reverse colour change takes place when the light source is removed, by thermal means, and therefore the coloured solutions again become colourless, or weakly coloured. [27] The importance of spirooxazines as a class of organic photochromes comes from the ability of these compounds to undergo a reversible photo-induced colour change when they are incorporated into appropriate

application media. The reasonable fatigue resistance and relative ease of synthesis of spirooxazines has extended the possible applications of these compounds, and therefore spirooxazines have been exploited in various successful ways, such as eye-protective glasses, molecular switches, memories, lenses, emissive displays, chemosensors and biosensors. [28-31]

Spironaphthoxazines and naphthopyrans represent two of the most important chemical classes of photochromic dyes produced industrially. [3, 31, 32] Photochromism of spironaphthoxazines (SNOs) has been the subject of extensive investigations owing to their higher photostability in comparison with well known indolinspiropyrans (ISPs). The mechanism of photochromism of SNOs is similar to that of ISPs and involves heterolytic cleavage of the C-O spiro bond of the oxazine ring to give highly coloured isomers, photomerocyanines, which undergo ring closure to reproduce SNOs either by heating or by irradiation with visible light. [33]



**Scheme 2.11** Synthetic route of spiroindolinonaphthoxazine

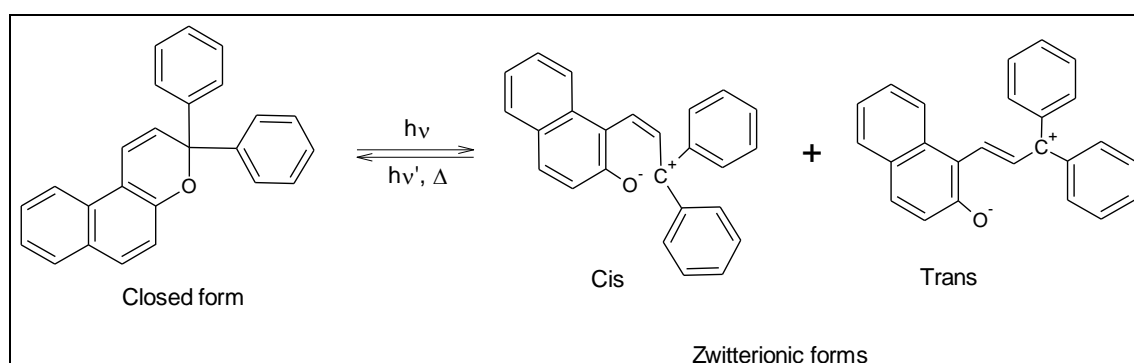
The synthetic route to the spiroindolinonaphthoxazine ring system involves the reaction of a 1-hydroxy-2-nitroso bearing aromatic ring with a 2-alkylidene heterocycle, such as Fischer's base, as shown in Scheme 2.11. Unsubstituted nitrosonaphthols can be synthesized by acidification of an aqueous solution of the corresponding phenolate and sodium nitrite. Condensation of nitrosonaphthols with the indolines is readily achieved by heating the mixture in methanol, or other polar solvents, under reflux. This synthetic route can be used as a general synthetic method for alkyl substituted naphthoxazines.

[1] The important positions for substitution are the 5-position at which substituents have a large effect on the colour, the 6'-position, at which there is also a major effect on both the colour of the open-ring form and properties such as light absorption, and molar absorption coefficient, which is a measurement of how strongly a chemical species absorbs light at a given wavelength, and the alkyl group on position 1, which has an effect on the kinetics of change of colour back to the colourless state. [1, 3]

The optical constants ( refractive index, extinction coefficient and thickness of a self assembled monolayer [34-36]) are important parameters when the selection of the photochromic materials for appropriate applications is made. [37] It is reported that the surface plasmon resonance system was employed, as an optical measurement method, for measuring the optical parameters, such as optical constants, dielectric constants and thickness, and other properties of spirooxazine derivatives, used as self assembled monolayers. This measurement showed that the structural changes of spirooxazine derivatives under UV-light irradiation resulted in changes in the optical constants, dielectric constant and thickness of the monolayer. [38]

### 2.3.3. Benzo- and naphtha- pyrans

Naphthopyrans have been reported to exhibit photochromism since the early 1960s. [39] Naphthopyran derivatives have attracted the attention of researchers due to their colour change in a wide range of the visible spectrum. [40-42] The industrial interest in naphthopyran derivatives for ophthalmic applications started in the early 1990s. [43, 44]

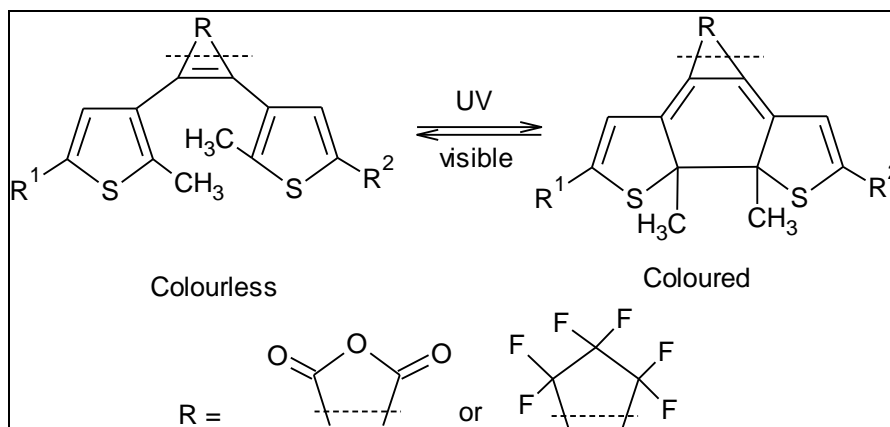


**Scheme 2.12** Photochromism of naphthopyrans

Scheme 2.12 shows the general structure and mechanism of photochromism of naphthopyrans. [45] The photochromic change is attributed to the breaking of the oxygen-carbon bond of the pyran. There is no consensus about which one of the electronic and geometric configurations best describes the open form, and therefore the open form may be represented by the zwitterionic, cis quinoidal or trans quinoidal

forms. [3, 46] Due to a neglect of naphthopyrans for many years since their discovery, spironaphthoxazines had at one time much greater commercial importance than naphthopyrans. [47] However, in the last two decades naphthopyrans have been much studied and are now the most commercially important class of photochromic molecules. [32]

#### 2.3.4. Diarylethenes

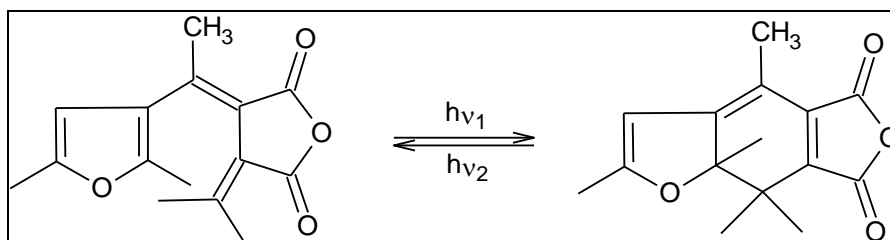


**Scheme 2.13** Photochromism of dithiophenes

The chemical structure and the reversible colour change of dithiophenylenes, an example of diarylethenes, are shown in Scheme 2.13. [1] The reversible change between the colourless ring-opened state and the coloured ring-closed state takes place on irradiation with light of different wavelengths. The reaction is not thermally reversible, and the fatigue resistance of these compounds is very high. [3, 48]

#### 2.3.5. Fulgides

Photochromism of fulgides was first observed by Stobbe, who synthesized some phenyl-substituted bismethylene succinic anhydrides and called them fulgides. [49]



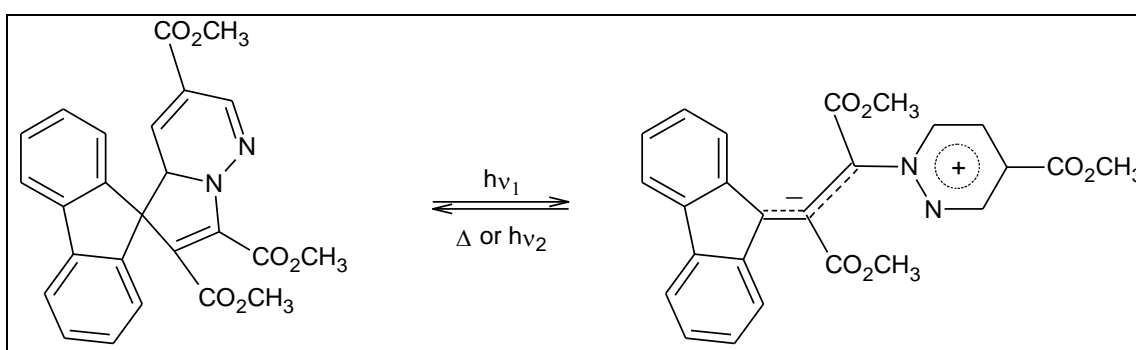
**Scheme 2.14** Photochromism of fulgides

The mechanism of the photochromic reaction of fulgides, and the general chemical structure of the colourless and coloured species are shown in Scheme 2.14. Both the

forward and the reverse reactions of fulgides are driven by light. The forward reaction, towards the coloured species, is stimulated by UV light while the reverse reaction is normally stimulated by visible light, and is not initiated thermally, so that the photochromism of fulgides is referred to as P-type, as mentioned in section 2.1.

### 2.3.6. Spirodihydroindolizines

Dihydroindolizines represent a class of photochromic compounds; their photochromism was first reported in 1979. [50]



**Scheme 2.15** Photochromism of spirodihydroindolizines

The photo-induced ring opening of the spirodihydroindolizine system gives the ring-open coloured species which can be reversed to give the colourless form either photochemically or by thermal means, as shown in Scheme 2.15. [1, 3]

## 2.4. Applications of Photochromic Compounds

### 2.4.1. General applications of photochromic materials

Basic research on photochromic materials has been increasing in recent years as a result of scientific interest and possible commercial applications. [3, 33, 51-55] Organic photochromic materials are of considerable current active interest because of their dynamic optical properties which offer potential for a wide range of applications such as responsive eyewear, including the familiar spectacles which become sunglasses when activated by sunlight, and potential applications in security printing, optical data storage, optical switching devices, cosmetics and electrophoretic displays[3, 31, 32, 56-58]. In the security printing field, photochromic inks may be used for cheque printing and document protection. The ink is invisible to the eye under normal lighting conditions, but it becomes visible under a UV lamp. [59, 60] The optical data storage may be another field for useful applications of photochromic materials. In this respect,

the use of photochromic materials was proposed to increase the memory density of optical memory storage devices such as compact disks (CD) and magneto-optical disks (MO) which are essential for audio and visual storage media and computer storage media. Thus, photochromic materials can undergo photon-mode recording based on photochemical reaction within the data storage medium. In this photon-mode recording, the memory density may be increased by multiplexing the light characteristics such as wavelength, polarization and phase. [61]

Selected photochromic materials have been reported as appropriate materials for cosmetic applications. [62-64] These photochromic cosmetics may be designed to allow sun blocking and change their colours when the user moves from place to place.

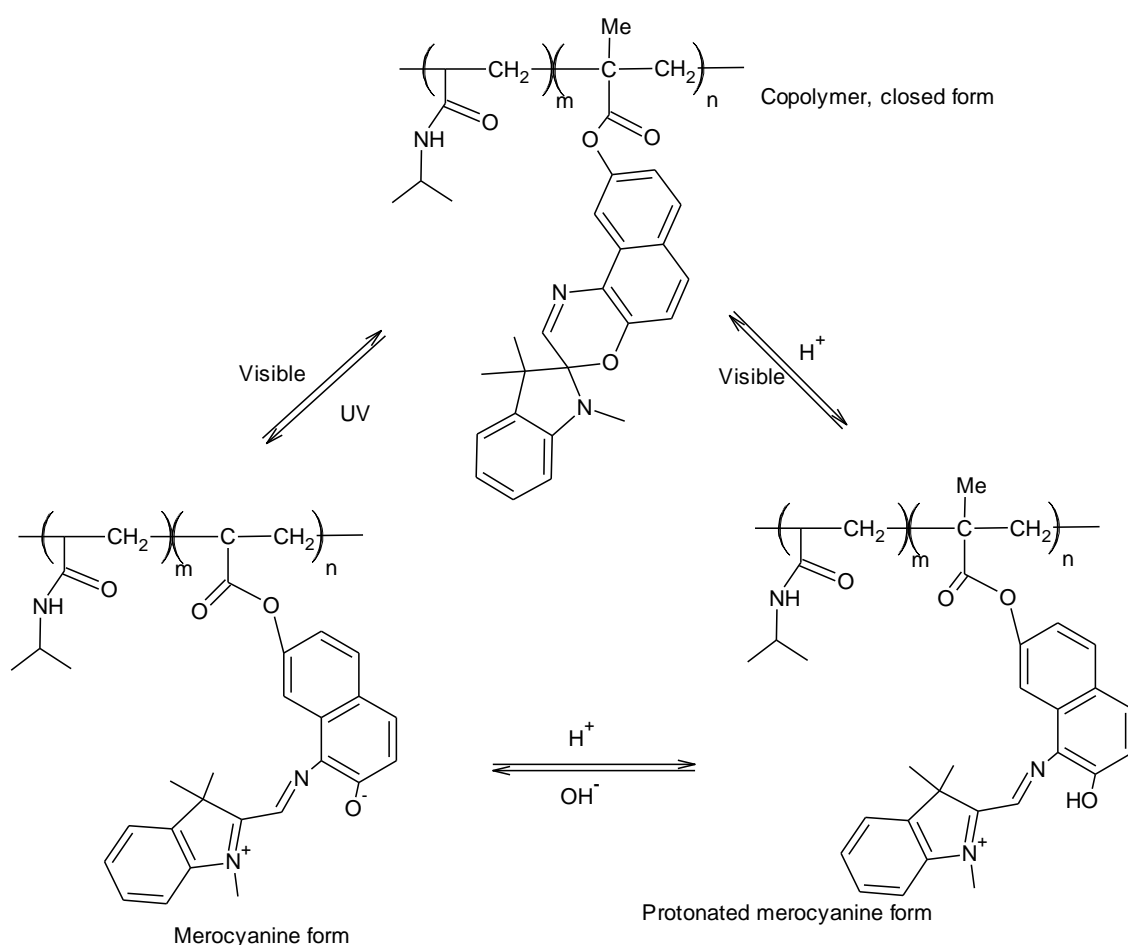
The molecular switching properties of photochromic compounds have opened the door for a wide range of applications involving the incorporation of the photochromic compounds into many systems, including molecular photoswitching devices, optical memory devices, drug delivery vesicles, holographic gratings, information processing and chemosensor systems. [48, 54, 65-87] As a recent example of the application of photochromic materials, the preparation and photochromic properties of functional spiropyran-based polymeric vesicles were investigated. The resulting vesicles displayed interesting photochromic properties. [88]

The potential applications of spiropyrans, fulgides and diarylethenes in optical devices have made these photochromic compounds an interesting subject of research and investigation for many decades. Photo-electronic applications of diarylethenes have been reported, facilitated by their excellent thermal stability, remarkable fatigue resistance, rapid response and fairly high photocyclization quantum yields. These applications include erasable-memory media, photo-optical switching, displays, photo-drive actuators, chemosensors and 3D optical data storage devices. [66, 89-92] The investigation of the application of diarylethenes, which is a class of photochromic compounds, for information processing was reported. [93] In this respect, the photoswitching properties of diarylethenes were utilized to the photoswitching of the flow of information through the molecule as a result of the changes in the electronic structure associated with the reversible photochromic colour change of the molecule.

As an example of a novel and recent application is the concept of the photo-induced colour change of a photochromic system based on spiropyran monolithic polymers which was applied to operate a novel photo-controllable micro-fluidic electroosmotic pump. [94] The photochromic monolithic polymer was made by copolymerization of the photoswitchable monomer, the spiropyran, with a divinylbenzene cross-linker, and

then it was encased within the channels of a microfluidic chip. Thus, the irradiation of the system with light of different wavelengths, which converts the spiroopyran between its two forms, may control the flow rate of the electroosmotic pump without the need to modify the electric field.

Thin film optical waveguide sensors have been designed to solve the several limits of conventional transmission of reflection measurements. These intrinsic waveguide type UV sensors can exploit the sensitivity of spirooxazine photochromism in constructing useful and more effective new UV sensor devices. [95]



**Scheme 2.16** Multiple switching process of photochromic poly(N-isopropylacrylamide) with spironaphthoxazine hydrogel

As a further example, the synthesis of a multiple switching photochromic poly(N-isopropylacrylamide) with a spironaphthoxazine hydrogel was reported. [96] This copolymer undergoes thermally-controlled photochromic reversible switching from solution phase to gel phase at a critical temperature. In addition to its photochromism, this polymer exhibited sensitivity to acid and base in aqueous solution, as shown in



Scheme 2.16. This complicated multiple switching may propose promising applications in the fields of electronic smart materials, logic gates, fluorescence sensors and other molecular photonic devices. Erasable and rewritable photoimaging on the hydrogel was demonstrated and, consequently, this copolymer can be proposed as a promising candidate for erasable data storage. [97]

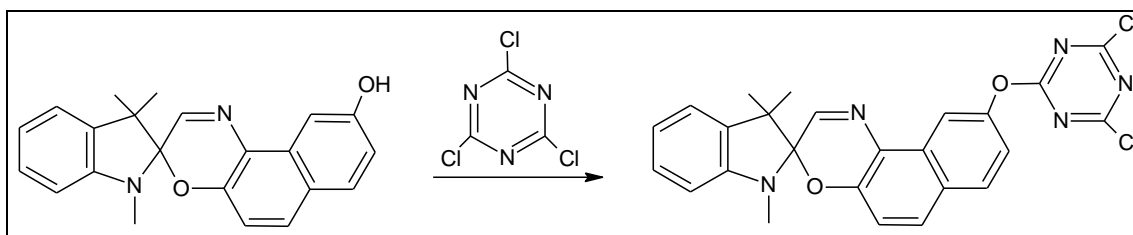
#### ***2.4.1. Textile applications of photochromic materials***

The interest in photochromic textiles, as a novel application field of photochromic dyes, has been growing apparently with expected applications in creative and intelligent designs, and in functional or smart textile products, for example in brand protection, responsive camouflage and as UV sensors. [26, 98-104] However, it has been suggested that the application of photochromic dyes to textiles has not attained significant commercial success, because of technical difficulties associated with application methodology and performance. [32] The application of a series of commercial photochromic dyes to textiles using a screen printing method was previously reported. The degree of photocolouration and fastness properties of the prints were investigated using a specifically-devised method for assessing the photocolouration properties using an independent source of irradiation and traditional colour measurement instrumentation. [102-104] There have been a number of previous reports of investigations of exhaust dyeing of synthetic textile fabrics using various specific photochromic dyes. In general, photochromic textiles were obtained, commonly characterized by rather low dye exhaustion. [98-101] In 2008, Billah et al reported the direct application of two simple spirooxazine photochromic dyes to polyester, nylon and acrylic by disperse dyeing. [101] Polyester fabric dyed with these photochromic dyes at typical application conditions for disperse dyes by high temperature dyeing method did not show any photochromic colour change under UV light. The resulting fabric, which acquired a brown colour, may indicate dye decomposition at high temperature under aqueous acidic conditions of dyebath for a prolonged time. In the same study, lower dyeing temperatures, 60°C and 90°C, were investigated for applying the photochromic dyes to polyester fabric at slightly acidic and neutral conditions without applying reduction clearing after dyeing. The resulting dyed fabric showed photochromism by changing colour on irradiation with UV light. When carrier was used for dyeing polyester at temperature of 90°C, the dyed fabric showed improved photochromism measured as an increase in the degree of photocolouration of the fabric on exposure to UV light. Acrylic fabrics dyed with the same dyes showed lower photochromism

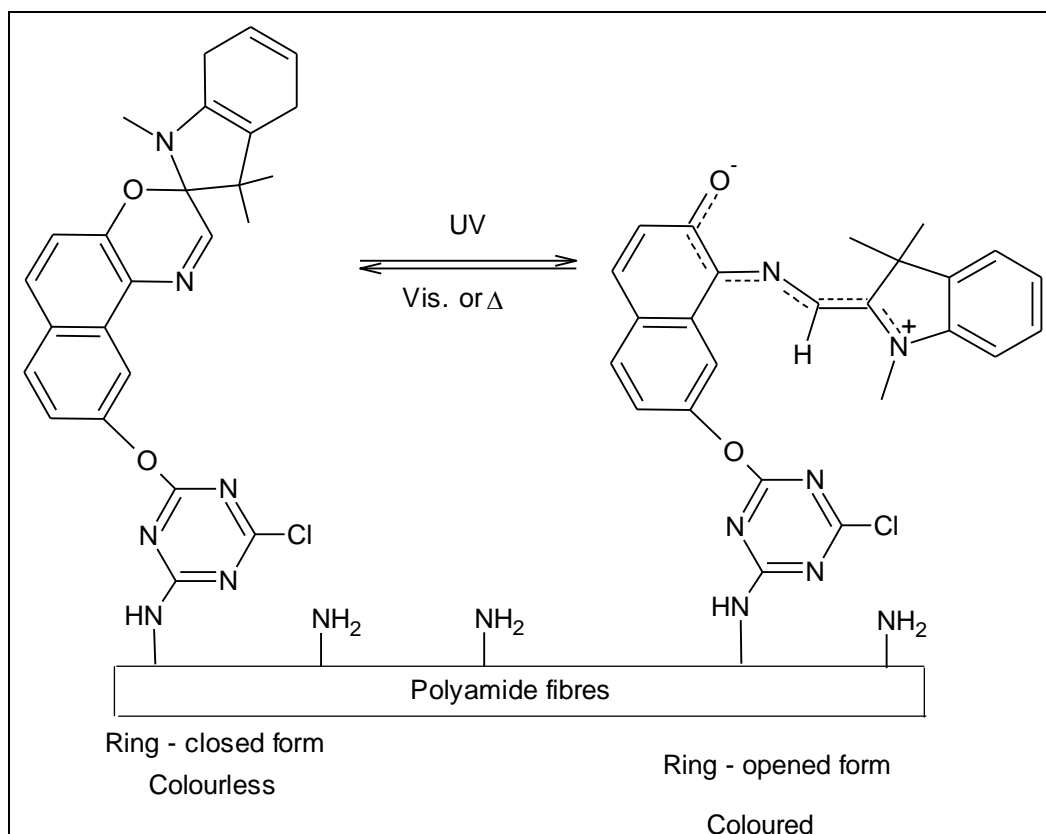
compared to polyester dyed at the same temperature, while nylon fabric, dyed at the same temperature, showed the highest photochromic colour change. In a further investigation of dye uptake and photochromic colour change [101], photochromic dyes with smaller molecules showed better photochromic performance when compared to photochromic dyes with larger molecules when they were both applied directly as disperse dyes to polyester fabric. This inferior photochromic performance of the dyes with higher molecular size may indicate the limited dye uptake by fabric, associated with the increase in the size of the dye molecule. In their investigation of the photochromic behaviour of four phenoxyanthraquinone dyes in solutions and on polyester substrates, Wang and Wu applied these dyes to polyester in a laboratory dyeing machine by a normal disperse dyeing procedure. Reduction clearing was carried out after dyeing and the resulting fabric exhibited photochromism by changing from pale yellow to deep yellow upon irradiation with UV light. The colour change was reversible and the fabric changed back to the original background colour upon exposure to the visible light. [98]

The exhaust dyeing method was also used for applying selected photochromic spiroxazine dyes to polyamide fabrics. [99] The dyed materials, at different dyeing temperatures between 80°C and 120°C, showed reversible photochromism on exposure to UV and visible light. The photochromic performance of the dyed fabrics was evaluated visually by comparing the depth of the colours built up by the dyed fabrics after irradiation with UV light. The study confirmed that the highest dye exhaustion was observed at dyeing temperatures of 100 – 110°C.

Synthetic textiles containing photochromic pigments were patented in 1993. [105] The photochromic pigments, encapsulated in thermoplastic materials, were extruded with synthetic fibres, such as poly(ethyleneterephthalate), nylon 6, nylon 66, nylon 8 and nylon 12, at a temperature of 250°C to give the relevant photochromic fibres which contain the photochromic pigments. For this application, photochromic dyes with high stability towards decomposition under conditions of a high temperature of 250°C for 10 minutes were required.



**Scheme 2.17** Synthesis of a reactive spirooxazine photochromic dye

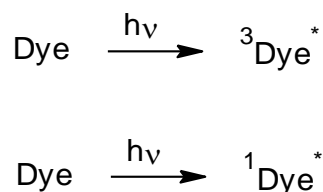


**Scheme 2.18** Reversible photochromism of a reactive spirooxazine photochromic dye on polyamide fibres

A novel spirooxazine dye was synthesized by introducing the dichloro-*s*-triazinyl reactive group into the spirooxazine dye molecule, as shown in Scheme 2.17. Successful coloration involving strong covalent bonding was clearly observed when the dye was applied to polyamide fibres. These results were also confirmed from photographs and absorption spectra demonstrating the photochromic reaction. Durable bonding between the spirooxazine and the fibre substrates was achieved by introducing a reactive group into the dye molecule which reacted with amino groups on the fibres, as shown in Scheme 2.18. [26]

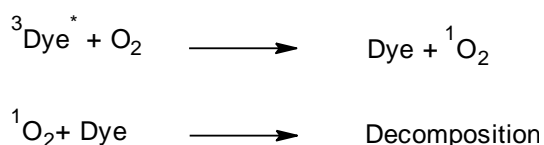
## 2.5. Photodegradation of Textile Dyes

Photodegradation of textile dyes can take place as a result of a photooxidation process, via singlet oxygen or superoxide, or by photoreduction via radical species. The two photodegradation processes are generally brought about when light promotes the dye to the excited singlet or triplet forms, as shown in Scheme 2.19.



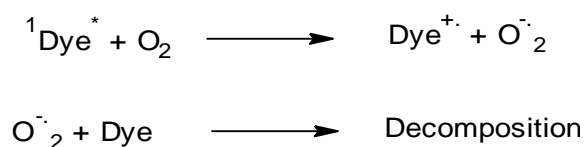
**Scheme 2.19** Dye transformation to an excited triplet state

When the excited triplet form of the dye reacts with molecular oxygen, the dye acts as a singlet oxygen sensitizer. Subsequently, the dye may be degraded by the singlet oxygen, as shown in Scheme 2.20.



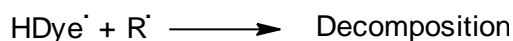
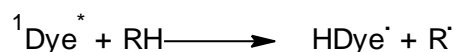
**Scheme 2.20** Photooxidation of the dye via singlet oxygen

Superoxide may be formed by an electron transfer reaction between the dye, in its singlet excited form, and oxygen, and in that case photooxidation of the dye via superoxide may be responsible for the dye degradation, as shown in Scheme 2.21.



**Scheme 2.21** Photooxidation of the dye via superoxide

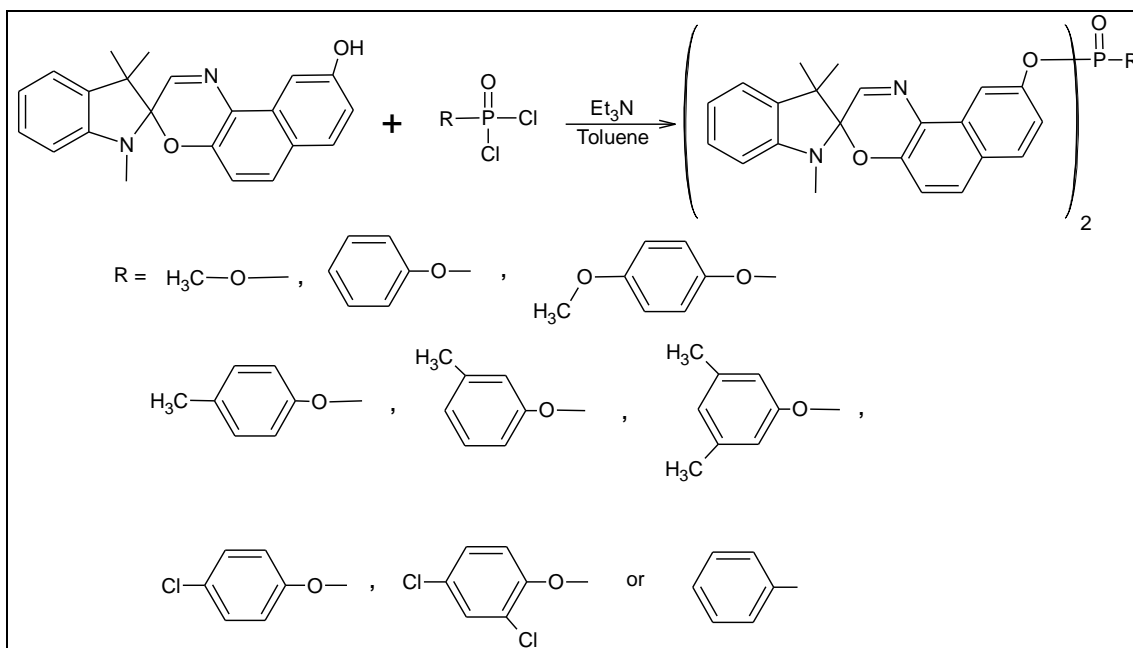
The third possible mechanism suggested for degradation of textile dyes, the photoreduction process, involves free radicals. This process is brought about when hydrogen is abstracted from nearby groups, such as on the substrate, or additives and/or impurities in the system. Scheme 2.22 shows one of the possible pathways of photoreductive degradation.



**Scheme 2.22** Photoreduction of the dye via free radicals

The lifetime of the excited triplet form of the dye plays an important role in determining which one of the three mechanisms is dominant when the dye photodegradation is initiated by UV light. The longer the lifetime of the triplet form, the higher the possibility that the dye can interact with oxygen, and therefore photooxidation may be more likely to take place than photoreduction. [106, 107]

The photodegradation of photochromic compounds, especially spirooxazines and spiropyrans, has been intensively studied because of its effect on restricting some industrial applications of these dyes. Although different theories have been proposed to explain the photodegradation of photochromic compounds, the photooxidation mechanism, via singlet oxygen or via superoxide, is the most important pathway as supported by experimental investigations. [108-111] The stability of photochromic compounds towards the photodegradation brought about by exposure to light is expressed by the term 'fatigue resistance'. The fatigue resistance of spirooxazines is a property that is commonly of special importance for the applications of these compounds. The mechanism of photodegradation of spirooxazines which involves an electron transfer between molecular oxygen and the triplet state of the photomerocyanine form leads to the formation of superoxide anion radicals. The superoxide anion radical can attack the photomerocyanine, leading to the photodegradation effect. [110]



**Scheme 2.23** Synthesis of functionalised spironaphthooxazines

An example of a method for improving the fatigue resistance of the spirooxazines, by the functionalization of spironaphthooxazines with a phosphoryl group, has been reported. The chemical structure of and synthesis route to the functionalized spironaphthooxazine are shown in Scheme 2.23. The improvement achieved in the fatigue resistance of the functionalised spirooxazines was confirmed by carrying out kinetic analysis of the photodegradation process in non-polar and polar solvents. [112]

## 2.6. Dyeing Mechanisms of Textile Fibres

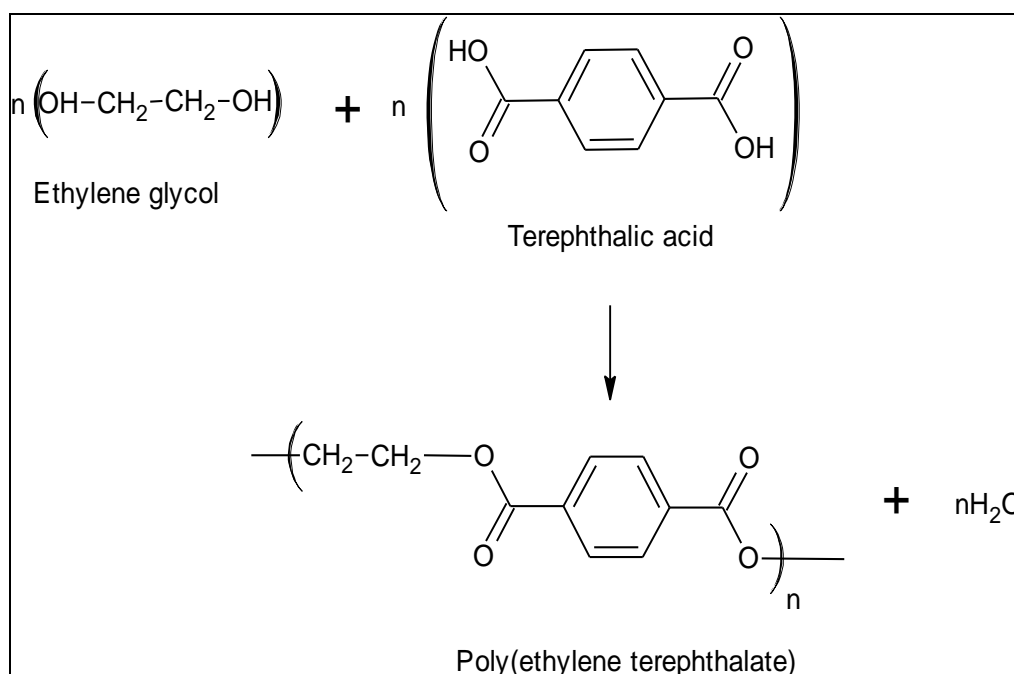
When a fibre is introduced into a dye bath, water moves into the fibre pores, and an interface between water and fibre is formed. Dye molecules, which are larger than water molecules, are in constant motion encouraging entry into the pores. This constant motion, in the pores, keeps the dye molecules closer than they are in the solution, and carries them to the walls of the larger pores. This process is assisted if the dye molecules carry an electrical charge opposite to that of the fibre. Another factor that contributes to this process is van der Waals forces. These forces cause the dye molecules to align parallel to and in contact with the molecular chains of the fibre polymer molecules. The larger the molecule, the greater is the effect of van der Waals forces. In the case of hydrophobic fibres in an aqueous dye bath, there is a less extensive pore system than in hydrophilic fibres. In this case, the dyeing process is attributed to the high affinity of the dye molecules for the fibre, which is a measure of the ability of the dye molecule to move from the solution to the fibre, due mainly to formation of

dipolar and hydrogen bonds, and as a result they penetrate into the fibre, forcing the polymer chains apart. [113]

Different techniques have been used for applying insoluble dyes, such as disperse dyes, to textiles. Solution dyeing, microcapsule binding and exhaust dyeing methods are commonly used for these applications. In the solution dyeing method, the dye is added at the extrusion stage. Problems may emerge in the spinning stage as a result of adding the dye to polymers. In the microcapsule method, using a binder can impart harsh handle to textiles. Therefore, an exhaustion dyeing is considered as a potentially successful and convenient dyeing method. [99]

## 2.7. Polyester Dyeing Technology

Polyester is generally made by condensing a dihydroxy aliphatic alcohol with a dicarboxylic acid. Most polyester fibres are based on poly(ethylene terephthalate), which was the first commercial fibre-forming polyester developed in 1941. [113, 114] Poly(ethylene terephthalate) may be synthesized by condensing ethylene glycol with terephthalic acid, as shown in Scheme 2.24. [115] It may also be synthesized by a transesterification reaction of dimethyl terephthalate with ethylene glycol.



**Scheme 2.24** Synthesis route of poly(ethylene terephthalate)

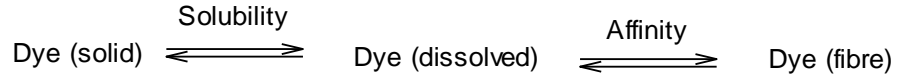
Polyester has the most crystalline structure among the man-made fibres that can be dyed by disperse dyes, so that dyeing from aqueous solution must be carried out at a high

temperature that can reach 140°C in order to have a practically sufficient rate of dyeing. The reason for the dependence of the rate of dyeing on the temperature is given in the discussion which follows. The other choice is using carriers as assisting materials to reduce the dyeing temperature to below the boiling point of water. [113]

A knowledge of the relationship between temperature and the physical properties of man-made fibres is essential to understand the dyeing mechanisms associated with these fibres. The dyeing transition temperature of an amorphous polymer is defined as the temperature at which the rate of diffusion of the dye into the polymer increases remarkably. [116, 117] At a relatively low temperature, the mobility of polymeric chains of an amorphous polymer is restricted, a condition referred to as the frozen state of the molecular chains of the polymer. When the temperature rises, the energy of the polymeric system increases, and therefore the amplitude of the vibrational motions of constituent atoms increases. Consequently, rotational movements about some of the covalent bonds in the backbone of the polymer begin. Polymer segments between two rotating bonds in the same polymer chain become able to change their positions. This change of the position is called a segmental jump, which is transferred to the neighbouring segments and so on to the whole polymer. This state in which there is a segmental mobility of the polymer chains may be called the rubbery state, and is detected by a sudden change in the physical properties of the polymer. The temperature at which these changes take place is referred to as the glass transition temperature  $T_g$ . [113] Polyester fibres are essentially undyeable below 70-80°C, leaving only 20-30°C range for increasing the dyeing rate before reaching the boiling temperature of water. The dyeing transition temperature of the polymer, which is the temperature at which dyeing of the polymer practically starts, is not far removed from its  $T_g$  as detected by physical means. [116, 117]

In general, polyester dyeing processes follow the same steps: preparation of goods, dyeing, rinsing, reduction clearing (if necessary) and soaping. [113] Polyesters have no ionic groups and are dyed almost exclusively with disperse dyes. Disperse dyes, which are none ionic dyes, are insoluble in water at room temperature and have only limited solubility at higher temperatures. These dyes possess substantivity for hydrophobic fibres, such as polyester and nylon, in which they are reasonably soluble. [114] Thus, disperse dyes have to be applied as aqueous dispersions of finely-dispersed solid dye particles in the dyebath. Generally accepted suggestions for the mechanism of disperse dyeing is that dye in the dyebath exists in two forms: solid dye and dye in solution. The following equilibria shown in Scheme 2.25, are set up in the presence of fibres: [113]





**Scheme 2.25** Disperse dyeing mechanism

Dyeing with disperse dyes involves the transfer of dye molecules from a molecular dispersion into the fibre. The factor which represents this situation is referred to as the partition coefficient, and is given by the following equation:

$$K = \frac{[D]_{ad}}{[D]_s} \quad (1)$$

Where  $[D]_{ad}$  is the amount of dye adsorbed

$[D]_s$  is the concentration of dye in the dyebath

The ‘standard affinity’ term is defined as ‘the difference between the chemical potential of the dye in its standard state on the fibre and the corresponding chemical potential in its standard state in the dyebath’. [118] The conditions of the standard state are a temperature of 298 K and a pressure of one atmosphere which are used as a reference point for the purpose of calculations. The standard affinity of the dyeing process is a measurement of the ability of the dye molecule to move from the solution to the fibre when it is in its standard state in each phase, and it is given by the following relationship:

$$-\Delta\mu^\theta = -(\mu_f^\theta - \mu_s^\theta) = RT \ln \frac{a_f}{a_s} \quad (2)$$

Where:

$-\Delta\mu^\theta$  is the standard affinity of the dye for the fibre

R is the gas constant  $J.K^{-1} mol^{-1}$

T is the absolute temperature of the system, Kelvin

$a_f$  is the activity of the dye in the fibre

$a_s$  is the activity of dye in the solution

The activity parameter is an idealization function of the real concentration of solutions. It replaces the concentration for the ideal solutions, i.e. a solution which is so dilute that the solute particles do not interact with each other. More information about the activity concept is given in the literature. [113] The shape of the sorption isotherm, which is a curve representing the dependence of the concentration of the dye in the fibre on its concentration in the bath, is a criterion for a dye sorption mechanism. [119, 120] In the

case of synthetic fibres, such as polyester, dissolution of the dye molecule in the amorphous regions of the polymer is adopted as the sorption mechanism. [119, 121] Studies showed that the isotherm of dyeing with disperse dyes is linear, resulting in the constancy of the partition coefficient K. [113] This implies that the dye is behaving ideally in both phases, so that the activities in equation (2) can be replaced by concentrations, i.e.

$$-\Delta\mu^\theta = RT \ln \frac{[D]_{ad}}{[D]_s} = RT \ln K \quad (3)$$

The concept of standard affinity is basically used to consider the dye distribution between the dye solutions and the fibres when different dyes are used under the same conditions, or when the same dye is used under different application conditions. The percentage exhaustion of the disperse dyebath is related to the partition coefficient K and the liquor-to-goods ratio L by equation (4).

$$\text{Exhaustion} = K / (K+L) \quad (4)$$

### ***2.7.1. Dyeing with carrier***

The term ‘carrier’ describes a material used as an accelerant in the dyeing or printing of hydrophobic fibers with disperse dyes. [113] Disperse dyes exhibit low diffusion into polyester fibres at the practical boiling point of water (98°C) under atmospheric pressure, an effect that is attributed to the compact nature of the arrangement of polymer chains within the polyester fibre. [122] To improve the diffusion of the dye into polyester fibres, and therefore to increase the rate of dyeing of polyester to a reasonable value, while avoiding dyeing under pressure at a temperature above 100°C, a carrier may be added to the dyebath. Researchers have proposed different theories concerning the action of carriers. Some of these theories propose that the carrier functions by its effect on the dye, while other theories take the view that the carrier operating mechanism is attributed to its effect on the fibre rather than the dye. In 1955, it was suggested that when a carrier is added to the dyebath, a complex is formed between the carrier and the dye. Diffusion of this complex into polyester is proposed to be easier than diffusion of the dye alone. However, this theory has not been strongly supported by evidence. [123] The concept of formation of a complex of the dye with the carrier was the reason for using the term ‘carrier’ which indicated that the complex could carry the dye into the fibre, and therefore increase the dyeing rate. [113]

In 1966, Balmforth et al. proposed that some carriers function by increasing both the equilibrium uptake of the dye by the fibre and the rate of dyeing, while other carriers cause only an increase in the rate of the dyeing process. [124]

Another theory suggested that carriers may function by modifying the structure of the fibre temporarily. This theory was based on the observation that the improvement in the dyeing of polyester attributed by carriers is accompanied by a swelling effect which is measured as an increase in the fibre diameter. [113] This theory has not yet been confirmed by evidence. In contrast, it was reported that monochlorobenzene, a carrier, is effective as a carrier without showing a noticeable swelling effect on polyester fibre. [113, 125]

The concept of the solubility parameter, which is a numerical value that indicates the relative behaviour, with regard to solvency, of specific solvents [126], was proposed to explain the effect of carriers. For most carriers, the closer the match between the solubility parameter of the carrier and that of the fibre, the more active the carrier is. The theory proposing that carriers operate by only modifying the fibre structure was argued by the fact that the most active carriers are not those with solubility parameters closest to the solubility parameter of polyester. Shrinkage of polyester filaments, as a measure of swelling according to a study carried out by Rawicz et al [127], was detected when polyester was immersed in an aqueous solution containing carrier compounds. This observation was extended by accounting for the swelling effect attributed to carriers on the basis of the temperature at which the swelling effect starts. It was reported that a reduction in the swelling initiation temperature of textile filaments was observed when a carrier was added to the aqueous dyebath. This reduction was equivalent to the reduction in the glass transition temperature  $T_g$  of the fibre. [128, 129] Consequently, as the swelling of polyester fibres can be considered as a plasticizing effect, it may be inferred that carriers function by lowering the temperature at which the fibre becomes plastic. This observation supports the theory that the carrier operates by loosening the molecular structure of the fibre, thus facilitating the penetration of dye molecules into the fibre. [113] As the decrease in  $T_g$  is a measure of the plasticizing effect exerted by solvents on fibres, it may be concluded that plasticization plays a vital role in enhancing dye uptake by fibres. [130] The effect of the carrier on the glass transition temperature of polyester, and hence on the dyeing transition temperature, is practically independent of the chemical structure of the carrier. This fact was supported by different researchers who found that similar amounts of different carriers caused the same decrease in the glass transition temperature of polyester. [131, 132] However it

was reported that the structure of the carrier affects the distribution of the carrier between the dyebath and the fibre. In this way, the role that the carrier plays in reducing the dyeing transition temperature may be affected by the chemical structure of the carrier. [133]

Waters divided carriers into four groups according to their chemical structure: phenolics, primary amines, hydrocarbons and esters. The solvent most commonly used as a carrier is benzyl alcohol which increases the rate of dyeing as a result of the plasticizing effect on the fibre. A large increase in the concentration of benzyl alcohol reduces the uptake of dye because the increased solubility of the disperse dye supports the dye movement from fibre to solution. [134]

Methylnaphthalene is a self-emulsifiable liquid carrier, added to the dyebath of polyester with disperse dyes. The amount required is 0.2-0.3 % of the dye liquor. The methylnaphthalene gives good colour yield at low cost. [113]

The use of the carrier as an accelerant for dyeing and printing of polyester with disperse dyes has been restricted by the fact that carriers possess many disadvantages, such as toxicity, unpleasant odour, poor lightfastness of dyed materials, volatility in steam, shrinkage effects on the dyed materials, high cost of waste water treatment and environmental contamination. [134-138] In addition to that, the use of carriers may affect the physical properties, such as the strength, of polyester badly by loosening the fibre structure. [139]

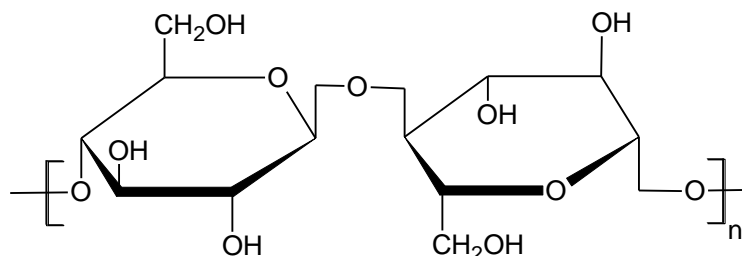
### ***2.7.2. High temperature dyeing***

It was discussed in section 2.7 that the use of a high temperature, usually between 125°C and 135°C, enables the rate of dyeing of polyester fibres to increase to a practically acceptable level without using carriers. The benefits of using the high temperature in the dyeing of polyester were demonstrated shortly after the commercial introduction of the fibre. [140] An investigation, carried out by Merian et al, demonstrated the dramatic increase in the rate of dyeing of polyester with disperse dyes, when the temperature was raised to between 100°C and 200°C, and showed that the dyeing rate increased approximately six-fold for a temperature increase of 10°C. [141] The advantages of the high temperature dyeing process over the carrier dyeing process are the reduced costs, improved levelness, improved technical properties, shorter dyeing times, excellent penetration, higher colour yield and, in some cases, superior fastness properties of dyed fabrics. [142] The higher rate of dyeing and higher dye penetration achieved by the high temperature dyeing, compared to the carrier dyeing, may be due to

the higher kinetic energy of the dye molecules, the greater segmental mobility of the molecular chains of polyester fibres and the higher aqueous solubility of the dye at the high temperature. [140] Thus, when heavy shades are needed, polyester is dyed at a high temperature without carriers. In the slightly acidic conditions of the dyebath, polyester does not suffer any degradation even at a temperature of 130°C. Degradation may become apparent when traces of alkali are present. Any alkali used during scouring must therefore be removed before high temperature dyeing. When scouring has been carried out, rinsing with water is required, followed by another rinse in water containing a small amount of acetic acid, to ensure that no alkali is left on the fibres. [115] Acetic acid is added to the dyebath to adjust the pH to 4.5-5.5, because, in addition to the degradation of polyester fibres in alkali conditions, many disperse dyes degrade if the pH is uncontrolled during aqueous dyeing. [140]

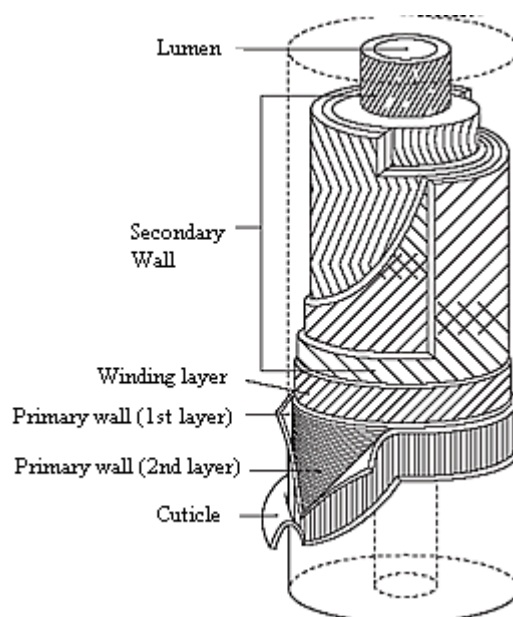
## 2.8. Cotton Dyeing Technology

Cotton fibre, which is the seed hair of plants of the genus *Gossypium*, is a natural fibre which represents the purest form of cellulose found in nature. [114, 143] The chemical structure of cellulose, which is a polymer derived from glucose monomers [144], is shown in Figure 2.3.



**Figure 2.3** Chemical structure of cellulose

Cotton is classified into three types, according to the average fibre lengths (staple lengths). Type 1 has the finest and longest staple of 25-60 mm, type 2 has coarser and shorter staple lengths of 13-33 mm, and type 3 has the shortest staple lengths of 9-25 mm. Cotton fibres are single cells with tubular shapes which have the appearance of flat, twisted ribbons, varying in width between 12 and 20µm, and are formed as the cotton fibres grow and dry out to collapse in the open boll. The fibre cross-section has a bean shape with the presence of a central canal or lumen. The fibrillar structure of cotton fibres consists of three main areas: a primary wall, a secondary wall and a lumen, as shown in Figure 2.4.



**Figure 2.4** Structure of cotton fibre

The network of cellulosic fibrils of the primary wall is covered with an outer layer of pectin, protein, mineral matter and wax. This outer layer, which is referred to as the cuticle, is removed when cotton is prepared for dyeing, and thus cotton becomes more water-absorbent. The primary wall, which contains most of the non-cellulosic materials of cotton fibres, disintegrates as a result of removing most of these materials when preparing cotton for dyeing and printing. [114, 143] A comparison between the composition of the primary wall and that of the cotton fibre as a whole is shown in Table 2.1. [144]

**Table 2.1** Composition of raw cotton

| <i>Constituent</i> | <i>Proportion of dry weight (%)</i> |                     |
|--------------------|-------------------------------------|---------------------|
|                    | <i>Whole fibre</i>                  | <i>Primary wall</i> |
| Cellulose          | 88.0 - 96.0                         | 52                  |
| Pectins            | 0.7 - 1.2                           | 12                  |
| Wax                | 0.4 - 1.0                           | 7                   |
| Proteins           | 1.1 - 1.9                           | 12                  |
| Ash                | 0.7 - 1.6                           | 3                   |
| Other substances   | 0.5 - 1.0                           | 14                  |

The secondary wall consists of successive layers of cellulosic fibrils arranged spirally around the fibre axis. The fibrils, in turn, consist of smaller microfibrils, the smallest being a combination of cellulose molecules. The fibre porosity of about 6 % is brought

about by the numerous channels between the fibrils. The greatest dye absorption tend to take place on the inside surface of the curved bean-shaped cross-section of the fibre. The lumen is the interior tunnel of the fibre formed as a result of the evaporation of the protoplasm in the cell interior as the fibre dries out during growth. The lumen consists of proteins, colouring matter and minerals in its wall. [114, 143]

The external and internal structure of a cotton fibre, and especially the specific surface area, affects its dyeing properties. The finer the fibre, the higher is its specific surface area and the higher is the rate of dyeing. [145]

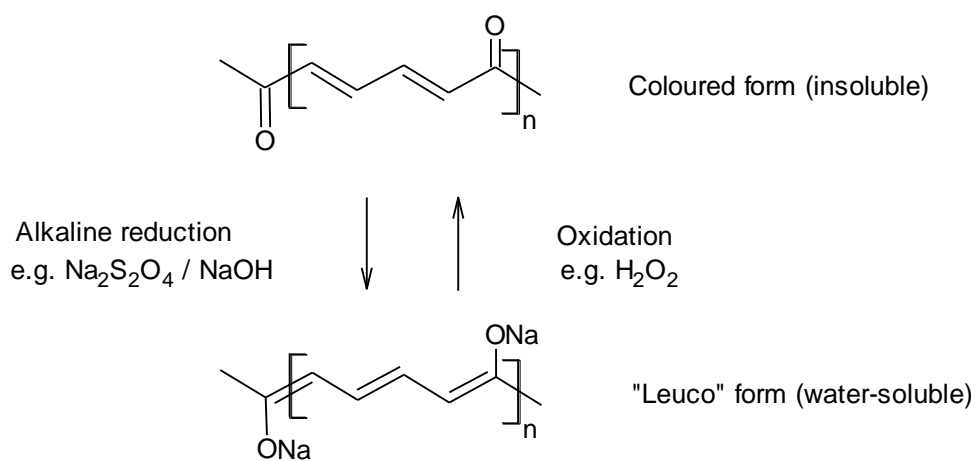
Cellulosic textiles may be dyed by several classes of dyes, including direct, vat, sulphur, azoic and reactive dyes.

### **2.8.1. Direct dyes**

Direct dyes form anions in the aqueous dyebath giving rise to their solubility in water. The substantivity of a dye for a fibre is defined as the tendency of the dye to move onto the fibre from the solution. [146] The substantivity of direct dyes for cellulosic fibres is attributed to the long, linear shape of the dye molecules, which are usually sulphonated azo compounds. Direct dyes are readily applied to cellulosic textiles. However, their washfastness properties are poor to moderate, because direct dyes are only loosely associated with the fibre molecules through their substantivity property, and therefore the intermolecular forces involved are weak. [147]

### **2.8.2. Vat dyes**

Vat dyes are mostly of the anthraquinonoid and the indigoid chemical types. Both of these classes contain carbonyl groups ( $\text{>C=O}$ ) in their structures. The general procedure of dyeing cotton fibres with vat dyes starts with reducing the insoluble vat dye to the leuco form, which, due to possessing hydroxyl groups, is soluble in the alkaline aqueous dyebath, as shown in Scheme 2.26.



**Scheme 2.26** Solubility of the leuco forms of vat dyes in alkali aqueous solutions [148]

When cotton textiles are impregnated with the alkaline solution of the anionic leuco form of the vat dye, the latter is adsorbed by the cellulosic fibre. The dye adsorption stage is carried out at the boiling point of the aqueous dyebath. Once the dye is adsorbed by the fibre, the leuco form is oxidized to its insoluble form using either atmospheric oxygen or oxidising agents such as potassium dichromate or hydrogen peroxide. Finally, dye particles adhering on the fibre surface are removed by treating with boiling soap or detergent solution which also induces crystallization of the dye giving improved performance. [113, 147]

### 2.8.3. Sulphur dyes

Sulphur dyes are characterized by their highly complicated structure and the presence of sulphur linkages in their molecules. The insoluble sulphur dyes are converted into soluble forms by reduction in alkaline solution. After dyeing, the dye is oxidized to its insoluble form. [147]

### 2.8.4. Azoic dyes

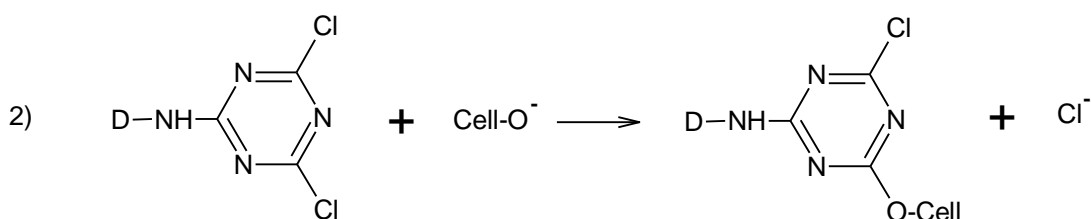
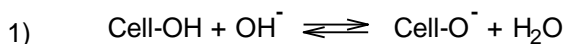
Coloured azoic dyes are formed within cellulosic fibres by carrying out the azo coupling reaction during the dyeing process. Cellulosic fibres are treated with the coupling component, and this is followed by adding the diazonium salt, which, in turn, reacts with the coupling component to produce the coloured azoic dye, which is insoluble in aqueous media, within the fibre. [147]

### 2.8.5. Reactive dyes

The main difference between reactive dyes and all other classes of dyes applied to cellulosic fibres is that the reactive dyes react chemically with the fibres and form



covalent bonds. The covalent bond between the reactive dye and the cellulosic fibre is the main factor that determines the fastness properties of these dyes. In general, reactive dyes are characterized by their high washfastness, good lightfastness and the availability of a wide range of bright shades. The reactive functional groups of reactive dyes are commonly based on heterocyclic rings containing nitrogen, such as triazinyl, pyrimidinyl and quinoxaliny. An example of the reaction of reactive dyes with cellulosic fibres under the alkaline conditions of the dye bath is shown in Scheme 2.27.



**Scheme 2.27** Reactive dyeing of cellulosic fibres

In the first stage, some of the hydroxyl groups of cellulosic chains are ionized in the presence of alkali. The next stage is the reaction between the reactive dye and the ionized cellulose by a nucleophilic substitution mechanism. [147]

## 2.9. The Use of Solvents in Textile Dyeing

Textile treatments based on ionic processes are carried out only in a medium with a high dielectric constant such as water, and therefore most organic solvents cannot replace water in these treatments. However, non-ionic processes can be carried out in organic solvents. In 1912, it was reported that cotton may be dyed from a mixture containing ethanol and water. A relatively high exhaustion of the dye on cotton was obtained when cotton was dyed from a solution consisting of 5% water and 95% alcohol. [149]

The concept of using recoverable organic solvents as an alternative to water in the wet-processing of textiles is supported by the pressure to reduce the pollution of the environment, and the high cost of clean water in many areas of the world. On the other hand, the ecological and toxicological problems associated with the most appropriate solvents for textile dyeing have limited the development of this field of application. Solvents of choice for dyeing must meet the following criteria: they must be inexpensive, readily available, readily recoverable, non-toxic and non-flammable. Chlorinated solvents have been the most intensively investigated solvents for the

purposes of textile dyeing applications. Perchloroethylene has attracted most attention with regard to commercial development due to the chemical stability of this solvent under the conditions of processing and the relative ease of solvent recovery. In addition, heating of perchloroethylene is less expensive than heating of water because of its lower specific heat, and perchloroethylene is more efficient than water in wetting out fabrics. Due to the non-polar nature of perchloroethylene, it readily dissolves non-ionic dyes, such as the disperse dyes used for polyester. [113] Another advantage of perchloroethylene is that it is available commercially on a large scale. [150]

It has been reported that the diffusion of disperse dyes in polyester is faster from a perchloroethylene dyeing bath than from an aqueous bath, but the partition coefficient in perchloroethylene is smaller than that in water. A comparison has shown that the glass transition temperature of polyester is reduced in the presence of perchloroethylene and consequently diffusion of disperse dyes in polyester occurs at such a low temperature of 80°C. [151]

When disperse dyes are applied to polyester from perchloroethylene, the partition coefficient between fibre and solvent is much lower than in the case of aqueous systems. Hence, the exhaustion of dye from perchloroethylene, which is related to the partition coefficient, is low resulting in low colour yield. The partition coefficient can be increased if the solubility of the dye in the dyebath is reduced. This requirement may be achieved with dyes of high solubility in the solvent by using a low liquor ratio and low temperature. However, the reduction in the solubility of the dye should not fall down a limit under which the rate of dyeing will decrease to an impractical level. [152]

To obtain the required distribution of the dye between a fibre and a solvent, it is necessary to use dyes having as low solubility in the solvent as possible at the dyeing temperature. The solubility of most commercial dyes in perchloroethylene is very high if used without any additives. The colour yield (A) from exhaust dyeing is given in equation 5.

$$A = \frac{KF}{KF + 1} \quad (5)$$

where:

A= the colour yield (bath exhaustion)

K= partition coefficient.  $K = \frac{C_F}{C_L}$ .

$C_F$ = concentration of dye in the fibre

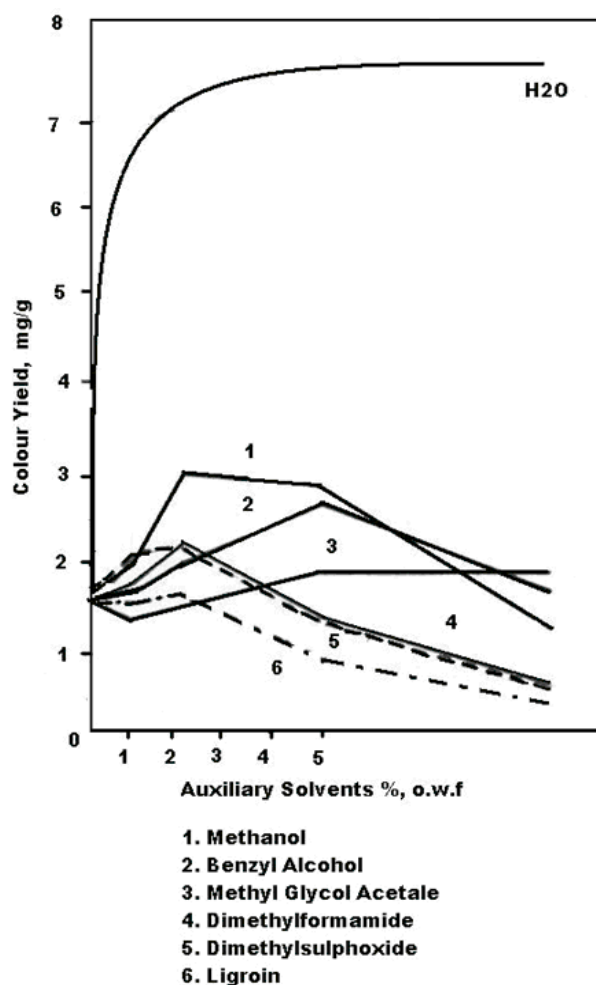
$C_L$  = concentration of dye in the solvent

F = liquor ratio (goods: liquor)

As an example, it may be shown using equation 5 that a colour yield of greater than 80% can be achieved with a partition coefficient of 25 for a liquor ratio of 1:5. Such considerations lead to the following two requirements:

- 1) Dyes used for dyeing from perchloroethylene must have the lowest possible solubility in perchloroethylene at 120°C (the boiling point of perchloroethylene), leading to a high partition coefficient. This requirement may be achieved by adding auxiliary solvents.
- 2) The dyeing process must be carried out with the smallest possible goods: liquor ratio.

An investigation of the effect of the addition of secondary or 'booster' solvents to the dyebath of polyester in perchloroethylene on the colour yield has been reported. [153] The secondary solvents investigated were methanol, benzyl alcohol, methyl glycol acetate, dimethylformamide, dimethylsulphoxide, ligroin and water. In all cases, the colour yield increased when a small amount of the secondary solvent, less than 1% o.w.f (of weight of fibre), was added, as shown in Figure 2.5.



**Figure 2.5** Effects of auxiliary solvents on colour yield of a disperse dye applied to polyester fabric from perchloroethylene (goods:liquor ratio 1:10; 30 min; 120° C)

When increasing amounts of the auxiliary solvents were added to the perchloroethylene, the colour yield was affected. In all cases there was a particular amount of the secondary solvent that caused a maximum increase in the colour yield. Higher amounts caused a significant decrease in the colour yield to less than the colour yield achieved without using a secondary solvent. The highest increase in the colour yield of polyester in perchloroethylene was obtained when an amount of 1% o.w.f of water was added as a secondary solvent. As perchloroethylene can dissolve only 1% of its mass of water; amounts in excess of 1% did not give further technical advantages. [113]

Another approach used to alter the partition coefficient in favour of the dye concentration in the fibre has been reported. The process, which is referred to as Dacsol, involved modifying the perchloroethylene dyeing bath by introducing a low viscosity silicone fluid into the perchloroethylene system leading to reduction in both the solubility of the dye and the liquor ratio. [154]

When auxiliary solvents are added to perchloroethylene liquors, three distribution equilibria of the dye have to be considered:

$K_1$  = Dye concentration in fibre/ dye concentration in perchloroethylene.

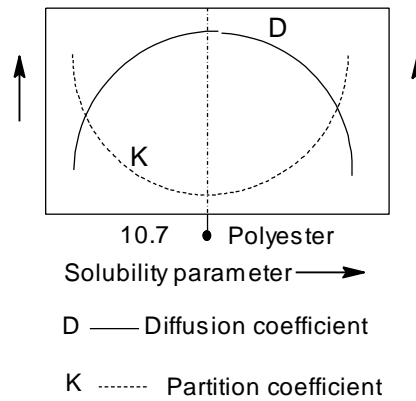
$K_2$  = Dye concentration in perchloroethylene/ dye concentration in auxiliary solvent.

$K_3$  = Dye concentration in fibre/ dye concentration in auxiliary solvent.

The difference in the solubilities of the dye in the fibre-perchloroethylene-water system results in the following relationship:  $K_1 < K_2 < K_3$

This relationship would suggest that the high colour yield resulting when water is used as an auxiliary solvent is caused by the high partition coefficient  $K_3$ , proposing that the actual dyeing process takes place through the aqueous phase. However, if the low solubility of the dye in water alone determined the partition coefficient, then a given dye would give a deeper dyeing from solvents in which the dye is only slightly soluble. As experiments confirmed that is not the case, it is most likely that the function of water in the dyeing process is to form hydrogen bonds between the fibre and the dye. In the first stage of the dyeing process, it is proposed that water attaches to the fibre and penetrates into it by means of a hydrogen-bonding mechanism. Thus, the intermolecular forces existing within the fibre are broken, so that its structure is opened up, and dyeing is facilitated. [153]

The availability of spaces into which the dye can penetrate the structure of textile materials is an essential requirement for a successful dyeing process to take place. These spaces may be an inherent property of the fibre structure, such as the capillary channels of cotton fibres. Alternatively, spaces may have to be created by separating the polymeric chains of textile materials, such as in polyester. The ability of a solvent to penetrate a polymer structure, and separate the polymer chains is determined by the match of its solubility parameter with that of the polymer. It is evident that the maximum equilibrium dye uptake of disperse dyes by poly(ethylene terephthalate) occurs when the association solubility parameter ( $\delta_a$ ) of the dye, which represents all the polar forces which cause molecules to associate, matches that of the fibre. [155] A similar match of the solubility parameters of solvent and fibre is required to facilitate dyeing. It may be inferred from this discussion that the solubility of the optimum dye in the optimum solvent will be high, and therefore the partition coefficient of the dye will be low and the dye diffusion inadequate. Thus, the solvent with the solubility parameter producing the maximum diffusion rate of the dye produces its lowest affinity, as shown in Figure 2.6. [156]

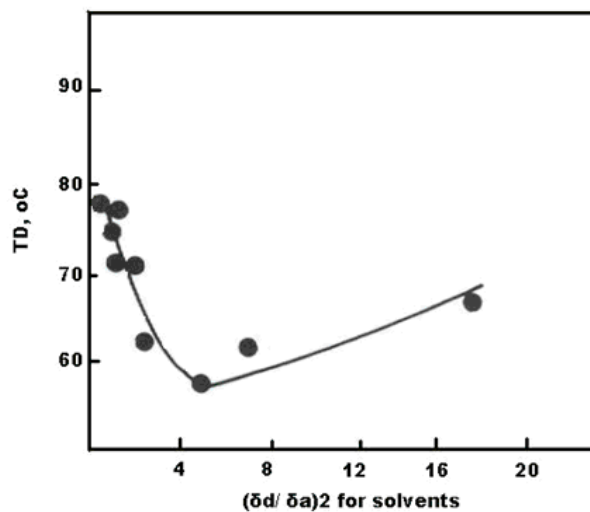


**Figure 2.6** Diffusion and partition coefficients as a function of solubility parameter of solvent

The total solubility parameter ( $\delta_t$ ) of a solvent is derived from the polar association solubility parameter ( $\delta_a$ ), and non-polar dispersion solubility parameter ( $\delta_d$ ), which represents contribution from dispersion forces, as given in equation 6. [157]

$$\delta_t^2 = \delta_a^2 + \delta_d^2 \quad (6)$$

It has been reported that from a particular dye-fibre combination, the affinity of the dye for the fibre and the effect of solvents on the dyeing process are determined by the relative magnitude of the polar and non-polar forces involved. [155] On the basis of this principle, it has been reported that a minimum value of the dyeing transition temperature for a disperse dye applied to polyester from an aqueous bath in the presence of a solvent can be achieved by selecting a solvent with a suitable value of the relative intensity of the association and dispersion forces represented by  $(\delta_d^2/\delta_a^2)$ , as shown in Figure 2.7.



**Figure 2.7** The effect of the  $(\delta_d/\delta_a)^2$  of solvents on the dyeing transition temperature ( $T_D$ ). Reproduced from [113]

Finally, since perchloroethylene and water form an azeotrope at 87°C, pressurized apparatus would be necessary for dyeing at 120°C. [153]

### **2.10. Dry heat-fixation**

The thermofixation process is a method for dyeing polyester fabrics or fabrics constructed from blends of polyester and cotton. In the case of polyester, the fabric is subjected to dry heat at about 200°C for about 1 minute after applying the disperse dye by padding. When polyester-cotton blends are dyed by the thermofix process, suitable dyes for both components are applied simultaneously by padding before transferring the fabric to the dry heat stage. After padding the fabric in the aqueous dyeing liquor, which contains either vat dyes or reactive dyes for the cotton and disperse dyes for the polyester, the fabric is dried and then heated to about 200°C to fix the dye on the polyester portion. [113] During the impregnation stage, the hydrophilic cotton fibres pick up much more pad-liquor than do the hydrophobic polyester fibres, and therefore, at this stage, more disperse dye is present on cotton than on polyester. This disperse dye is transferred from the cellulose to the polyester through the vapour phase, due to the higher substantivity of polyester for the dye vapour, when the dye sublimates off the cellulose during heating at the high temperature. [158]

It has also been reported that the dry heat-fixation process may be used for fixing disperse dyes applied to polyester from a non-aqueous dyeing bath. In an early report, polyester fabric was dyed with disperse dyes by impregnating the fabric in a solution containing the dyestuff in tetrachloroethylene. [159] After squeezing the fabric, it is dried at 80°C for 1 minute. This stage is followed by the thermal fixation of the dye by heating the fabric at temperature between 190° – 220°C for 45 seconds. The non-fixed dye is washed off by treating the fabric in cold tetrachloroethylene for 20 seconds. Similar satisfactory results were obtained when tetrachloroethylene was replaced by any one of the following solvents: dichloromethane, chloroform, carbon tetrachloride, tetrachloroethane, dichloropropane, 1,1,1-trichloropropane, chlorobutane and dichlorobutane.

### **2.11. Textile Printing**

Textile printing is one of the most versatile methods for introducing colours and designs to textile fabrics. [160] There are various methods of textile printing, such as block printing, engraving printing process, copper roller printing, screen printing and digital inkjet printing. The block printing, which is the earliest method of printing textile

materials, uses blocks with raised printing surfaces, which are inked and then pressed on the fabric. The use of block printing declined greatly during the mid-18<sup>th</sup> century due to the introduction of engraving printing, and later the copper roller printing, methods which exhibited much higher production speed compared to the block printing method. Screen printing, which was initially developed in 1850, replaced the roller printing and became the most commercially important method for textile printing around 1967, with steadily increasing importance until the mid-1990s. Inkjet printing, which is the newest method of textile printing, is discussed in detail in section 2.12.

## **2.12. Inkjet Printing**

### ***2.12.1. Introduction***

Inkjet is a non-impact printing method involving the delivery of a liquid ink to a substrate by the deposition of ink droplets to an image recording element in response to digital data signals. [161] The basis of inkjet printing was first suggested in 1686 by Mariotte who studied the fluid dynamics and observed drop formation of fluid passing through a nozzle. [162] The first patent published for an inkjet printing system was in 1867. Eleven years later, the role of surface tension in drop formation, which has proved to be an important concept for the inkjet technology, was described by Rayleigh. [163] The first patents for inkjet recording devices were issued between the 1920s and 1930s. [164]

In 1965, Hertz and Simonsson invented the high-resolution continuous inkjet method, which led to development of a type of continuous inkjet technology using mutual charge droplet repulsion that produces very fine ink droplets at a very high frequency. This continuous inkjet technology opened the door to the production of high resolution images which, since then, have found applications in the textile and fashion industries.

The principle of the thermal inkjet process was discovered in 1977 when the exposure of the side of a pipette containing liquid to a flame caused the pipette to emit a drop of the liquid. This concept was applied by Canon to introduce the thermal printers in the 1980s. [165] Subsequently, a twelve-colour inkjet textile printer, using thermal inkjet print heads, was exhibited at ITMA 1999 in Paris. The high prices and limited production capabilities of these machines did not enable them to be accepted widely in the textile printing market. Significant market adoption of inkjet printers which used piezoelectric print heads was attained by Ichinose and DuPont who installed a high number of printers by February 2006.



### ***2.12.2. Inkjet technologies and mechanisms***

The inkjet printing system has many advantages over the traditional screen printing process. In the case of the screen printing, sample preparation is a long, complex and expensive process. Each separated colour requires a screen coated with light sensitive material, a film positive and a light source to transfer the positive image to the light sensitive screen. In addition, huge print rooms are necessary for the screen printing process. On the other hand, inkjet printing has made a breakthrough in textile printings by eliminating the need for preparing colour-separated positives and printing in such large rooms. The inkjet sampling system replaced the manual colour separation process by direct computed control over the appearance of the design on the fabric. The inkjet printing process requires consideration of three basic components to work properly to produce an acceptable printed fabric. These three components are the print head, the ink and the substrate.

Inkjet technology may be classified in two classes: continuous inkjet (CIJ) and drop-on-demand inkjet (DOD). In CIJ, a constant pressure is applied to squirt the ink at a constant speed. Drops are formed after leaving the nozzles and either come into contact with the substrate to form the image, or are deflected to a gutter when no colour is needed in the area of the image. In DOD, drops are ejected only when needed to form the image. There are two main mechanisms for drop generation, namely piezoelectric inkjet (PIJ) and thermal inkjet (TIJ). In PIJ, ink is squeezed out of the nozzle by quickly reducing the volume inside the nozzle using a piezoelectric actuator. In TIJ, ink is heated by thermal means located inside the nozzle. The heated ink forms a bubble which in turn expands explosively pushing the ink outside the nozzle. The conductivity of the inks used in CIJ print heads needs to be high, because the droplets generated by the CIJ process are charged after ejection. The CIJ print heads tend to be expensive, because of the complexity associated with this technology including the need to charge and deflection of the ink drops, in addition to ink circulation and pressurization. On the other hand, the operation frequencies of the CIJ print heads are at least an order of magnitude higher than in DOD systems, because of the active refill of the nozzles by the positive pressure operation associated with the CIJ technology, and therefore large scale industrial applications use the CIJ systems. In DOD-PIJ technology, the drop formation process is controlled by waveforms of different complexities. The waveforms may be defined as the pressure waves formed inside the ink channel causing a deformation in the cross-section of the channel by the inverse piezo-electric effect which results in firing a droplet through the nozzle connected to the channel. The

waveforms are generated by applying an electric voltage using a piezo actuator element with each channel. In the DOD-TIJ technology, water based inks are preferred, because water is more efficient in formation of explosive bubbles than other solvents. The main drawback of the PIJ technology is that drop ejection requires a change in the chamber volume of the order of twice the drop volume, and this in turn reduces the number of nozzles per inch in the direction of the nozzle array. The presence of trapped air bubbles in the ink causes problems in both PIJ and TIJ technologies, because these bubbles can absorb a portion of the pressure pulse reducing its efficiency or even disabling it. Air bubbles trapped in the ink may be caused by the low pressure areas generated by the PIJ waveforms and by heating the ink during the firing pulse in TIJ print heads. TIJ is superior to PIJ in dealing with gas bubbles, because in TIJ the drop generator energy device is very close to the nozzle, and therefore it causes a gas removal effect from the critical region. On the other hand, pre-degassing is required for inks to be used in the PIJ print heads, because of the complexity of the path between the firing chamber and the nozzle which makes gas bubble generation more likely. An important advantage of the PIJ technology over the TIJ technology is that TIJ devices favour water based inks, while the PIJ devices can easily fire any fluid. Commercial TIJ print heads are effective for low viscosity water-based ink systems (less than 4 cps), and hence PIJ print heads are the industrial choice where operation outside this viscosity range is required. [162]

### ***2.12.3. Ink systems for textiles***

#### ***a) Reactive dye-based inks***

Reactive inks are most commonly used for printing on cellulosic substrates. These dyes form covalent bonds with the fibre polymers under alkaline conditions. Reactive dye molecules contain reactive groups which can undergo substitution or addition reactions with hydroxyl groups on the fibre to form the stable covalent bonds. A purification process of reactive inks is required to be carried out to remove the majority of the salt that can cause corrosion of jet nozzles. [162] Reactive inks contain, in addition to the dye, hygroscopic agents to prevent ink drying in the nozzles, surfactants and phosphoric acid-based buffers. The buffer is added to control the pH, and hence delay reactive dye hydrolysis. Fixation of reactive inks on cellulosic substrates is carried out by steaming for 10 minutes at 102°C followed by a wash-off. [166]

*b) Acid dye-based inks*

These dyes are generally used for printing wool, silk and nylon. When they are dissolved in water, acid dyes become anionic, so that they are attracted to the positively charged sites that are formed on the fibres under acidic conditions. Acid dye inks include hygroscopic agents and surfactants in their formulations. Acid dye prints are fixed by steaming at 102°C for 30-40 minutes, followed by washing. [167]

*c) Pigment-based inks*

Pigments are applied to textiles as finely dispersed particles, because they are insoluble in water. The particles do not diffuse into fibres, but they adhere to the surface by means of being contained in a polymeric, self-cross-linking binder. The fixation step after printing is carried out by dry heating. The possible aggregation of pigment particles in the ink may increase the risk of jet nozzle blockage. The presence of binder in the pigment ink system may lead to an increase in the ink viscosity to such high levels that it makes the ink system incompatible with the print head. Another drawback associated with the presence of the binder into the ink system is the risk of jet nozzle blockage, and therefore it may be necessary to apply the binder to substrates as a post-treatment.

*d) Disperse dye-based inks*

Disperse dyes have very limited solubility in water, and hence they are applied to synthetic textiles as finely dispersed particles. Ink systems used for disperse inkjet printing of polyester are classified into two types: the vapour phase transfer type and the direct printing type. In vapour phase transfer printing, the disperse dye ink is printed into a specific paper, and then thermally transferred to polyester fabric by treating at a temperature of 210°C for 30 seconds. For this type of process, neither pre-treatment nor wash off is required. [168] Relatively low molecular weight and hence more volatile disperse dyes are required for vapour transfer printing. [162] On the other hand, direct printing reduces the extra expenses of paper and avoids a second printing operation. Disperse dyes, after application, are bonded to polyester mainly by van der Waals forces and hydrogen bonding.

Fixation of prints is carried out by high temperature steaming at 170-180°C, or by dry heat at temperature of 190-200°C, and is followed by a wash-off cycle and reduction clearing.

Aqueous-based ink systems are composed of dye, water-soluble organic solvents, surfactant, pH modifier, water and additives. The water-soluble organic solvents are referred to as co-solvents and as humectants depending on their function. Co-solvents

assist water to incorporate other ingredients into the ink system. Examples of co-solvents include alcohols, ketones, keto-alcohols, ethers, thiodiglycol, sulfonate, 2-pyrrolidone, 1,3-dimethyl-2-imidazolodione and propanediols. The selection of a suitable mixture depends on the application requirements such as surface tension, viscosity, colorants used and compatibility with substrate and the print head. [169] Humectants are used to prevent the ink from drying and clogging the nozzles of the print head. They work by attracting water vapour from the air and returning it to the liquid phase. 2-pyrrolidone serves as both a co-solvent and a humectant. Other materials may be used as humectants such as polyethylene or propylene glycols, glycerol and sorbitols. [162] The water-soluble organic solvents and the surfactant are used to adjust the ink viscosity and surface tension. These parameters have very important effects on the printing process properties, such as the ink reliability and adsorption speed. Ink properties must be optimized to the print head in use. Drop formation from a liquid stream in air is controlled according to equations 8 and 9.

Weber Number:

$$We = \rho U^2 D / \sigma \quad (8)$$

Reynolds Number:

$$Re = UD / \nu \quad (9)$$

Where:

$\rho$  = Specific gravity ( $\text{kg m}^{-3}$ ),

$U$  = Flight speed of liquid ( $\text{m s}^{-1}$ ),

$D$  = Diameter of flight liquid (m)

$\sigma$  = Surface tension ( $\text{N m}^{-1}$ ),

$\nu$  = Dynamic viscosity number ( $\text{m}^2 \text{s}^{-1}$ ).

Drop formation is closely related to the values of these two numbers. Consequently they are required to be within a certain range to create a drop. Thus, it is important to measure the dynamic viscosity and surface tension of the ink formula. The rheological behavior of the ink ejected from the nozzles has a direct effect on drop formation. The surface tension has important effects on both the drop formation and the image formation. The latter quality is related to the ink dot placement, spreading and penetration inside the fabric. Ink behaviour can be controlled by the careful selection of the organic solvents and additives and their concentrations in the ink formulation. The

addition of water soluble organic solvents of a hydrophilic nature can also increase the ink reliability by reducing water evaporation, and hence avoiding the start-up failure resulting from increasing the solid component concentration near the nozzle where water evaporates quickly. Surfactants are added to control surface tension and wetting properties of the ink. Examples of surfactants commonly used in ink formulation include ethoxylated acetylene diols, ethoxylated primary and secondary alcohols, sulfosuccinates, organosilicones and fluoro surfactants. The typical amount of surfactants in the ink formula is preferably about (0.2 – 2) % of the total weight of the ink. Other additives are also added to the ink formulation to the extent that they do not interfere with the stability and jetability of the ink. The appropriate amounts of these additives are determined by routine experimental work. Anti-oxidizing agents are also used as additives to reduce the dye decomposition and hence avoid changing the ink physical properties. [169]

Disperse dye-based inks for inkjet are different from screen printing inks in terms of particles size, dispersing agents and ink viscosity. Inks for polyester are prepared by using low viscosity, highly particulated dispersions. Dispersions for inkjet inks are prepared as concentrations (10-20) % of dispersion in water and are highly purified. The mean particle size is between (100-250) nm. This particle size is obtained by the purification process and careful selection of dispersing agent. Purification is also important to achieve the targeted levels of storage and ejection stability. The viscosity range of the concentrated dispersion is from 10 to 50 mps.

The preparation process of disperse dye ink passes through the following stages:

1. Purification of disperse dye (elimination of salts and organic impurities)
2. Dispersion
3. Further purification including:
  - Coarse particles which are removed by ultra-centrifugation and ultra-filtration.
  - Inorganic impurities which are removed by reverse osmosis
4. Addition of additives
5. Ink preparation
6. Ageing
7. Purification
8. Bottling

Different proportions of components can be used for ink formulation to achieve desired ink properties. [169] Examples of typical disperse dye ink systems are given in Table 2.2. [170]

**Table 2.2** Disperse dye ink system formulation

| <i>Material</i>  | <i>Weight % of weight of the ink</i>  |   |
|--|---|---|
|  | <i>Black</i>  | <i>Light Magenta</i>  |
| Ethylene Glycol (co-solvent)   | 23.0  | 23.0  |
| Glycerol (co-solvent)  | 8.0   | 13.0  |
| LEG- 1   | 4.0   | 9.0   |
| Dowanol DPM (Dipropylene Glycol Methyl Ether), humectant   | 5.0   | 5.0   |
| Surfynol 440, surfactant   | 1.0   | 1.0   |
| Polyethylene glycol  | -   | 1.0   |
| Proxel GXL (Biocide for the preservation of industrial water-based products against spoilage from bacteria, yeasts and fungi.) | 0.15  | 0.15  |
| 2-Pyrrolidone (co-solvent)   | 0.72  | 0.4   |
| Disperse dye in dispersion   | 10-11   | 5.0   |
| Water  | Balance to 100%   | Balance to 100%   |
| Properties   | pH = 8.5<br>Viscosity (cps, 25°C) = 8.1<br>Surface tension (dyne/cm at 25°C)=31.3 | pH = 8.3<br>Viscosity (cps, 25°C) = 8.0<br>Surface tension (dyne/cm at 25°C)=30.0 |

An example is reported of a dispersed ink system developed by mixing either a disperse dye or a pigment to an amphiphilic compound in aqueous solution. [171] The amphiphilic compound consists of a hydrophilic portion and a hydrophobic portion. In the ink system, the hydrophobic portions of the amphiphilic compound are adsorbed on

hydrophobic groups on the surface of the pigment, or disperse dye particles. The hydrophilic portions extend into the aqueous medium resulting in dispersing the pigment, or disperse dye particles. According to this invention, a fine particulated and re-dispersible ink has been prepared successfully, so that high definition print quality may be achieved. A compromise must be maintained between the ink re-dispersability and the ability of the amphiphilic compound to defragment particles of the disperse dye or pigment. This target can be attained by controlling the amphiphilic compound molecular weight and the pigment or disperse dye particle size to meet the following relationship:

$0.004 \leq \text{the particle diameter (nm) of the pigment or the disperse dye} / \text{the molecular weight of the amphiphilic compound} \leq 0.04.$

Ink properties can be adjusted to become compatible with the print head in use and to improve the ink storage ability by adding the following components:

- Water-soluble organic solvents: Ethylene glycol, diethylene glycol or glycerol

The total amount of water-soluble organic solvents is between 8 and 25% based on the weight of the ink.

- Surfactant
- Defoaming agent
- Humectant
- Drying-preventing agent
- Agent for preventing crusting at the print head
- Bactericides

The print quality can also be improved by incorporating fine polymer particles into the ink. Examples of commercial fine polymer particles are, Joncryn 7001, joncryn 711 and Joncryn 775. [171]

Conventional printing processes, such as screen printing, produce brilliant colours and soft fabric handle. These properties are difficult to achieve by digital inkjet printing techniques. The reason is the low viscosity required by inks to comply with the print head. This low viscosity causes the ink to spread on the fabric, and this, in turn, reduces the brilliance and definition of the printed fabric. The simplest solution to overcome this problem is the pre-treatment of textiles with thickeners to absorb excess fluid and prevent the ink bleeding on the fabric. This method has an associated drawback which may lead to a hard handle of the printed fabric. New products have been developed to replace the thickener, such as 'Luprejet HD', which is available commercially and

padded onto the fabric, or alternatively applied as a spray. This material, and other commercial products, is used to prevent the bleeding effect of the ink but with no associated hard handle on the printed fabric. [134] Typical pre-treatments, disperse inkjet printing and fixation processes for polyester fabric are given in Table 2.3. [162]

**Table 2.3** Typical process route for direct disperse dye inkjet printing of polyester fabric

| Process            | Material   | Instrument  | condition               |
|--------------------|--|---|-------------------------|
| Pre-treatment      | (sodium alginate (thickener) 100-200g + Citric acid 0.2g)<br>OR<br>(Luprejet HD (thickener) 440.5 g +Defoamer DC 0.2 g)<br>+<br>Water to 1000g |   |                         |
| Padding            |  |   | Pick- up ratio 70 – 80% |
| Drying             |  | Tenter  | 100-120°C               |
| Printing           | Disperse dye based ink   | Inkjet printer  |                         |
| fixation           |  | High temperature steam (e.g. 170-180°C for 6-8 min.)<br>or, thermosol (e.g. 190°C for 60 seconds) |                         |
| Wash off           | Cold water   |   |                         |
| Soaping            | 1 g l <sup>-1</sup> non-ionic surfactant   |   | 40°C                    |
| Reduction clearing | 1-2 g l <sup>-1</sup> sodium dithionite<br>2 g l <sup>-1</sup> sodium hydroxide<br>1g l <sup>-1</sup> surfactant                               |   | 60-90°C                 |
| Wash               | Hot water  |   | 40-60°C                 |
| Wash               | Cool water   |   |                         |



## **2.13. Colour Measurement**

### ***2.13.1 Introduction***

The measurement of colour is an important feature of the detailed analysis of the properties of dyes, pigments and coloured products, such as colour and application properties, which aims to ascertain that these properties of dyes and pigments are of consistent quality, or to ensure that the colours of the products are exactly as required and are consistent from one item to another. Colour measurement has found applications in different fields such as textiles, food, paper products, toiletries and prints. [147]

Colour measurement analysis can be conducted either on solutions, by measuring their transmission properties, or on solid materials, by measuring their reflectance characteristics. An example of the colour measurement of materials in solution is the application to dyes to establish the hue and strength of the dyes. The outcome of the colour measurement of solid materials, such as textiles, which is based on the reflectance measurements, is referred to by the colour co-ordinates. These co-ordinates define the colour and allow decisions to be made as to whether the samples tested match the standard sample to which they are compared. This method may also be used to evaluate the colour difference between two coloured samples. A further useful application of colour measurement, which is used routinely by the users of colorants, is the computation of the quantities of dyes or pigments that must be applied to a substrate to produce a desired colour. The technology of colour measurement has been developed in an attempt to achieve automatical control of quality and to provide feedback on coloration processes, such as textile dyeing and printing processes.

### ***2.13.2 Colour physics***

Light may be defined as the part of the spectrum of the electromagnetic radiation that human eyes can detect. [172] The properties of electromagnetic radiation may be described by both the wave model and the particle model; neither of these models alone gives a completely satisfactory explanation of the properties of radiation. [173] The wave model describes radiation as a wave motion consisting of electric and magnetic fields moving at right angles to each other and to the direction of propagation. The electromagnetic spectrum consists of regions which are characterized by different wavelengths, as shown in Table 2.4. [174]

**Table 2.4** Regions of electromagnetic spectrum (approximate)

| <i>Type of radiation</i> | <i>Wavelength m</i>   | <i>Frequency Hz</i> |
|--------------------------|-----------------------|---------------------|
| Cosmic rays              | $10^{-17} - 10^{-13}$ | $10^{22} - 10^{18}$ |
| Gamma rays               | $10^{-12} - 10^{-11}$ | $10^{17} - 10^{16}$ |
| X- rays                  | $10^{-10} - 10^{-9}$  | $10^{15} - 10^{14}$ |
| Ultraviolet              | $10^{-8}$             | $10^{13}$           |
| Visible                  | $10^{-7} - 10^{-6}$   | $10^{12} - 10^{11}$ |
| Infrared                 | $10^{-5}$             | $10^{10}$           |
| Far infrared             | $10^{-4}$             | $10^9$              |
| Microwave                | $10^{-3}$             | $10^8$              |
| Radar                    | $10^{-2}$             | $10^7$              |
| Television               | $10^0$                | $10^5$              |
| VHF radio                | 10                    | $10^4$              |
| Medium wave radio        | $10^2$                | $10^3$              |
| Long wave radio          | $10^3$                | $10^2$              |

The shorter the wavelength of the radiation, the higher is its energy. The frequency of radiation is related to the wavelength of this radiation by Plank's equation (10). [173]

$$E = h \nu = h \frac{c}{\lambda} \quad (10)$$

where

$h$  is referred to as Plank's constant and has a value of  $6.626 \times 10^{-34}$  (J s).

$E$  is the energy of radiation, (J).

$\nu$  is the frequency of the radiation ( $s^{-1}$ ) which may be defined as the number of waves which pass a given point in one second.

$c$  is the velocity of electromagnetic radiation,  $c = 3.00 \times 10^8$  [m.s<sup>-1</sup>].

$\lambda$  is the wavelength of the radiation, (m).

Thus, radiation of the shortest wavelengths, such as cosmic and x-rays, have high energy and therefore have high ability to penetrate materials. Ultraviolet radiation, which is a component of sunlight, possesses higher energy than visible light, which, in turn, has higher energy than infrared radiation. However, the latter brings about a heating effect when it is incident on objects. Radiation of longer wavelengths is popular because of the common applications, for example in microwave ovens, radar, television and radio.

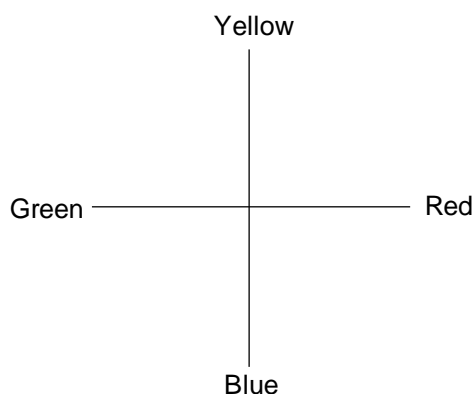
Colour measurement instruments are used for the measurement of the visible light which represents a narrow region in the electromagnetic spectrum from approximately  $3.6 \times 10^{-7}$  to  $7.8 \times 10^{-7}$  m (360 to 780 nm) where  $1 \text{ m} = 10^9 \text{ nm}$ . The practical sensitivity of the human eye to light lies in the region 380 – 710 nm. The colours of the visible light of various wavelengths perceived by the human eye are shown in Table 2.5. [175]

**Table 2.5** Visible colours of spectral light

| <i>Wavelength <math>\lambda</math> (nm)</i> | <i>Colour</i> |
|---|---------------|
| 380 - 400                                   | Violet        |
| 400 – 435                                   | Indigo        |
| 435 – 480                                   | Blue          |
| 480 – 490                                   | Greenish blue |
| 490 – 500                                   | Bluish green  |
| 500 – 560                                   | Green         |
| 560 – 580                                   | Yellow green  |
| 580 – 595                                   | Yellow        |
| 595 – 605                                   | Orange        |
| 605 - 740                                   | Red           |

The reason why an object possesses a particular colour is the selective absorption of radiation of specific wavelengths by this object. [176] This selective absorption is explained on the basis of changes in the various types of energies possessed by the molecules present in the coloured object. A molecule possesses three types of energy, which are relevant in giving rise to colour: rotational energy, which is produced by the rotation of the whole molecule about its centre of gravity; vibrational energy, which arises from the stretching or bending of chemical bonds; electronic energy, which is brought about by the continuous motion of the electrons which occupy the molecular orbitals around the nuclei. The ability of a molecule to absorb incident radiation in a particular wavelength region is determined by the correspondence between the energies of the frequencies of this region of radiation and the differences between the various energy levels in the molecule. Thus, the absorption of particular frequencies of radiation such as in the ultraviolet or visible region of the spectrum may bring about an electronic transition as a result of promoting an electron from the orbital it occupies in the ground state to an orbital of higher energy. The excited state which is formed in this way has a short life, so that the molecule returns very quickly to the ground state, usually

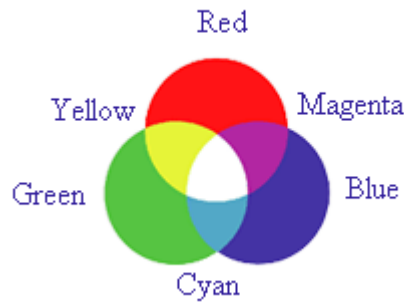
dissipating the absorbed energy as heat. Absorption of radiation in the visible region, which is responsible for the colour of dyes and pigments, is brought about essentially by the electronic transition although there are also superimposed vibrational and rotational transitions. Thus, the selective absorption of light by coloured objects in specific regions of the visible spectrum is responsible for their individual colours. Hence, the colour perceived by the eye represents the wavelengths of light not absorbed by the dye or pigment. The 'opponent colours' diagram represents a useful method for determining the colours of objects perceived by the human eye depending on the opposite, or complementary, colours absorbed by coloured objects, as shown in Figure 2.8. [177] For example, according to the opponent colours diagram, a green dye absorbs light in the red region of the spectrum, and vice-versa.



**Figure 2.8** 'Opponent colours' diagram

### ***2.13.3 Additive and subtractive colour mixing***

A sound understanding of the laws of colour mixing is essential for colour specification. Additive colour mixing refers to mixing coloured lights when they are shone together on a white screen, which reflects most of the incident light to the eye. [147] The three primary coloured lights, which are referred to as primary because they cannot be produced by mixing any other two colours, are red, green and blue. A mixture of equal proportions of the three primary coloured lights gives white, while equal mixtures of two primary colours produce the secondary colours, namely magenta, yellow and cyan. White is also produced when equal proportions of the three secondary colours are mixed, as shown in Figure 2.9.



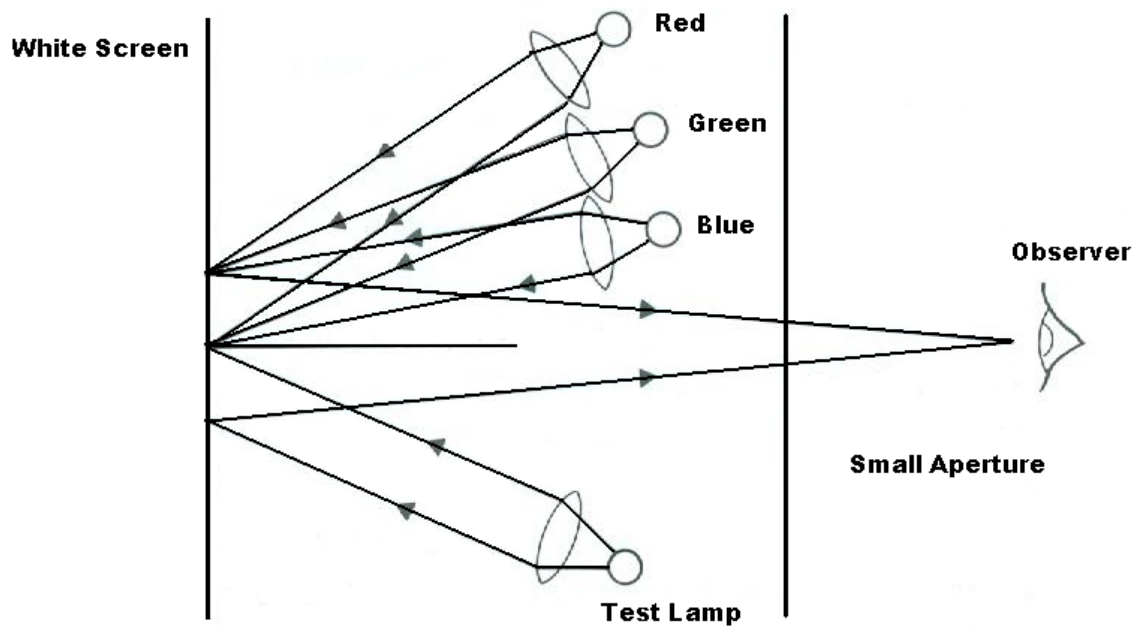
**Figure 2.9** Additive colour mixing

The relationship of colours to each other is represented by the colour space, which is a description of the colour circle made by spacing the three primary colours equally round a circle and placing the secondary colours on the circle between their two primary components. White is placed in the centre of the circle. More details about the colour space concept are given in section 2.13.5.

Subtractive colour mixing is brought about by the selective absorption of light by dyes and pigments, which absorb light in particular regions of the visible spectrum and reflect the rest of the light thus providing the perceived colour. For example, a cyan coloured object absorbs light most strongly in the red region of the spectrum, which is referred to as the complementary component of cyan, and reflects light in the blue and green regions, which are the primary components of the cyan.

#### ***2.13.4 The C.I.E system of colour specification***

Colour measurement systems are mostly based on the C.I.E system. This system was initially agreed in 1931. The initials C.I.E stand for Commission International de l'Eclairage, which is an organization devoted to international cooperation and exchange of information among its member countries on all matters relating to the art and science of lighting. [178] The experiment illustrated in Figure 2.10 represents the properties of the additive mixture of coloured lights, which is the basis of the C.I.E system. This experiment showed that a wide variety of coloured lamps can be matched by adjusting the properties of the red, green and blue lights in agreement with the principles of the additive mixing of coloured lights.



**Figure 2.10** The additive mixtures of coloured lights

This situation can be represented by the colour matching equation (11):

$$C[C] = R[R] + G[G] + B[B] \quad (11)$$

which represents that C units of a colour [C] can be matched by R units of the red primary [R], G units of the green primary [G] and B units of the blue primary [B]. The symbols [R], [G] and [B] represent the primary colours red, green and blue respectively, while R, G, and B, which are referred to as the tristimulus values, represent the amounts of these primaries required to match the colour [C]. It has been found that not all colours can be matched by a given set of primary colours. Some very pure colours may be more saturated than the colours obtained by mixing any set of primaries. [173] For example, the colour matching equation for pure magenta light cannot be derived without reducing its richness by adding green light, because the green primary has to be added to the magenta, so that it can be matched by a mixture of the blue and red primaries, as shown in equations 12 and 13.

$$C[C] = R[R] + B[B] - G[G] \quad (12)$$

$$\text{or} \quad C[C] + G[G] = R[R] + B[B] \quad (13)$$

where [C] is the pure magenta.

To overcome the problem of the inconvenient negative values of the tristimulus values required to match some colours, the C.I.E. adopted three imaginary primaries [X], [Y] and [Z] which represent very saturated red, green, and blue primaries respectively. Thus, the imaginary primaries [X], [Y] and [Z] have been defined mathematically as spectral lights at wavelengths of 700.0, 546.1 and 436.8 nm respectively. According to

this definition, white light would be matched by equal amounts of the imaginary primaries, as shown in equation 14.

$$S_E = 0.333[X] + 0.333[Y] + 0.333[Z] \quad (14)$$

where  $S_E$  is white light from equal amounts of each wavelength.

The amounts of the imaginary primaries required to match unit energy of light at each wavelength of the spectrum have been calculated, from the tristimulus values (R, G, B), by using transformation equations. Thus, the amounts of the imaginary primaries are referred to by  $\bar{x}_\lambda, \bar{y}_\lambda, \bar{z}_\lambda$  and their values at each wavelength have been published by the C.I.E.

The tristimulus values (X, Y, Z) of surface colour, which represent the amounts of the imaginary primaries required to match the white light when all the wavelengths of this light are viewed simultaneously, are given by the sums of the amounts of the imaginary primaries required. Thus the values of X, Y and Z can be calculated by using equations 15, 16 and 17 respectively.

$$X = \int_{360}^{780} \bar{x}_\lambda d\lambda \quad (15)$$

$$Y = \int_{360}^{780} \bar{y}_\lambda d\lambda \quad (16)$$

$$Z = \int_{360}^{780} \bar{z}_\lambda d\lambda \quad (17)$$

As the source of light emits different amounts of light at each wavelength, and the surface does not reflect the entire light incident on it, equations 15, 16 and 17 must be amended to give equations 18, 19 and 20 respectively.

$$X = k \int_{360}^{780} E_\lambda \bar{x}_\lambda R_\lambda d\lambda \quad (18)$$

$$Y = k \int_{360}^{780} E_\lambda \bar{y}_\lambda R_\lambda d\lambda \quad (19)$$

$$Z = k \int_{360}^{780} E_\lambda \bar{z}_\lambda R_\lambda d\lambda \quad (20)$$

$$\text{where } k = \frac{1}{\int_{360}^{780} E_\lambda \bar{y}_\lambda d\lambda} \quad (21)$$

$E_\lambda$  = relative energy of the source

$R_\lambda$  = reflectance of the surface

This is simplified by using an approximation method called the weighted-ordinate method to calculate X, Y and Z, as shown in equations 22, 23, and 24 respectively.

$$X = \sum E_\lambda \bar{x}_\lambda R_\lambda \quad (22)$$

$$Y = \sum E_\lambda \bar{y}_\lambda R_\lambda \quad (23)$$

$$Z = \sum E_\lambda \bar{z}_\lambda R_\lambda \quad (24)$$

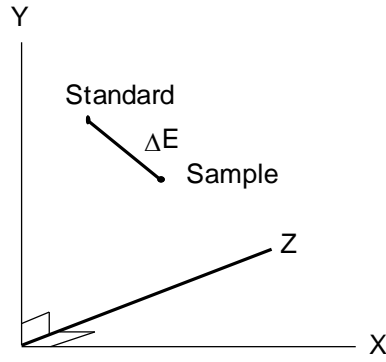
Equations 22 – 24 can be used to specify the appearance of a coloured material under any source, without needing to measure the reflectance of the material under that particular source. The values of  $E_\lambda \bar{x}_\lambda$ ,  $E_\lambda \bar{y}_\lambda$ ,  $E_\lambda \bar{z}_\lambda$  at each wavelength are published by the C.I.E. for different illuminants and wavelength intervals. Since the values of  $E_\lambda \bar{x}_\lambda$ ,  $E_\lambda \bar{y}_\lambda$ ,  $E_\lambda \bar{z}_\lambda$  and  $R_\lambda$  are known, the tristimulus values of a coloured material, and therefore the colour appearance under a particular illuminant, can be measured by using equations 22, 23 and 24.

### **2.13.5 Colour difference assessment**

Modern instruments are able to measure the tristimulus values, which are used then in the colour difference equation to give a single number which represents the magnitude of the visual difference between two colours. The principle of the measurement of colour difference is based on calculating the distance between the colours of the standard and the sample in the colour space. If the colour space used to calculate the colour difference is the three dimensional X, Y, Z tristimulus space, as shown in Figure 2.11, the distance between two colours in the colour space is given by equation 25, which is referred to as the colour difference equation.

$$(\Delta E)^2 = (\Delta X)^2 + (\Delta Y)^2 + (\Delta Z)^2 \quad (25)$$





**Figure 2.11** The three dimensional X, Y, Z colour space

Experiments have showed that pairs of colours with equal visual differences in colour may not give the same colour difference values as calculated by equation 25. Hence, many equations have been proposed to replace equation 25 by modifying the X, Y, Z scales to produce a visually uniform colour space, in which equal changes in the measured co-ordinates correspond to equal perceived differences. Thus, the C.I.E. has proposed the CIELAB equation, which uses the LAB visually uniform colour space derived from the XYZ space. The values of the three perpendicular axes of this colour space,  $L^*$ ,  $a^*$ ,  $b^*$  are calculated from X, Y, Z by using equations 26, 27, and 28.

$$L^* = 116 \left( \frac{Y}{Y_n} \right)^{\frac{1}{3}} - 16 \quad (26)$$

$$a^* = 500 \left[ \left( \frac{X}{X_n} \right)^{\frac{1}{3}} - \left( \frac{Y}{Y_n} \right)^{\frac{1}{3}} \right] \quad (27)$$

$$b^* = 200 \left[ \left( \frac{Y}{Y_n} \right)^{\frac{1}{3}} - \left( \frac{Z}{Z_n} \right)^{\frac{1}{3}} \right] \quad (28)$$

where  $X_n$ ,  $Y_n$ ,  $Z_n$  are the tristimulus values of the reference white under the source used. The colour difference between a standard and a sample in CIELAB space is given by using  $L^*$ ,  $a^*$ ,  $b^*$ , as shown in equation 29.

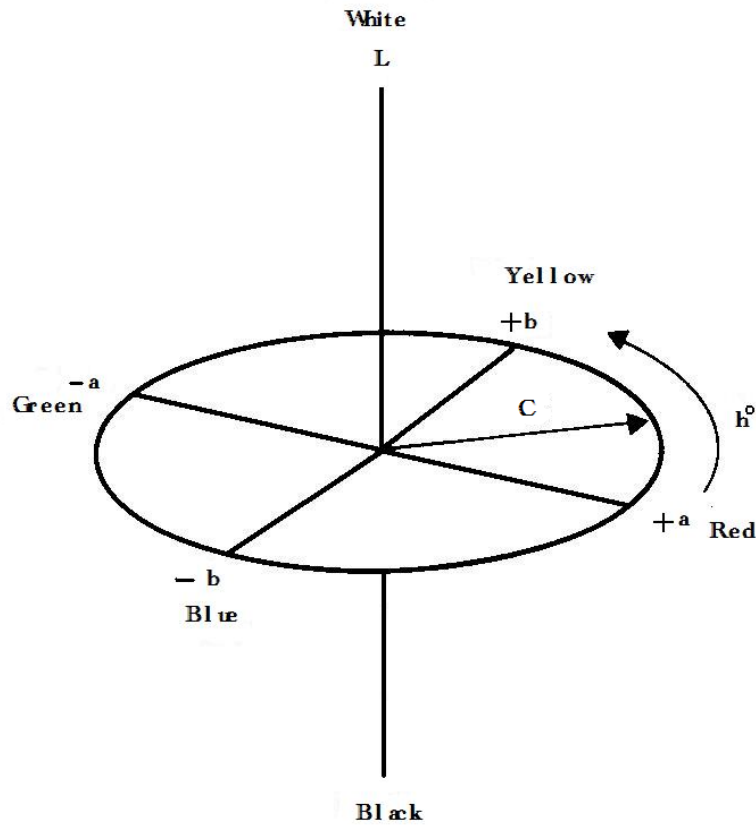
$$\Delta E = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{\frac{1}{2}} \quad (29)$$

The cylindrical co-ordinates ( $L^*$ ,  $C^*$ , and  $h$ ) can be used to define the location of colours in the  $L^*$ ,  $a^*$ ,  $b^*$  space.  $L^*$ ,  $C^*$ , and  $h$  represent the three attributes of colour vision, namely lightness, chroma and hue respectively, where:

$$C^* = \left( a^{*2} + b^{*2} \right)^{\frac{1}{2}} \quad (30)$$

$$h = \arctan\left(\frac{b^*}{a^*}\right) \quad (31)$$

The CIELAB colour space is illustrated in Figure 2.12.



**Figure 2.12** CIELAB colour space

The colour difference between two colours in the CIELAB space is expressed by equation 32.

$$\Delta E = \left[ (\Delta L^*)^2 + (\Delta C^*)^2 + (\Delta H^*)^2 \right]^{\frac{1}{2}} \quad (32)$$

Although equation 32 is still widely accepted for colour difference calculation, alternative equations for calculating colour differences have been developed to overcome the drawbacks of other available equations such as the inconsistent performance of equation 32 through the colour space and the need to use different tolerances according to the colours viewed. For example, a further equation was proposed by the Society of Dyers and Colourists to quantify the colour difference between colours. This equation (33), which is referred to as the CMC (1:c) equation,

may have the best overall performance compared to any equations published before, and therefore it was adopted as a British standard (BS6923:1988) in 1988, and then an ISO standard in 1996.

$$\Delta E = \left[ \left( \frac{\Delta L^*}{L.S_L} \right)^2 + \left( \frac{\Delta C^*}{c.S_c} \right)^2 + \left( \frac{\Delta H^*}{S_H} \right)^2 \right]^{\frac{1}{2}} \quad (33)$$

$$\text{Where } S_L = \frac{0.040975 L_1^*}{(1 + 0.01765 L_1^*)} \quad (34)$$

Unless  $L_1^* < 16$  when  $S_L = 0.511$

$$S_c = \left[ \frac{0.0638 C_1^*}{1 + 0.0131 C_1^*} \right] + 0.638 \quad (35)$$

$$S_H = S_c (T \cdot f + 1 - f) \quad (36)$$

$$f = \left\{ \frac{(C_1^*)^4}{[(C_1^*)^4 + 1900]} \right\}^{\frac{1}{2}} \quad (37)$$

$$T = 0.36 + |0.4 \cos(h_1 + 35)| \quad (38)$$

Unless  $h_1$  is between  $164^\circ$  and  $345^\circ$ , when

$$T = 0.56 + |0.2 \cos(h_1 + 168)| \quad (39)$$

## Chapter 3 - The Application of Photochromic Dyes to Polyester as Disperse Dyes by an Exhaustion Method

### 3.1. Introduction

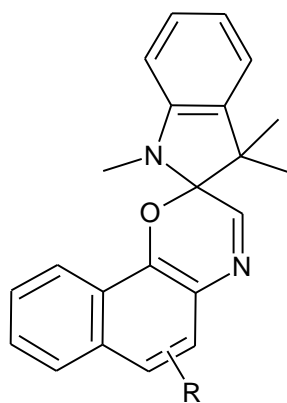
The hydrophobic and highly crystalline nature of polyester fibres makes it difficult for water to penetrate the fibre structure, and therefore polyester is one of the most difficult man-made fibres to dye. Successful dyeing methods using disperse dyes have been developed for this purpose. The most common methods that have been developed are carrier dyeing, high temperature pressurised dyeing and dry heat dyeing. [179] In each one of the dyeing methods, the rate of dye diffusion into the highly-crystalline structure of polyester was increased, by the use of carrier solvent in the case of the carrier dyeing method and the use of high temperatures in the other two dyeing methods.

In an aqueous dyebath, non-ionic disperse dyes are relatively insoluble, and transfer to the hydrophobic polyester fibres for which they have substantivity. [114] The commercial photochromic dyes investigated in this thesis are non-ionic, and therefore it was of interest to apply them to polyester fabric as disperse dyes. The series of commercial photochromic dyes (1-6) used in this investigation represents a range of colours and chemical types, as listed in Table 3.1. The exact chemical structures of the dyes are not disclosed for reasons of industrial confidentiality.

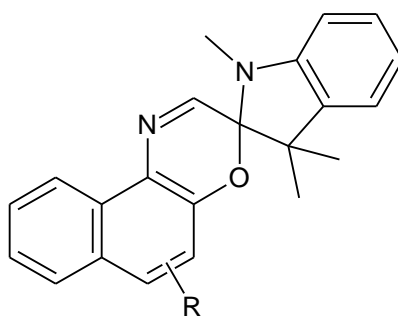
**Table 3.1** Commercial photochromic dyes

| <i>Dye</i> | <i>Commercial name</i> | <i>Chemical Type</i>           |
|------------|------------------------|--------------------------------|
| <b>1</b>   | Aqua Green             | Naphtho[1,2- <i>b</i> ]oxazine |
| <b>2</b>   | Oxford Blue            | Naphtho[1,2- <i>b</i> ]oxazine |
| <b>3</b>   | Palatinate Purple      | Naphtho[2,1- <i>b</i> ]oxazine |
| <b>4</b>   | Plum Red               | Naphtho[2,1- <i>b</i> ]oxazine |
| <b>5</b>   | Ruby                   | Naphtho[2,1- <i>b</i> ]pyran   |
| <b>6</b>   | Corn Yellow            | Naphtho[2,1- <i>b</i> ]pyran   |

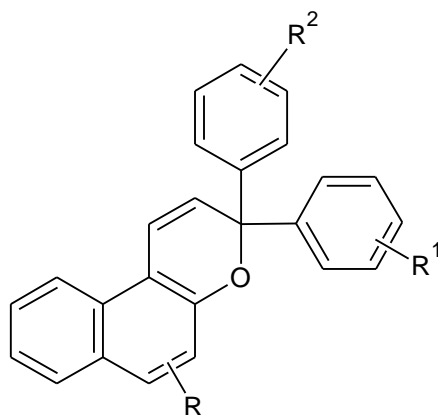
The dyes used were Aqua Green and Oxford Blue, naphtho[1,2-*b*]oxazine (Figure 3.1); Palatinate Purple and Plum Red, naphtho[2,1-*b*]oxazine (Figure 3.2); and Ruby and Corn Yellow, both based on naphtho[2,1-*b*]pyrans (Figure 3.3).



**Figure 3.1** Naphtho[1,2-b]oxazine



**Figure 3.2** Naphtho[2,1-b]oxazine



**Figure 3.3** Naphtho[2,1-b]pyran

Naphthoxazines and naphthopyrans represent two of the most important chemical classes of photochromic dyes produced industrially. [3, 31, 32] In terms of chemical structures, there are certain similarities between photochromic dyes **1-6** and the range of traditional disperse dyes used for the coloration of synthetic textile fibres, notably polyester, in that they are neutral molecules with a balance of hydrophilic and

hydrophobic character. [140, 148] A significant difference, however, is that the photochromic dyes are non-planar in their original colourless form, because the ring systems of the molecules are connected through an  $sp^3$  C-atom, so that the two halves of the molecules are orthogonal to one another. Molecular planarity is generally important in disperse dyeing to facilitate uptake and penetration into the tightly-packed crystalline structure of polyester.

## **3.2. Experimental**

For colour measurement, the specifically-devised methodology described below was used. [103]

### ***3.2.1. The optimum calibration conditions of the spectrophotometer***

Photochromic samples, at a controlled temperature, were irradiated for an appropriate time using a Philips TL20W/05 UVA bulb (emission maximum 365nm). The UV light source was set up horizontally, below which samples were mounted at a distance of 4.5 cm. Colour measurement was carried out using a Datacolor Spectraflash SF600 spectrophotometer, processed using Datamatch 3.1 software, using the small aperture, specular reflectance included and UV component excluded, under D65 illumination.

According to the spectrophotometer used in the experimental work described in this thesis, a colour difference value of 0.75 or less is considered within experimental variation. This spectrophotometer is set up, by the manufacturer, to match any two colours if the difference between them is equal to or less than 0.75.

### ***3.2.2. Temperature variations***

Temperature has been shown to have a significant effect on the equilibrium between the closed ring (spiro), and the open ring (merocyanine) forms, especially of the naphthoxazine dyes. [103] The UV light source and the spectrophotometer used for colour measurement were located in a conditioned laboratory with controlled temperature (20°C) and humidity (65%  $\pm$  2%).

### ***3.2.3. Time lapse***

As the available UV irradiation source is separate from the colour measurement instrument, it takes time to move samples to the spectrophotometer after irradiation. The fade rates of the photochromic dyes are high, so that variations in the time needed to take samples from the UV light source to the spectrophotometer has the potential to cause differences in the measurement results. In the practical procedure used, a lapse of 3 seconds is the shortest possible time between irradiation and measurement. The time

lapse was kept at 3 seconds which was achieved by operator practice. All measurements were repeated four times and averaged.

#### **3.2.4. Materials**

The fabric used was woven twill, heat-set polyester (Toray Textiles). A series of commercial photochromic dyes supplied by James Robinson from the Reversacol range was used as given in Table 3.1.

#### **3.2.5. Variation in dye concentration, dyeing time and temperature**

Dyeing of polyester fabric using different dye concentrations was carried out to investigate the effect of dyeing concentration on the degree of photocolouration and the background colours of the dyed fabrics. The concentrations investigated were 0.1, 0.2, 0.5, 1, 1.5, and 2% o.w.f. A set of experiments was carried out with Oxford Blue, as an example of the naphthooxazine dyes, and Corn Yellow, as an example of the naphthopyran dyes. Different concentrations of both dyes were applied to polyester fabric at different temperatures for different dyeing times. The degree of photocolouration was represented by  $\Delta E_1$  which is the colour difference between the background colour of the dyed fabric before irradiation with UV light and the developed colour after irradiating the fabric with UV light. The background colour of the dyed fabric was represented by  $\Delta E_2$ , which is the colour difference between the undyed fabric and the fabric after dyeing, without UV light irradiation. The UV light irradiation time was optimised by measuring  $\Delta E_1$  values of a selected dyed fabric sample after irradiation with UV light for different periods of time. The optimisation process aimed at achieving a compromise between the requirements of a high degree of photocolouration, represented by  $\Delta E_1$  values, and low background colours, represented by  $\Delta E_2$  values, of the photochromic fabrics tested. The optimum conditions were then applied to all dyes.

#### **3.2.6. Disperse dyeing of polyester with photochromic dyes by an exhaustion method**

The following general procedure was adopted. Specific conditions are given in section 3.3. Dyeing was carried out in a Pyrotec S laboratory dyeing machine with an infra-red heating system. The photochromic dye at the appropriate concentration (o.w.f) was dissolved in the minimum volume of acetone and the solution added to the aqueous dyebath solution containing Matexil DA-AC as a dispersing agent (1% o.w.f). This material assists in maintaining a stable dispersion and increases the dye solubility, and thus improving leveling by decreasing the affinity of the dye molecules for polyester

fibres. [115, 147] As described in section 3.3, acetic acid was added to adjust the pH to 4.5 in the initial experiment, although subsequently no acidification was used. The mixture was boiled for 5-10 minutes to evaporate the acetone from the dyebath. Polyester fabric (4g) was added to the dyebath. The dyebath volume was adjusted to give a liquor ratio of 50:1. Dyeing was carried out at the prescribed temperature for the prescribed time as discussed in section 3.3. After a cold water rinse, reduction clearing was carried out at 70°C for 20 minutes using an aqueous solution containing sodium hydroxide (2 g l<sup>-1</sup>), sodium dithionite (2 g l<sup>-1</sup>) and Synperonic BD100, a non-ionic surfactant (1 g l<sup>-1</sup>), at a liquor ratio of 30:1. The samples were then rinsed with water, washed with an aqueous solution of Synperonic BD100 (1 g l<sup>-1</sup>) for a few minutes, rinsed again and then air dried.

### ***3.2.7. Fading characteristics, fatigue resistance and shelf life***

#### *a) Fading time*

The optimally dyed samples were irradiated with UV light for 4 minutes and then  $\Delta E_1$  values for all samples were measured and recorded against a fading time of up to 60 minutes. Fading charts were produced and compared. These charts consist of plots of  $\Delta E_1$  versus fading time of up to 60 minutes in the dark after irradiation with UV light.

#### *b) Fatigue resistance*

The optimally dyed samples were irradiated with UV light for 4 minutes and then left in the dark for 2 hours to fade back to their original unexposed states.

This irradiation and fading cycle was repeated 20 times for each sample.  $\Delta E_1$  values were measured after 20 irradiation cycles, and then compared to the values recorded after the original UV exposure.

#### *c) Storage stability/ shelf life*

The optimally dyed samples were irradiated with UV light for 4 minutes, measured and then kept in the dark at room temperature for 170 days and re-measured.

### ***3.2.8. Colour fastness to light of polyester fabric dyed with photochromic dyes by an exhaustion method***

Lightfastness test was carried out according to BS1006: 1990, Group B. Colour Fastness to Light and Weathering B02. Colour Fastness to Artificial Light: Xenon arc fading lamp test. [180]

The lightfastness test was carried out on a Heraeus Xenotest 150S machine. Samples were cut into a size of 2×4 cm, and then attached to cards and exposed to light in the



Xenotest for periods of 0.5, 1, 2, 4, 6, 8, 12 and 24 hours. Samples were removed and assessed by colour measurement with the spectrophotometer. Calibration conditions of the spectrophotometer used were the same conditions as given in 3.2.1, except for the aperture which was changed from small to ultra small due to the small size of samples.

### ***3.2.9. Additives used in an attempt to improve lightfastness***

#### ***a) Hindered amine light stabilizers (HALS)***

Tinuvin 144 was added to the dyeing dispersion of Oxford Blue before applying to polyester fabric. The same optimum dyeing procedure for disperse dyeing of polyester with Oxford Blue, as given in sections 3.2.6 and 3.3.3 was followed, but Tinuvin 144, 0.5% o.w.f, was dissolved with the dye in acetone before adding the solution to the dispersion bath.

Eversorb 90 (0.5% o.w.f) was applied with Oxford Blue in the same way as with Tinuvin 144.

To investigate the optimum concentration of Tinuvin 144 that could provide the maximum improvement in the light fastness of Oxford Blue applied to polyester fabric by the exhaustion method, Oxford Blue (0.5% o.w.f) was applied to polyester with the following different concentrations of Tinuvin 144, 0.1%, 0.2%, 0.5%, 1%, 1.5% and 5% o.w.f.

All dyes were then applied to polyester, at their optimum concentrations, by the exhaustion method with the optimum concentration of Tinuvin 144 (0.5% o.w.f).

#### ***b) UV absorbers***

Tinuvin P (0.5% o.w.f) was applied with the spironaphthooxazine dyes in the same way as with Tinuvin 144 and Eversorb 90.

#### ***c) UV absorbers + HALS***

A mixture of Tinuvin P (0.5% o.w.f) and Tinuvin 144 (0.5% o.w.f) was applied with Oxford Blue (0.5% o.w.f) to polyester fabric by the exhaustion method.

### ***3.2.10. Colour fastness to washing of polyester fabric dyed with photochromic dyes by the exhaustion method***

Washfastness test was carried out according to the British standard BS1006:1990, Group C. Colour Fastness to Domestic and Commercial Laundering. A solution of 5 g l<sup>-1</sup> standard soap and 2 g l<sup>-1</sup> sodium bicarbonate in water was prepared. Dyed polyester samples were placed in the container of the Roaches Washtec-P washfastness test machine. The necessary amount of soap solution previously heated to the specific test temperature was added to give a liquor ratio of 50:1. Samples were treated in the

solution at the specific temperature for a specific time (Test 1: Temperature 40°C, time 30 minutes; Test 3: Temperature 60°C, Time 30 minutes). Samples were removed from the containers, rinsed twice with distilled water, and then with cold, running tap water for 10 minutes, then squeezed and air dried. [181]

*a) Test 1 (Temperature 40°C, time 30 minutes)*

Samples of the six dyes applied to polyester were washed in the washing solutions for 30 minutes at a temperature of 40°C. After rinsing and air drying, samples were measured on the spectrophotometer.  $\Delta E_1$  values were recorded for washed fabrics and compared to the values of  $\Delta E_1$  of the non-washed fabrics.

*b) Test 3 ( Temperature 60°C, Time 30 minutes)*

Samples of the six dyes applied to polyester were washed in the washing solutions for 30 minutes at a temperature of 60°C. After rinsing and air drying, samples were measured on the spectrophotometer.  $\Delta E_1$  values were recorded for washed fabrics and compared to the values of  $\Delta E_1$  of the non-washed fabrics.

### ***3.2.11. Carrier dyeing of polyester with photochromic dyes***

All the photochromic dyes were applied to polyester fabric at their optimum concentrations by a carrier dyeing method. Benzyl alcohol was selected to be used as a carrier.

*a) Materials*

Photochromic dyes at their optimum dyeing concentrations, as identified in section 3.3.5

Benzyl alcohol (3 g l<sup>-1</sup>)

Dispersing agent (1% o.w.f)

Water (50:1 o.w.f)

*b) Carrier dyeing procedure*

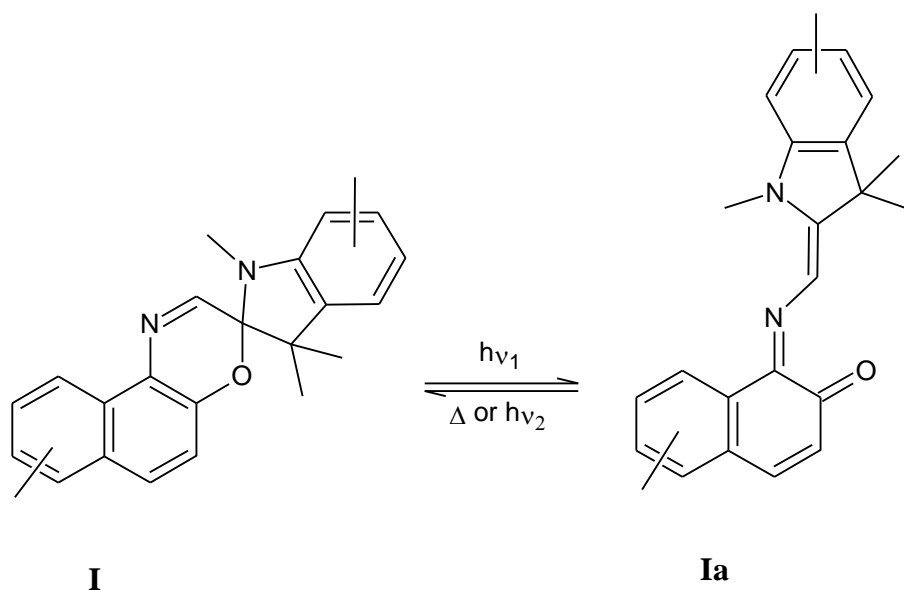
Dyeing was carried out in a Pyrotec S laboratory dyeing machine with an infrared heating system. The photochromic dyes, at their optimum concentrations, were dissolved in minimum volumes of acetone and the solutions were added to the aqueous dyebath solutions containing Matexil DA-AC as a dispersing agent (1% o.w.f). The mixtures were boiled for 5-10 minutes to evaporate the acetone from the dyebath. The dyebath volumes were adjusted to give a liquor ratio of 50:1. Polyester fabric (4g) was added to each dyebath. The dyebath temperature was increased to 65°C, and then benzyl alcohol (the carrier solvent) was added. The dyeing bath was heated to 100°C at a rate of 1°C/min. Dyeing was carried out at a temperature of 100°C for 90 minutes. After a

cold water rinse, reduction clearing was carried out in the same way as described in section 3.2.6. The samples were then rinsed with water, washed with aqueous solutions of Synperonic BD100 ( $1 \text{ g l}^{-1}$ ) for a few minutes, rinsed again and then air dried.

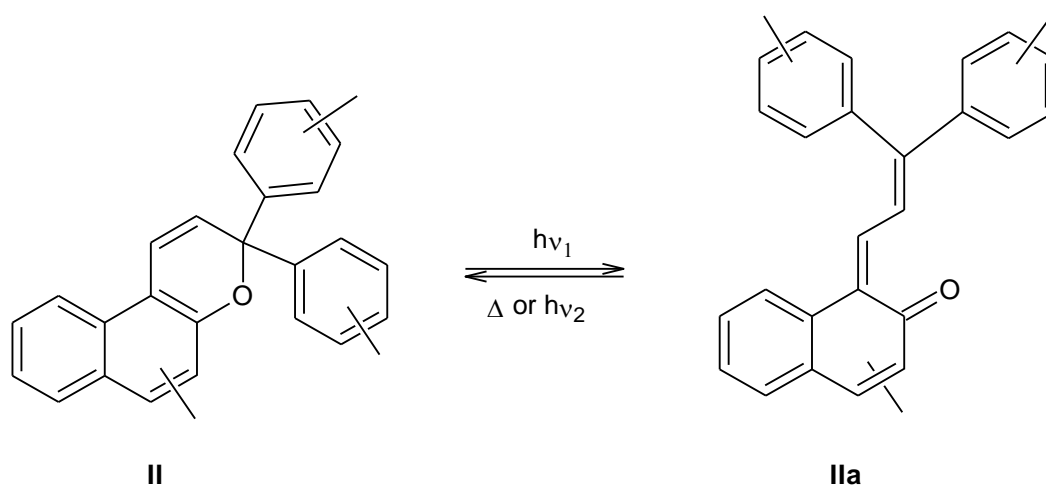
### 3.3. Results and Discussion

#### 3.3.1. Dyeing at a temperature of $120^{\circ}\text{C}$ ; dyeing time of 45 minutes

For a preliminary investigation of the dyeing performance of the photochromic dyes applied to polyester fabric by an exhaustion method, aqueous dispersions of Oxford Blue and Corn Yellow dyes were prepared, adjusted to pH 4.5 with acetic acid, and dyeing was carried out at a concentration of 1% (o.w.f.) and a temperature of  $120^{\circ}\text{C}$  for 45 minutes. The normal recommended conditions for dyeing polyester by the high temperature dyeing method are: temperature  $125\text{-}130^{\circ}\text{C}$ ; time 30-60 minutes. [140, 182] A lower temperature of  $120^{\circ}\text{C}$ , and an intermediate time of 45 minutes were selected initially to ensure that the photochromic dyes were applied under mild conditions, and thus to minimise the possibility of dye degradation at dyeing conditions. These initial conditions used are referred to as conditions D in a subsequent investigation aimed at an optimized procedure (see Table 3.2 and section 3.3.3). Oxford Blue and Corn Yellow were selected as representatives of the spironaphthoxazine and naphthopyran classes respectively.



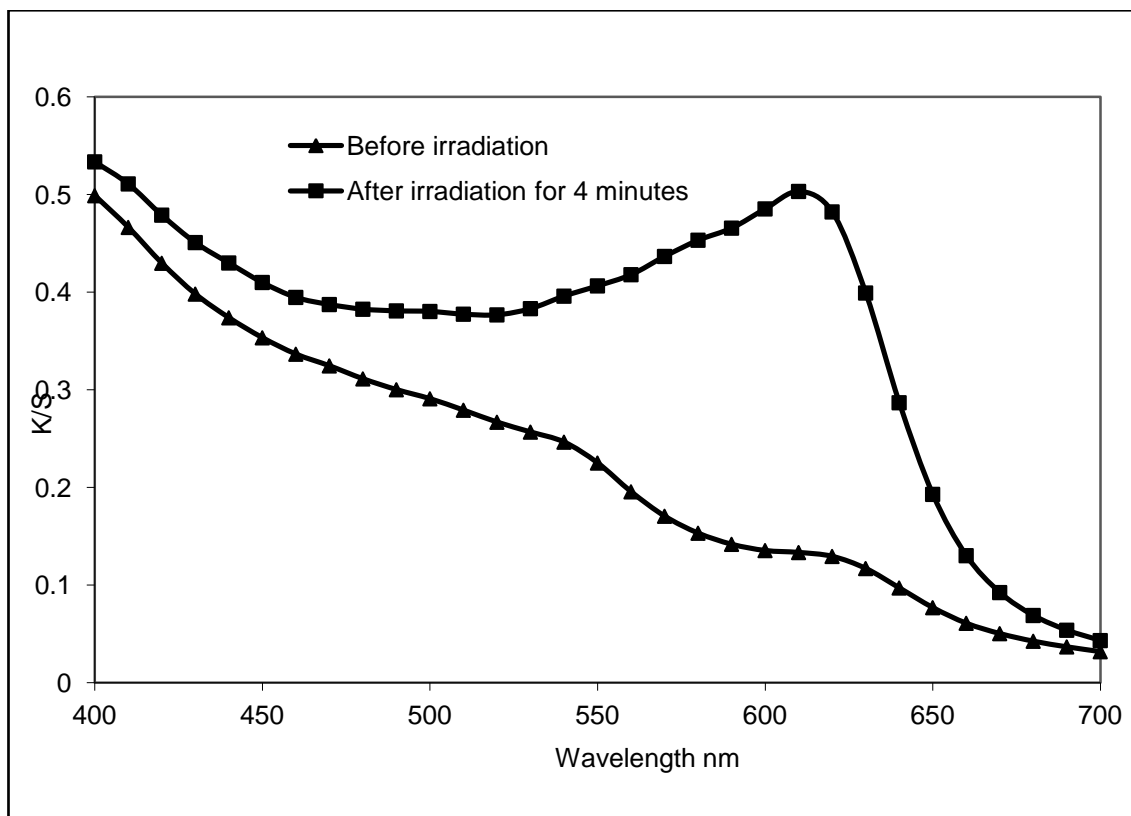
**Scheme 3.1** The photochromism of spironaphthoxazines (I)



**Scheme 3.2** The photochromism of naphthopyrans (II)

Generalised structures of the spironaphthoxazine (**I**) and naphthopyran (**II**) dye classes are shown respectively in Schemes 3.1 and 3.2, which also illustrate the mechanism of the photoinitiated conversion to the coloured forms. The photochromism of both dye classes involves the UV-initiated cleavage of a C-O bond resulting in the formation of an approximately planar ring-opened structure which has extended  $\pi$ -conjugation giving rise to absorption of light in the visible region. Schemes 3.1 and 3.2 show only one of several possible isomers of the coloured forms (**Ia** and **IIa** respectively). In fact, the ring-opening is believed initially to proceed through metastable cisoid isomers which subsequently rearrange to one or more of the more stable transoid isomers, such as those illustrated. [1]

Two measured colour difference values were used.  $\Delta E_1$  refers to the colour difference between the background colour and the colour developed on irradiating the photochromic fabric with the UV light, as a measure of the degree of photocolouration.  $\Delta E_2$  refers to the colour difference between the undyed and dyed polyester fabric before UV irradiation, as a measure of the background colour developed as a result of the dyeing process. Under these initial dyeing conditions, Oxford Blue gave a relatively weak coloured polyester fabric ( $\Delta E_2 = 11.0$ ) which became a moderately intense blue when irradiated with UV light for 3 minutes ( $\Delta E_1 = 20.2$ ). Weakly acidic conditions were used in these initial experiments which is typical in traditional disperse dyeing of polyester, to minimize degradation of the dyes by hydrolysis or reduction. [140]



**Figure 3.4** K/S Curves for Oxford Blue (1% o.w.f) applied to polyester fabric by the exhaustion method

Another method for representing colour change is shown in Figure 3.4, which is a plot of K/S against wavelength, as a means of illustrating colour strength difference between background and developed colour.

The  $\Delta E_1$  value of 20.2 and the K/S difference between background and developed colour, as shown in Figure 3.4, indicate a significant colour change attributed to the ring opening reaction of the dye molecules inside the polyester fibres under the influence of the UV light.

### ***3.3.2. Dyeing at neutral conditions pH~7, temperature 120°C and time 45 minutes - Conditions D***

When Oxford Blue was applied under the same conditions but at neutral pH, the background colour was reduced ( $\Delta E_2 = 8.6$ ), while a similar degree of photocoloration was observed ( $\Delta E_1 = 19.9$ ). In view of the possibility indicated by this result, that the dye may be unstable to aqueous acidic conditions at elevated temperatures contributing towards the development of background colour, neutral dyeing conditions were used subsequently.

### 3.3.3. Investigation of dyeing conditions

In order to investigate further the effect of dyeing conditions, a set of experiments was carried out in which Oxford Blue and Corn Yellow were applied at different temperatures and for different times, as given in Table 3.2.

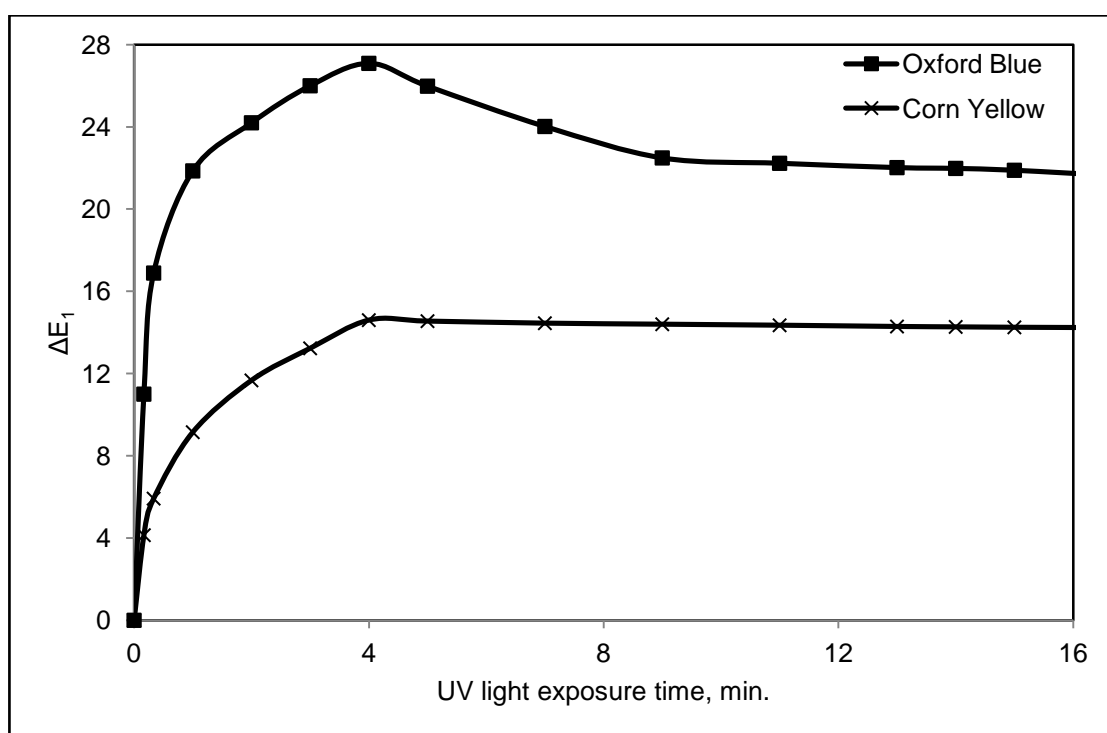
**Table 3.2** Degree of photocoloration ( $\Delta E_1$ ) and background colour ( $\Delta E_2$ ) of polyester dyed with Oxford Blue and Corn Yellow (1% o.w.f) by the exhaustion method

| <i>Dyeing Conditions</i> | <i>Oxford Blue</i> |              | <i>Corn Yellow</i> |              |
|--------------------------|--------------------|--------------|--------------------|--------------|
|                          | $\Delta E_1$       | $\Delta E_2$ | $\Delta E_1$       | $\Delta E_2$ |
| A (130°C, 20min)         | 24.8               | 10.0         | 13.2               | 16.7         |
| B (130°C, 45min)         | 18.1               | 10.4         | 10.0               | 17.0         |
| C (120°C, 20min)         | 12.9               | 8.0          | 6.3                | 15.0         |
| D (120°C, 45min)         | 19.9               | 8.6          | 10.1               | 14.9         |

The aim of the study was to maximize the degree of photocoloration while minimizing the background colour. The results are also given in Table 3.2. Fabrics dyed with Oxford Blue at 130°C (conditions A and B) showed similar background colours but a significantly higher degree of photocoloration with the shorter dyeing time (conditions A). With these dyes applied at 120°C (conditions C and D), lower background colours appear to be achievable, but the degree of photocoloration is also lower. Fabrics dyed with Corn Yellow showed a higher background colour and a reduced level of photocolorability compared with Oxford Blue under all conditions. Indeed, with Corn Yellow under all application conditions the colour difference ( $\Delta E_1$ ) between the background colour and the colour developed with UV irradiation is smaller than the colour difference ( $\Delta E_2$ ) between the undyed and dyed polyester fabric before UV irradiation. The results for both dyes indicate that an optimum photochromic effect may be achieved when the dyes are applied at the higher temperature for a shorter time. Thus, conditions A were selected as optimal for all subsequent dyeing experiments, although this involves an element of compromise in view of the slightly higher background colour obtained at the higher application temperature, especially with Corn Yellow. A number of factors may be proposed to explain these observations. The non-planar molecular structures of the dyes limit their ability to penetrate into the crystalline polyester fibres, although exhaustion is enhanced, as expected, at the higher temperature. Two factors may influence the development of a background colour on the unexposed fabric. The first of these is a degree of thermochromism resulting in the

formation of the ring-opened planar coloured form of the dye at the high application temperature which is above the glass transition temperature ( $T_g$ ) of polyester. The dye molecules become fixed in this form within the crystalline structure of polyester as it cools below its  $T_g$ , giving rise to a permanent colour. More details about  $T_g$  are given in section 2.7. This may well be the dominant factor. A second factor is possible thermal instability of the dyes under the aqueous application conditions at elevated temperatures. Both of these effects will be more significant as the temperature is raised. The thermal instability of the dyes may also explain the reduced degree of photocolouration with increased dyeing time at the higher temperature.

### 3.3.4. Optimisation of UV light irradiation time



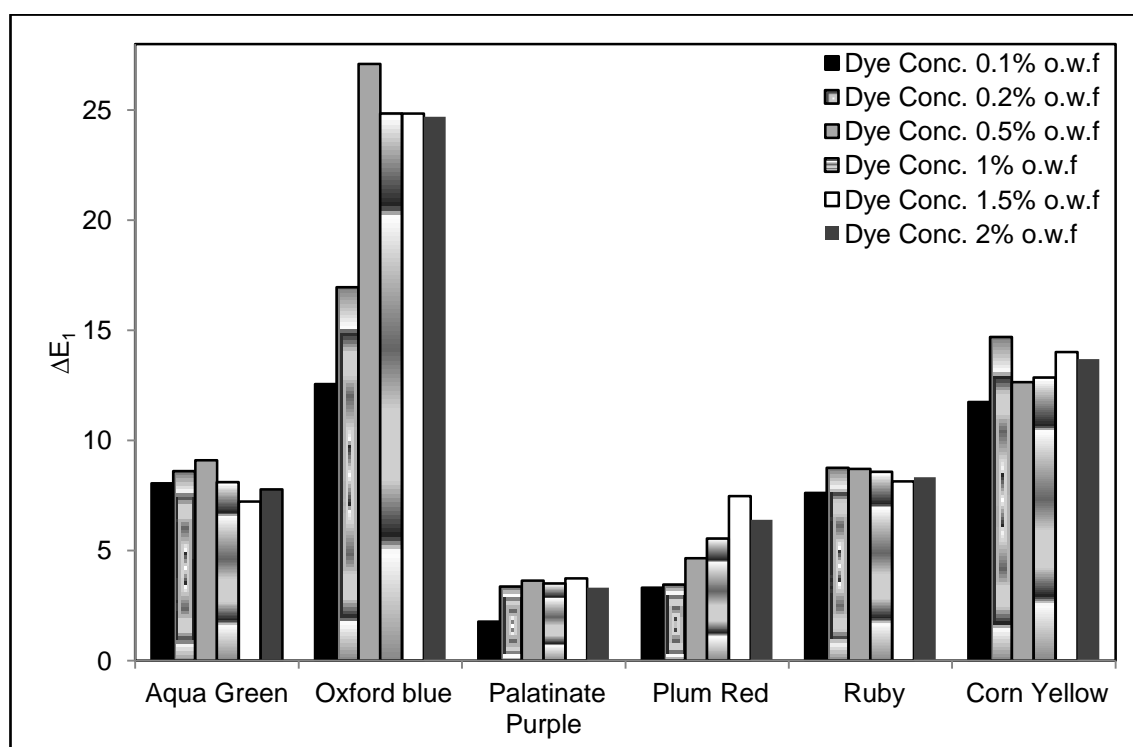
**Figure 3.5** Degree of photocolouration, with increased UV light irradiation time, of polyester fabric dyed with Oxford Blue and Corn Yellow (1% o.w.f)

The colour development properties of polyester dyed with Oxford Blue and Corn Yellow under the optimal conditions at a dye concentration of 1% o.w.f are illustrated in Figure 3.5. Both dyed fabrics show fairly rapid colour development initially, leveling to a maximum  $\Delta E_1$  value after around 4 minutes in both cases. The slight decrease in  $\Delta E_1$  with extended UV exposure, more pronounced with Oxford Blue, is likely to be associated with experimental difficulties in controlling the tendency of the dyed fabrics to rise marginally in temperature with prolonged exposure under the UV lamp, which

will accelerate the thermal reverse reaction leading to a reduction in colour strength. It has been reported previously that the photochromism of spironaphthoxazines, such as Oxford Blue, is more sensitive to temperature than that of naphthopyrans such as Corn Yellow. [1, 103] On the basis of this observation, a UV exposure time of 4 minutes was used for subsequent studies.

### 3.3.5. Degree of photocoloration and background colours of all dyes applied to polyester fabric by an exhaustion method at different dyeing concentrations

The degree of photocoloration ( $\Delta E_1$ ) for all dyes applied to polyester under the conditions optimised for Oxford Blue and Corn Yellow, after 4 minutes of UV light exposure and the background colours ( $\Delta E_2$ ) are illustrated in Figures 3-6 and 3.7 respectively.

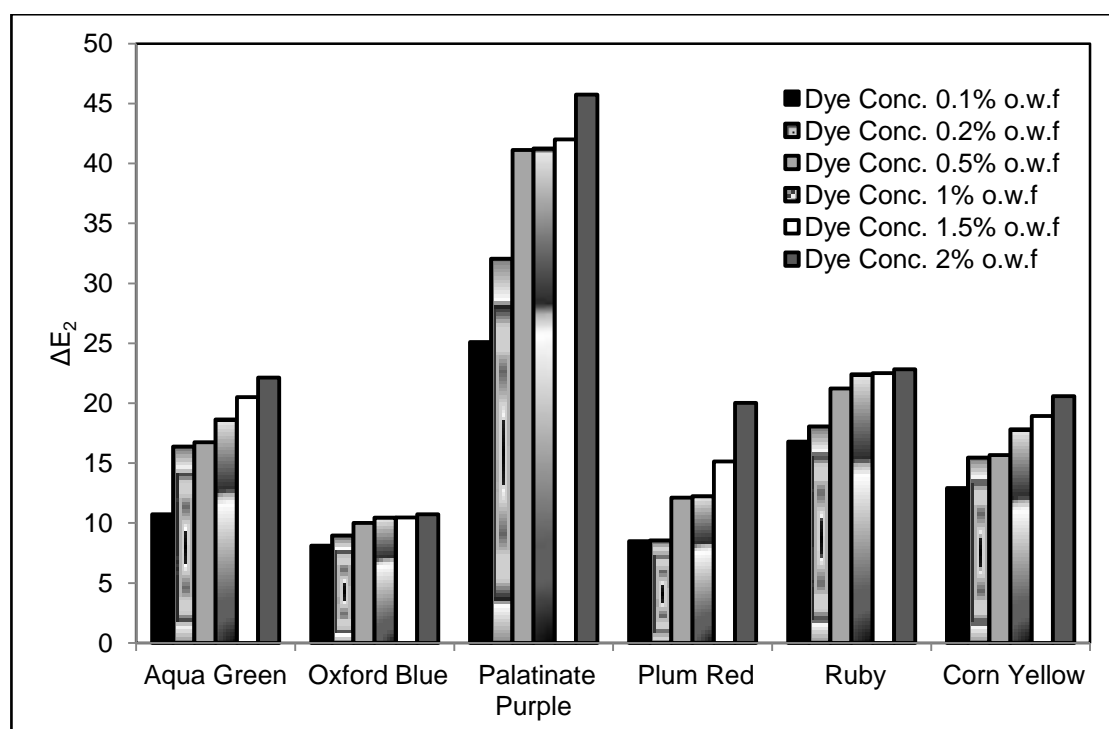


**Figure 3.6** Degree of photocoloration ( $\Delta E_1$ ) for all dyes applied to polyester by an exhaustion method

Figure 3.6 shows that the photochromic response varies considerably with the particular dye. Oxford Blue, a spironaphthoxazine, gives by far the highest degree of photocoloration, followed by Corn Yellow, a naphthopyran. Palatinate Purple, a naphthoxazine, gives the weakest colour change. There is thus no apparent correlation between the degree of photocoloration and the chemical class of dye, implying that this property is specific to particular chemical features of the individual dye structures.

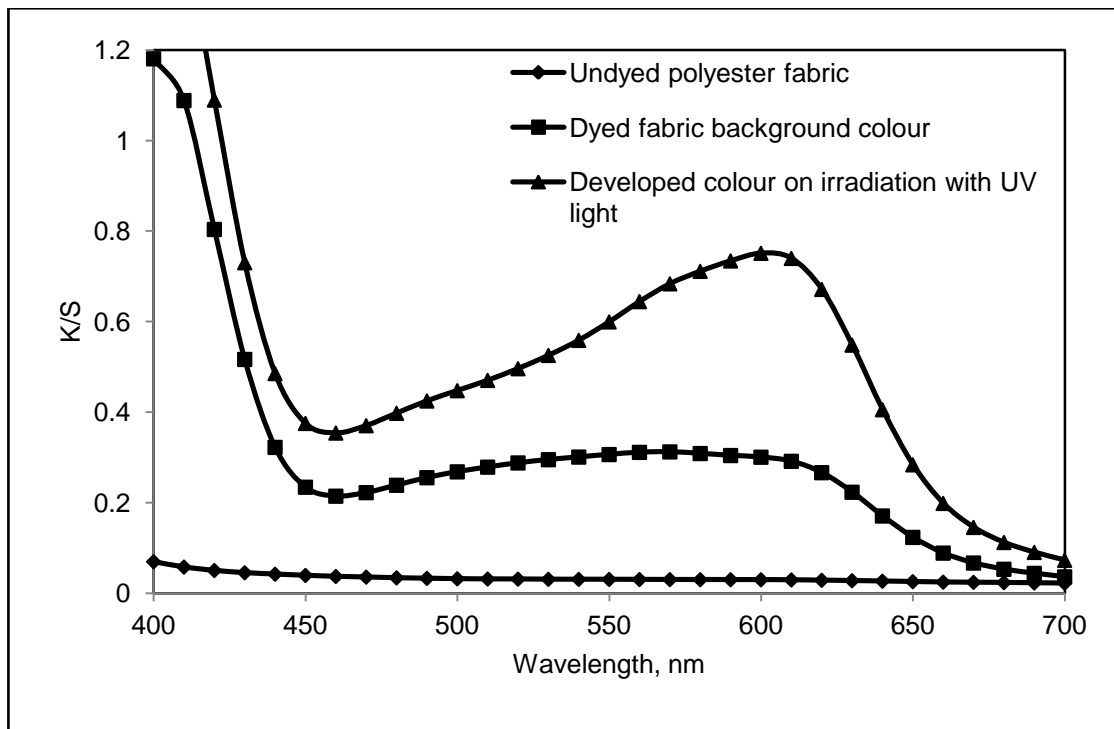


There is in all cases an initial increase in the degree of photocoloration with increasing concentration, although in general it does not increase further above concentrations of 0.2-0.5%. One reason may be that the dyes in their highly non-planar ring-closed form are unable to exhaust further under the conditions used, especially with the short dyeing time. A further possibility is that the dye may be located mainly close to the surface, leading to suppression of photochromism through aggregation effects at higher concentrations. There is thus no advantage in applying the dyes at a higher concentration.

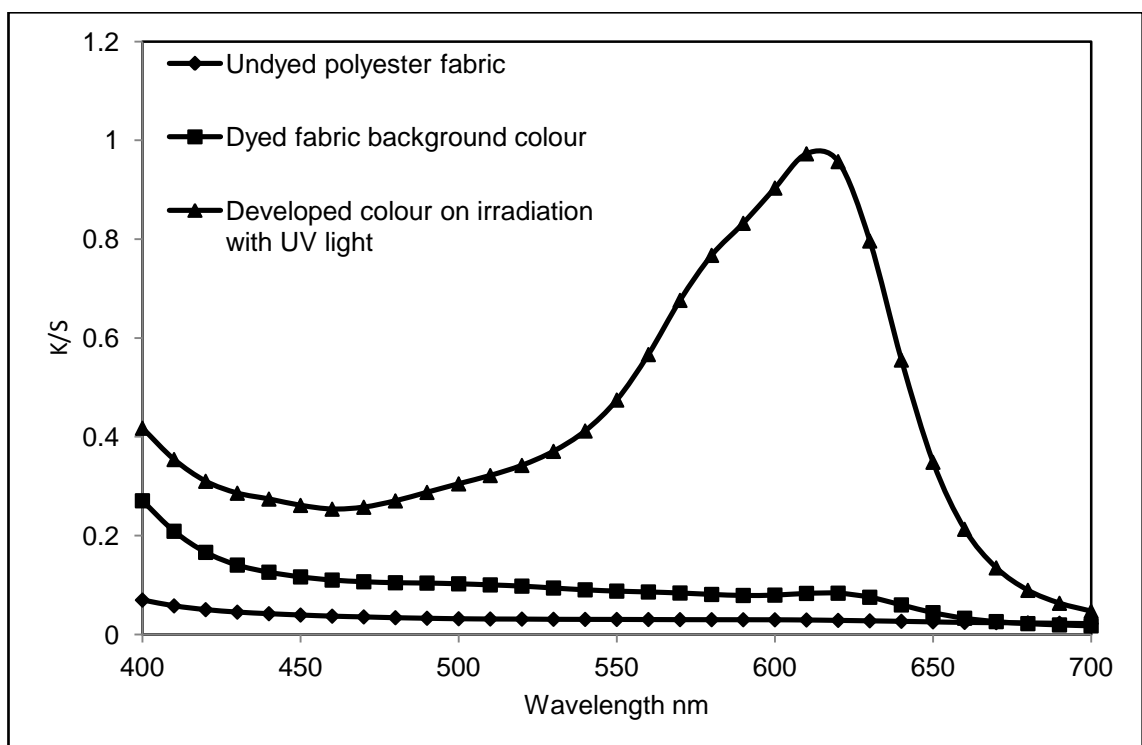


**Figure 3.7** Background colours ( $\Delta E_2$ ) for all dyes applied to polyester by an exhaustion method

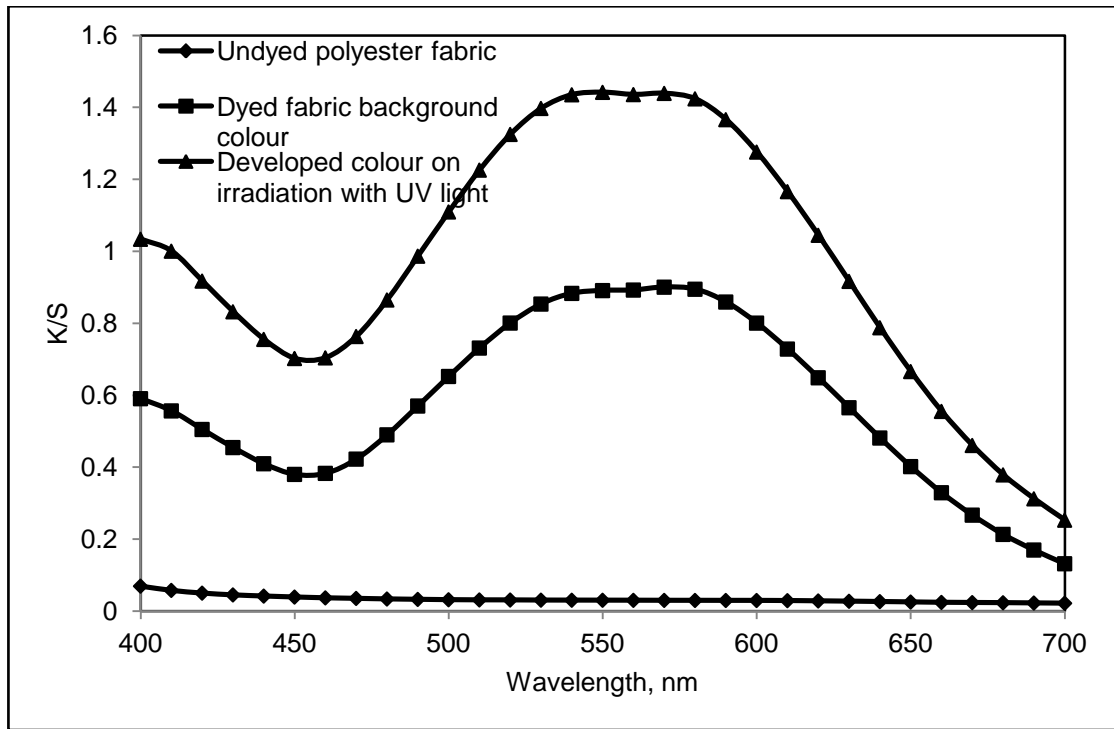
In fact, as illustrated in Figure 3.7, the level of background colour increases more or less steadily with dye concentration in all cases, possibly because the thermally-generated planar coloured form of the dye continues to exhaust on to the fabric as the concentration is increased. On the basis of attempting to maximize  $\Delta E_1$  while minimizing  $\Delta E_2$ , it was considered that the optimal dyeing concentrations were 0.2% o.w.f for Palatinate Purple, Plum Red, Ruby and Corn Yellow, and 0.5% o.w.f for Aqua Green and Oxford Blue, with an element of compromise being required in some cases. Palatinate Purple proved to be particularly unsuccessful in this application, giving a fairly strong background colour and limited colorability.



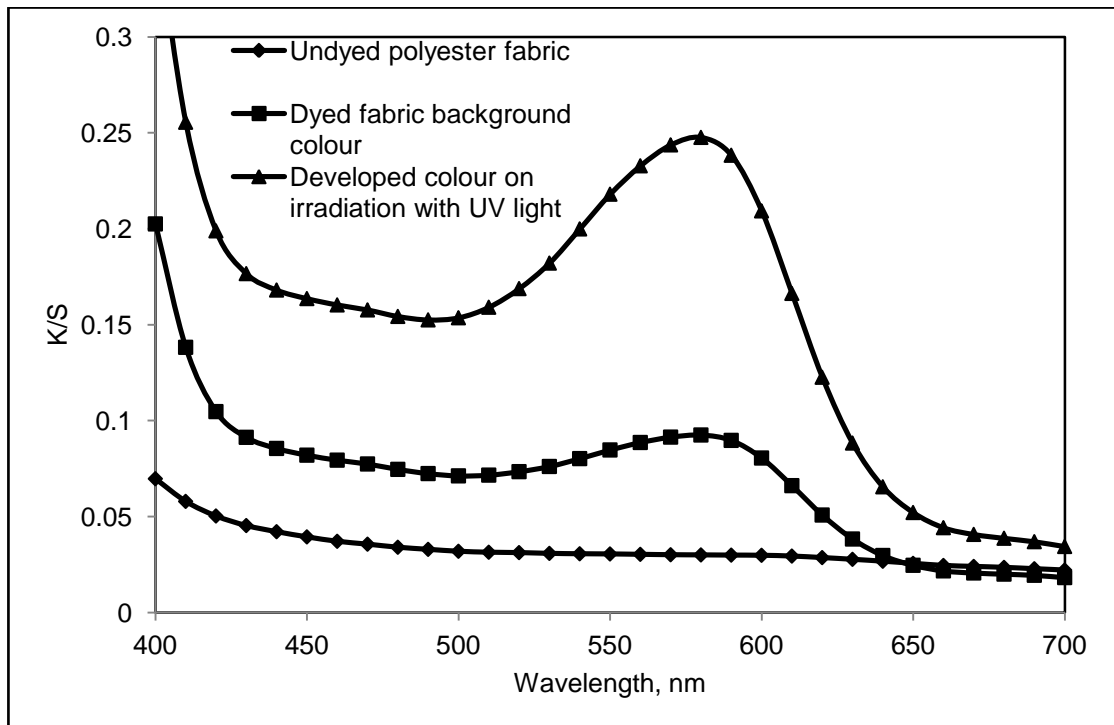
**Figure 3.8** K/S curves for polyester fabric dyed with Aqua Green (0.5% o.w.f) before and after UV light exposure for 4 minutes



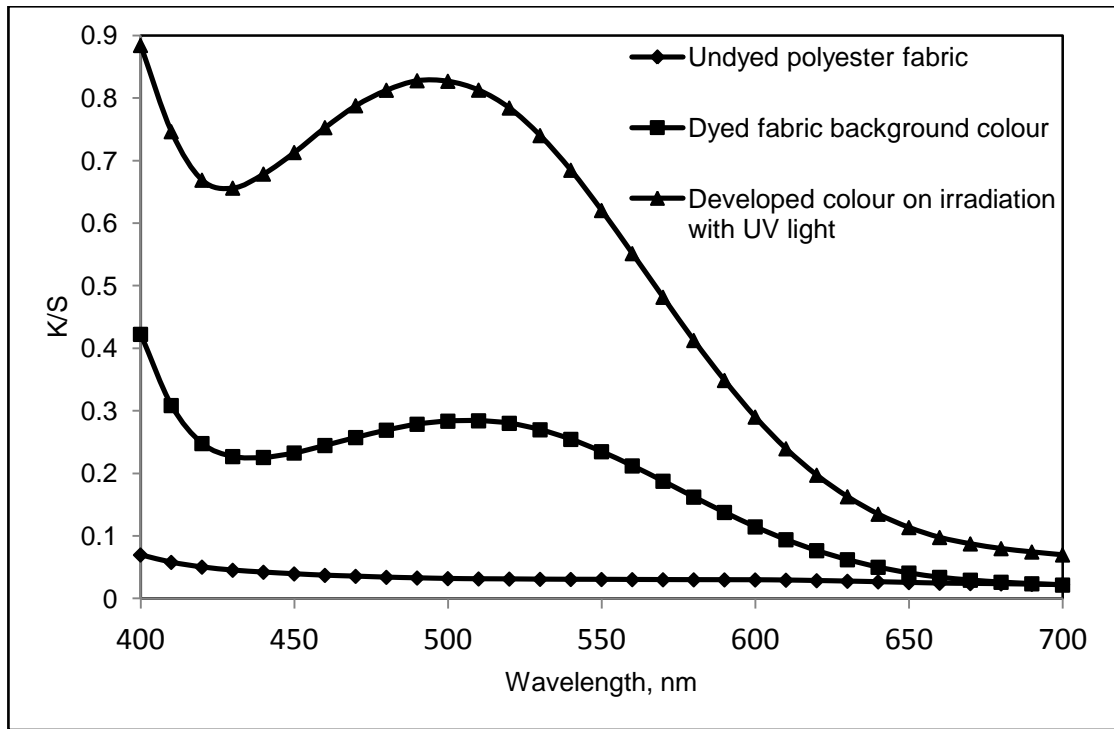
**Figure 3.9** K/S curves for polyester fabric dyed with Oxford Blue (0.5% o.w.f) before and after UV light exposure for 4 minutes



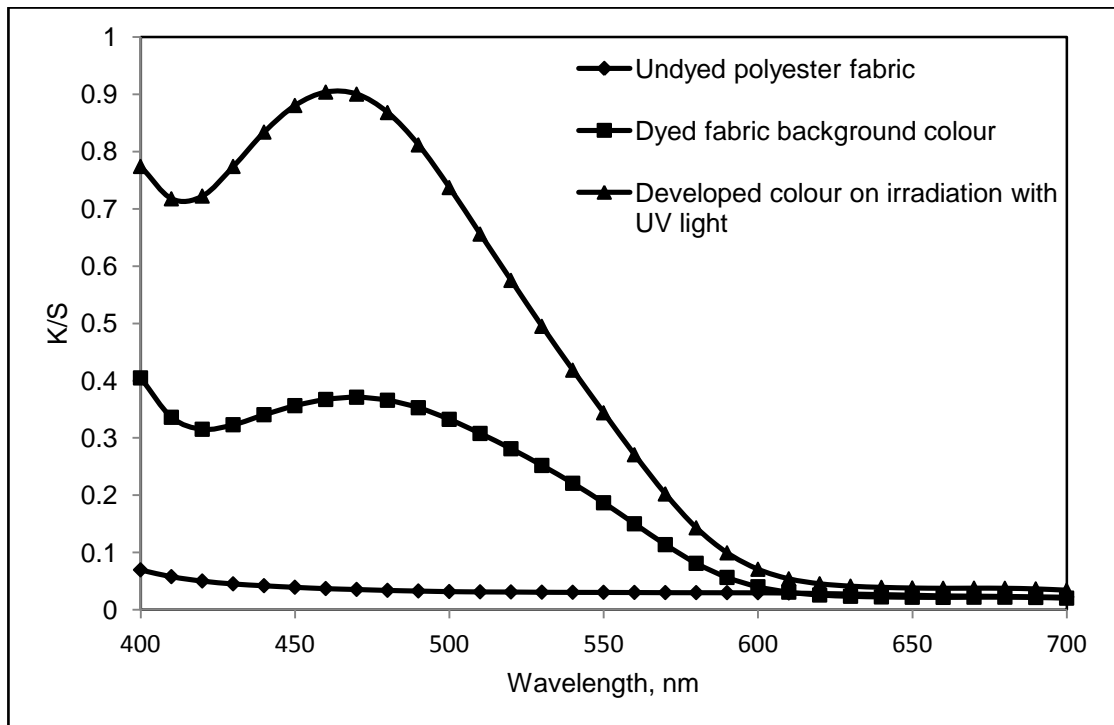
**Figure 3.10** K/S curves for polyester fabric dyed with Palatinate Purple (0.2% owf) before and after UV light exposure for 4 minutes



**Figure 3.11** K/S curves for polyester fabric dyed with Plum Red (0.2% o.w.f) before and after UV light exposure for 4 minutes



**Figure 3.12** K/S curves for polyester fabric dyed with Ruby (0.2% owf) before and after UV light exposure for 4 minutes



**Figure 3.13** K/S curves for polyester fabric dyed with Corn Yellow (0.2% o.w.f) before and after UV light exposure for 4 minutes

Figures 3.8 – 3.13 show the degree of photocolouration and the developed background colours, in these cases expressed as K/S curves, for all dyes applied to polyester fabric by an exhaustion method at the optimum concentrations and under optimised conditions. They demonstrate that Oxford Blue produces pronounced photocolouration from a weak background colour, while the background colour is much more pronounced with Corn Yellow. The similarity between the K/S curves for the background and developed colours for all dyes are consistent with the background colour being derived mainly from the ring-opened structure.



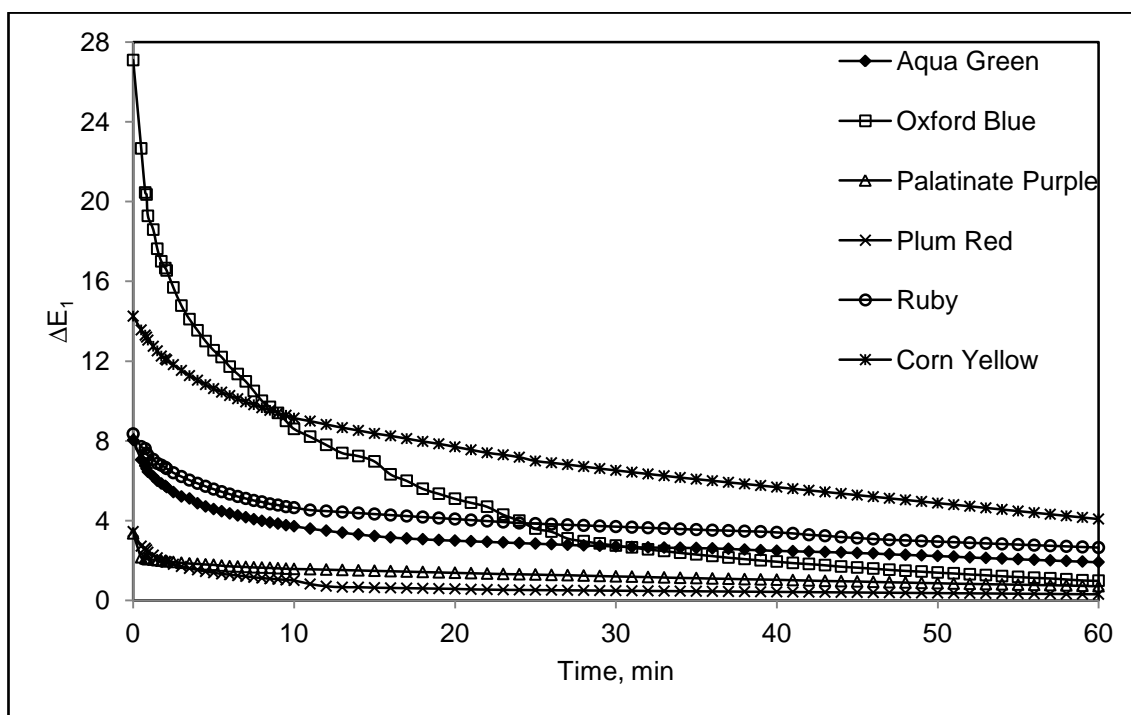
**Figure 3.14** Polyester fabric dyed with Aqua Green by the exhaustion method



**Figure 3.15** Polyester fabric dyed with Oxford Blue by the exhaustion method

Figures 3.14 and 3.15 show photographs taken of the background colours and developed colours after irradiation with UV light of polyester dyed with Aqua Green and Oxford Blue respectively in an attempt to provide an illustration of the colour change. Photographs were taken within 5 seconds after removing the samples from the UV light exposure area. Practically, significant difficulties were encountered in obtaining clear photographs for other dyes applied to polyester, because under the available light conditions the colour difference did not reproduce well in the photographs. Photographs of polyester dyed with Aqua Green and Oxford Blue are thus presented as examples of the visually-observed colour differences, under the UV light irradiation, of polyester fabric dyed with photochromic dyes by the exhaustion method.

**3.3.6. Fading time of polyester fabric dyed with all dyes applied by the exhaustion method**



**Figure 3.16** Fading curves all dyes applied to polyester fabric by the exhaustion method

Figure 3.16 illustrates how the photochromic polyester fabrics, dyed with all dyes at their optimal concentrations and exposed to UV light for 4 minutes, fade over a period of 60 minutes after the UV light source is removed. Spiroanthoxazines Aqua Green, Oxford Blue, Palatinate Purple and Plum Red fade quite rapidly after removal of the UV source, with naphthopyrans Ruby and Corn Yellow fading rather more slowly, a factor which has been observed previously with fabrics screen-printed by this set of dyes. [103] However, the fading is rather slower than observed with screen printing, and the

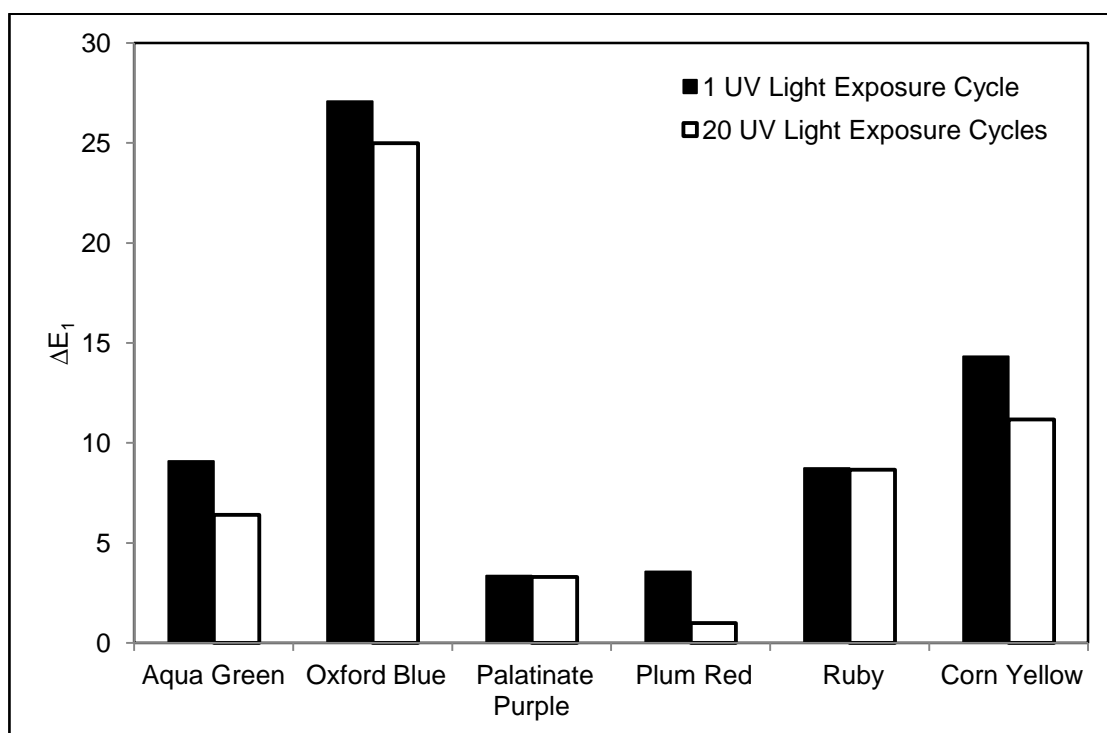
dyed fabrics continue to show some residual colour after fading for a few hours, especially Ruby and Corn Yellow.

**Table 3.3** Residual colour during fading, after removal of UV source, over several hours with all dyes applied to polyester

| <i>Dye</i>           | $\Delta E_1$   |                |                |                 |
|----------------------|----------------|----------------|----------------|-----------------|
|                      | <i>2 Hours</i> | <i>3 Hours</i> | <i>4 hours</i> | <i>24 Hours</i> |
| Aqua Green           | 1.0            | 0.8            | 0.7            | 0.3             |
| Oxford Blue          | 1.7            | 1.4            | 1.0            | 0.4             |
| Palatinate<br>Purple | 0.6            | 0.5            | 0.4            | 0.3             |
| Plum Red             | 0.2            | 0.2            | 0.1            | 0.1             |
| Ruby                 | 2.6            | 2.2            | 1.5            | 0.7             |
| Corn Yellow          | 2.9            | 2.0            | 1.3            | 0.7             |

Table 3.3 illustrates the residual colours which remain over several hours after removal of the UV source from the irradiated fabrics, measured as  $\Delta E_1$  values, the colour difference between the samples and their original unexposed states. The observation that the naphthopyrans show perceptible residual colours for longer than the spironaphthoxazine dyes may simply be due to the kinetics of fading of these particular dyes. However, it has also been reported that certain naphthopyran-based photochromic dyes may form two different stable, coloured isomers on irradiation, the major component, a short-lived, strongly coloured species, which is the *transoid-cis* isomer, and the minor component, a long-lived, paler coloured *transoid-trans* isomer. [102, 183-185] All dyed samples had effectively returned to their original state after 24 hours in the dark, as judged by a  $\Delta E_1$  value of less than 0.75. According to the recommendations associated with the spectrophotometer used in the experimental work in this thesis, a colour difference value of 0.75 or less is considered within experimental variation, as mentioned in section 3.2.1.

### 3.3.7. *Fatigue resistance of polyester fabric dyed with all dyes by an exhaustion method*



**Figure 3.17** Fatigue resistance of all dyes applied to polyester fabric by the exhaustion method

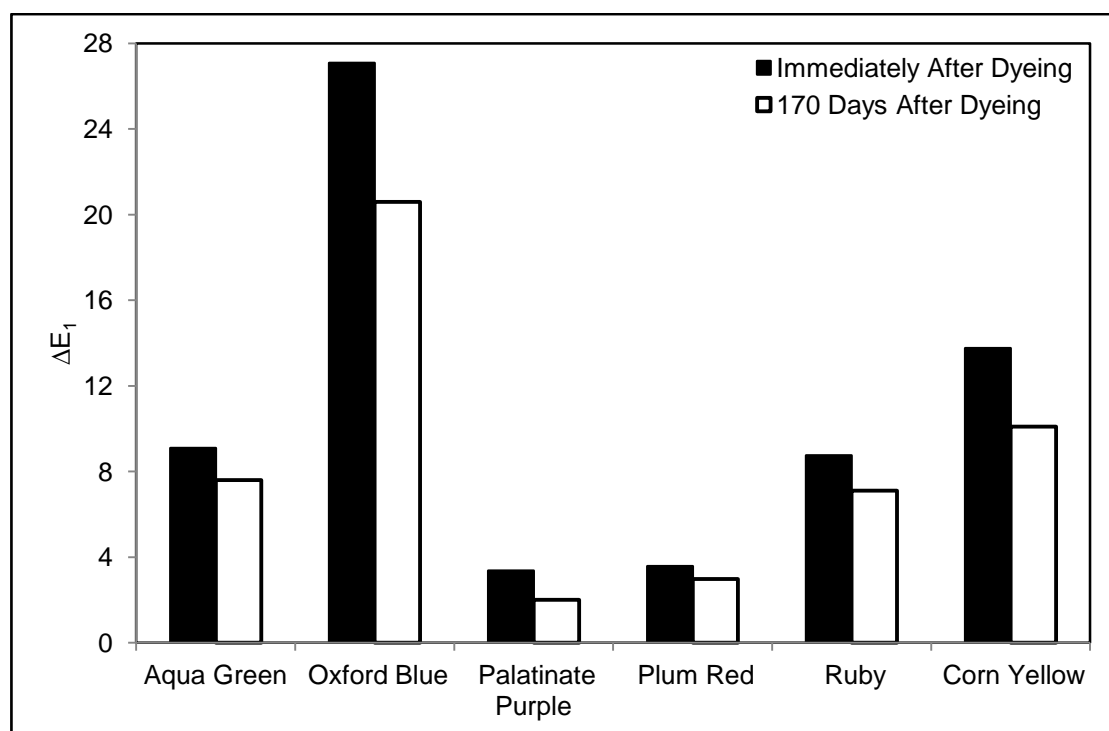
Fatigue resistance was assessed as the ability of the dye to retain its ability to undergo UV-induced coloration after repeated exposure/fading cycles. Figure 3.17 shows that after 20 cycles of exposure to UV light for 4 minutes in each case followed by fading in the dark for 2 hours, the dyed fabrics retained their photochromic response to different extents. Ruby was of particular interest in showing virtually no deterioration during this test while Oxford Blue and Palatinate Purple retained more than 90% of the photochromic response. Aqua Green and Corn Yellow showed 70-80% retention of photocolouration, while Plum Red exhibited rather low fatigue resistance in this application. There is no obvious correlation of this property with the chemical class of the dye.

### 3.3.8. *Storage stability of polyester fabric dyed with all dyes by an exhaustion method*

Ageing or storage stability of the dyed fabrics was assessed by retaining the fabric samples in the dark at room temperature and re-measuring after 170 days. This evaluation would not normally be relevant with traditionally-dyed fabric, but is of interest with photochromic fabric, because it has been observed that these special dyes



are generally significantly less stable than traditional dyes. The test complements the fatigue resistance tests, providing information on the potential longevity of products exposed to UV light infrequently or only intermittently in their lifetime.



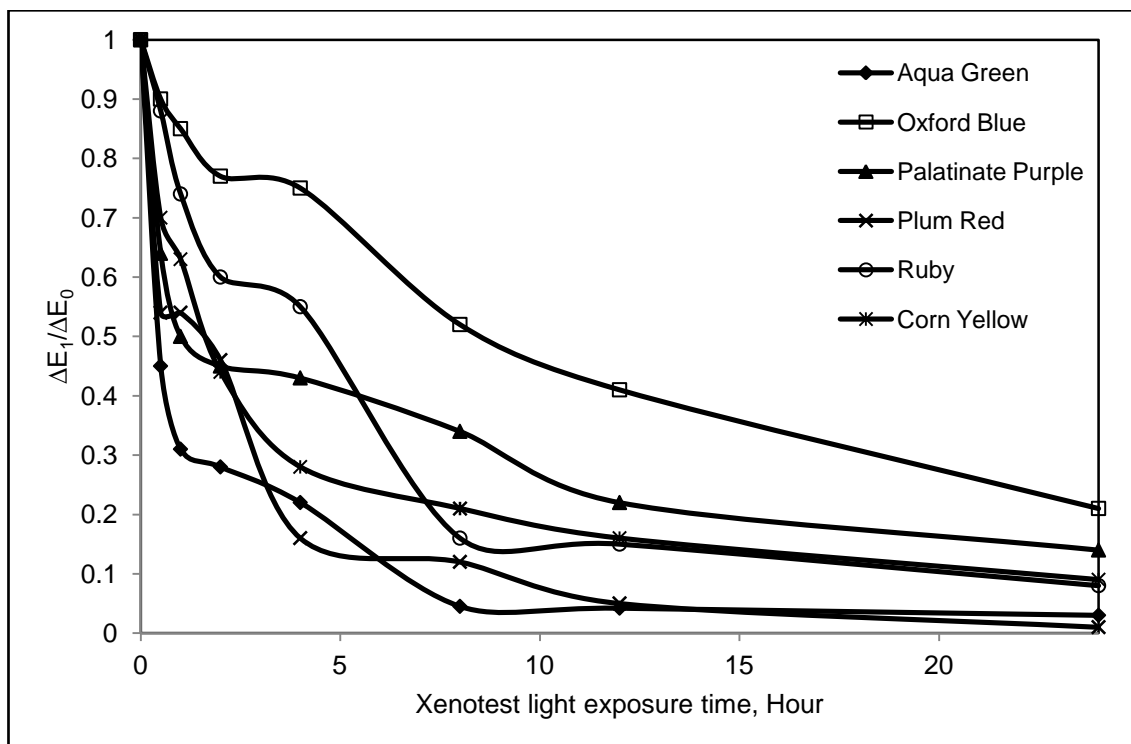
**Figure 3.18** Storage stability of all dyes applied to polyester fabric by the exhaustion method

Figure 3.18 shows a comparison between the degree of photocoloration of each dyed fabric on the day of dyeing and after 170 days of dark storage. The level of photocoloration retained by the dyes after this time was found to be in the range 60-84%, Aqua Green giving the best retention (84%) and Palatinate Purple the lowest (60%).

### ***3.3.9. Colour fastness to light of polyester fabric dyed with photochromic dyes by an exhaustion method***

The test provides an assessment of the resistance of colours of textiles of all kinds and in all forms to the action of an artificial light source representative of natural daylight. [180] The blue wool scale, which is routinely used to assess this property of traditionally dyed fabrics, was unsuitable as a means of assessing lightfastness in the case of photochromic dyes, because of the dynamic colour changing nature of samples dyed with these dyes. Instead of the blue wool scale, colour measurement was employed to assess the lightfastness by measuring  $\Delta E_1$  values between background and developed

colours for samples exposed to the Xenotest light and comparing them with those measured without light exposure.



**Figure 3.19** Normalized lightfastness curves for all dyes applied to polyester fabric by an exhaustion method

For this purpose, the degree of photocoloration, represented by  $\Delta E_1$  values between background and developed colours, was plotted against the light exposure period on the Xenotest. The degree of photocoloration ( $\Delta E_1$ ) of the samples after exposure to the Xenotest light was then converted to a fraction of the initial degree of photocoloration ( $\Delta E_0$ ) before light exposure. In this way using normalized values, comparison between lightfastness of different dyes was made possible, as shown in Figure 3.19.

Photochromic dyes on polyester lost a considerable amount of their photocoloration ability after light exposure over a relatively short period of time, as shown in Figure 3.19. After 24 hours of light exposure, the photochromic dyes on polyester were found to retain different fractions of their photocoloration ability. Oxford Blue showed the highest value with 21% retention of the original degree of photocoloration followed by Palatinate Purple, Corn Yellow and Ruby which retained 14%, 9% and 8% of their degree of photocoloration respectively. Aqua Green retained only 3% of its original degree of photocoloration while Plum Red effectively lost its photocoloration completely after 24 hours of light exposure. It may be inferred from these results that the lightfastness of each dye is a property of the dye itself, related to its specific

chemical structure, rather than to the general chemical structure of the photochromic system from which the dye is derived.

**Table 3.4** Half life of all dyes applied to polyester by an exhaustion dyeing method

| <i>Dye</i>        | <i>Half Life, Hour</i> |
|-------------------|------------------------|
| Aqua Green        | 0.5                    |
| Oxford Blue       | 9.4                    |
| Palatinate Purple | 1.0                    |
| Plum Red          | 1.5                    |
| Ruby              | 4.5                    |
| Corn Yellow       | 1.5                    |

Table 3.4 shows the half life of dyes on polyester, which in this particular case refers to the time of exposure to Xenotest light which causes the degree of photocolouration of the polyester fabric dyed with a photochromic dye to decrease to half of the initial value before exposure to Xenotest light. This particular definition of ‘half life’ should not be confused with the use of the term to describe the time for a photochromic dye to fade from its fully developed colour on UV irradiation to half of that value when allowed to fade in the dark.

The half life of dyes, when exposed to the Xenotest, applied to polyester by the exhaustion method, varies between half an hour in the case of Aqua Green to 9.4 hours in the case of Oxford Blue. As these dyes were not compared with the blue wool standard, for the reasons given in this section, an estimation of the lightfastness could not be expressed as a fixed value representing the number of the blue wool sample which is observed visually to have similar lightfastness of the dyed sample in question. A method of instrumental measuring of lightfastness of dyed and printed fabrics without the need for the visual comparison with the blue wool scale was established. An evaluation of this method against the possibility of using the blue wool scale is included in Chapter 8 of this thesis. The photochromic dyes used have clearly different lightfastnesses. Photochromic dyes from within the same general photochromic system, spironaphthooxazine or spironaphthopyran, had very different values of the half life as shown in Table 3.4. As a result, the lightfastness of photochromic dyes is clearly a property of each individual dye related to the specific chemical structure of the dye.

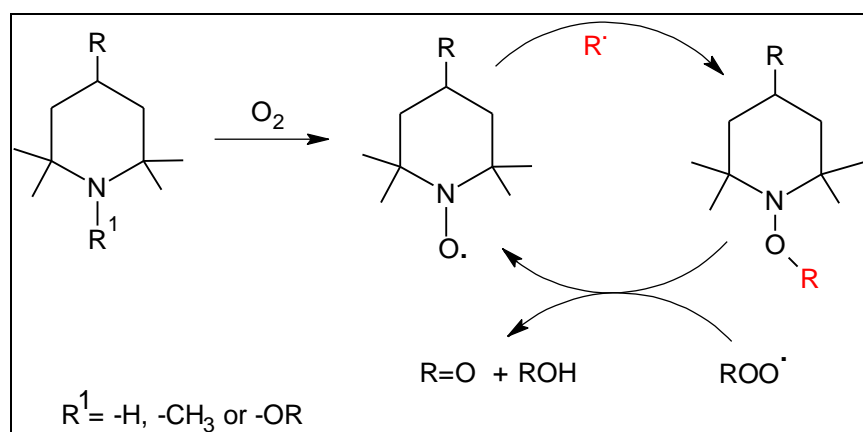
### 3.3.10. Using additives in an attempt to improve lightfastness

Three general mechanisms may be involved in the UV light-initiated degradation of textile dyes. These mechanisms are photooxidation via singlet oxygen, photooxidation via triplet oxygen and photoreduction via free radical species, as discussed in section 2.5. The protection of dyes from photodegradation can be performed either by incorporating additives which shield the dye molecules from the incident UV light, and therefore prevent the light-initiated process of dye transformation to the excited triplet form, or by reacting with the free radicals formed, for example, when the excited dye abstracts hydrogen from nearby groups. These free radicals may be responsible for the dye degradation process, as explained in section 2.5. The dye shielding effect can be brought about by using UV absorbers, while the free radical consuming effect can be brought about by using hindered amine light stabilizers. When photochromic dyes were applied to cotton and polyester fabrics by screen printing, as reported in a previous study [104], it was evident that some hindered amine light stabilizers (HALS) had a positive effect on the lightfastness of both naphthooxazine and naphthopyran dyes when the HALS were applied at a specific concentration. This effect was demonstrated on the basis of a significant increase in the half life of the dyes when exposed on the Xenotest instrument. In the same study, UV absorbers had a positive effect on the lightfastness of naphthooxazine dyes while they had a negative effect on the lightfastness of naphthopyran dyes. In all cases, UV light absorbers caused a decrease in the degree of photocolouration of screen-printed fabrics, due to their mechanism of operation which involves shielding the dye from the UV light. [186]

On the basis of these observations, the effect of HALS on the lightfastness in the case of the dyed fabrics was investigated for both naphthooxazine and naphthopyran dyes, while UV absorbers were investigated for the naphthooxazine dyes only. Oxford Blue was employed in an attempt to optimize the concentration of the HALS, because this dye showed the highest degree of photocolouration, and therefore it was envisaged that the differences in the lightfastness which might be brought about by the additives might be most noticeable with Oxford Blue compared to the other dyes.

#### a) *Hindered amine light stabilizers (HALS)*

Hindered amine light stabilizers improve lightfastness by inhibiting degradation of dye under the influence of UV light when the mechanism involves free radicals. This effect is attributed to the cyclic regeneration of these materials during the light stabilizing process, and therefore the HALS is not consumed, as shown in Scheme 3.3. [187]

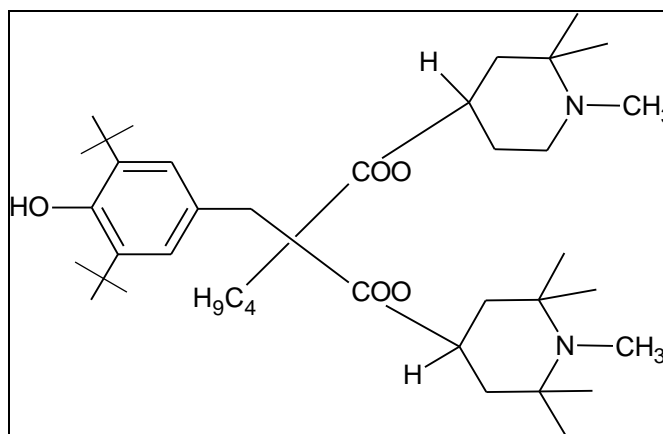


**Scheme 3.3** Mechanism of the light stabilizing process of the HALS

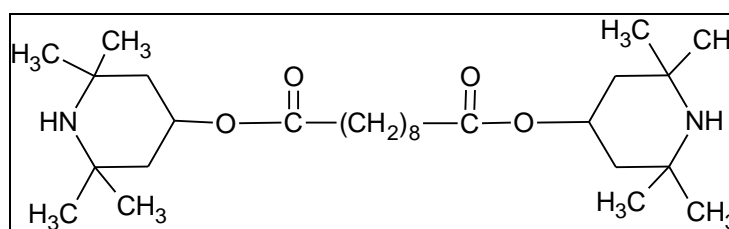
For most polymers, hindered amine light stabilizers are efficient stabilising agents against light-induced degradation. The efficiency of HALS arises from the ability of these materials to inhibit the photochemically initiated degradation reactions. Scheme 3.3 shows that the light stabilization process by the HALS involves three steps, as follows [188]:

1. Oxidation of the HALS species to the nitroxyl radical ( $NO\cdot$ )
2. The formation of non-radical hindered aminoethers (NOR) by the reaction between nitroxyl radicals and free radicals  $R\cdot$  generated in the photodegradation process
3. The reaction between (NOR) and peroxy radicals to re-generate nitroxyl radical species ( $NO\cdot$ )

The transformation products of the HALS, such as nitroxyl radicals and hydroxylamino ethers, are responsible for the light stabilisation process. And thus, the photodegradation of the dye under the effect of UV light is reduced by removing damaging radical species and preventing them from coming into contact with the dye.

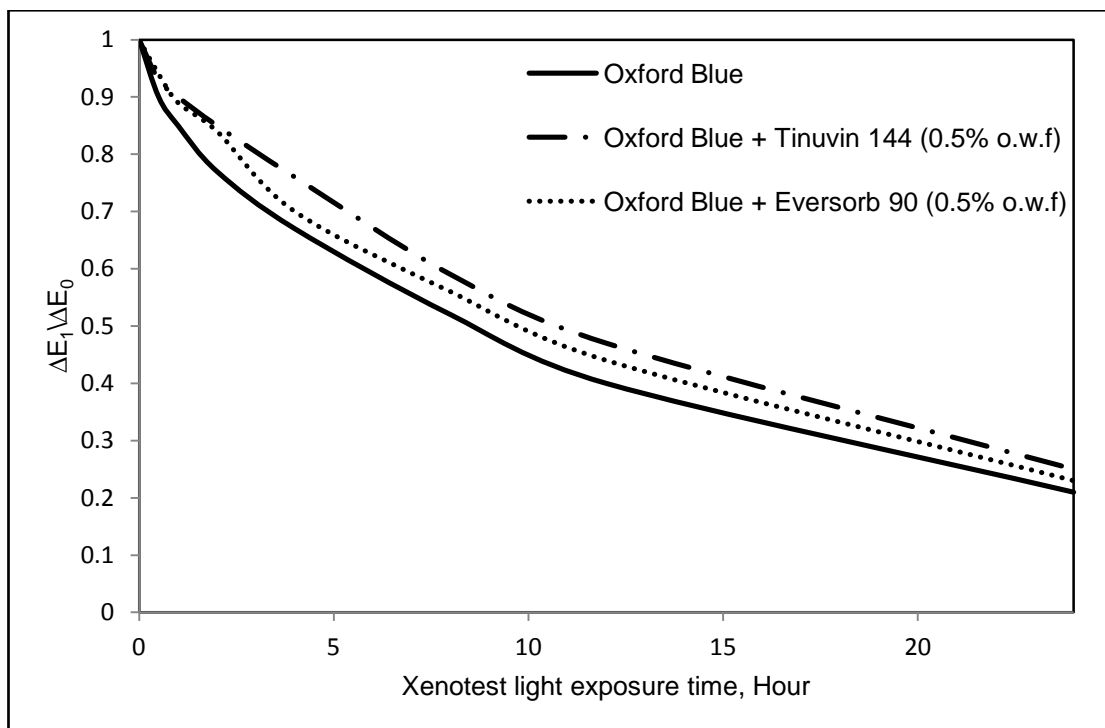


**Figure 3.20** Tinuvin 144. Bis(1,2,2,6,6-pentamethyl-4-piperidiny)-[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl] butylmalonate



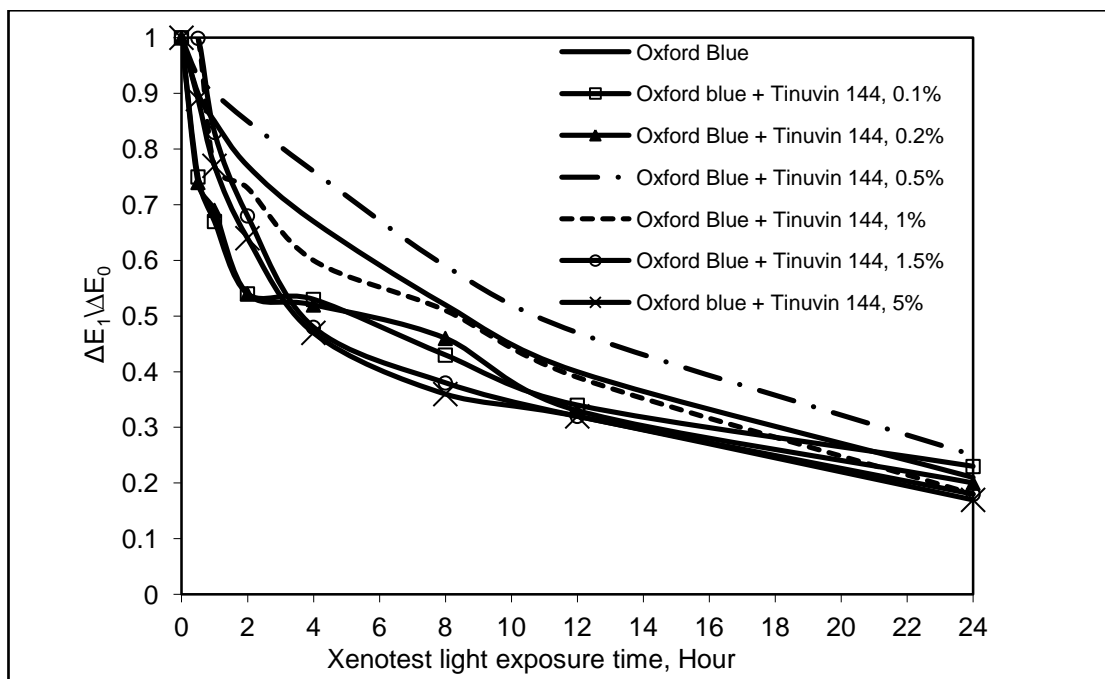
**Figure 3.21** Eversorb 90. Bis(2,2,6,6-tetramethyl-4-piperidyl)-sebacate

Tinuvin 144, which is an important industrial example of the HALS, was found to increase the half life of screen-printed fabrics against light exposure when it was incorporated in the screen printing paste with Palatinat Purple, Aqua Green and Plum Red printed on cotton. [103] The chemical structures of Tinuvin 144 and Eversorb 90, two examples of the HALS, are given in Figures 3.20 and 3.21 respectively. The lightfastness of dyed fabric was expressed in terms of the fraction of the degree of photocolouration of dyed polyester samples remaining after exposing to Xenotest light for different periods of time. This fraction was normalised to allow comparisons between dyes to be made. The effects of Tinuvin 144 and Eversorb 90 on the lightfastness of Oxford Blue on polyester were investigated.



**Figure 3.22** Normalised curves for lightfastness of Oxford Blue applied to polyester fabric with two different HALS incorporated

Figure 3.22 shows that Tinuvin 144 and Eversorb 90 provided only a slight improvement in the lightfastness of Oxford Blue applied to polyester fabric by the exhaustion method. The half life of Oxford Blue on polyester fabric with Tinuvin 144 (0.5% o.w.f) added increased by around 10% of the original half life of this dye without added Tinuvin 144, as shown in Table 3.5. The improvement in the lightfastness delivered by Eversorb 90 was slightly less than with Tinuvin 144, as shown in Figure 3.22. The half life of Oxford Blue with Eversorb 90 (0.5% o.w.f) added increased by 9.6% compared with its half life with no additives, as shown in Table 3.5. As both of the HALS used achieved an improvement of the lightfastness of Oxford Blue on polyester fabric, Tinuvin 144 slightly better than Eversorb 90, the latter was not investigated further. Different concentrations of Tinuvin 144 were used with Oxford Blue to investigate the effect of its concentration on the lightfastness of the dye applied to polyester fabric by the exhaustion method.



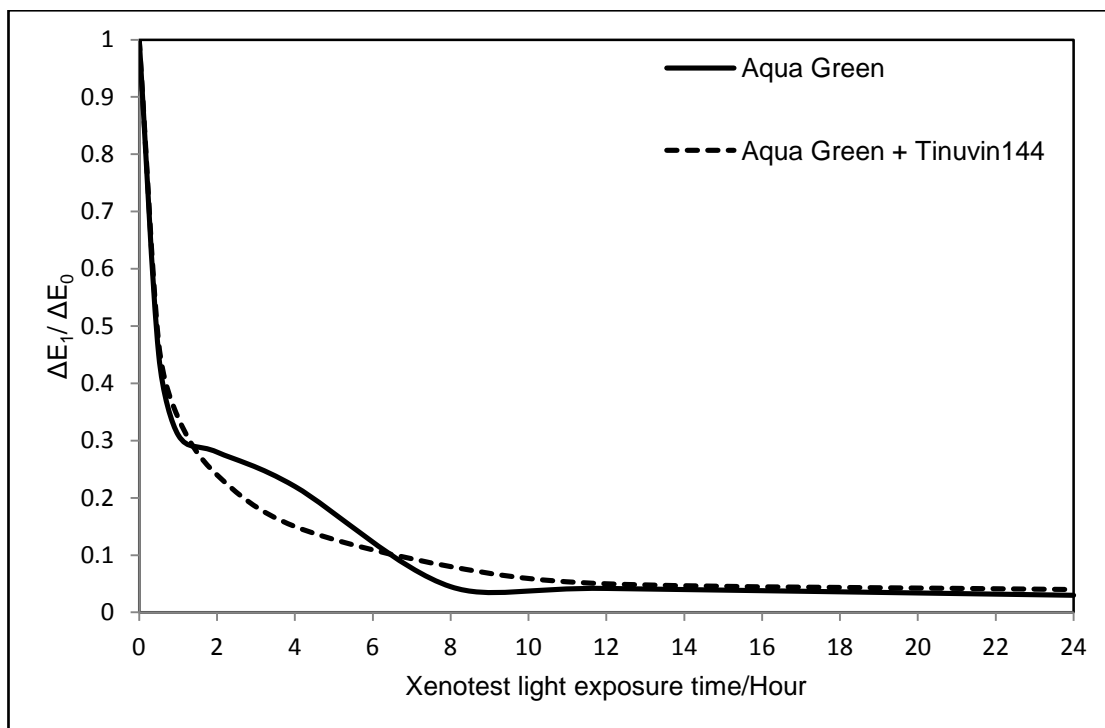
**Figure 3.23** Normalised curves for lightfastness of Oxford Blue + Tinuvin144 on Polyester

**Table 3.5** Half life of Oxford Blue with HALS applied to polyester by an exhaustion method

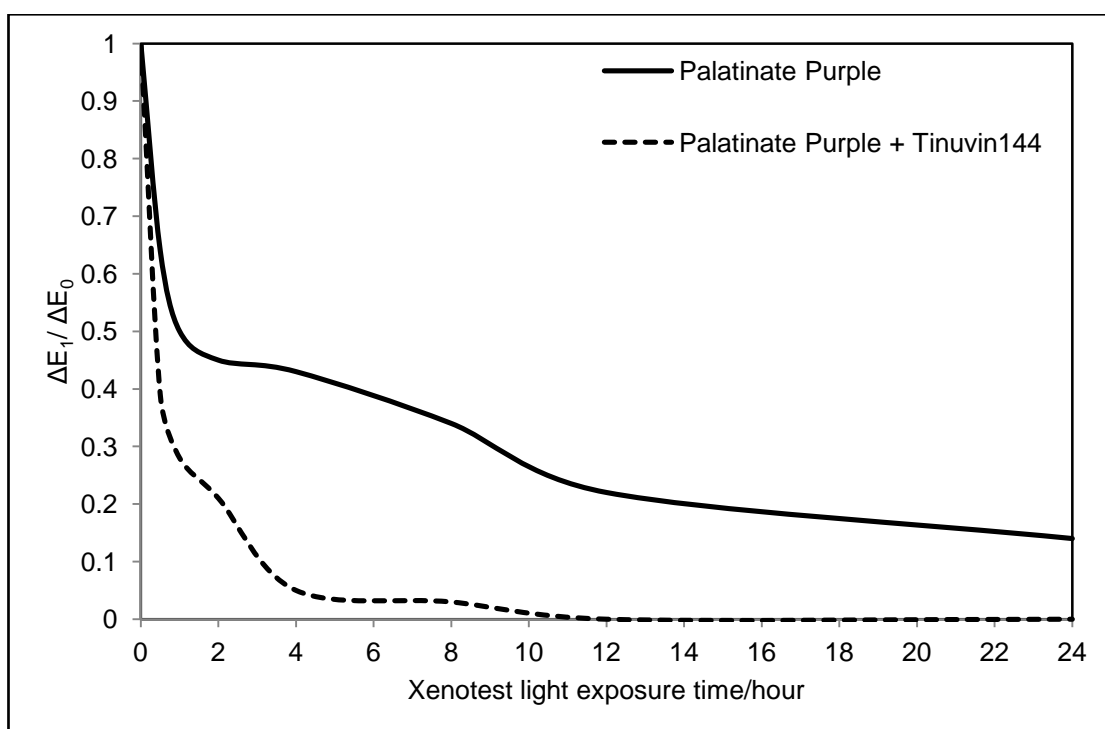
| <i>Dye + additives</i>                 | <i>Half life, Hour</i> |
|--|------------------------|
| Oxford Blue                            | 9.4                    |
| Oxford Blue + Tinuvin 144 (0.1% o.w.f) | 5.2                    |
| Oxford Blue + Tinuvin 144 (0.2% o.w.f) | 5.3                    |
| Oxford Blue + Tinuvin 144 (0.5% o.w.f) | 10.4                   |
| Oxford Blue + Tinuvin 144 (1% o.w.f)   | 8.3                    |
| Oxford Blue + Tinuvin 144 (1.5% o.w.f) | 3.8                    |
| Oxford Blue + Tinuvin 144 (5% o.w.f)   | 3.6                    |
| Oxford Blue + Eversorb 90 (5% o.w.f)   | 10.3                   |

Figure 3.23 shows that the optimum concentration of Tinuvin 144 was 0.5% o.w.f. In fact, both lower and higher concentrations reduced the lightfastness as measured by retention of degree of photocolouration and the half life, as shown in Figure 3.23 and Table 3.5 respectively. On the basis of this result, Tinuvin144 (0.5% o.w.f) was thus applied to polyester with all of the other dyes at this optimum concentration.

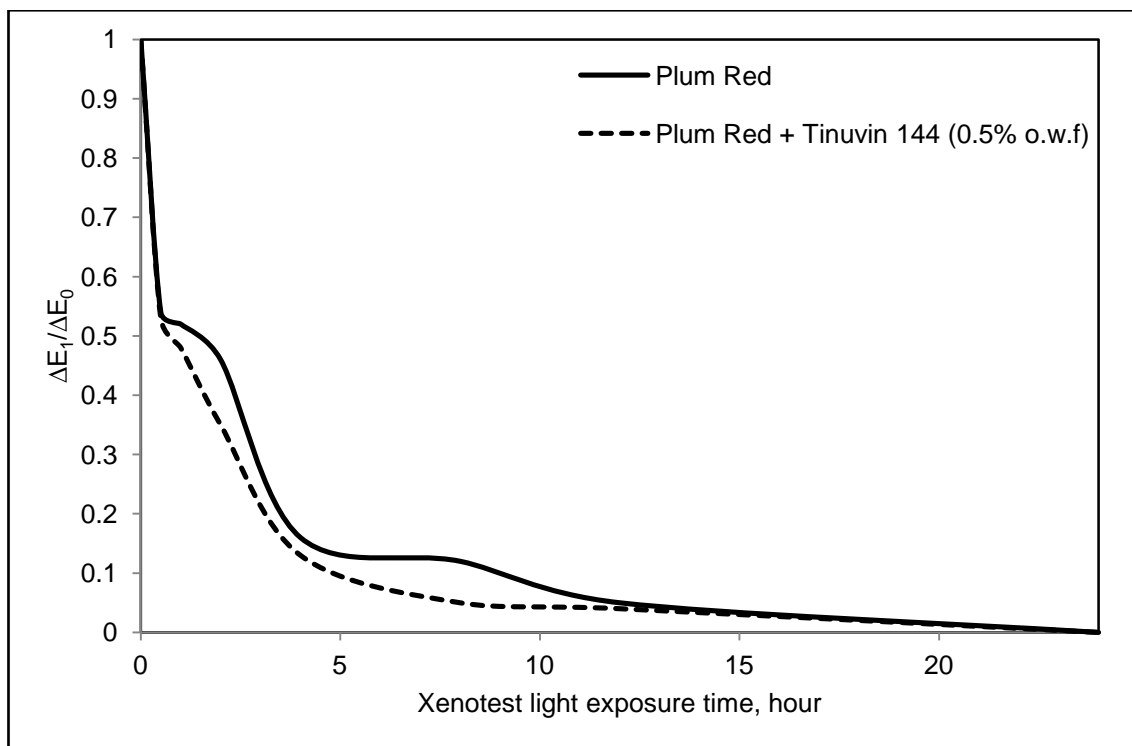




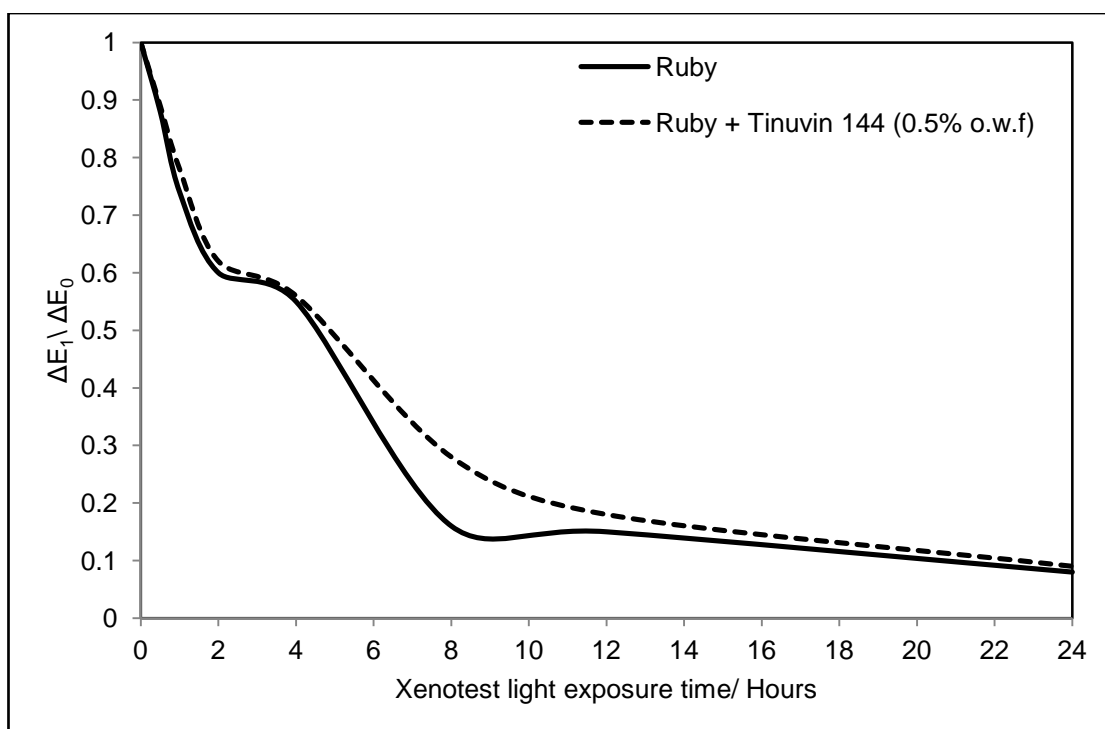
**Figure 3.24** Normalised curves for lightfastness of Aqua Green + Tinuvin 144 (0.5% o.w.f) for polyester



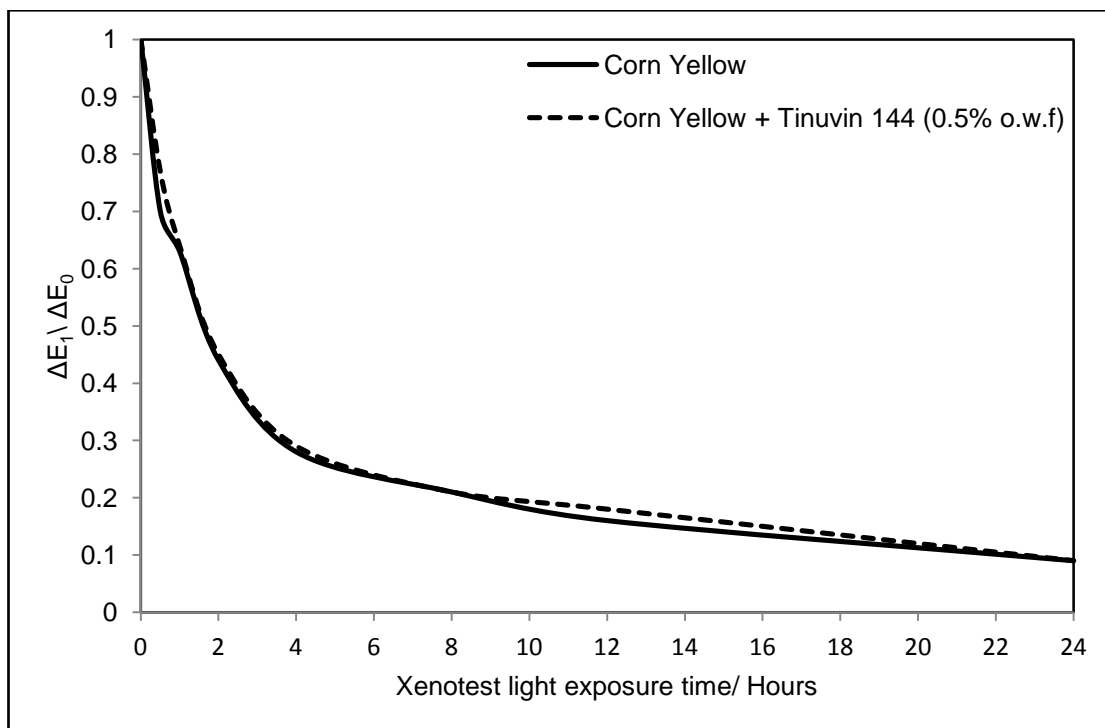
**Figure 3.25** Normalised curves for lightfastness of Palatinate Purple + Tinuvin 144 (0.5% o.w.f) on polyester



**Figure 3.26** Normalised curves for lightfastness of Plum Red + Tinuvin 144 (0.5% o.w.f) on polyester



**Figure 3.27** Normalised curves for lightfastness of Ruby + Tinuvin 144 (0.5% o.w.f) on polyester



**Figure 3.28** Normalised curves for lightfastness of Corn Yellow + Tinuvin 144 (0.5% o.w.f) on polyester

**Table 3.6** Half life of all dyes with Tinuvin 144 (0.5% o.w.f) applied to polyester fabric by an exhaustion method

| <i>Dye + additives</i>                       | <i>Half life. hour</i> |
|--|------------------------|
| Aqua Green                                   | 0.5                    |
| Aqua Green + Tinuvin 144 (0.5% o.w.f)        | 0.5                    |
| Oxford Blue                                  | 9.4                    |
| Oxford Blue + Tinuvin 144 (0.5% o.w.f)       | 10.4                   |
| Palatinate Purple                            | 1.0                    |
| Palatinate Purple + Tinuvin 144 (0.5% o.w.f) | 0.4                    |
| Plum Red                                     | 1.5                    |
| Plum Red + Tinuvin 144 (0.5% o.w.f)          | 0.8                    |
| Ruby   | 4.6                    |
| Ruby + Tinuvin 144 (0.5% o.w.f)              | 4.9                    |
| Corn Yellow                                  | 0.7                    |
| Corn Yellow + Tinuvin 144 (0.5% o.w.f)       | 0.7                    |

Figures 3.24 – 3.28 and Table 3.6 show that Tinuvin 144 did not significantly improve the lightfastness of any of the five other dyes. In fact, there was a significant decrease in the lightfastness of Palatinate Purple and Plum Red when Tinuvin 144 was added. In the cases of Aqua Green and Corn Yellow, Tinuvin 144 had no discernible effect on the lightfastness. Although it may be within the limits of experimental variation, there is tentative evidence for a slight improvement in the half life of Ruby.

The photochromic dyes in question thus responded to the addition of Tinuvin 144 in different ways in terms of its effect on their lightfastness. Oxford Blue responded positively with an increase in its half life by 10%, while Palatinate Purple and Plum Red responded negatively by a decrease in their half life by 60% and 53% respectively. Lightfastness of Aqua Green, Ruby and Corn Yellow were not affected by the addition of Tinuvin 144.

It was thus observed that the effect of the HALS on the lightfastness of polyester fabric dyed with the photochromic dyes by the exhaustion method are not consistent with the result obtained when the same dyes were screen-printed on cotton fabric in a previous study. [186]

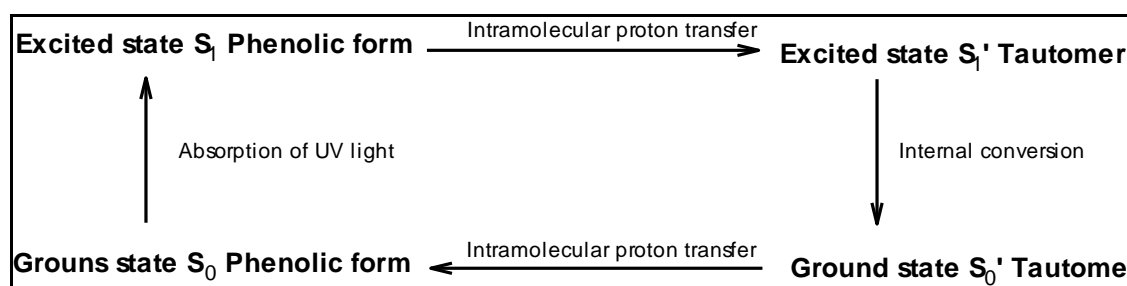
In the case of the screen-printed cotton, the dye and the light stabiliser are contained in the printing binder used, while in the case of dyed polyester, the dye and the light stabiliser operate in polyester fibres. It is conceivable that both the mechanism of photodegradation of the dye and the mechanism of the light stabilising action of the HALS may be different when they operate in different media. Another factor might play a role in this respect, which is associated with the highly crystalline structure of polyester. This structure may prevent the complete diffusion of the HALS into polyester fibres, and therefore only small concentrations, if any, of the HALS will be present to operate in the dyed polyester fibres. Tinuvin 144 is a relatively hydrophobic neutral molecule, which contains ester groups, as shown in Figure 3.20, and so it might be expected to be compatible with the structure of polyester. However, it is a fairly big molecule and this may prevent it from penetrating into the tightly-packed crystalline structure of the polyester fibres. No commercially-available HALS products with more suitable chemical structures were found. A final explanation is supported by the outcome of the investigation of the effect of the concentration of the HALS on the lightfastness of screen-printed cotton with the same dyes. According to this previous study [186], the same concentration of the HALS may have different effects on the lightfastness of the different photochromic dyes. Thus, the HALS may have different

effects on the lightfastness of different photochromic dyes when only a small concentration of the HALS exists in polyester fibres dyed with these dyes.

In conclusion, the lightfastness of the photochromic dyes is not predictable on the basis of the general photochromic system of the dye, and hence it may be related directly to the specific chemical structure of the dye. The various chemical structures of the dyes may give rise to different photodegradation mechanisms, and therefore they may respond in different ways to the light stabilizing mechanism of the HALS. Further investigation of the different mechanisms of photodegradation of the photochromic dyes requires a full knowledge of the specific chemical structures of the dyes which are not disclosed by the manufacturer of the dyes.

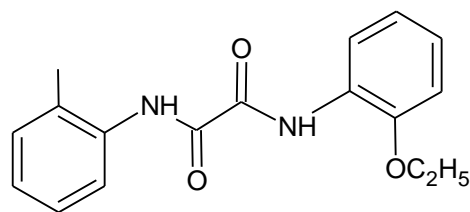
*b) UV absorbers*

UV absorbers possess the ability to absorb UV light and convert it to heat. [186] Hence, they can improve colour fastness to light by shielding the dye from UV light which may cause degradation of the dye. As the name suggests, UV light absorbers may be expected, in addition to improving lightfastness, to reduce the degree of photocoloration of photochromic dyes due to absorbing the UV light which is essential for initiating the colour change of photochromic dyes, as explained in section 2.3. UV absorbers may be classified chemically as either phenolic or non-phenolic UV absorbers. The cyclic mechanism of the UV absorbing process by the phenolic UV absorbers is shown in Scheme 3.4. [186]

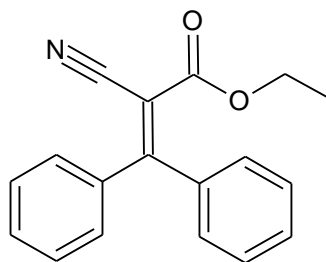


**Scheme 3.4** The cyclic UV absorption by phenolic UV absorbers

There is much less literature available for non-phenolic UV absorbers than that available for phenolic UV absorbers. The non-phenolic UV absorbers includes oxanilides and cyanoacrylates; their chemical structures are shown in Figure 3.29 and Figure 3.30 respectively. The oxanilides may undergo an excited state proton transfer, and the large number of vibrational modes of the cyanoacrylates allows radiational energy to be converted to thermal energy. [189]



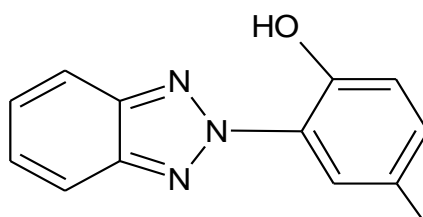
**Figure 3.29** Oxanilides UV absorber



**Figure 3.30** Cyanoacrylates UV absorber

Tinuvin P, a phenolic UV absorber, was selected to investigate the effect of UV absorbers on the lightfastness of photochromic dyes applied to polyester by the exhaustion method. The small, planar structure of the Tinuvin P molecule, as shown in Figure 3.31, may facilitate its penetration into the compact structure of the molecular chains of polyester fibres, and therefore facilitate its ability to improve the lightfastness of dyes applied to polyester fabric by the exhaustion method.

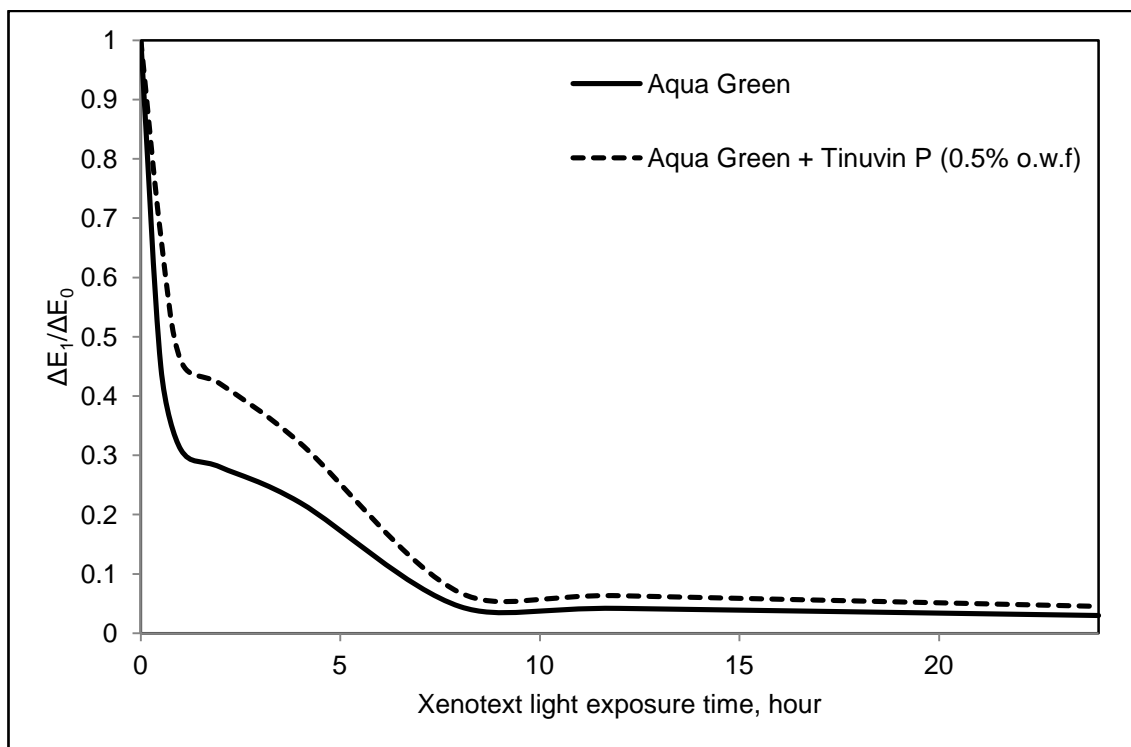
The lightfastness of Palatinate Purple on cotton was proved to increase when Tinuvin P, was added to the screen printing paste in a previous study. [186]



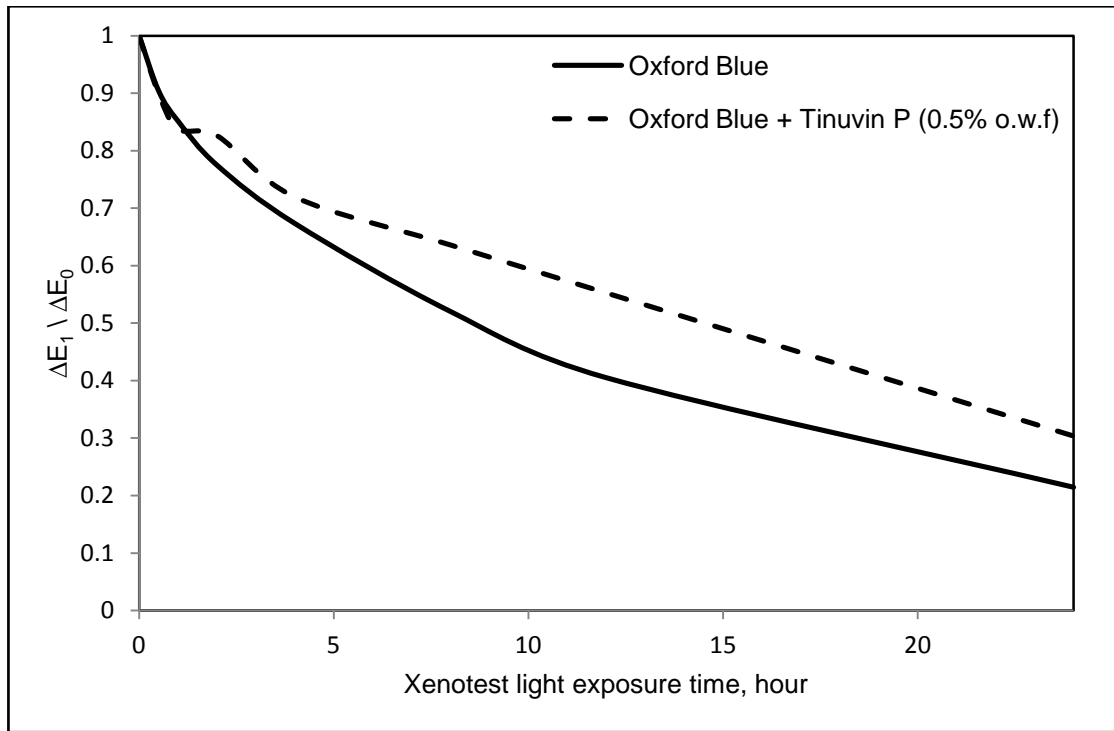
**Figure 3.31** Tinuvin P

The investigation of the effect of UV absorbers on the lightfastness of polyester fabric dyed with photochromic dyes was limited to the naphthooxazine-based photochromic dyes ( Aqua Green, Oxford Blue, Palatinate Purple and Plum Red), on the basis that the UV light absorbers had proved in a previous study to have a negative effect on the

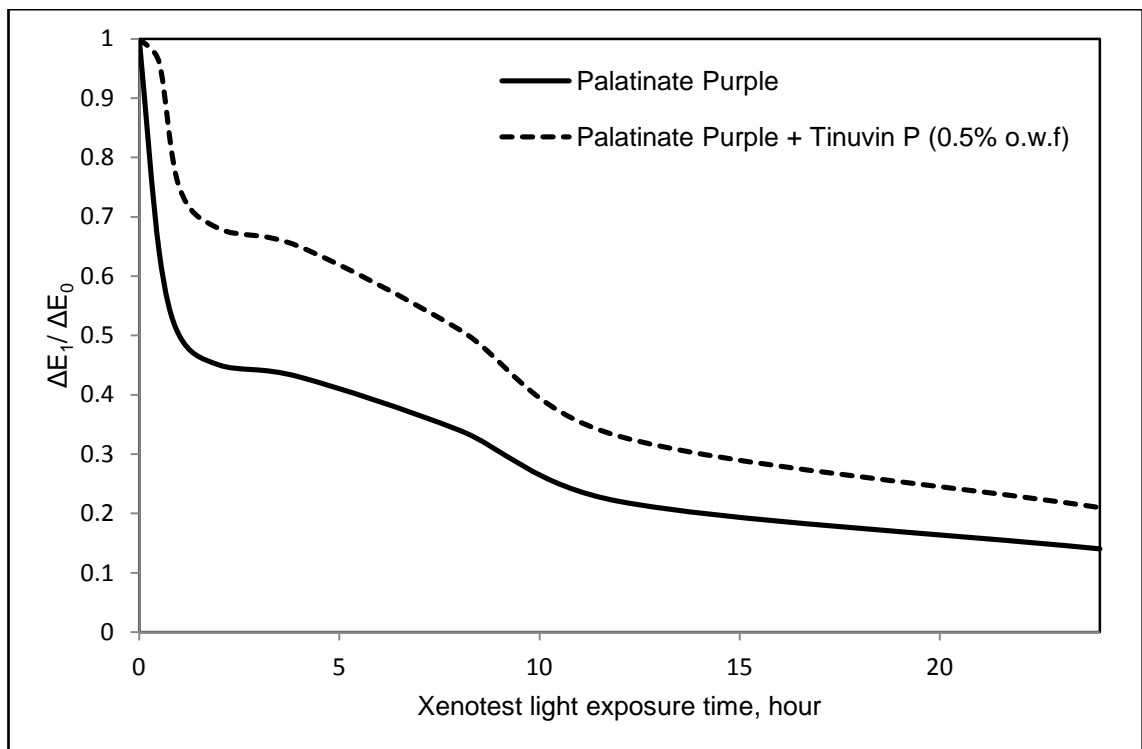
lightfastness of naphthopyran-based photochromic dyes when these dyes were applied to polyester fabric by screen printing. [186]



**Figure 3.32** Normalised curves for lightfastness of Aqua Green applied to polyester fabric with Tinuvin P.

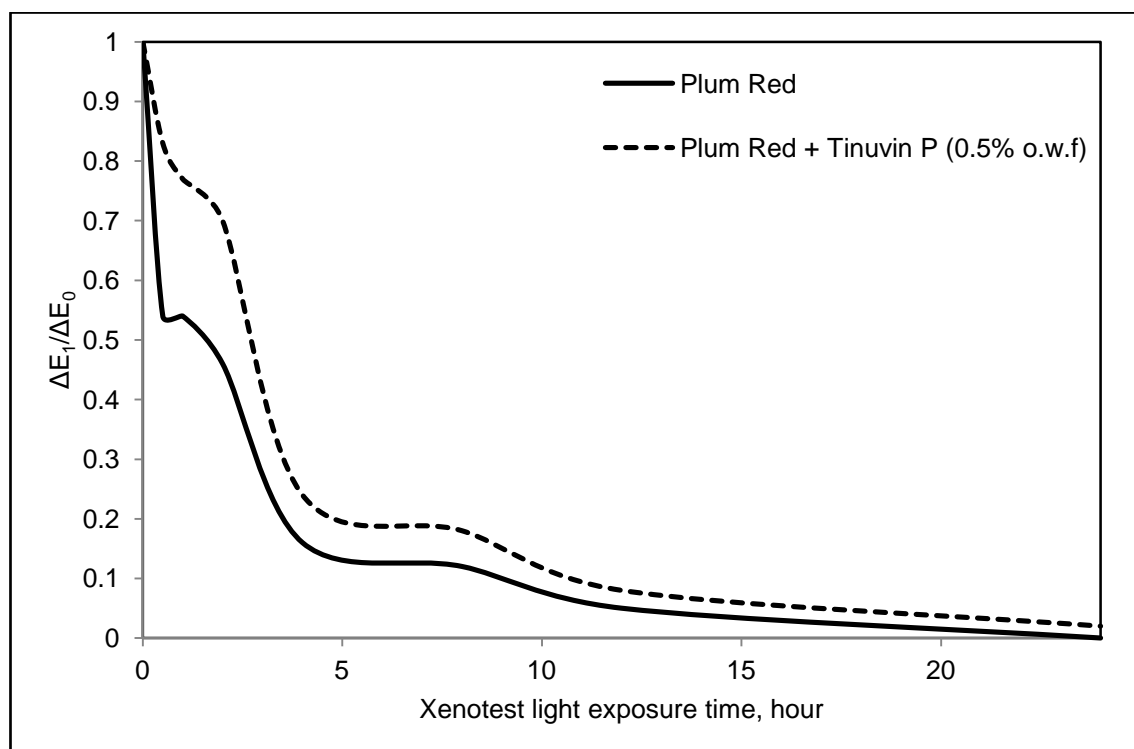


**Figure 3.33** Normalised curves for lightfastness of Oxford Blue applied to polyester fabric with Tinuvin P



**Figure 3.34** Normalised curves for lightfastness of Palatinate Purple applied to polyester fabric with Tinuvin P





**Figure 3.35** Normalised curves for lightfastness of Plum Red applied to polyester fabric with Tinuvin P

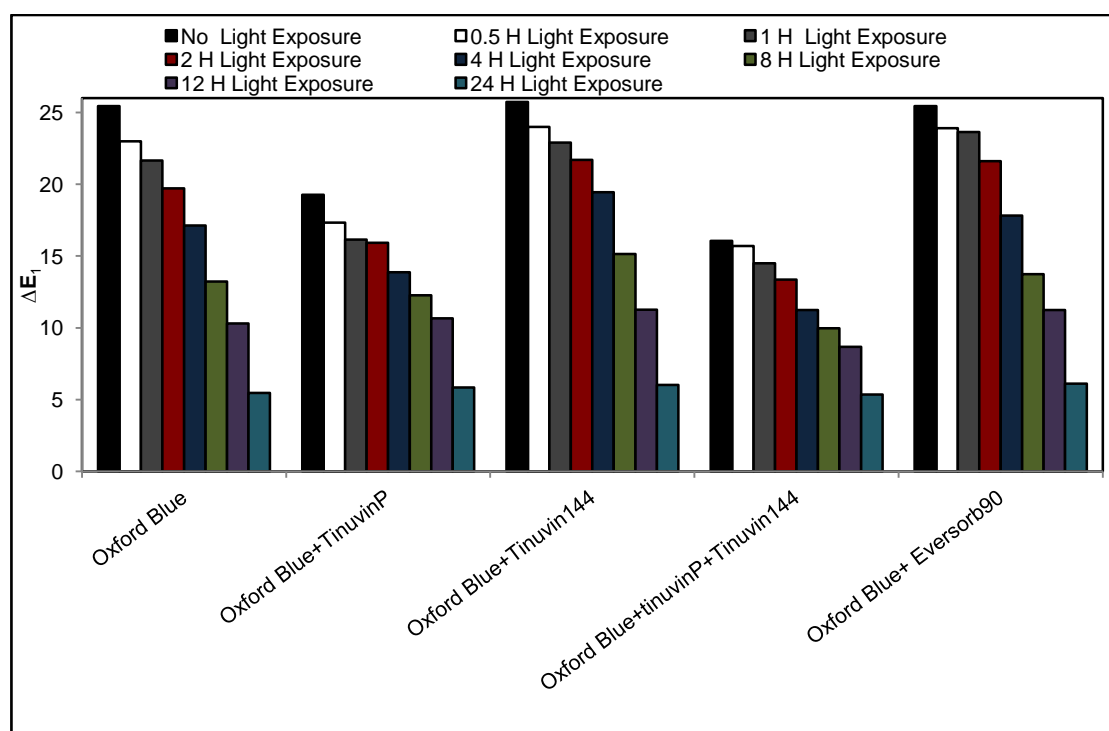
**Table 3.7** Half life of the spironaphthooxazine dyes with Tinuvin P applied to polyester fabric by an exhaustion method

| Dye               | Half life, hour |                        |
|-------------------|-----------------|------------------------|
|                   | No additives    | Tinuvin P (0.5% o.w.f) |
| Aqua Green        | 0.5             | 0.74                   |
| Oxford Blue       | 9.4             | 14.5                   |
| Palatinate Purple | 1.0             | 1.5                    |
| Plum Red          | 1.5             | 2.3                    |

Figures 3.32 – 3.35 show that Tinuvin P gave rise to an increase in the lightfastness of all of the spironaphthooxazine dyes applied to polyester fabric by the exhaustion dyeing method. The half life of the dyes recorded an increase of 48% - 54% of the original half life without additives, as shown in Table 3.7.

As a UV absorber, Tinuvin P may be expected to cause a decrease in the degree of photocolouration of photochromic dyes, because of its mechanism of operation which involves shielding the dye molecules from UV light. Hence, it is conceivable that the

photoinduced transformation of the dye from its closed form to its open form may be inhibited. This fact was supported by measuring the degree of photocolouration of the spironaphthooxazine dyes without adding Tinuvin P, and then repeating the same measurement after adding Tinuvin P together with the dyes. As Oxford Blue showed the highest degree of photocolouration it may be expected to show the clearest indication of the influence of light stabilisers, measured as the effect on the degree of photocolouration.



**Figure 3.36** The effect of different additives on the lightfastness and degree of photocolouration of Oxford Blue on Polyester

Figure 3.36 shows that the degree of photocolouration of polyester fabric dyed with Oxford Blue by the exhaustion method decreased by 24% of its original value when Tinuvin P (0.5% o.w.f) was added to the dyebath.

In conclusion, the use of Tinuvin P as a UV absorber to improve the lightfastness of the spironaphthooxazine photochromic dyes has higher potential to improve lightfastness of these dyes compared to the other light stabilizers investigated in this study. This result may be explained by the fact that the chemical structure of the Tinuvin P molecule is significantly smaller than the molecules of the other light stabilizers used in this study. The ability of this relatively small molecule to penetrate into the highly crystalline structure of polyester fibres may be higher than the ability of the other larger molecules,

and therefore its influence on the lightfastness of the dyes on polyester will be more significant.

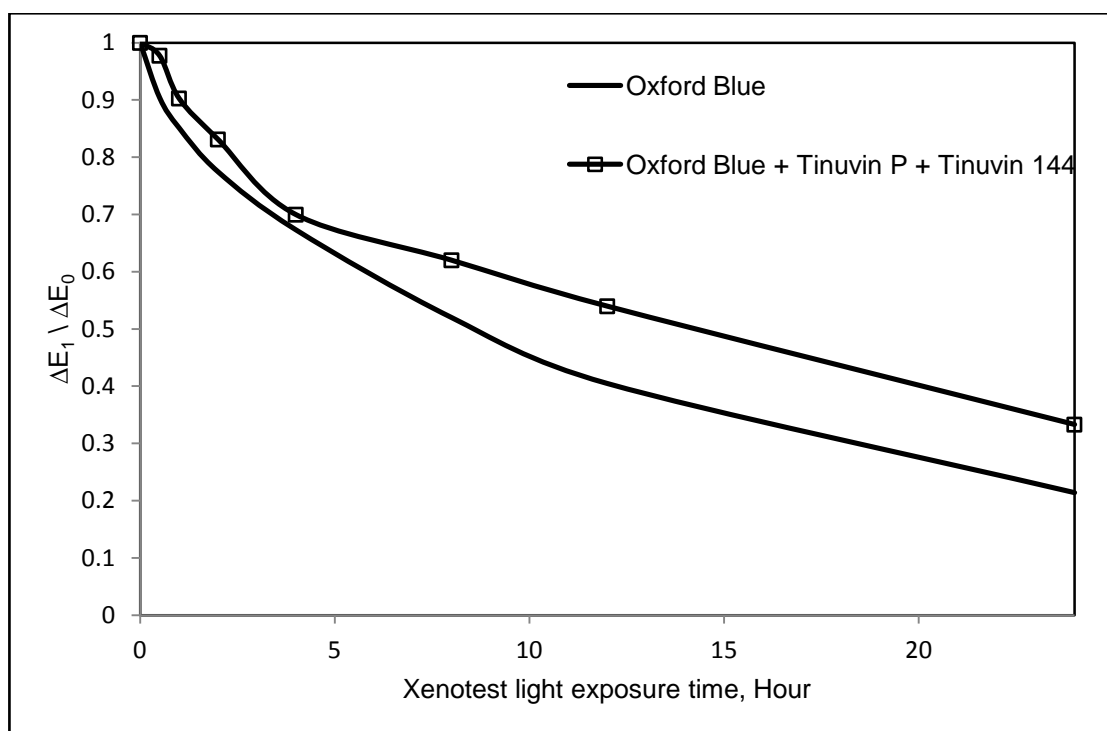
**Table 3.8** Half life of Oxford Blue with different additives applied to polyester by an exhaustion method

| <i>Dye and additives (0.5% o.w.f)</i> | <i>Half life, Hour</i> |
|---------------------------------------|------------------------|
| Oxford Blue                           | 9.4                    |
| Oxford Blue + Tinuvin 144             | 10.4                   |
| Oxford Blue + Tinuvin P               | 14.5                   |
| Oxford Blue + Tinuvin 144 + Tinuvin P | 14.3                   |
| Oxford Blue + Eversorb 90             | 10.3                   |

*c) UV light absorbers and HALS*

In the next step, a mixture of a UV absorber and a HALS was investigated in an attempt to obtain a compromise between the highest level of improvement of lightfastness, brought about by Tinuvin P, while maintaining the degree of photocolouration of the dye, which is brought about by Tinuvin 144.

As discussed previously in this section, UV light absorbers and HALS operate in different ways. It was envisaged that the use of a mixture of a UV light absorber and a HALS might lead to a synergistic effect with both lightfastness enhancement mechanisms operating at the same time. The degradation inhibition and UV shielding mechanisms, attributed to HALS and UV light stabilizers respectively, might maximize the lightfastness improvement when they are applied together.



**Figure 3.37** Normalised curves for lightfastness of Oxford Blue applied to polyester fabric with a mixture of Tinuvin 144 and Tinuvin P

Figure 3.37 shows the effects on the lightfastness of polyester dyed with Oxford Blue when it was applied with a mixture of equal quantities of Tinuvin P (0.5% o.w.f) and Tinuvin 144 (0.5% o.w.f). The half life of Oxford Blue was observed to increase from 9.4 to 14.3 hours, as shown in Table 3.8. As Tinuvin P is a UV light absorber, it may cause a decrease in the photocolouration of photochromic dyes due to shielding the dye molecules from the UV light; the latter is essential to initiate the photochromic colour change of the dyes. Figure 3.36 shows the effects of additives on both the lightfastness and the degree of photocolouration of Oxford Blue on polyester. Tinuvin 144 gave rise to an increase of 10% in the half life of Oxford Blue on polyester, as shown in Table 3.8, with no negative effect on the degree of photocolouration of the dye, as shown in Figure 3.36. The half life of the spironaphthooxazine dyes on polyester increased by 48% - 54% when Tinuvin P was added, as shown in Table 3.7, but at the same time Tinuvin P caused a decrease of 24% in the original degree of photocolouration of Oxford Blue, as shown in Figure 3.36.

A mixture of Tinuvin P and Tinuvin 144 resulted in a significant decrease of 35% in the degree of photocolouration of Oxford Blue applied to polyester, as shown in Figure 3.36. However the half life of the dye on polyester increased by 53% compared with the original half life of the dye with no additives, as shown in Table 3.8.

In conclusion, the selection of the light stabilizer for lightfastness improvement of polyester fabric dyed with photochromic dyes by the exhaustion method depends on the requirements of the final use of the dyed fabric. If the original degree of photocolouration of the dye is required to be maintained, while lightfastness is secondary in importance, then UV absorbers may not be used as light stabilizers for lightfastness improvement of the fabric. On the other hand, if lightfastness is essential in the final use and, at the same time, the degree of photocolouration comes second in importance, then the use of a UV absorber is recommended in the case of the spironaphthooxazine dyes, as shown in Table 3.7 and Figure 3.36. The use of a mixture of a UV absorber and a HALS gave rise to a significant increase in the lightfastness of Oxford Blue. However, this increase in the lightfastness is still less than the increase brought about by Tinuvin P, as shown in Table 3.8 and, at the same time, the decrease in the degree of photocolouration, brought about by using a mixture of Tinuvin 144 and Tinuvin P is higher than the decrease brought about by using Tinuvin P alone, as shown in Figure 3.36. As a result, the use of Tinuvin P, a UV absorber of a relatively small molecular size, has the potential to improve the lightfastness of the spironaphthooxazine dyes while keeping a minimum decrease in the degree of photocolouration compared to the use of a mixture of a HALS and a UV absorber.

Finally, photochromic dyes behave differently in terms of their response to light stabilizers. Thus, the knowledge of the chemical structures of the photochromic dye and the light stabilizer might help to predict the final effect of the light stabilizer on the lightfastness of the photochromic dye, especially if there is an understanding of the photodegradation mechanisms.

### ***3.3.11. Colour fastness to washing of polyester fabric dyed with photochromic dyes by an exhaustion method***

The washfastness test was carried out according to the British Standard BS 1006:1990, Group C. Colour Fastness to Domestic and Commercial Laundering. According to this standard, there is a series of five washing tests established to measure fastness to washing of coloured textiles. The five washing tests, with gradually increasing washing time and temperature, with the same formulation of the washing solution, cover the range of washing procedures from mild to severe. [181] When textiles dyed with normal dyes are tested for washfastness, a specimen of the textiles with one or two adjacent fabrics is washed in a soap solution under specific conditions of time and temperature, then rinsed and dried. The change in the colour of the specimen and the staining of the

adjacent fabrics are assessed against the grey scales. In the case of the photochromic dyes, the grey scale was inappropriate to assess the washfastness of fabrics dyed with these dyes, because of the dynamic colour-changing nature of photochromic dyes. There is no stable state of developed colour of fabrics dyed with photochromic dyes for comparison with the grey scale. An alternative approach involving assessing the degree of photocolouration of the dyes before and after being subjected to the washfastness test process was adopted to evaluate the washfastness of fabrics dyed with photochromic dyes. The  $\Delta E_1$  value between background and developed colours measured for the samples before and after the washing process was adopted to assess the stability of the degree of photocolouration of dyed samples when subjected to the washing process. The remaining ability of the washed fabric to build up its colour when exposed to UV light was considered as a measure of the washfastness of fabrics dyed with photochromic dyes.

The method used to assess the colour fastness to washing in the research described in this thesis is based on the principle of the gradual increase in the washing conditions in terms of temperature and/or time, from mild to severe, testing the degree of photocolouration after washing and comparing it with that before washing. Conditions of Test 1 are a temperature of 40°C and a time of 30 minutes; conditions of Test 3 are a temperature of 60°C and a time of 30 minutes. The washfastness test procedure started with the mildest conditions (Test 1), and the severity was increased until a decrease in the colour fastness to washing began to be observed.

When the samples showed no deterioration when subjected to Test 1, Test 2 was skipped and Test 3 was carried out. As the conditions of Test 3 showed only a modest decrease in the degree of photocolouration, then it was decided that there was no value in using the milder conditions of Test 2 (Temperature 50°C, time 45 minutes ).

a) Test 1 (Temperature 40°C, time 30 minutes)

**Table 3.9** Washfastness of the dyes applied to polyester fabric by an exhaustion method - Washfastness Test 1 and Test 3

| <i>Dyes</i>       | $\Delta E_1$             |                                   |                                   |
|-------------------|--------------------------|-----------------------------------|-----------------------------------|
|                   | <i>Non-washed fabric</i> | <i>Washed at 40°C, for 30 min</i> | <i>Washed at 60°C, for 30 min</i> |
| Aqua Green        | 11.1                     | 11.1                              | 10.0                              |
| Oxford Blue       | 27.1                     | 27.1                              | 24.1                              |
| Palatinate Purple | 3.4                      | 3.4                               | 3.0                               |
| Plum Red          | 3.5                      | 3.5                               | 3.0                               |
| Ruby              | 9.2                      | 9.2                               | 8.1                               |
| Corn Yellow       | 13.1                     | 13.1                              | 11.8                              |

Table 3.9 shows no difference in the degree of photocolouration, expressed as  $\Delta E_1$ , on irradiation with UV light between fabrics washed under the conditions of Test 1 and non-washed fabrics. Hence the degree of photocolouration was not affected by the mild conditions of washing Test 1.

**Table 3.10** The effect of the washing process on the background colours of all dyes applied to polyester fabric by an exhaustion method

| <i>Dyes</i>       | $\Delta E_2$             |                                    |                                    |
|-------------------|--------------------------|------------------------------------|------------------------------------|
|                   | <i>Non-washed fabric</i> | <i>Washed at 40°C, for 30 min.</i> | <i>Washed at 60°C, for 30 min.</i> |
| Aqua Green        | 14.1                     | 14.0                               | 14.4                               |
| Oxford Blue       | 9.0                      | 8.8                                | 8.7                                |
| Palatinate Purple | 28.3                     | 28.0                               | 28.1                               |
| Plum red          | 8.5                      | 8.1                                | 8.0                                |
| Ruby              | 18.8                     | 18.3                               | 18.5                               |
| Corn Yellow       | 13.1                     | 12.8                               | 12.7                               |

The background colours of samples before and after washing were also compared.  $\Delta E_2$  values between background colours and undyed fabric colours for both washed and non-washed samples were used to express the effect of the washing process on the background colour of polyester fabric dyed with photochromic dyes by an exhaustion

method. Table 3.10 shows that the background colours of dyed samples did not change significantly after washing at 40°C for 30 minutes. According to the spectrophotometer used in the experimental work in this thesis, a colour difference value of 0.75 or less is considered within experimental variation, as mentioned in 3.2.1. Coloured samples showing such small differences are considered to match usually. As colour differences in Table 3.10 are smaller than 0.75, they may be considered within experimental variation. In conclusion, polyester fabrics dyed with all of the six photochromic dyes are resistant to the washing conditions of the washfastness Test 1.

*b) Test 3 ( Temperature 60°C, Time 30minutes)*

It is observed from Table 3.9 that washing at temperature of 60°C for 30 minutes resulted in a decrease in the degree of photocolouration of the six dyes applied to polyester fabric. The decrease in the degree of photocolouration varied between 10% in the cases of Aqua Green and Corn Yellow, and 13% in the case of Plum Red.

Table 3.10 shows that there is no difference between the background colours of non-washed and washed polyester samples dyed with any of the six dyes. As the difference between every two figures of the same dye in Table 3.10 is smaller than 0.75, then they are considered as within experimental variation and do not express a real difference, as mentioned in 3.2.1.

In conclusion, the washfastness of polyester fabrics dyed with the six photochromic dyes started to show a modest decrease when the washing conditions of Test 3 were applied.

**3.3.12. Carrier dyeing of polyester with photochromic dyes**

The hydrophobic nature of polyester fibres requires special methods to be employed to dye these fibres. Three methods have been used for applying disperse dyes to polyester, which are carrier dyeing, high temperature and the dry heat dyeing. The main advantage of using the carrier is to facilitate the dye diffusion into polyester fibres at a temperature of 100°C by changing the physical properties of polyester. [179]

The theories proposed to explain the carrier operating mechanism are discussed in section 2.7.1.

The effect of the carrier may be explained as lowering the glass transition temperature of polyester by loosening its chemical structure and initiating the motion of the segments of the molecular chains of polyester fibres. This segmental mobility is responsible for creating free volume between the molecular chains of polyester fibres, and therefore increasing the ease of the diffusion of disperse dyes into polyester fibres.



The temperature at which the dye diffusion increases dramatically is called the dyeing transition temperature which is not far from the glass transition temperature, as mentioned in section 2.7 [113, 114].

The dye structure plays a vital role in the effect of the carrier on the dyeing rate. [190] Various compounds have been used as carriers, e.g. diphenyl, ortho-phenyl phenol, para-phenylphenol, chlorinated benzenes and methyl salicylate. [179] The use of benzyl alcohol, as a carrier, has been recommended because of its effect in increasing the rate of dyeing of synthetic fibres. [129]

All the photochromic dyes were applied to polyester fabric by the carrier dyeing in an attempt to investigate the effect of this dyeing method on the final outcome of the dyed samples in terms of their degree of photocoloration and background colours.

**Table 3.11** The degree of photocoloration polyester fabric dyed with all of the photochromic dyes by two different dyeing methods

| <i>Dye</i>        | $\Delta E_1$          |                                |
|-------------------|-----------------------|--------------------------------|
|                   | <i>Carrier dyeing</i> | <i>High temperature dyeing</i> |
| Aqua Green        | 8.3                   | 11.1                           |
| Oxford Blue       | 20.5                  | 27.1                           |
| Palatinate Purple | 2.6                   | 3.4                            |
| Plum Red          | 2.7                   | 3.5                            |
| Ruby              | 6.9                   | 9.2                            |
| Corn Yellow       | 10.0                  | 13.1                           |

Table 3.11 shows that the values of the degree of photocoloration, represented by  $\Delta E_1$  values, of polyester samples dyed with the photochromic dyes by the carrier dyeing method are less than the values achieved by the high temperature exhaustion dyeing method. The percentage decrease in the degree of photocoloration of samples dyed by the carrier dyeing method, compared to those dyed by the high temperature dyeing method, ranged between 23%, in the case of Plum Red, and 25%, in the cases of Aqua Green, Oxford Blue and Ruby. This decrease in the degree of photocoloration may be a result of low diffusion of the dyes into polyester fibres dyed by the carrier dyeing method. The free volume, created by the carrier, between the polyester molecular chains may not be enough for the relatively large dye molecules to penetrate into polyester fibres.

This explanation was also supported by the low values of the background colours of polyester fabrics dyed by the carrier dyeing, expressed by  $\Delta E_2$  values shown in Table 3.12.

**Table 3.12** The background colour of polyester fabric dyed with the photochromic dyes by two different dyeing methods

| <i>Dye</i>        | $\Delta E_2$          |                                |
|-------------------|-----------------------|--------------------------------|
|                   | <i>Carrier dyeing</i> | <i>High temperature dyeing</i> |
| Aqua Green        | 1.5                   | 14.1                           |
| Oxford Blue       | 1.4                   | 9.0                            |
| Palatinate Purple | 2.9                   | 28.3                           |
| Plum Red          | 1.1                   | 8.5                            |
| Ruby              | 2.3                   | 18.8                           |
| Corn Yellow       | 1.4                   | 13.1                           |

Table 3.12 shows that polyester samples dyed by the carrier dyeing method showed a significant decrease in the background colours compared to those samples dyed by the high temperature dyeing method. This decrease may be brought about by three factors. The first factor is the low diffusion of the dyes brought about by the relatively small volume created, by the carrier, between the molecular chains of polyester, and therefore less dye may penetrate into polyester fibres. The second factor may be the lower thermal degradation of the dyes at a temperature of 100°C, compared to a temperature of 130° in the case of the high temperature dyeing method. The third factor may be related to the degree of thermochromism shown by the photochromic dye under the dyeing conditions. Since the dyes are applied at a temperature of 100°C, which is lower than the temperature of 130°C in the case of the high temperature dyeing method, then less dye will undergo the thermochromic change during the dyeing process, and therefore less dye will be trapped inside the polyester fibres in its open-ring form, as explained in section 3.3.3.

One or more of the three factors explained above may be involved in the reduction in the background colours observed for polyester fabric dyed by the carrier dyeing method.

### 3.4. Conclusions

Six commercial photochromic dyes, four spironaphthoxazines and two naphthopyrans, were applied to polyester fabric as disperse dyes by an exhaustion dyeing method. The dyeing procedure was optimized in terms of temperature, time and pH for two of the dyes, a spironaphthoxazine (Oxford Blue) and a naphthopyran (Corn Yellow). Dyeing concentrations were optimized for each dye individually. Oxford Blue gave the most successful outcome showing pronounced photocolouration from a relatively low background colour, developing maximum intensity after 4 minutes of UVA irradiation, while the other dyes gave varying levels of performance. Palatinate Purple, a spironaphthoxazine-based dye, was particularly unsuccessful in this application, giving a fairly strong background colour and limited colorability. The fading characteristics of the dyed fabrics after removal of the UV source were investigated. The naphthopyran dyes took longer to fade to their unexposed state than the spironaphthoxazine dyes. Fatigue resistance was variable, but very good in some cases and the dyes showed reasonable stability when stored in the dark for a prolonged period. In these respects, there was no obvious correlation with the dye class.

The lightfastness and washfastness properties of the six dyes on polyester were investigated. Because of the dynamic colour-changing nature of the photochromic dyes, it was not possible to carry out these investigations by following the same procedures followed in the case of the normal dyes. The ability of the dye to retain its degree of photocolouration after exposure to the Xenotest light was used to represent the dye lightfastness.

With regard to the lightfastness, the half life of the six dyes varied from half an hour in the case of Aqua Green to 9.4 hours in the case of Oxford Blue. The half life of each of the other dyes was between these two values. It was clear that there was no relation between the dye class and the lightfastness of the dye, because dyes of the same class showed very different values of the half life. Two different types of light stabilizers were used in an attempt to improve lightfastness properties of the dyes on polyester. In this respect, a hindered amine light stabilizers (HALS) caused a slight increase in the lightfastness of Oxford Blue when applied at a concentration of (0.5% o.w.f). Higher and lower concentrations caused a decrease in the lightfastness of Oxford Blue. A slight positive effect of the HALS, at a concentration of 0.5% o.w.f, on the lightfastness was observed in the case of Ruby, while a significant negative effect on the lightfastness was observed in the cases of Palatinate Purple and Plum Red. Lightfastness of Aqua Green, and Corn Yellow were not affected by adding the HALS. Tinuvin P, a UV absorber,

caused a significant increase in the lightfastness of all the spironaphthooxazine dyes, but at the same time the degree of photocolouration of these dyes was affected negatively by adding Tinuvin P. An element of compromise between the degree of photocolouration and the lightfastness of photochromic dyes is necessary in the selection of a HALS as a UV light absorber. A mixture of both Tinuvin 144, a HALS, and Tinuvin P, a UV absorber brought about a significant increase in the lightfastness of Oxford Blue, but at the same time caused a higher decrease in the degree of photocolouration of this dye compared to the decrease brought about by Tinuvin P.

All dyes showed good resistance to the washfastness conditions applied. All dyes maintained their abilities to develop colours, upon irradiation with UV light, when they were washed under the conditions of washfastness Test 1 according to the British standard BS 1006:1999. When the dyed samples were washed under the conditions of Test 3 of the same standard, all the dyes on polyester started losing their abilities to build up their colours upon irradiation with the UV light. The decrease in the degree of photocolouration of the dyed fabric was expressed by the difference between  $\Delta E_1$  values before and after the washing test. All samples showed a decrease in their degree of photocolouration after washing under the conditions of Test 3. This decrease varied between 10%, in the case of CornYellow, and 13% in the case of Plum Red.

Finally, the application of photochromic dyes to polyester fabric by carrier dyeing was investigated briefly. The investigation showed that the carrier dyeing method brought about a lower degree of photocolouration and background colours of the photochromic dyes applied by this dyeing method compared to the same dyes applied by the high temperature dyeing method.

## **Chapter 4 -The Application of Photochromic Dyes To Polyester Fabric by a Solvent-Based Pad Dry-Heat Dyeing Method**

### **4.1. Introduction**

Disperse dyes are normally applied to polyester from aqueous dispersions. The non-ionic nature of disperse dyes and the hydrophobic nature of polyester mean that it is a reasonable proposition to investigate other application methods of these dyes to polyester using non-ionic processes from organic solvents rather than water which is a highly polar solvent. Due to the very low solubility of disperse dyes in water at room temperature, and the hydrophobic nature of polyester fibres, disperse dyes do not penetrate the fibre sufficiently from aqueous dispersion at room temperature. Hence, a high temperature of about 130°C, or the use of a carrier which is an organic solvent with a dyeing temperature of about 100°C, is essential for applying disperse dyes to polyester from an aqueous dyebath. In this respect, the high dyeing temperature operates by increasing the kinetic energy of dye molecules, increasing the solubility of the dye in water and increasing the segmental mobility of polymeric chains of polyester, and therefore facilitating the dyeing process by increasing the rate of dye diffusion into polyester fibres. Further discussion of the roles of carriers and the high temperature in aqueous-based dyeing of polyester is given in sections 2.7.1, and 2.7.2 respectively.

The possibility of dyeing polyester from organic solvents has attracted attention as an alternative to the aqueous-based dyeing method due to certain advantages associated with the use of solvents instead of water in the dyeing process of polyester with disperse dyes. These advantages include the high solubility of disperse dyes in some organic solvents, the higher ability of these solvents to penetrate the hydrophobic structure of polyester compared with water, the lower energy required to heat some organic solvents to their boiling points compared with the energy required to heat water to its boiling point and finally the possibility of carrying out the dyeing process from solvents at room temperature.

The criteria for selecting a suitable solvent for the dyeing of polyester with disperse dyes include various factors such as the match between the solubility parameter of the solvent and those of the dye and the fibre, toxicity, recoverability and cost. The definition of the solubility parameter concept is given in section 2.7.1. Further details on the selection of appropriate solvents for dyeing are given in section 2.9.

There have been few recent reports about the solvent dyeing of textiles, probably due to the ecological and toxicological issues associated with those solvents appropriate for

textile dyeing applications. Most of the studies that investigated the use of solvents for textile dyeing were published in the 1970s and 1980s. [150, 151, 153, 154, 156, 191-193] Chlorinated organic solvents have been the most widely accepted as alternatives to water for non-aqueous dyeing of polyester with disperse dyes. From a commercial point of view, perchloroethylene has been the most extensively investigated solvent for textile dyeing. As perchloroethylene is non-polar, most disperse dyes, which are non-ionic, possess high solubility levels in this solvent. Other properties of perchloroethylene that may account for why it is the most investigated solvent for textile dyeing applications are its low specific heat,  $0.205 \text{ Kcal kg}^{-1} \text{ deg}^{-1}$ , which means that the energy required to heat this solvent to its boiling point is relatively low, its efficiency in wetting out synthetic fibres rapidly, ease of solvent recoverability and low production cost.

An investigation of the application of the six commercial photochromic dyes (**1-6**) described in section 3.1 to polyester fabric by a solvent-based dyeing method is discussed in this chapter. The dyeing method investigated in this study, which is referred to as solvent-based pad dry-heat dyeing method, is based on a published report of a study of disperse dyes applied to polyester fabric from a solution containing the dyes in perchloroethylene at room temperature, followed by thermal fixation of dyes on the fabric. [159] In this study, dichloromethane is used instead of perchloroethylene for the reasons given in section 4.3.1. In addition, the dyeing method was optimized in terms of solvent/fabric ratio, dyeing concentration and the temperature and time of thermal fixation to improve the application of the photochromic dyes to polyester fabric.

## **4.2. Experimental**

### ***4.2.1. Colour measurement methodology and conditions***

For colour measurement, the specifically-devised methodology in terms of the optimum calibration conditions of the spectrophotometer, the temperature variations and the time lapse described in sections 3.2.1, 3.2.2 and 3.2.3 respectively were used.

### ***4.2.2. Materials***

Polyester fabric as described in section 3.2.4 was used in this study. The series of commercial dyes (**1-6**) described in section 3.2.4 and their names and chemical classes given in Table 3.1 were used. Dichloromethane of a laboratory grade as supplied by Sigma-Aldrich (UK) and stabilized by amylene was used as a medium for all dyeing processes of polyester fabric by a solvent-based pad dry-heat dyeing method.

#### ***4.2.3. Variations in dye concentrations***

The effect of the dyeing concentration on the degree of photocolouration and background colours of dyed fabrics was investigated by applying the photochromic dyes (**1-6**) to polyester fabric at five different dyeing concentrations, namely 0.1%, 0.2%, 0.5%, 1%, 1.5% and 2% o.w.f. The degree of photocolouration and the background colour were represented by  $\Delta E_1$  and  $\Delta E_2$  respectively; both of these terms were defined in section 3.2.5. The UV light irradiation time was adjusted at 4 minutes, which proved to be the optimum irradiation time that brings about the maximum degree of photocolouration of polyester fabrics dyed with photochromic dyes, as discussed in section 3.3.4.

#### ***4.2.4. Solvent-based pad dry-heat dyeing of polyester fabric with photochromic dyes***

All dyeing processes were carried out manually. The dye solution in dichloromethane was prepared in a beaker, and then poured into a shallow tray. The optimum solvent/fabric ratio was 2.5:1. In each case, 10g of dichloromethane and 4g of polyester fabric were used with the appropriate amounts of dye to give dyeing concentrations of 0.1%, 0.2%, 0.5%, 1%, 1.5% or 2 % o.w.f. Polyester fabric was impregnated in the dye solution manually by passing it slowly under the surface of the dye solution. This process was repeated twice for each sample, and then the fabric was squeezed under pressure by a padding machine consisting of two rubber-coated rolls prior to transferring it to the oven for thermal fixation of the dyes into polyester fabric. For thermal fixation of dyes on the fabrics, a Roaches TFO, 500 mm laboratory oven and steamer was used. The machine was set up to operate as a dry heat oven. In the oven, fabrics were subjected to dry heat at a temperature of 190°C for 45 seconds. In each case the dyeing processes were followed by a cold water rinse, followed by reduction clearing, as described in section 3.2.6. The dyed samples were then rinsed with water, washed with an aqueous solution of Synperonic BD100 (1 g l<sup>-1</sup>) for a few minutes, rinsed and then air dried.

#### ***4.2.5. Fading characteristics, fatigue resistance and shelf life***

Fading characteristics, fatigue resistance and shelf life of polyester fabrics dyed with the photochromic dyes (**1-6**) at optimum concentrations by a solvent-based pad dry-heat dyeing method were investigated according to the methods described in section 3.2.7.

#### ***4.2.6. Colour fastness to light of polyester fabrics dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method***

Lightfastness tests were carried out according to the British standard BS1006: 1990, group B, colour fastness to light and weathering B02, colour fastness to artificial light: Xenon arc fading lamp test. [180] The same testing method and conditions given in section 3.2.8 were used.

#### ***4.2.7. Using additives in an attempt to improve lightfastness of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method***

Tinuvin P (0.5% o.w.f) was dissolved in dichloromethane with dyes **1-4**, and Tinuvin 144 (0.5% o.w.f) was dissolved in dichloromethane with dyes **5** and **6** individually at their optimum dyeing concentrations. The same optimised dyeing procedure for solvent-based pad dry-heat dyeing of polyester with photochromic dyes, as given in section 4.2.4 was followed, but Tinuvin 144 and Tinuvin P were dissolved together with the dyes in dichloromethane before impregnating polyester fabrics in the dyebath. The same testing method and conditions given in section 3.2.8 were used.

#### ***4.2.8. Colour fastness to washing of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method***

Washfastness tests were carried out according to the British standard BS1006:1990, Group C, colour fastness to domestic and commercial laundering, test 3 (Temperature 60°C, Time 30 minutes) and test 4 (Temperature 95°C, Time 30 minutes). [181] The same Roaches Washtec-P washfastness test machine given in section 3.2.10 was used to carry out the washfastness test of polyester fabric dyed with photochromic dyes (**1-6**) by the solvent-based pad dry-heat dyeing method.  $\Delta E_1$  values were recorded for washed fabrics and compared with the values of  $\Delta E_1$  of the unwashed fabrics.

### **4.3. Results and Discussion**

#### ***4.3.1. Dyeing polyester fabric with photochromic dyes by a solvent-based pad dry-heat dyeing method***

As shown in Table 3.1 the photochromic dyes (**1-6**) used in this study belong to two different chemical classes which are spironaphthoxazine and naphthopyran; their general chemical structures and the mechanism of photochromism are illustrated in Schemes 3.1 and 3.2 respectively.

For a preliminary investigation of dyeing conditions, Oxford Blue, a spironaphthoxazine-based dye, was applied to polyester fabric by the solvent-based



pad dry-heat dyeing method to investigate the dyeing performance. Oxford Blue was selected because it showed the highest degree of photocolouration when it was applied to polyester as a disperse dye by the aqueous exhaust method, as discussed in section 3.3.5. Using this dye, the dyeing procedure was optimized in terms of solvent/fabric ratio and the temperature and time of thermal fixation. The optimization of the dyeing procedure was based on attempting to achieve the highest degree of photocolouration of polyester fabrics dyed with photochromic dyes on exposure to UV light, which is expressed by the values of  $\Delta E_1$  (see section 3.2.5), and the minimum background colours of these fabrics, expressed by the values of  $\Delta E_2$  (see section 3.2.5).

For the dyeing process of thermoplastic fibres, such as polyester, to be successful, the amorphous zone of the polymer must have sufficient energy for entire segments of the polymer chains to become mobile. The motion of the polymeric chains creates sufficient free volume to allow dye molecules to penetrate into the polymer. The temperature at which an increase in the ease of diffusion of dye molecules into the polymer takes place is referred to as the dyeing transition temperature ( $T_d$ ) which is not far removed from the glass transition temperature ( $T_g$ ). Further details concerning  $T_d$ ,  $T_g$  and the relationship between the effect of temperature on the physical structure of man-made fibres and the mechanism of dyeing of these fibres are given in section 2.7. Thus, the efficiency of solvents or water in the dyeing process of synthetic textile fibres may be assessed by their ability to create a space in the fibre structure to facilitate penetration of dye molecules into the fibre. For a solvent to be able to create a space between the polymer chains, to enable dye molecules to penetrate the polymer structure, the solvent solubility parameter should closely match that of the polymer. As different fibres have different solubility parameters, there is no particular solvent that can be suitable for solvent-based dyeing of all fibres. Perchloroethylene, as the most investigated solvent for solvent-based dyeing, and dichloromethane have solubility parameters of  $20.3 \text{ J}^{0.5} \text{ cm}^{-1.5}$  and  $20.2 \text{ J}^{0.5} \text{ cm}^{-1.5}$  respectively, while the solubility parameter of poly(ethyleneterephthalate) is  $21.4 \text{ J}^{0.5} \text{ cm}^{-1.5}$ . [194-196] Since the value of the solubility parameter of dichloromethane is very close to that of perchloroethylene, it might be expected that dichloromethane will exert a similar effect to that of perchloroethylene as a medium for solvent-based dyeing of polyester. Another factor that supports the use of dichloromethane instead of perchloroethylene is the toxicological issues associated with the latter solvent. [197] Thus dichloromethane was selected as an appropriate solvent to replace perchloroethylene for dyeing polyester fabric by the solvent-based dyeing method investigated in this study.

The first stage of the dyeing process, which essentially involves dye adsorption on the fibre surface by impregnating the fabric in the dye solution, was carried out at room temperature. In the next stage, which is the padding process, the excess solvent absorbed by polyester is removed, and therefore the dye concentration at the surface of the fabric may increase to a level at which the dye diffusion in the subsequent stage becomes more effective. In addition, the removal of the excess solvent may improve the even distribution of the dye on the fabric by restricting the free spread of the dye on the fabric. Dye diffusion into polyester fibres takes place during the thermal fixation stage where the temperature is raised above  $T_d$  to allow the initiation of segmental motion of polymeric chains of polyester, and thus the dye molecules from the highly concentrated solution have the ability to diffuse into the spaces generated between the polymeric chains of the polyester fibres. The initial conditions used for applying photochromic dyes to polyester by the solvent-based pad dry-heat dyeing method were a dye concentration of 1% o.w.f, solvent/fabric ratio of 10:1 o.w.f and a thermal fixation temperature and time of 200°C for 45 seconds respectively. Polyester fabric dyed with Oxford Blue under these conditions was pale blue and developed a deep blue colour on irradiation with UV light for 4 minutes. The degree of photocoloration measured using the spectrophotometer was recorded on the basis of a  $\Delta E_1$  value of 21.7, while the background colour was characterised by a  $\Delta E_2$  value of 9.8, as shown in Table 4.1

**Table 4.1** Degree of photocoloration ( $\Delta E_1$ ) and background colour ( $\Delta E_2$ ) of polyester fabric dyed with Oxford Blue 1% o.w.f from a solvent/fabric ratio of 10:1 under different conditions of thermal fixation

| <i>Thermal fixation conditions</i> | $\Delta E_1$ | $\Delta E_2$ |
|------------------------------------|--------------|--------------|
| Temperature 200°C, Time 20 seconds | 0.6          | 3.9          |
| Temperature 200°C, Time 45 seconds | 21.7         | 9.8          |
| Temperature 200°C, Time 60 seconds | 17.9         | 10.9         |

When the thermal fixation time was reduced from 45 to 20 seconds at a temperature of 200°C, the dyed fabric showed very low photocoloration expressed by  $\Delta E_1 = 0.6$  on

exposure to the UV light. The reason for this may be that the short treatment time at the high temperature may not be sufficient to initiate the segmental motion of polyester polymeric chains, and therefore the amount of dye able to diffuse into the polyester fibres is low. This result was also consistent with the low background colour, represented by  $\Delta E_2 = 3.9$ , of dyed fabrics when the thermal fixation temperature was reduced to 20 seconds. When a 60 second thermal fixation time was used, the dyed fabric showed a decrease in the degree of photocolouration to  $\Delta E_1 = 17.9$ , and an increase in the background colour to  $\Delta E_2 = 10.9$  compared to the values obtained by the thermal fixation time of 45 seconds. This result may be due to thermal degradation of the dye with prolonged exposure to the high temperature. Consequently, for the next phase of investigation the thermal fixation time was fixed at 45 seconds which shows the highest degree of photocolouration and a reasonable background colour, as shown in Table 4.1.

In an attempt to improve the degree of photocolouration of dyed fabric, lower solvent/fabric ratios were investigated. It was envisaged that when the solvent/fabric ratio is decreased, the dye concentration in the dyeing solution increases, and the amount of dye adsorbed by fabric may also increase. Thus, the amount of dye diffusing into fabric during the thermal fixation stage may also increase. In this respect, when the solvent/fabric ratio was reduced to 2.5:1, dye uptake by the fabric increased and this in turn increased the degree of photocolouration to a value of  $\Delta E_1 = 26.7$ , as shown in Table 4.2. Further investigation of the effect of solvent/fabric ratio on the dye uptake was carried out by applying the dye from even lower solvent/fabric ratios. When a solvent/fabric ratio of 1:1 was used, the photochromic fabric gave a value of  $\Delta E_1 = 25.3$ . This reduction in the solvent/fabric ratio to such a low level was associated with practical difficulties in the fabric impregnation stage, because of the relatively small amount of solvent used. Another disadvantage associated with this low solvent/fabric ratio was the significant increase in the background colour of the dyed fabric, which is expressed by an increase in the value of  $\Delta E_2$  to 10.1, as shown in Table 4.2. This increase in the value of  $\Delta E_2$  may be a result of the increase in the dye uptake by fabric due to the increased amount of dye in the fixed amount of dye solution adsorbed by the fabric when the solvent/fabric ratio was reduced to a low level of 1:1 o.w.f. This increase in the dye uptake brings about two opposite effects. The first effect is a decrease in the degree of photocolouration as a result of reducing the colour difference between the background and developed colours and restricting the photocolouration ring opening reaction of dye molecules due to the limited space available for the high number of these molecules. The second effect is an increase in the degree of

photocoloration due to the increased amount of dye transferred into fabric, and therefore the increased number of the dye molecules that perform their photochromic colour change on UV light exposure. The total outcome of these two effects may be either an increase or a decrease in the degree of photocoloration of the dyed fabric. Thus, the decrease in the degree of photocoloration from 26.7 to 25.3 which was associated with the reduction of the solvent/fabric ratio from 2.5:1 to 1:1, may be a result of a compromise between the two opposite effects in favour of the decreased colour difference between the background and developed colours.

**Table 4.2** Degree of photocoloration ( $\Delta E_1$ ) and background colour ( $\Delta E_2$ ) of polyester dyed with Oxford Blue 1% o.w.f at different solvent-to goods ratios, and thermal fixation temperature of 200°C and time 45 seconds

| <i>Solvent/fabric ratio</i><br><i>o.w.f</i> | $\Delta E_1$ | $\Delta E_2$ |
|---|--------------|--------------|
| 10:1  | 21.7         | 9.8          |
| 2.5:1                                       | 26.7         | 9.4          |
| 1:1   | 25.3         | 10.1         |

Further reduction in the solvent/fabric ratio was impractical because it was impossible to impregnate the fabric with such a small amount of the dye solution. Hence, the optimum solvent/fabric ratio was selected as 2.5:1 which achieved the highest degree of photocoloration shown by dyed fabric, and a reasonable background colour, with a moderate value of  $\Delta E_2 = 9.4$ , compared to the values brought about by higher and lower ratios, as shown in Table 4.2.

The final parameter investigated in an attempt to optimize the dyeing procedure of polyester fabrics by maximizing  $\Delta E_1$  and minimizing  $\Delta E_2$  was the temperature of the thermal fixation stage. For this purpose, Oxford Blue at 1% o.w.f was applied to polyester fabric by a solvent-based pad dry-heat dyeing method, from a dyeing solution using a solvent/fabric ratio of 2.5:1, and a fixed time of 45 seconds for the thermal fixation process.

**Table 4.3** Degree of photocolouration ( $\Delta E_1$ ) and background colour ( $\Delta E_2$ ) of polyester fabric dyed with Oxford Blue 1% o.w.f from a solvent/fabric ratio of 2.5:1 under different conditions of thermal fixation

| <i>Thermal fixation conditions</i> | $\Delta E_1$ | $\Delta E_2$ |
|------------------------------------|--------------|--------------|
| Temperature 200°C, Time 45 seconds | 26.7         | 9.4          |
| Temperature 190°C, Time 45 seconds | 27.7         | 8.9          |
| Temperature 180°C, Time 45 seconds | 4.7          | 3.8          |

When the thermal fixation temperature was reduced from 200°C to 190°C, the degree of photocolouration of dyed fabric increased to a value of  $\Delta E_1 = 27.7$ , while the background colour decreased to give a value of  $\Delta E_2 = 8.9$ . A thermal fixation temperature lower than 190°C resulted in a significant decrease in the degree of photocolouration of dyed fabrics. When the thermal fixation process was carried out at a temperature of 180°C, the dyed fabric developed a very low colour after irradiation with UV light, and colour measurement showed small values of  $\Delta E_1 = 4.7$ , and  $\Delta E_2 = 3.8$  of dyed fabric. These observations may be explained by the low diffusion of dye into polyester fibres due to the restricted segmental mobility of polymeric chains of polyester at the relatively low temperature of 180°C. As a result, the thermal fixation temperature was fixed at 190°C which brought about a compromise between the highest value of  $\Delta E_1$ , and a moderate value of  $\Delta E_2$ , as shown in Table 4.3.

On the basis of the investigations carried out to optimize the process for application of Oxford Blue to polyester by a solvent-based pad dry-heat dyeing method, the optimum conditions shown in Table 4.4 were used for applying all the other photochromic dyes to polyester fabric by this dyeing method.

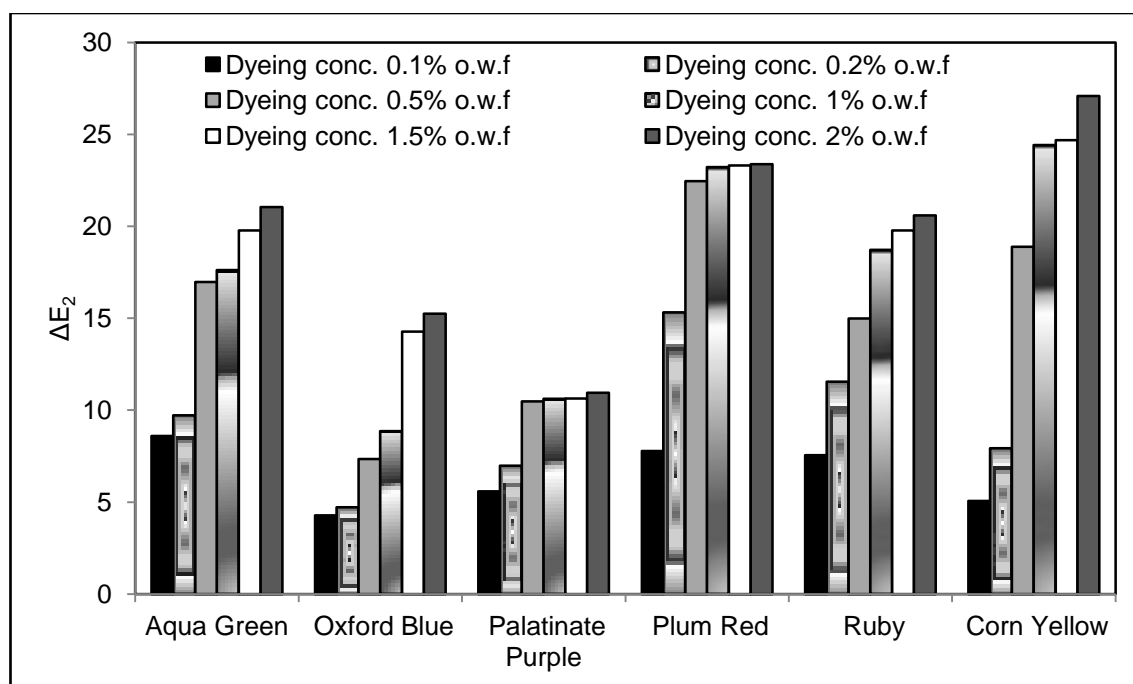
**Table 4.4** The optimum conditions for applying photochromic dyes to polyester by a solvent-based pad dry-heat dyeing method

|                              |         |
|------------------------------|---------|
| Solvent-to goods ratio       | 2.5:1   |
| Thermal fixation temperature | 190°C   |
| Thermal fixation time        | 45 sec. |

This optimum dyeing procedure in terms of solvent/fabric ratio, thermal fixation time and temperature was followed to apply dyes **1-6** to polyester fabric by a solvent-based pad dry-heat dyeing method. Each dye was applied at six different dyeing concentrations of 0.1, 0.2, 0.5, 1, 1.5 and 2% o.w.f, in an attempt to obtain the optimum dyeing concentration which brings about the maximum degree of photocoloration and minimum background colours of dyed fabrics.

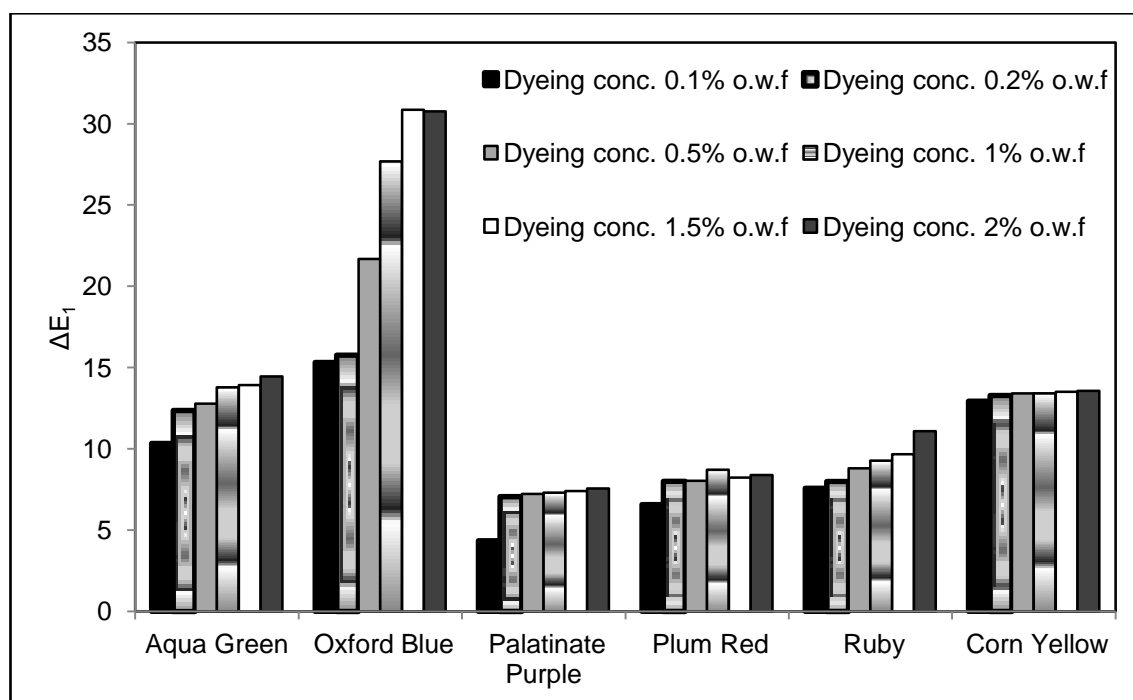
**4.3.2. Degree of photocoloration and background colours of polyester fabric dyed with photochromic dyes at different dyeing concentrations by a solvent-based pad dry-heat dyeing method**

Photochromic dyes **1-6** were applied to polyester fabric at different concentrations under the dyeing conditions optimised for Oxford Blue. Figures 4.1 and 4.2 show the background colours, and the degree of photocoloration of the dyed fabrics after 4 minutes of UV light exposure respectively.



**Figure 4.1** Background colours ( $\Delta E_2$ ) for dyes **1-6** applied to polyester by a solvent-based pad dry-heat dyeing method

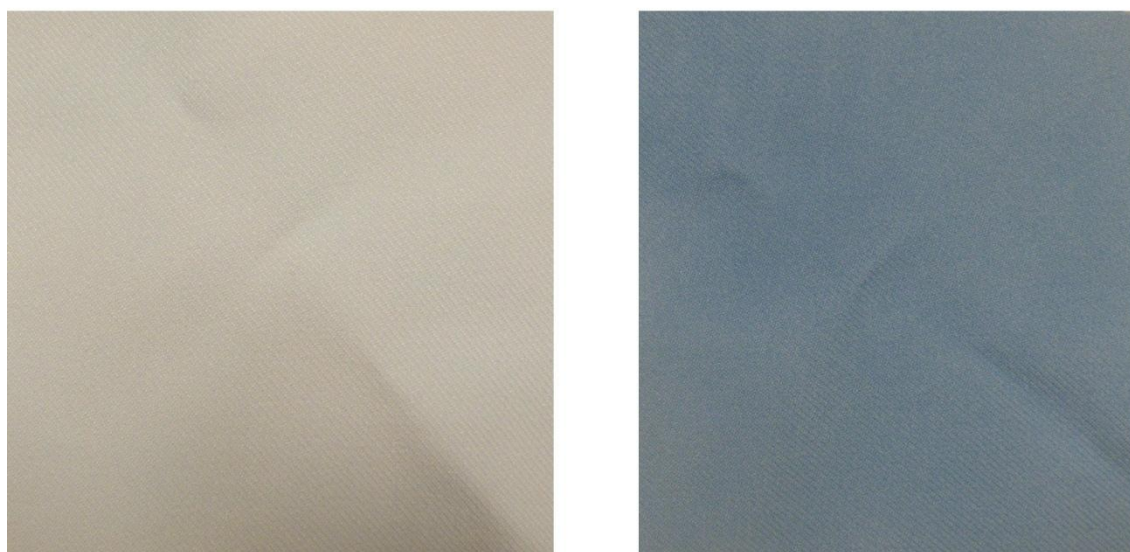
In all cases, the increase in the dyeing concentrations gave rise to a consistent increase in the values of  $\Delta E_2$ , referring to consistent increases in the background colours, as shown in Figure 4.1.



**Figure 4.2** Degree of photocoloration ( $\Delta E_1$ ) for dyes **1-6** applied to polyester by a solvent based pad dry-heat dyeing method

Figures 4.1 and 4.2 show that polyester fabrics dyed with photochromic dyes **1-6** at a dyeing concentration of 0.1% o.w.f showed low values of  $\Delta E_1$  and  $\Delta E_2$ . These low values are likely to be due to the low dye uptake by fabrics at this low dyeing concentration. A dye concentration of 1.5% o.w.f of Oxford Blue recorded the highest value of  $\Delta E_1$ , but at the same time showed a significant increase in the background colour compared to the background colours of samples dyed at lower dyeing concentrations of the same dye. It is observed that an increase in the dyeing concentration of Aqua Green, Oxford Blue, and Corn Yellow from 1.5% to 2% o.w.f causes a significant increase in  $\Delta E_2$  with a small effect on  $\Delta E_1$ , as shown in Figures 4.1 and 4.2 respectively. This result may be explained by the increased restriction applied on the ring opening process of dye molecules associated with the colour change reaction of the dye on UV light exposure in the limited space between polymeric chains of polyester fibres when the dye is present in the fibre at a high concentration. Thus, there is no advantage in increasing the dyeing concentrations of these dyes to 2% o.w.f. Oxford Blue gave rise to a significant increase in  $\Delta E_1$  value and a marginal increase in  $\Delta E_2$  value when the dye concentration was increased from 0.5% to 1% o.w.f, while the increase in the dyeing concentration from 1% to 1.5% o.w.f brought about a higher increase in  $\Delta E_2$  compared to the increase in  $\Delta E_1$ , as shown in Figures 4.1 and 4.2. As a result of these observations, the dye concentration of 1% o.w.f was selected as the

optimum dyeing concentration for Oxford Blue on polyester. For all other dyes, the dye concentration of 0.2% showed relatively high values of  $\Delta E_1$  and small values of  $\Delta E_2$  compared to the values given at higher concentrations. The small increase in the degree of photocolouration of fabrics dyed at higher concentrations of these dyes was associated with high background colours of the dyed fabrics, and therefore the dye concentration of 0.2% was selected as the optimum dyeing concentration for Aqua Green, Palatinate Purple, Plum Red, Ruby and Corn Yellow applied to polyester fabric by a solvent-based pad dry-heat dyeing method.



**Figure 4.3** Photocolouration of polyester fabric dyed with Oxford Blue by a solvent-based pad dry-heat dyeing method

In an attempt to provide an illustration of the colour change, photographs were taken of the background colour and developed colour after irradiation with UV light for polyester fabric dyed with Oxford Blue, as shown in Figure 4.3. The photograph was taken within 5 seconds after removing the sample from the UV light exposure area. Photographs of other dyes were not taken because of the difficulties associated with the process of taking photographs in the available lighting conditions.



**Table 4.5** Background colours and degree of photocoloration of polyester fabric dyed with photochromic dyes **1-6** by two different dyeing methods

| <i>Dye</i>        | $\Delta E_1$                |                             | $\Delta E_2$                |                             |
|-------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                   | <i>Aqueous-based dyeing</i> | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> | <i>Solvent-based dyeing</i> |
| Aqua Green        | 9.1                         | 12.4                        | 16.8                        | 9.7                         |
| Oxford Blue       | 27.1                        | 27.7                        | 10.0                        | 8.9                         |
| Palatinate Purple | 3.4                         | 7.1                         | 32.0                        | 7.0                         |
| Plum Red          | 3.5                         | 8.0                         | 8.5                         | 15.3                        |
| Ruby              | 8.8                         | 8.0                         | 18.8                        | 11.5                        |
| Corn Yellow       | 14.7                        | 13.3                        | 15.5                        | 7.9                         |

A comparison between the degree of photocoloration and background colours of polyester fabrics dyed with photochromic dyes **1-6** by the solvent-based pad dry-heat dyeing method and those of polyester fabrics dyed with the same dyes as disperse dyes by the aqueous-based exhaust dyeing method, which was discussed in chapter 3, was made in an attempt to evaluate the two dyeing methods in terms of producing optimum photochromic fabrics. The results showed that the general trend was towards the improved performance of fabrics dyed with photochromic dyes by the solvent-based dyeing method compared to those dyed by the aqueous-based dyeing methods with a few exceptions, as shown in Table 4.5. Thus, fabrics dyed with Aqua Green, Oxford Blue and Palatinate Purple by the solvent-based dyeing method showed superior properties in terms of the higher degree of photocoloration and lower background colours compared to the results obtained for the same dyes applied by the aqueous-based dyeing method. The highest improvement was observed in the case of polyester fabrics dyed with Palatinate Purple by the solvent-based dyeing method which showed an increase of more than 100% in the degree of photocoloration and a significant decrease in the background colour compared to the same fabric dyed by the aqueous-based dyeing method, as shown in Table 4.5. The solvent-based dyeing method, compared to the aqueous-based dyeing method, brought about a significant decrease in the background colours of polyester fabrics dyed with Ruby and Corn Yellow, and a slight decrease in the degree of photocoloration in both cases, as shown in Table 4.5. Although the degree of photocoloration of polyester fabric dyed with Plum Red by the solvent-based dyeing method increased by more than a 100% compared to that achieved

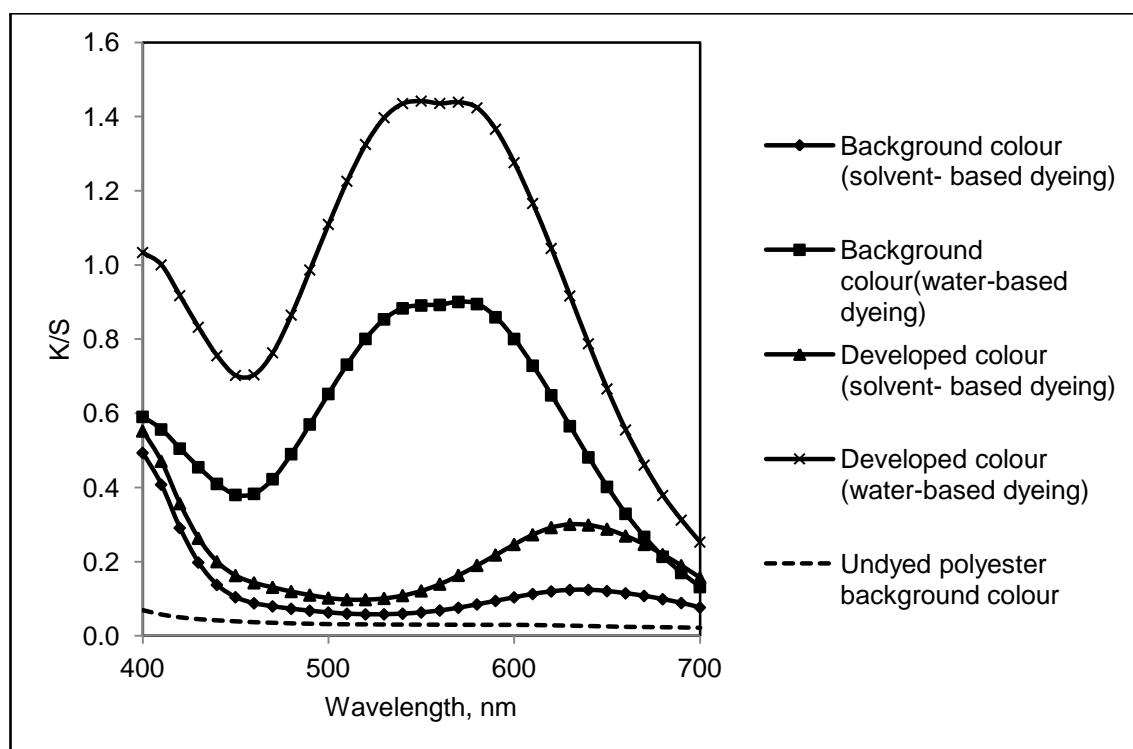
by the aqueous-based dyeing method, its background colour recorded a significant increase in  $\Delta E_2$  from 8.5 to 15.3.

In an attempt to explain the different performance of polyester fabrics dyed by the two dyeing methods, it is proposed that the uptake of photochromic dyes by polyester fabric generally increases when the dyes are applied by the solvent-based pad dry heat dyeing method due to the higher solubility of the dyes in dichloromethane used as a dyeing medium, compared to the limited solubility of these dyes in water which is the medium of applying the dyes to polyester fabric as disperse dyes by the aqueous-based exhaust dyeing method, as discussed in chapter 3. This increased dye uptake may lead to an increase in the diffusion of the dye molecules into polyester fibres. These dyes exist in two molecular forms, the non-coloured ring-closed form and the coloured ring-opened form which may be formed thermally to a certain extent under the dyeing conditions in both dyeing methods. The general structures of the ring-opened and ring-closed forms of photochromic dyes **1-6** are given in section 3.3.1. The probable contribution of the coloured ring-opened form of photochromic dyes to the background colour of polyester fabrics dyed with these dyes and the factors that may enhance the formation of the ring-opened form under dyeing conditions have been discussed in section 3.3.3. Thus, the increase in the dye diffusion into polyester fabrics dyed with photochromic dyes by the solvent-based dyeing method compared to that achieved by the aqueous-based dyeing method may account for the observed increase in the degree of photocolouration and/or the background colours of the dyed fabrics. The dye molecules that have diffused as non-coloured ring-closed molecules bring about an increase in the degree of photocolouration, while the coloured ring-opened molecules are likely to cause an increase in the background colours of the dyed fabrics. The uptake of the ring-opened molecules may be limited due to their relatively large size, depending on the specific chemical structure of each dye, and the space created between the molecular chains of polyester fabric as a result of the segmental mobility of these chains at the temperature of dyeing or the thermal fixation process. The concept of the segmental mobility of molecular chains and its effect on facilitating the dyeing process of thermoplastic fibres is discussed in section 2.7. In another respect, the formation of the ring-opened form of the dye molecules may be determined by the conditions of the dyeing method used and the interaction between the dye and the dyeing solvent. On the basis of this explanation, the compromise between the increased diffusion of the dye molecules in both ring-opened and ring-closed forms, the ease of formation of the ring-opened form under the dyeing conditions and the interaction of each dye with the

dyeing solvent and the restrictions applied to the amount of the ring-opened molecules taken up determine the final effect on the degree of photocolouration and background colours of the dyed fabrics. These factors depend on the solubility of the dye in the dyeing medium, the chemical structure of the dye, and the geometry of its ring-opened form. Thus, if the dye is highly soluble in the dyeing solvent, and, at the same time, the dyeing conditions and the interaction between the dye molecules and the dyeing solvent do not favour the formation of the ring-opened form, this will result in an increased uptake of the ring-closed and a decreased uptake of the ring-opened forms. As a result, there will be a higher degree of photocolouration and the background colour will decrease, as shown in the cases of Aqua Green, Oxford Blue and Palatinate Purple dyed by the solvent-based dyeing method compared to the same dyes applied by an aqueous-based dyeing method.

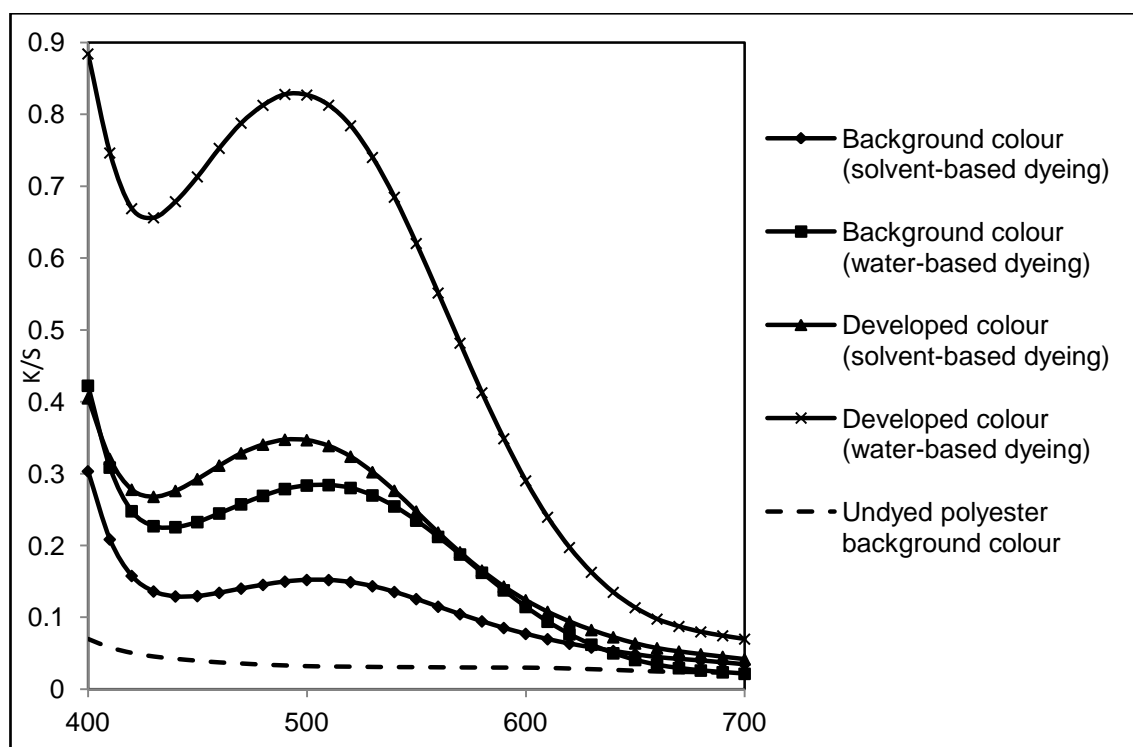
If the ring-opened form of the dye molecules is relatively small and planar, and the formation of this form is enhanced by both the interaction between the dye and the dyeing solvent and the dyeing conditions, the dye uptake by the fabric of dye molecules in their ring-opened and ring-closed forms may increase, and therefore both the background colour and the degree of photocolouration may increase, as shown in the case of Plum Red applied by the solvent-based dyeing method.

If the solubility of the dye in the dyeing solvent is limited ( not much higher than the solubility in water ) and, at the same time, the interaction between the dyeing solvent and the dye does not enhance the formation of the ring-opened form, the degree of photocolouration may not be significantly affected by changing the dyeing method, while the background colour will significantly decrease, as shown in the cases of Ruby and Corn Yellow.



**Figure 4.4** K/S curves for polyester fabric dyed with Palatinate Purple (0.2% o.w.f) by two different dyeing methods

It was observed that when Palatinate Purple was dissolved in dichloromethane, the colour of the dye solution was unexpectedly light green. It was subsequently found that the background colour of polyester fabric dyed with Palatinate Purple by a solvent-based pad dry-heat dyeing method was also light green. This colour change phenomenon was investigated by comparing the colours of polyester fabrics dyed with Palatinate Purple by a solvent-based pad dry-heat dyeing method with the colour of the same fabric dyed with the same dye as a disperse dye by the aqueous-based dyeing method, as discussed in chapter 3. The light absorption characteristics changed from two maximum wavelengths at around 540 nm and 570 nm in the case of the water-based dyed fabric to an absorption at around 630 nm in the case of the solvent-based dyed fabric, as shown in Figure 4.4. The other photochromic dyes showed similar colours when they were dissolved in dichloromethane compared to their colours in water, and also the colours of polyester fabrics dyed with the same dye by the two different dyeing methods were similar in the cases of all photochromic dyes except Palatinate Purple. An example showing that polyester fabrics dyed with Ruby by the solvent-based and the water-based dyeing methods have similar light absorption characteristics at around 500 nm is illustrated in Figure 4.5.



**Figure 4.5** K/S curves for polyester fabric dyed with Ruby (0.2% o.w.f) by two different dyeing methods

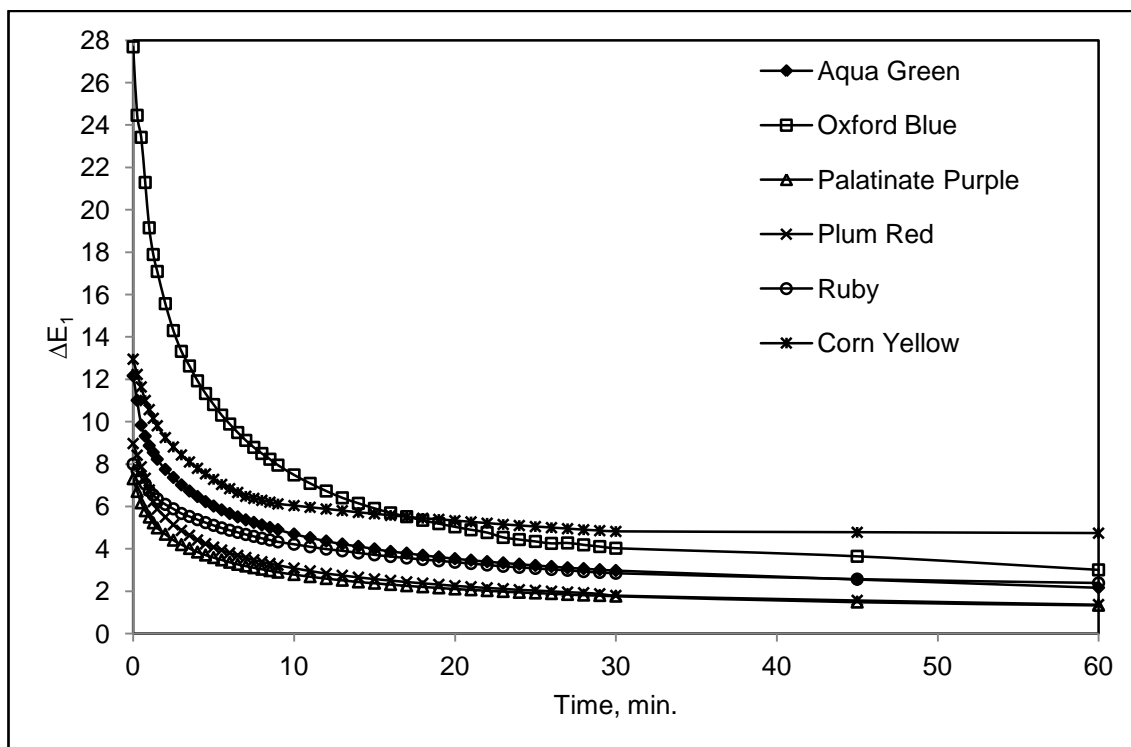
This permanent colour change of Palatinat Purple brought about by dissolving this dye in two different solvents, water and dichloromethane, may be due to negative solvatochromic properties associated with this dye. The principles of solvatochromism have been discussed in section 2.2.4. Thus, on the basis of proposed negative solvatochromic properties of Palatinat Purple, the observed colour change of this dye may be brought about by the low polarity of dichloromethane, which was used in a solvent-based pad dry-heat dyeing method, compared to the higher polarity of water used in the aqueous-based dyeing method.

Another interesting observation is the similarity between the colour of the dyeing solution and the permanent background colour transferred to the dyed fabric. This observation may give evidence that the main factor in the presence of background colours of fabrics dyed with photochromic dyes is the transfer of dye molecules in their coloured ring-opened form to the fabric under conditions of the dyeing process.

#### ***4.3.3. Fading time of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method***

The fading characteristics of photochromic dyes **1-6** applied to polyester fabrics using their optimum dyeing concentrations were investigated by irradiating the dyed fabrics

with UV light for 4 minutes and recording the values of  $\Delta E_1$  over fading times of up to 60 minutes in the dark at room temperature.



**Figure 4.6** Fading curves for dyes **1-6** applied to Polyester by the solvent-based pad dry-heat dyeing method

All colours developed on polyester fabric after UV light exposure started fading to their original background colours immediately after removing the UV light source, as shown in Figure 4.6. A notable observation in Figure 4.6 is the slow fading of naphthopyran-based dyes (Ruby and Corn Yellow) compared to the spironaphthooxazine-based dyes (Aqua Green, Oxford Blue, Palatinate Purple and Plum Red). This feature was confirmed by measuring the time required by photochromic dyes **1-6** on polyester to fade in the dark to half the values of  $\Delta E_1$  recorded immediately after UV light exposure and referring to this value by the term 'half life of fading'. Thus, the half life of fading of the spironaphthooxazine-based dyes varied from 3 minutes in the case of Oxford Blue to 4.5 minutes in the cases of Aqua Green and Palatinate Purple. Ruby and Corn Yellow, which are naphthopyrans, showed higher values of the half life of fading, 11.5 and 14 minutes respectively, as shown in Table 4.7. These results of the half life of fading, in terms of the order of magnitude, are broadly consistent with those given by the same dyes applied to polyester fabric as disperse dyes by the aqueous-based exhaust dyeing method, which has been discussed in section 3.3.6. In addition, it was observed

that the value of half life of fading of each dye applied to polyester fabric by the solvent-based dyeing method is lower than that of the same dye applied to polyester fabric by the aqueous-based exhaust dyeing method, except Plum Red which showed the opposite behavior, as shown in Table 4.7. In conclusion, the rate of fading of the photochromic dyes applied to polyester fabric may be affected by the interaction between the dye and the dyeing solvent which may in turn have influenced the location and distribution of the dye in the fibre. In addition, the differences in the dyeing temperature and the thermal fixation temperature in the cases of the aqueous-based and the solvent-based dyeing methods respectively and the dyeing media used in both cases may have different effects on polyester fibre during the dyeing process. It has been reported that the rigidity of polymeric systems and the free volumes available to the photochromic dye strongly influence its kinetics of photochromism leading to altering its rate of photocolouration and fading. [32, 198] Thus, it is a possibility that the non-polar nature of dichloromethane and the high temperature of thermal fixation in the solvent-based dyeing method may have led to a structure with freer segmental mobility of polyester molecular chains due to the penetration of the solvent into the fibre and the high temperature conditions, which in turn creates larger spaces between the chains when the polyester cools down to room temperature after dyeing. Hence, dye molecules may be in a less restricted matrix when applied by the solvent-based dyeing method compared to the same dyes applied by the aqueous-based dyeing method. As a result, photochromic dyes applied by the solvent-based dyeing method possessed higher fading rates, during the time of half life of fading, compared to the same dyes applied by the aqueous-based dyeing method, as shown in Table 4.6. Thus, the overall effect may be determined by various factors including the specific interaction between the dye and dyeing solvent, the interaction between the solvent and polyester fibres and finally the effect of the dyeing temperature or thermal fixation temperature on the fibre structure during the dyeing process.

**Table 4.7** Half life of fading of photochromic dyes **1-6** applied to polyester fabric by two different dyeing methods

| <i>Dye</i>        | <i>Half life of fading, min.</i> |                             |
|-------------------|----------------------------------|-----------------------------|
|                   | <i>Solvent-based dyeing</i>      | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 4.5                              | 7.6                         |
| Oxford Blue       | 3.1                              | 4.2                         |
| Palatinate Purple | 4.5                              | 7.1                         |
| Plum Red          | 4.2                              | 3.1                         |
| Ruby              | 11.5                             | 18.1                        |
| Corn Yellow       | 14.1                             | 19.8                        |

The relatively slow fading of the naphthopyran-based dyes has been observed in a previous study of the application of dyes **1,3,4,5** and **6** to polyester fabrics by screen printing. [103] In another respect, photochromic dyes **1-6** showed residual colours on polyester fabric after fading in the dark for 60 minutes compared to the background colours of these fabrics before irradiation with UV light. The residual colour after 60 minute of fading in the dark was assessed by calculating the value of  $(\Delta E_1)_{60} / (\Delta E_1)_0$ , where:

$(\Delta E_1)_0$  is the degree of photocolouration measured immediately after the UV light exposure for 4 minute.

$(\Delta E_1)_{60}$  is the remaining degree of photocolouration measured after 60 minutes of fading in the dark.

On the basis of this assessment method, the residual colours of photochromic dyes **1-6** on polyester fabric after 60 minutes of fading in the dark are given as fractions of the values of  $(\Delta E_1)_0$  expressed as percentages. These values varied between 11-18% in the case of the spironaphthooxazine-based dyes, and 30-37% in the case of the naphthopyran-based dyes, as shown in Table 4.8. An explanation of the factors that may give rise to the higher residual colour of naphthopyran-based dyes compared to that of the spironaphthooxazine-based dyes has been given in section 3.3.6.

A comparison between the residual colours of the photochromic dyes applied to polyester fabric by the solvent-based dyeing method and those of the same dyes applied to polyester fabric as disperse dyes by an aqueous-based dyeing method showed that there was no apparent consistency between the results obtained by both dyeing methods in terms of the order of the values and the trend of the effect of the dyeing method on



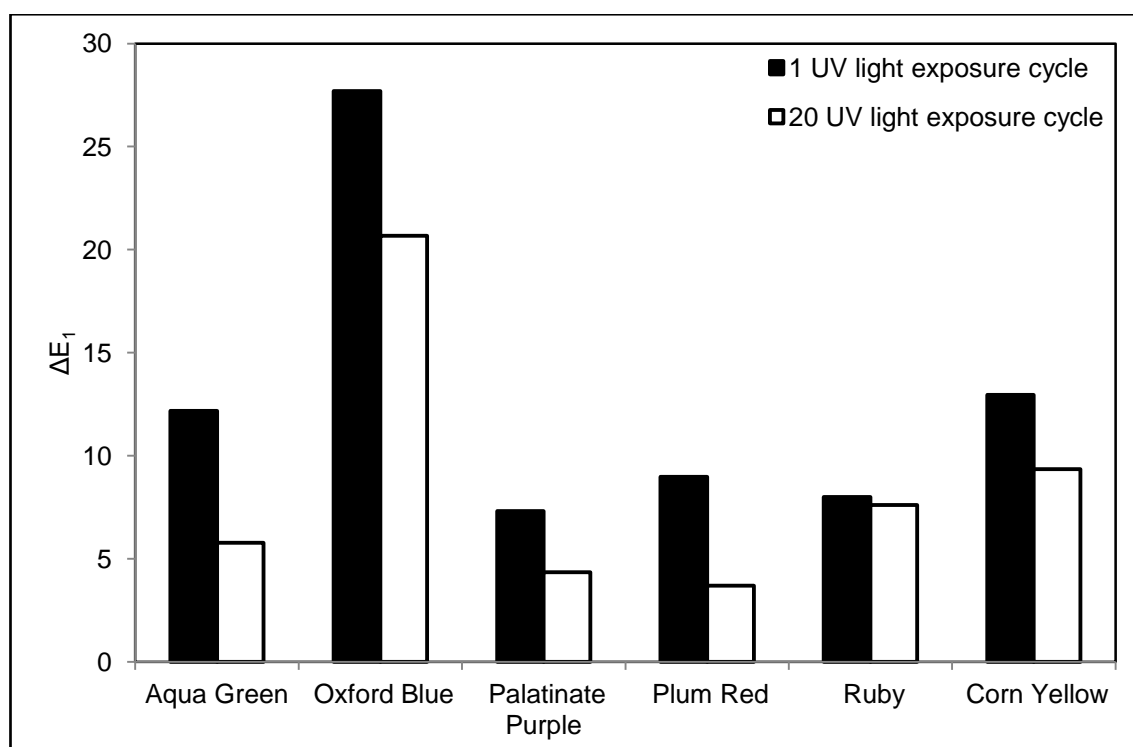
the value of the residual colour of each dye, as shown in Table 4.8. The property may be determined by the interaction between each dye and the dyeing solvent under the dyeing conditions in such a way that depends on the specific chemical structure of the dye. Although the results of the half life of fading showed reasonable consistency with regard to the effect of the dyeing method, the effect on the residual colours retained after 60 minutes of fading in the dark showed inconsistency. A tentative explanation is that the dyeing method may have a dominant influence on the fading time at the beginning of fading compared to its effect after a 60-minute time of fading when there may be dominance of another factor after this relatively long time of fading. This factor which may arise from the outcome of the interactions associated with each dye, the dyeing solvent and the dyeing conditions arises after longer fading time is relatively lower restriction in the matrix in which each dye is located towards the ring closure reaction at the time when most of the dye molecules have undergone the reaction in the first few minutes of fading. Thus, the remaining molecules of each dye will experience similar low levels of restriction towards their fading reactions after longer fading time compared to the same dye applied by different dyeing method. Therefore, the rate of fading of each dye will be determined by its specific chemical structure and the outcome of its interaction with the dyeing solvent under dyeing conditions. Consequently, the residual colours of the dyes applied by different dyeing methods will be affected in different ways, as shown in Table 4.8.

**Table 4.8** Residual colours after 60 minutes in the dark of developed colours of photochromic dyes **1-6** applied to polyester fabrics by two different dyeing methods

| <i>Dye</i>        | $(\Delta E_{1})_{60} / (\Delta E_{1})_0$ |                             |
|-------------------|--|-----------------------------|
|                   | <i>Solvent-based dyeing</i>              | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 18 %                                     | 24 %                        |
| Oxford Blue       | 11 %                                     | 4 %                         |
| Palatinate Purple | 18 %                                     | 21 %                        |
| Plum Red          | 15 %                                     | 9 %                         |
| Ruby              | 30 %                                     | 32 %                        |
| Corn Yellow       | 37 %                                     | 29 %                        |

#### 4.3.4. Fatigue resistance of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method

Samples of polyester fabric dyed with photochromic dyes **1-6** at their optimum dyeing concentrations were irradiated with UV light for 4 minutes. The irradiated samples were left to fade to their background colours over a period of 2 hours in the dark at room temperature. This cycle of UV exposure and fading was repeated 20 times, and then  $\Delta E_1$  was measured and compared with the value of  $\Delta E_1$  recorded after the first UV light exposure.



**Figure 4.7** Fatigue resistance of dyes **1-6** applied to polyester fabric by a solvent-based pad dry-heat dyeing method

Figure 4.7 shows that the dyed fabrics retained different levels of their photochromic response after 20 cycles of UV light exposure. Ruby showed the highest fatigue resistance retaining 95% of its photochromic response after 20 cycles of UV light exposure compared to its response after the first cycle, as shown in Table 4.9. Oxford Blue and Corn Yellow came next by retaining 75% and 72% of their photochromic response respectively. Aqua Green, Palatinate Purple and Plum Red were the dyes that deteriorated most by retaining 47%, 60% and 41% respectively of their photochromic response after 20 cycles of UV exposure.

**Table 4.9** Retention of photochromic response of polyester fabrics dyed with photochromic dyes **1-6** by a solvent-based pad dry-heat dyeing method after 20 cycles of UV light exposure as a fraction of the photochromic response after the first exposure cycle, expressed as a percentage.

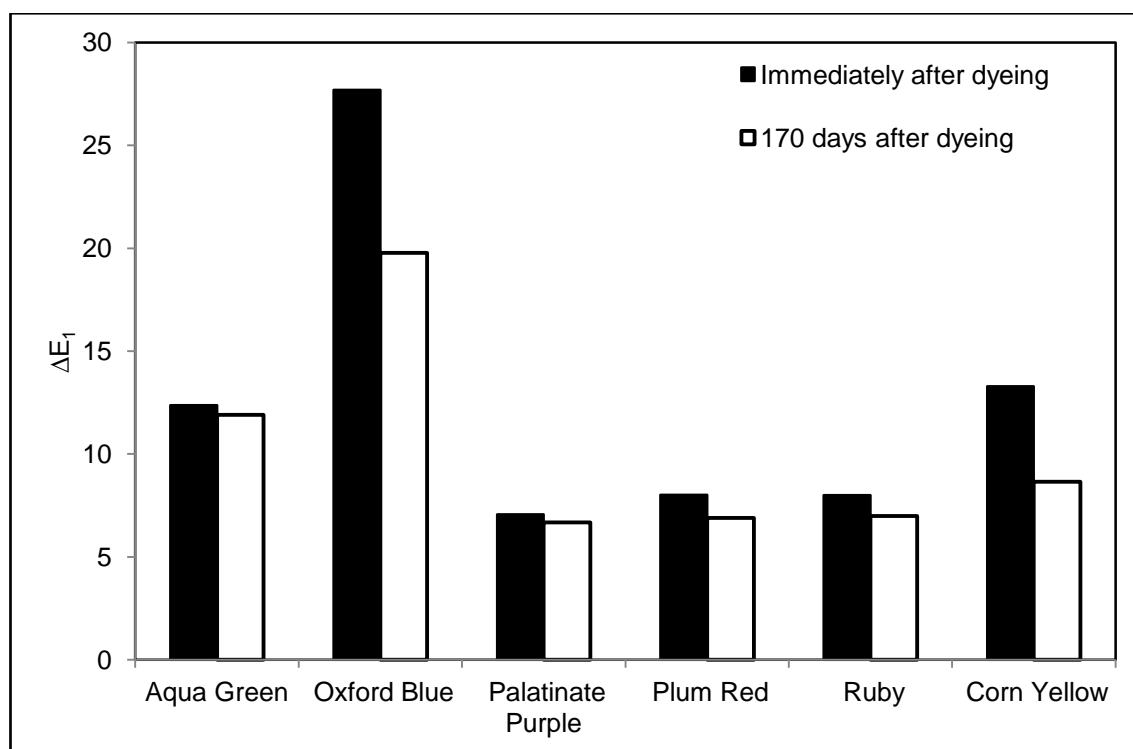
| <i>Dye</i>        | <i>Retention of photochromic response after 20 cycles of UV light exposure</i> |                             |
|-------------------|--|-----------------------------|
|                   | <i>Solvent-based dyeing</i>  | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 47 %   | 70 %                        |
| Oxford Blue       | 75 %   | 92 %                        |
| Palatinate Purple | 60 %   | 98 %                        |
| Plum Red          | 41 %   | 28 %                        |
| Ruby              | 95 %   | 99 %                        |
| Corn Yellow       | 72 %   | 78 %                        |

These results indicate that the general chemical class of photochromic dyes may not have the determining effect on the fatigue resistance of the dyes. In addition, the order of magnitude of fatigue resistance of photochromic dyes **1-6** applied to polyester by a solvent-based pad dry-heat dyeing method is not completely consistent with that of the same dyes applied to the same fabric as disperse dyes by an exhaust dyeing method. However, fabrics dyed with Ruby showed the highest fatigue resistance while fabrics dyed with Plum Red showed the lowest fatigue resistance in both dyeing methods, as shown by comparing the results in this section with those given in section 3.3.7 which are shown in Table 4.9. In addition, it is observed that the fatigue resistance of each photochromic dye applied by an exhaust dyeing method is higher than that of the same dye applied to the same fabric by the solvent-based pad dry-heat dyeing method, with one exception which is Plum Red, as shown in Table 4.9. Thus, the dyeing method for applying photochromic dyes to polyester fabric produces similar trends in the fatigue resistance of these dyes on the fabric, but the specific chemical structure of each dye, its interaction with the dyeing solvent and the dyeing conditions may determine the specific value of its fatigue resistance. This resistance shows a dependence on the mechanism of photodegradation of the dye, which is brought about by the repetitive exposure to UV light in this case, which will vary with the chemical structure of the dye, as discussed in section 2.5. On the other hand, there is a similarity of the effect of the dyeing solvent on the trend of the fatigue resistance and there is an increase in the

fatigue resistance of each dye when dichloromethane is replaced by water as a dyeing solvent. This effect may be explained by the outcome of the influence of the solvent on the polyester fabric substrate. Thus, the more rigid matrix of polyester treated with water compared to that of the same fabric treated with dichloromethane, as discussed in section 4.3.3, appears to be providing the dyes with some protection against photodegradation as a result of interaction with UV light. The protection may involve this environment reducing the possibility of contact of the dye with reactive species, such as molecular oxygen, which would be involved in the photooxidative mechanism discussed in section 2.5, by limiting its penetration into the polymer matrix, or by a degree of filtering the penetrating UV light by the matrix. Thus, the relatively higher-shielded dyes which are applied to polyester fabric by the aqueous-based dyeing method compared to the same dyes applied by the solvent-based dyeing method may provide higher protection towards the photodegradation effect brought about by the repetitive exposure to UV light, and therefore they possess higher fatigue resistance, as shown for most dyes in Table 4.9.

#### ***4.3.5. Storage stability of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method***

Ageing or storage stability of the dyed fabrics was assessed by retaining the fabric samples in the dark at room temperature and re-measuring after 170 days. This evaluation would not normally be relevant with traditionally-dyed fabrics, but is of interest with photochromic fabric, because the dyes are generally significantly less stable than traditional dyes. The test complements the fatigue resistance tests, providing information on the potential longevity of products exposed to UV light infrequently or only intermittently in their lifetime. The degree of photocoloration of the dyed samples after UV exposure was measured after the 170 days storage and the values compared to the values measured on the day of dyeing, as shown in Figure 4.8.



**Figure 4.8** Storage stability of dyes 1-6 applied to polyester fabric by a solvent-based pad dry-heat dyeing method

The ability to develop colour on UV light exposure retained by the dyes after 170 days storage in the dark was found to be in the range 64-96%. The highest storage stabilities were shown by Aqua Green and Palatinate Purple which retained 96% and 94% of their degrees of photocoloration respectively. Ruby and Plum Red retained 87% and 86% of their degrees of photocoloration respectively. Corn Yellow possessed the lowest storage stability, retaining only 64% of its degree of photocoloration, while Oxford Blue retained 71% of its degree of photocoloration after 170 days of storage in the dark, as shown in Table 4.10.

**Table 4.10** Retention of photochromic response of polyester fabrics dyed with photochromic dyes **1-6** by a solvent-based pad dry-heat dyeing method after 170 days storage in the dark as a fraction of their photochromic response on the day of dyeing

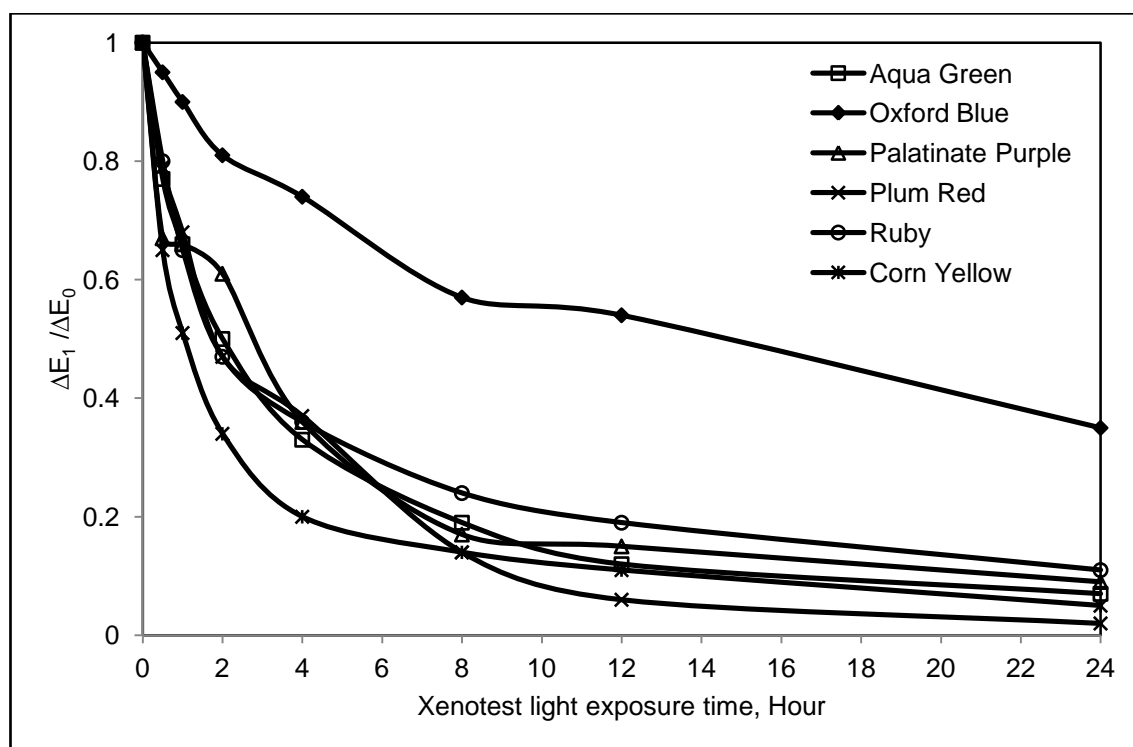
| <i>Dye</i>        | <i>Retention of photochromic response after 170 days storage in the dark</i> |                             |
|-------------------|--|-----------------------------|
|                   | <i>Solvent-based dyeing</i>  | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 96 %   | 84 %                        |
| Oxford Blue       | 71 %   | 76 %                        |
| Palatinate Purple | 94 %   | 60 %                        |
| Plum Red          | 86 %   | 83 %                        |
| Ruby              | 87 %   | 81 %                        |
| Corn Yellow       | 64 %   | 73 %                        |

It may be inferred from the investigation of the storage stability of photochromic dyes **1-6** applied to polyester fabric by a solvent-based pad dry-heat dyeing method that this property is not related to the general chemical class of the dye, but it may be determined by the specific chemical structure of each dye. There is no apparent consistency between the order of magnitude of storage stability of photochromic dyes **1-6** applied by a solvent-based pad dry-heat dyeing method and that of the same dyes applied as disperse dyes by an exhaust dyeing method, as shown by comparing the results in this section with those in section 3.3.8 which are given in Table 4.10. In addition, the values of storage stability of the same dye applied to polyester fabric by the two different dyeing methods were different, with no apparent relation between the dyeing method and the directions of this difference, either an increase or a decrease, in the storage stability of the dyes. Thus, the dyeing method may affect the storage stability of the dye as a result of the interaction between the dye, the dyeing solvent and the dyeing conditions rather than the effect of the solvent on the dyed substrate, and therefore this effect is related to the specific chemical structure of each dye. This result is anticipated, because the storage stability represents a property of the dye affected by the dye behaviour in the dark rather than its behaviour under UV light exposure. Therefore, this property is not affected by the factors associated with the effect of the dyeing conditions on the dyed fabric, such as the geometrical changes in the physical structure of polyester fibres which in turn affect other properties, such as the fading time and fatigue resistance by restricting the ring-closure reaction after removing the UV exposure in the former case and shielding the dye molecules from UV exposure in the latter case when

the solvent-based dyeing medium was replaced by the aqueous-based dyeing, as discussed in sections 4.3.3 and 4.3.4.

#### 4.3.6. Colour fastness to light of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method

The test used for assessing lightfastness of traditional dyes applied to fabrics was not appropriate to assess lightfastness of photochromic dyes, due to the reasons discussed in section 3.3.9. Thus, the lightfastness of photochromic dyes applied to polyester fabrics was assessed using colour measurement, whereby the degree of photocolouration of dyed fabrics exposed to the Xenotest light was compared with that of the fabric measured without such exposure.



**Figure 4.9** Normalized lightfastness curves of photochromic dyes 1-6 applied to polyester fabric by a solvent-based pad dry-heat dyeing method

A plot of  $\Delta E_1/\Delta E_0$  versus the period of time of exposure of the dyed fabrics to Xenotest light was used to illustrate the photostability of photochromic dyes 1-6 applied to polyester fabric, as shown in Figure 4.9.  $\Delta E_0$  represents the initial degree of photocolouration of the dyed fabric before Xenotest exposure, and  $\Delta E_1$  represents the degree of photocolouration of the dyed fabric after exposure. All dyed fabrics started to lose significant amounts of their degree of photocolouration after a relatively short period of time of light exposure. The degree of photocolouration retained by the dyed fabrics

after 24 hours of light exposure varied from one dye to another with no obvious correlation with the chemical classe of the dyes. The most significant retention was shown by Oxford Blue which retained 35% of its original degree of photocoloration. Palatinate Purple, Plum Red, Corn Yellow and Aqua Green showed lower abilities to retain their photocoloration abilities with the retention values of 11%, 9%, 7% and 5% respectively. The lowest ability to retain the degree of photocoloration was shown by Ruby which retained only 2% of the original value before light exposure, as shown in Table 4.11. There was no consistency between the order of magnitude of the values of retention of degree of photocoloration after 24 hours of Xenotest light exposure of photochromic dyes applied to polyester fabric by the solvent-based dyeing method and those of the same dyes applied by an aqueous-based exhaust dyeing method, which was discussed in section 3.3.9, as shown in Table 4.11. In addition, the dyes responded differently in terms of their retention values when they were applied to the fabric by the two different dyeing methods, as shown in Table 4.11. This trend may be explained by the different interaction between each dye and the dyeing solvent, during the dyeing process, depending on the specific chemical structure of the dye. This interaction may affect the dye performance in terms of its lightfastness by the dependence of photodegradation mechanism of the dyes on the outcome of the interaction between each dye and the dyeing solvent under dyeing conditions.

**Table 4.11** Retention of degree of photocoloration of photochromic dyes **1-6** applied to polyester fabric by two different dyeing methods after 24 hours of Xenotest light exposure

| <i>Dye</i>        | <i>Retention of degree of photocoloration after 24 hours of Xenotest light exposure</i> |                             |
|-------------------|---|-----------------------------|
|                   | <i>Solvent-based dyeing</i>   | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 5 %   | 3 %                         |
| Oxford Blue       | 35 %  | 21 %                        |
| Palatinate Purple | 11 %  | 14 %                        |
| Plum Red          | 9 %   | 1 %                         |
| Ruby              | 2 %   | 8 %                         |
| Corn Yellow       | 7 %   | 9 %                         |



Another parameter which may assist in the assessment of lightfastness of photochromic dyes is the half life of the dyes. The special meaning of the term ‘half life’ in this case was given in section 3.3.9.

**Table 4.12** Half life of dyes **1-6** applied to polyester by a solvent-based pad dry-heat dyeing method, following Xenotest exposure.

| <i>Dye</i>        | <i>Half Life/ Hour</i>      |                             |
|-------------------|-----------------------------|-----------------------------|
|                   | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 1.8                         | 0.5                         |
| Oxford Blue       | 14.5                        | 9.4                         |
| Palatinate Purple | 2.9                         | 1.1                         |
| Plum Red          | 2.1                         | 1.5                         |
| Ruby              | 1.1                         | 4.5                         |
| Corn Yellow       | 1.9                         | 1.5                         |

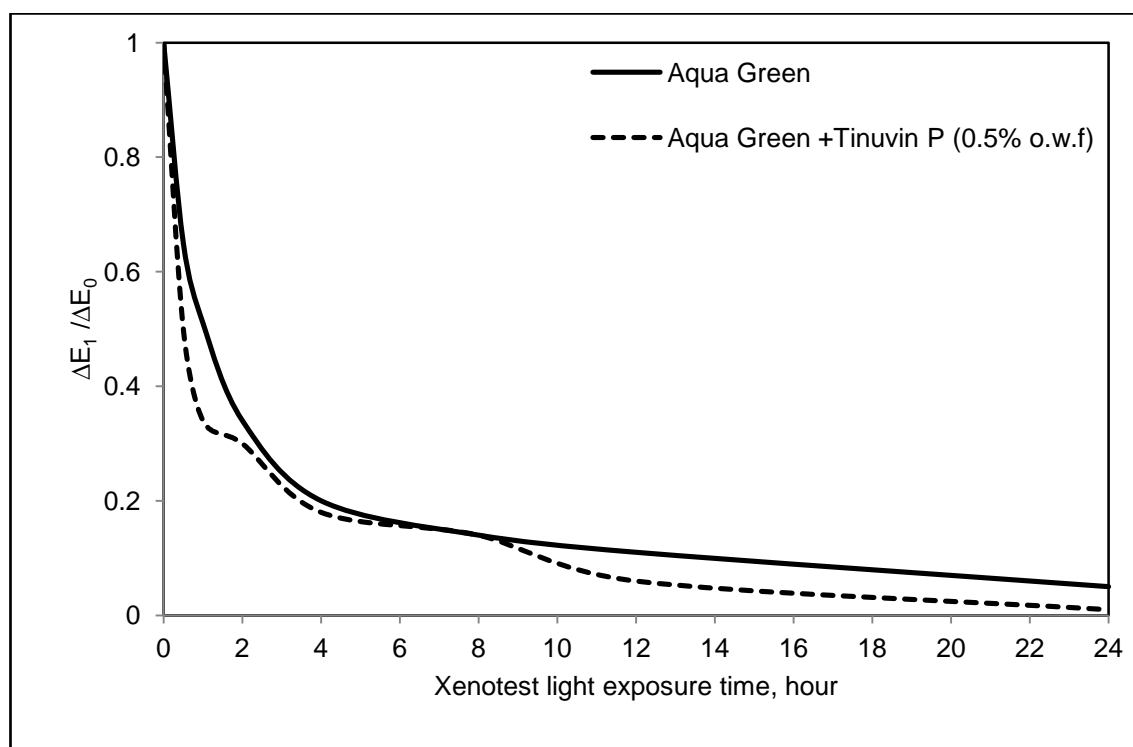
The half life of dyes **1-6** varied from 14.5 hours in the case of Oxford Blue to 1.1 hours in the case of Ruby, as shown in

Table 4.12. The various values of half life of all dyes confirm the observation that lightfastness of the investigated photochromic dyes is not correlated with the general chemical class of the dye, and it may be related to the specific chemical structure of each dye. The comparison between the half life of polyester fabrics dyed with photochromic dyes **1-6** by two different dyeing methods indicates that the dyeing method brings about different effects on the half life of the dyed fabrics in each case, and therefore there is no correlation between the general chemical class of the dye and the response of its lightfastness towards the two different dyeing methods, as shown in Table 4.12.

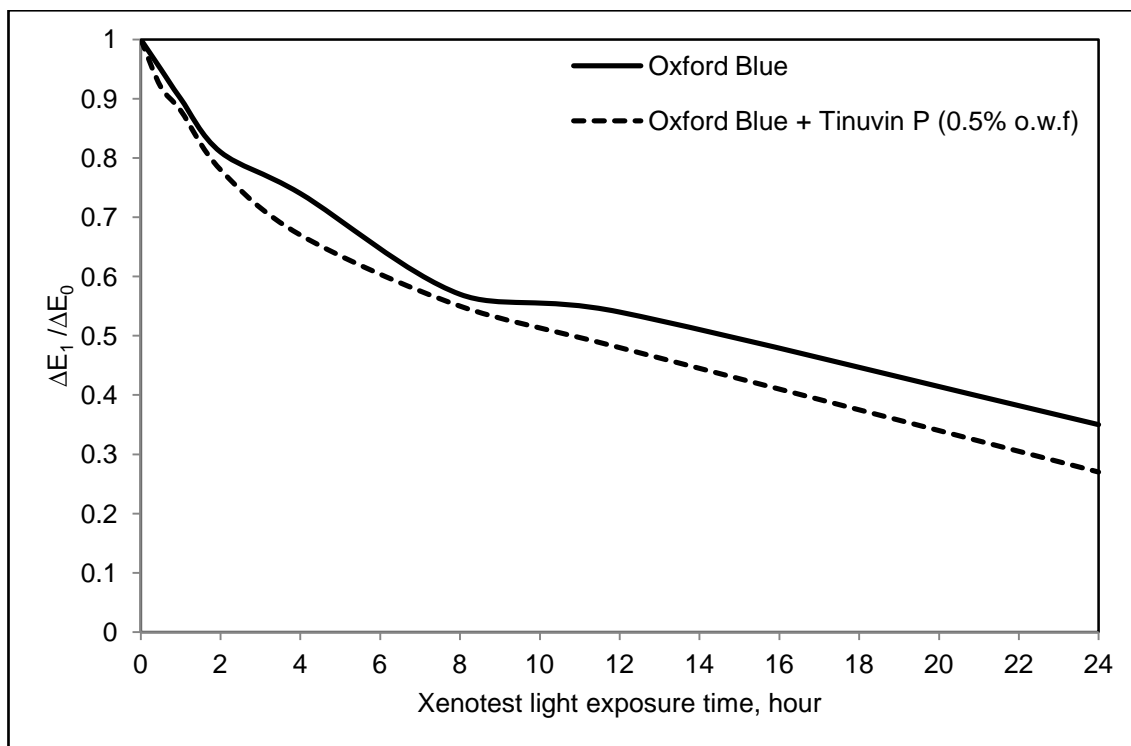
***4.3.7. Additives used in an attempt to improve lightfastness of photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method***

An investigation of the effect of different additives with the aim to improve lightfastness of photochromic dyes applied to polyester fabric as disperse dyes by an exhaust method was discussed in section 3.3.10. On the basis of the investigation of the aqueous dyeing process, there was no single additive identified suitable for all dyes in term of improving their lightfastness while maintaining their degree of photocolouration, as explained in section 3.3.10. It was evident that Tinuvin P, which is a UV absorber,

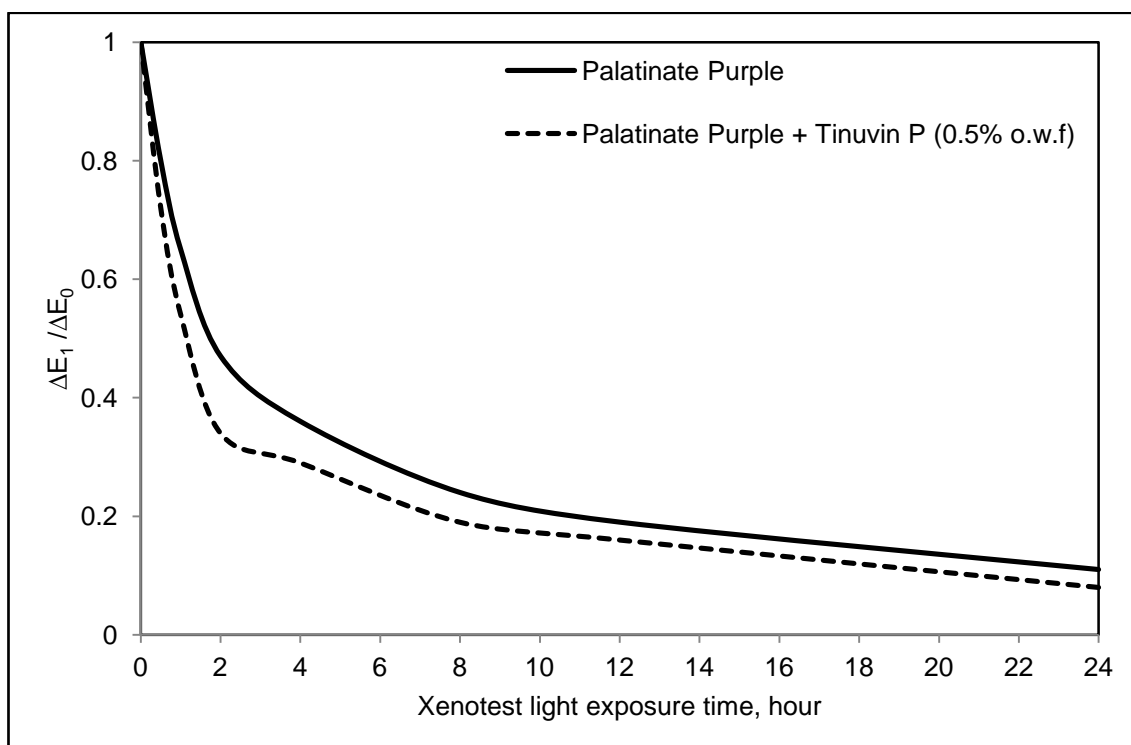
improved lightfastness of the spironaphthooxazine-based photochromic dyes, as shown in Table 3.7, while Tinuvin 144, which is a HALS, improved the lightfastness of Corn Yellow but did not affect lightfastness of Ruby; both of these are naphthopyran-based dyes, as shown in Table 3.6. Consequently, in this part of the investigation Tinuvin P was applied to polyester fabric with spironaphthooxazines (Aqua Green, Oxford Blue, Palatinate Purple and Plum Red), while Tinuvin 144 was applied with naphthopyrans (Ruby and Corn Yellow) by the solvent-based pad dry-heat dyeing method. It was anticipated that the stabilisers might be more effectively applied from an organic solvent in which they are soluble rather than from water in which they are insoluble.



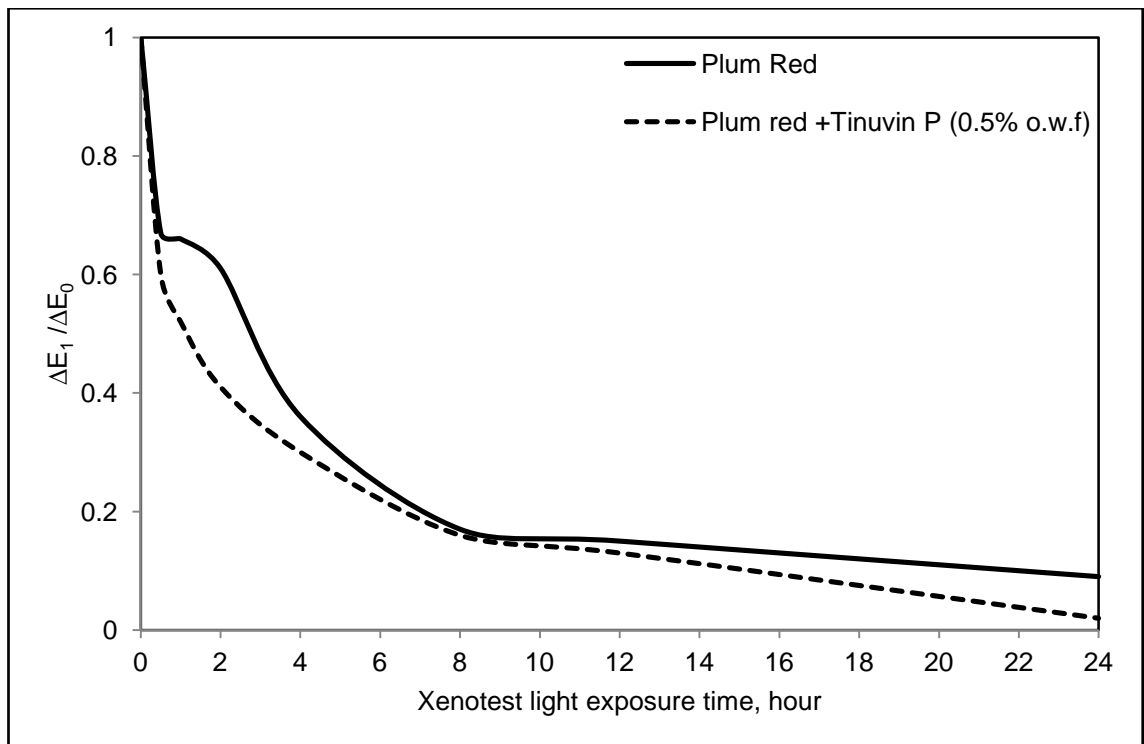
**Figure 4.10** Normalised curves for lightfastness of Aqua Green applied to polyester fabric with Tinuvin P



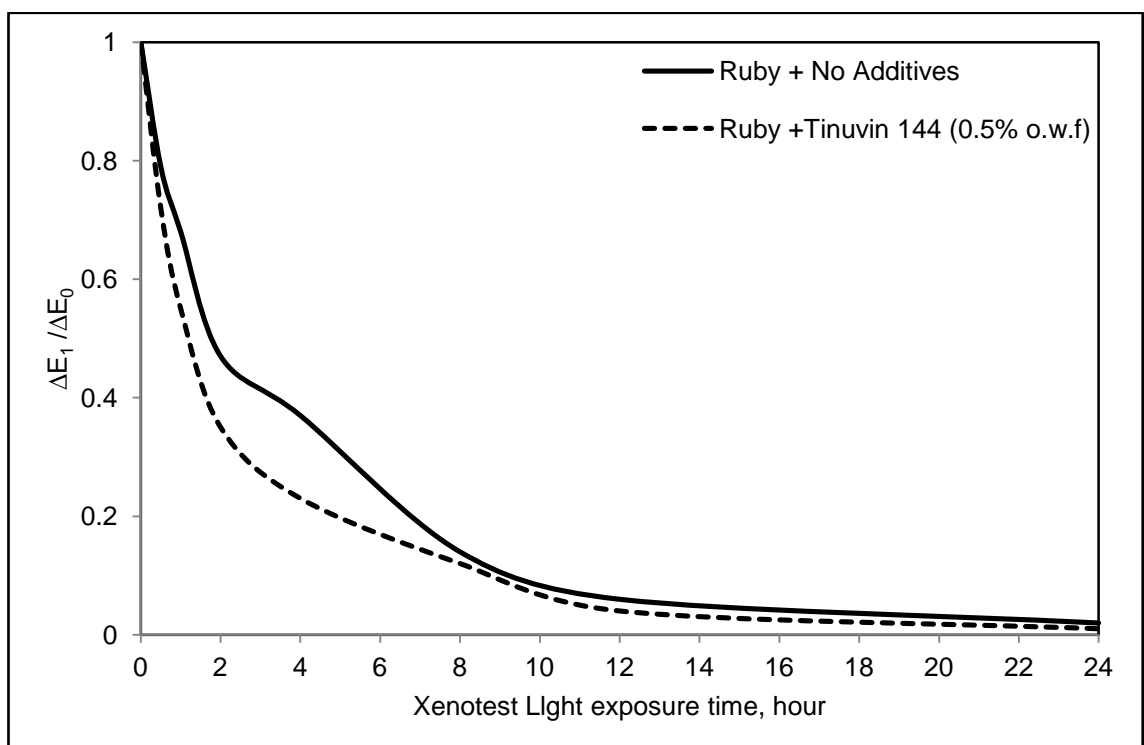
**Figure 4.11** Normalised curves for lightfastness of Oxford Blue applied to polyester fabric with Tinuvin P



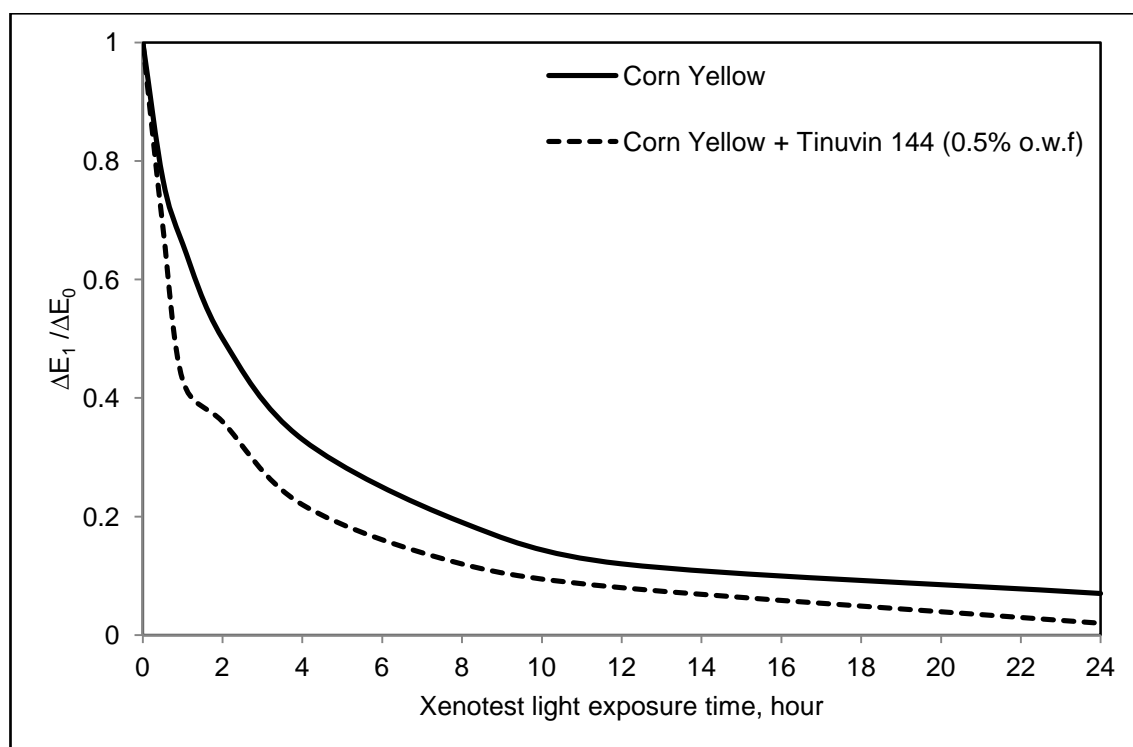
**Figure 4.12** Normalised curves for lightfastness of Palatinate Purple applied to polyester fabric with Tinuvin P



**Figure 4.13** Normalised curves for lightfastness of Plum Red applied to polyester fabric with Tinuvin P



**Figure 4.14** Normalised curves for lightfastness of Ruby applied to polyester fabric with Tinuvin 144



**Figure 4.15** Normalised curves for lightfastness of Corn Yellow applied to polyester fabric with Tinuvin 144

Figures 4.10 – 4.15 show that both additives had a negative effect on the lightfastness of all photochromic dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method. The half life of all dyes on polyester was observed to decrease when the light stabilizers were incorporated with the dye, as shown in Table 4.13

**Table 4.13** Half life of photochromic dyes 1-6 applied to polyester fabric by a solvent-based pad dry-heat dyeing method

| <i>Dye</i>        | <i>Half Life/ Hour</i> |                       |
|-------------------|------------------------|-----------------------|
|                   | <i>No Additives</i>    | <i>With additives</i> |
| Aqua Green        | 1.1                    | 0.5                   |
| Oxford Blue       | 14.5                   | 10.8                  |
| Palatinate Purple | 1.8                    | 1.2                   |
| Plum Red          | 2.9                    | 1.1                   |
| Ruby              | 1.9                    | 1.3                   |
| Corn Yellow       | 2                      | 0.9                   |

This is a disappointing result which is difficult to explain. It may be inferred that the interaction between dichloromethane, as the dyeing medium and the light stabilisers when applied to polyester may have suppressed or badly affected the mechanism by

which the light stabiliser operates, and therefore the light stabilisers brought about deterioration of the lightfastness of photochromic dyes.

#### ***4.3.8. Colour fastness to washing of polyester fabric dyed with photochromic dyes by a solvent-based pad dry-heat dyeing method***

The washfastness test was carried out according to the British Standard BS 1006:1990, Group C, Colour Fastness to Domestic and Commercial Laundering. [181] The comparison between the degree of photocoloration of dyed fabrics before and after the washing test was used to assess the washfastness of these fabrics. This assessment method was used as an alternative to the normal assessment method used in the case of traditional dyes due to the special requirements involved in assessing the washfastness of photochromic dyes, as discussed in section 3.3.11. A series of five washfastness tests are given in the British Standard with the testing conditions increasing gradually from mild to severe in terms of the test time and temperature. On the basis of the results of the washfastness test for the series of photochromic dyes applied to polyester fabric as disperse dyes by an exhaust method, the mild conditions of Test 1, as described in the series of standard washfastness tests, did not cause any deterioration in the photochromic response of the dyed fabrics. The photocoloration of these fabrics started to decrease when they were washed under the conditions of Test 3 which uses a temperature of 60°C and a time of 30 minutes. In the light of these results, the samples of polyester fabric dyed with photochromic dyes **1-6** by a solvent-based pad dry-heat dyeing method were subjected to the washfastness test under this last set of conditions, and their degree of photocoloration were measured and compared to the degree of photocoloration of the unwashed fabrics.

**Table 4.14** Washfastness of polyester fabric dyed with photochromic dyes **1-6** by a solvent-based pad dry-heat dyeing method

| <i>Dye</i>        | $\Delta E_1$           |                                    |                                    |
|-------------------|------------------------|------------------------------------|------------------------------------|
|                   | <i>Unwashed fabric</i> | <i>Washed at 60°C, for 30 min.</i> | <i>Washed at 95°C, for 30 min.</i> |
| Aqua Green        | 12.4                   | 12.3                               | 11.1                               |
| Oxford Blue       | 27.7                   | 27.6                               | 24.8                               |
| Palatinate Purple | 7.2                    | 7.1                                | 6.3                                |
| Plum Red          | 8.0                    | 8.0                                | 7.0                                |
| Ruby              | 8.0                    | 7.6                                | 7.1                                |
| Corn Yellow       | 13.3                   | 13.2                               | 11.6                               |

Table 4.14 shows that the difference between the degree of photocoloration of each dye on an unwashed fabric and on the fabric washed at 60°C for 30 minutes is less than 0.75. Therefore, the degree of photocoloration of dyed fabrics washed under the conditions of Test 3 did not decrease significantly compared to that of the unwashed fabrics. The value of 0.75 was used on the basis of the explanation given in section 3.3.11, a. Thus, the photocoloration of dyed samples effectively showed no deterioration when they were subjected to the relatively mild conditions of Test 3. Consequently, Test 4 was carried out. All dyed samples lost varying levels of their degree of photocoloration when they were washed under the conditions of Test 4, which uses a temperature of 95°C for 30 minutes, compared to the unwashed samples, as shown in Table 4.14. The decrease in the degree of photocoloration varied from 10% in the cases of Aqua Green and Oxford Blue to 13% in the cases of Palatinate Purple, Plum Red and Corn Yellow.

#### **4.4. Conclusions**

Six commercial photochromic dyes, four spironaphthooxazines and two naphthopyrans, were applied to polyester fabric by a solvent-based pad dry-heat dyeing method. This dyeing method was developed based on a previously reported study concerning the application of traditional disperse dyes to polyester fabric from perchloroethylene followed by a thermal fixation of the dyes on the fabric. The dyeing procedure was optimized in terms of the solvent/fabric ratio, the time and temperature of the thermal fixation step and used dichloromethane as a more powerful and less toxic solvent compared to perchloroethylene. The optimisation process was carried out using Oxford

Blue, which is a spironaphthooxazine-based photochromic dye. Dyeing concentrations were optimized for each dye individually by applying the criteria of maximizing the degree of photocolouration and minimizing the background colour of polyester fabric dyed with the photochromic dye by this dyeing method. The degree of photocolouration and the background colour were expressed by  $\Delta E_1$  and  $\Delta E_2$  respectively, as defined in section 3.2.5. On the basis of these optimisation criteria, polyester fabric dyed with Oxford Blue showed the best performance by possessing a relatively low background colour and showing the highest degree of photocolouration on UV light exposure for 4 minutes. This result is consistent with the results of the aqueous exhaust dyeing methods investigated in chapter 3, where Oxford Blue also showed the best performance compared to the other dyes investigated. The other dyes showed variable performance, with a common feature which was the relatively high background colour compared to the degree of photocolouration, which is also consistent with the results given by the same dyes applied to the same fabric by an exhaustion method as discussed in chapter 3. The lowest performance was shown by Plum Red, a spironaphthooxazine, which gave the highest background colour and a low degree of photocolouration. In addition, the solvent-based pad dry-heat dyeing method brought about an improvement of the performance of most of the photochromic dyes applied to polyester fabric by this dyeing method compared to the same dyes applied to the same fabric by the aqueous-based exhaust dyeing method. This improvement was represented by an increase in the degree of photocolouration and a decrease in the background colour in the cases of polyester fabrics dyed with Aqua Green, Oxford Blue and Palatinate Purple or a significant decrease in the background colour accompanied with only a slight decrease in the degree of photocolouration in the cases of the fabrics dyed with Ruby and Corn Yellow. Plum Red was the only dye which showed a significant increase in both the degree of photocolouration and the background colour when it was applied to polyester fabric by the solvent-based pad dry-heat dyeing method.

A notable solvatochromic effect was given by Palatinate Purple which showed a colour change to light green when it was dissolved in dichloromethane, compared to its purple colour in water. This light green colour was also transferred to the fabric after applying the dye from dichloromethane by a solvent-based pad dry-heat dyeing method. The permanent light green background colour of the fabric may be explained by the diffusion of dye molecules to the fabric at their coloured form.

Fading characteristics of dyed fabrics were investigated by recording the decrease in their degree of photocolouration over 60 minutes after removing the UV light source.



The results showed that fading rates of the naphthopyran-based dyes were lower than those of the spironaphthooxazine-based dyes, due to the reasons proposed in section 3.3.6 to explain the same behaviour of these dyes when they were applied to polyester fabric by an exhaust method. Fatigue resistance was variable, but lower than that shown by the same dyes applied to polyester fabric as disperse dyes by an exhaust method. The investigation of the storage stability over 170 days showed variable values of the storage stabilities of the dyes. For both fatigue resistance and storage stability characteristics there was no obvious correlation with the chemical class of each dye.

The colour fastness properties to light and washing were investigated. These properties were assessed by a special method designed to meet the requirements of the dynamic nature of colour change of photochromic dyes. According to this method, the retention of the degree of photocolouration was used to represent the lightfastness and washfastness of the photochromic dyes **1-6** on polyester fabric.

With regards to lightfastness, the half life values of dyes **1-6** applied to polyester fabric by a solvent-based pad dry-heat dyeing method were between 1.1 and 14.5 hours, which are higher than those of the same dyes applied to polyester as disperse dyes by an exhaust method with one exception which is Ruby, a naphthopyran-based dye, which showed a lower lightfastness compared to that achieved when the dye was applied by an exhaust dyeing method.

An attempt to improve the lightfastness of dyed fabrics was carried out by adding the light stabilizers Tinuvin P and Tinuvin 144 to the spironaphthooxazine-based and naphthopyran-based dyes respectively. In contrast with the results achieved by the disperse dyeing by an aqueous exhaust method, the lightfastness of the dyes applied to polyester fabric by a solvent-based pad dry-heat dyeing method decreased when the light stabilizers were added, compared to the lightfastness of the same dyes with no additives.

The washfastness test of the photochromic dyes **1-6** was carried out by subjecting the dyed fabrics to gradually increased severity of washing conditions and measuring the decrease in their abilities to develop colours on UV light exposure. Thus, all dyes were stable under the washing conditions of Test 3, while the conditions of Test 4 (Temperature 95°C; time 30 min.) brought about a decrease of 10-13% in the washfastness of the dyed fabrics compared to the washfastness of the unwashed fabrics. Nevertheless, this represents a highly appropriate level of washfastness for commercial applications. A further observation was that the washfastness of the photochromic dyes

**1-6** applied to polyester fabric by a solvent-based pad dry-heat dyeing method is higher than that of the same dyes applied as disperse dyes by an exhaust method.

## **Chapter 5 - Digital Inkjet Printing of Polyester Fabric with Photochromic Dyes**

### **5.1. Introduction**

Inkjet printing may be defined as a process of building up coloured patterns by projecting tiny drops of inks of different colours onto a substrate surface such as textile fabrics. [160] In spite of the challenges facing the development of inkjet printing technology of textiles which have commercial implications for industry, such as the low productivity, weaknesses in washfastness due to the difficulties associated with incorporating fixing agents into printing inks and the need for pretreatment of fabrics to improve the print quality, this technology has attracted attention in recent years. This is due to the associated advantages compared to the traditional flat and rotary screen printing and roller printing technologies, as explained in section 2.12. [199-204]. Further details of the principles of inkjet printing have been given in section 2.12. Ink formulation is one of the most important factors affecting the print quality and reliability due to the dependence of the jetability of the ink by the printhead on the physical properties of the ink which are optimized to comply with the printhead in use and to provide practically acceptable ink storage stability. [205] An ink formulation process consists basically of mixing ink ingredients, purifying and characterising the ink to optimize its physical properties such as its viscosity, surface tension and average particle size.

The ink system, which refers to the dye or pigment used and the nature of the medium, solvent or water, used to incorporate the ingredients of the ink, is determined mainly by the substrate onto which the ink will be applied. Further details about ink systems and their compatibility with various substrates have been given in section 2.12.3. Thus, inkjet printing of polyester fabric, which is invariably dyed by disperse dyes, is normally carried out by using aqueous dispersion-based ink systems. After printing by this method, the prints are fixed onto polyester fabric thermally by treating the fabric at high temperature either by steaming or using dry heat. Further details about aqueous dispersion-based inks for printing polyester have been given in section 2.12.3, d. In an aqueous dispersion-based ink, the dye is not dissolved in the ink, but it exists as finely dispersed particles due to the limited solubility of disperse dyes in water. Special techniques are required to prepare the concentrated dye dispersions used for formulating aqueous dispersion-based inks to achieve the required fine particle size of the dye. These techniques involve the use of special dispersing agents and high purification to

give a mean particle size in the range from 10 to 250 nm, which addresses storage and ejection stabilities and the elimination of the risk of nozzle blockage due to aggregation of dye particles by obtaining the targeted mean particle size. An issue is that there is limited availability of some of the chemicals, especially the dispersing agents, used for producing the concentrated dispersions required for ink formulations. In fact, dispersing agents that are designed especially for this purpose are often used which means that this process may be difficult to achieve outside of industry involved. As an example, one of the methods used for preparing concentrated dispersions for aqueous dispersion-based ink systems has been referred to in section 2.12.3, d. [171]

In this study, attempts to prepare aqueous dispersion-based inks for inkjet printing were unsuccessful due to the issues described above which include the difficulties associated with achieving the targeted particle size and stable dispersions of the photochromic dyes using the available dispersing agents. Consequently, the concept of using aqueous dispersion-based inks for inkjet printing of polyester fabrics with photochromic dyes was not further investigated. As an alternative choice, a solvent-based ink system was used to investigate the application of photochromic dyes to polyester fabric by an inkjet printing method.

On the basis of the results of the solvent-based dyeing method of polyester fabric with photochromic dyes as described in chapter 4, the properties of dichloromethane in terms of the good solubility of the non-ionic photochromic dyes in this non-polar solvent, the ease of diffusion of the dyes into the fabric from this solvent and other criteria for selecting the appropriate solvent for the solvent-based dyeing, as given in section 4.1, dichloromethane was selected for a preliminary investigation as the solvent for formulations of solvent-based ink systems. However, this preliminary selection proved to be unsuccessful due mainly to the inability to achieve the targeted viscosity of the formulated inks within the range of values which are compatible with the printhead. A detailed study of the investigation using dichloromethane for ink formulation is given in section 5.3.1. As an alternative solvent, isopropanol was selected due to the reasons discussed in section 5.3.1.

The application of the commercial photochromic dyes (**1-6**) described in section 3.1 to polyester fabric by a digital inkjet printing method is discussed in this chapter. Solvent-based ink systems using the dyes were formulated. The inks were characterised in terms of their physical properties which are related to the jetability of the inks, and finally the prints were fixed onto polyester fabrics by thermal fixation prior to carrying out colour measurement of the printed fabrics.

## 5.2. Experimental

### 5.2.1. Colour measurement methodology and conditions

The specifically–devised methodology for colour measurement in terms of the optimum calibration conditions of the spectrophotometer, the temperature variation and the time lapse described in sections 3.2.1, 3.2.2 and 3.2.3 respectively were used in this study.

### 5.2.2. Materials

Polyester fabric and the series of commercial photochromic dyes (**1-6**) used were as described in section 3.2.4. Isopropanol and dichloromethane of a laboratory grade were used as solvents for ink formulations. Ethylene glycol and polyethylene glycol used as humectants were also of laboratory grade. Dowanol DPM 2-(2-methoxypropoxy) propan-1-ol, and triethylene glycol monomethyl ether (TGME), both from Wolfram Alpha, were also used as humectants. Polyvinylpyrrolidone (PVP) from Sigma Aldrich, with average molar weight of 40000, was used to increase the viscosity of the ink to the required level. 2-Pyrrolidone from Sigma Aldrich was used in ink formulations to improve the solubility of solid components in the ink. Some physical properties of these materials are given in Table 5.1. [206-209]

**Table 5.1** Physical properties of materials used for ink formulation

| Material             | Phase  | Viscosity<br>(cP, at<br>25°C) | Surface tension<br>(mN m <sup>-1</sup> ) | Vapour pressure<br>(mmHg, at 25°C) |
|----------------------|--------|-------------------------------|--|------------------------------------|
| Glycerol             | Liquid | 934                           | 64.8                                     | 0.001316                           |
| Ethylene glycol      | Liquid | 16.1                          | 48.4                                     | 0.0001052                          |
| Polyethylene glycol  | Liquid | 58.3                          | 44                                       | < 0.01                             |
| Polyvinylpyrrolidone | Solid  | N/a                           | N/a                                      | N/a                                |
| 2-pyrrolidone        | Liquid | 13.1                          | 45.81                                    | 7.501                              |
| Dowanol DPM          | Liquid | 3.7                           | 28.8                                     | 0.4                                |
| TGME                 | Liquid | 6.25                          | 37.8                                     | 0.009998                           |

### 5.2.3. Ink formulation

The procedure for the optimized ink is given here. Similar procedures were used for other inks as discussed in section 5.3.1. 0.1 g of each photochromic dye (**1-6**) was dissolved in isopropanol to give 40 g of the dye solution which was stirred for 1 hour

using a magnetic stirrer to dissolve the dye. While stirring the dye solution, 30 g of ethylene glycol and 5 g of polyethylene glycol were added, and then 5 g of polyvinylpyrrolidone was added over 10 minutes. The solution was stirred for a further two hours to ensure complete dissolution of polyvinylpyrrolidone. After stirring, the ink was filtered through a filter paper of a pore diameter of 1  $\mu\text{m}$ , and then the filtered ink was left to stand in the dark at room temperature overnight. The ink was then filtered again using the same kind of the filter paper to remove any traces of precipitated components. After the second filtration, the ink was degassed for 2 hours using a Decon Minor ultrasound device to remove air from the ink. Air within the ink can cause reliability problems due to generating gas bubbles in the piezoelectric inkjet (PIJ) printhead used in this study, as discussed in section 2.12.2. After degassing, the inks are ready to be applied to polyester fabric by inkjet printing. Viscosity and surface tension of the ink formulations were measured at room temperature using a Brookfield DV-II+ Pro viscometer and a Kruss surface tension measuring device respectively.

#### ***5.2.4. Digital inkjet printing of polyester fabric with photochromic dyes***

All inkjet printing processes were carried out using Xennia inkjet printer operating a Xaar 760 print unit which is fitted with a drop-on-demand piezoelectric inkjet (DOD-PIJ) printhead. The printer is operated by a computer with XUSB windows application software. The print unit has two rows of nozzles with each row containing 390 nozzles at a pitch of 141.1  $\mu\text{m}$ . The ink is poured slowly into the ink tank which is connected to the print unit, and then the ink tank is closed tightly with the air tight lid. Any air trapped in the print unit is removed using a syringe which is connected manually to the printhead through a pipe supplied with a manual valve. The XUSB software enables the user to carry out the printing process which starts with opening the image, adjusting the printing system parameters and finally starting the printing process. The adjustment of the printing system parameters allows the user to set-up the waveform for each row of the printhead. The fabric is laid on the printing board and then the printhead is passed manually over the fabric. During the passage of the printhead over the fabric, nozzles jet the ink on the fabric according to the image selected which was a square shape in all cases investigated in this study. After printing, fabrics were transferred to a preheated oven for thermal fixation of the prints onto fabric at a temperature of 190°C for 45 seconds. This was followed by a cold water rinse, and then reduction clearing, as described in section 3.2.6. The printed samples were then rinsed with water, washed

with an aqueous solution of Synperonic BD100 ( $1 \text{ g l}^{-1}$ ) for a few minutes, rinsed with water and then air dried.

#### ***5.2.5. Fading characteristics, fatigue resistance and shelf life***

Fading characteristics, fatigue resistance and shelf life of polyester fabrics inkjet printed with photochromic dyes **1-6** using the optimum numbers of printing passes were investigated according to the method described in section 3.2.7.

#### ***5.2.6. Colour fastness to light of polyester fabric inkjet printed with photochromic dyes***

Lightfastness tests were carried out according to the British standard BS1006: 1990, group B, colour fastness to light and weathering B02, colour fastness to artificial light: Xenon arcfading lamp test. [180] The same testing method and conditions given in section 3.2.8 were used in this study.

#### ***5.2.7. Colour fastness to washing of polyester fabric inkjet printed with photochromic dyes***

Washfastness tests were carried out according to the British standard BS1006:1990, Group C, colour fastness to washing and laundering, test 3 (Temperature  $60^{\circ}\text{C}$ , Time 30 minutes). [181] The Roaches Washtec-P washfastness test machine and test conditions discussed in section 3.2.10 were used to assess the washfastness of polyester fabric inkjet printed with photochromic dyes (**1-6**).

### **5.3. Results and Discussion**

#### ***5.3.1. The application of photochromic dyes to polyester fabric by an inkjet printing method***

Photochromic dyes **1-6**, their commercial names and general chemical classes given in Table 3.1, were used to formulate the inks used for application to polyester fabrics by an inkjet printing method. The jetability of an ink by a printhead is determined mainly by the values of the viscosity and surface tension of the ink. These values should be within the ranges compatible with the printhead which are given by the manufacturer of the printing unit. In the case of the printer used in this study, the viscosity of the ink used for printing is required to be in the range between 4 and 7 cP (centipoises) as measured at room temperature, and the surface tension in the range between 28 and 35  $\text{mN m}^{-1}$ . In addition, ink purification and degassing must be carried out to achieve the other

necessary properties of the ink in terms of the targeted particle size of  $\leq 1 \mu\text{m}$  and removing the trapped air to avoid nozzle blockage and print reliability problems.

The optimization process of the inkjet printing method was carried out by applying Oxford Blue, a spironaphthooxazine photochromic dye, and investigating the properties of the printed fabric in terms of achieving the maximum degree of photocolouration, expressed by the value of  $\Delta E_1$ , and minimum background colour expressed by the value of  $\Delta E_2$ . Both of these terms have been defined in section 3.2.5.

For preliminary investigation of ink formulation, dichloromethane was used as the solvent due to the reasons given in section 4.1 and related to the success achieved in using this solvent for dyeing polyester fabric. The first formulation investigated consisted of dichloromethane, ethylene glycol, TGME, glycerol, Dowanol DPM, polyvinylpyrrolidone and 2-pyrrolidone according to the amounts given in Table 5.2. The function of each of these components has been given in section 5.2.2. The ink was formulated according to the method described in section 5.2.3. Measurement of physical properties of the ink prepared according to formulation 1 gave a viscosity of 2.24 cP and a surface tension of  $32 \text{ mN m}^{-1}$ . This ink was applied to polyester fabric by the inkjet printing method described in section 5.2.4. The printed fabric showed a presence of unprinted strips distributed randomly on the printed area due to the presence of a significant number of missing nozzles in the printhead. This observation may be a result of the incompatibility between the ink and the printhead due to a lower viscosity of the ink than the range 4-7 cP which is recommended by the manufacturer of the printhead used in this study.



**Table 5.2** Formulation of dichloromethane-based inks

| <i>Material</i>            | <i>Weight, g per 100 g of ink</i>   |   |   |   |   |
|----------------------------|---|---|---|---|---|
|                            | <i>Formulation 1</i>  | <i>Formulation 2</i>  | <i>Formulation 3</i>  | <i>Formulation 4</i>  | <i>Formulation 5</i>  |
| Ethylene glycol            | 19  | 19  | 19  | 19  | 19  |
| TGME                       | 8   | 8   | 8   | 8   | 8   |
| Glycerol                   | 3   | 3   | 3   | 3   | 3   |
| 2-pyrrolidone              | 2   | 2   | 3   | 5   | 7   |
| Dowanol DPM                | 6   | 6   | 0   | 0   | 0   |
| Polyvinylpyrrolidone (PVP) | 0   | 6   | 2   | 5   | 7   |
| Dye                        | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   |
| Dichloromethane            | As required to make up to a 100g  | As required to make up to a 100g  | As required to make up to a 100g  | As required to make up to a 100g  | As required to make up to a 100g  |
| <i>Ink properties</i>      | Viscosity = 2.24 cP<br>Surface tension = 32 mN m <sup>-1</sup><br>(before and after filtration) | Viscosity = 4.23 cP<br>Surface tension = 31.5 mN m <sup>-1</sup><br>(before filtration) | Viscosity = 2.04 cP<br>Surface tension = 30.5 mN m <sup>-1</sup><br>(before and after filtration) | Viscosity = 3.06 cP<br>Surface tension = 29 mN m <sup>-1</sup><br>(before and after filtration) | Viscosity = 4.03 cP<br>Surface tension = 26 mN m <sup>-1</sup><br>(before and after filtration) |
| <i>Observations</i>        | Unprinted strips in the printed area  | Filtration not successful   | Unprinted strips in the printed area  | Unprinted strips in the printed area  | Unprinted strips in the printed area  |

In an attempt to overcome the problem of the low ink viscosity, polyvinylpyrrolidone (PVP), 6 g per 100 g of the ink was added to the ink formulation with no change in the amounts of the other ingredients, as shown in Table 5.2. The result was an increase in the viscosity and a decrease in the surface tension of the ink to 4.23 cP and 31.5 mN m<sup>-1</sup> respectively. The ink, referred to as formulation 2, showed difficulties in the filtration

process due to the formation of a gel-like material of high viscosity precipitated on the filtration paper which prevented the ink from passing through the paper. This gel-like material may be formed as a result of the interaction between the excessive amount of polyvinylpyrrolidone which is not completely dissolved in dichloromethane and the other ingredients of the ink. Thus, the next stage aimed at improving the formulation was carried out by decreasing the amount of polyvinylpyrrolidone, from 6% to 2% in an attempt to avoid the formation of the gel-like material, and increasing the amount of 2-pyrrolidone from 2% to 3% aiming to improve the solubility of polyvinylpyrrolidone in formulation 3, as shown in Table 5.2. At the same time Dowanol DPM which has a low viscosity, as shown in Table 5.1, was not used in formulation 3 in an attempt to avoid reducing the viscosity to a low level which might result from reducing the amount of polyvinylpyrrolidone. Although these changes resulted in overcoming the issue of the formation of a gel-like material, the viscosity of the formulated ink decreased to 2.04 cP, which is lower than the range recommended. Consequently, the prints produced by applying this ink to polyester fabric showed too many missing nozzles demonstrated by unprinted strips in the printed area on the fabric.

In the next stage, the amount of polyvinylpyrrolidone was increased to 5% in an attempt to increase the viscosity to within the recommended range and, at the same time, the amount of 2-pyrrolidone was increased to 5% to improve the solubility of the additional polyvinylpyrrolidone. The resulting ink, referred to as formulation 4 in Table 5.2, showed, as expected, an increase in the viscosity to 3.06 cP due to the increased level of polyvinylpyrrolidone, and a decrease in the surface tension due to the increased level of 2-pyrrolidone. Inkjet printing of polyester fabric using this ink gave rise again to unprinted strips in the printing area as a result of inactivating some of the nozzles in the printhead due to the incompatibility of the ink with the printhead.

Further attempts to increase the ink viscosity by increasing the amounts of polyvinylpyrrolidone, and 2-pyrrolidone, as is necessary to improve the solubility of polyvinylpyrrolidone, led to an increase in the viscosity to 4.03 cP and a decrease in the surface tension to  $26 \text{ mN m}^{-1}$  than the recommended range for compatibility with the printhead, as shown for formulation 5 in Table 5.2. Consequently, the ink formulated according to formulation 5 was not jetted successfully by the printhead giving rise to the presence of missing nozzles.

On the basis of the results obtained using dichloromethane as the solvent, it was not possible to achieve the required values of viscosity and surface tension of the ink at the same time. Therefore, the next stage was an investigation into the use of isopropanol,

instead of dichloromethane, as the solvent. Isopropanol was selected on the basis of its higher viscosity compared to dichloromethane, as shown in Table 5.3. [210-212], which is closer to the range recommended for the printhead. It was envisaged that this may contribute towards achieving the required viscosity without the necessity to use a high level of polyvinylpyrrolidone. This in turn may eliminate the necessity to use 2-pyrrolidone to improve the solubility of polyvinylpyrrolidone. The elimination of using 2-pyrrolidone, which has a low surface tension, may compensate for the expected lower surface tension of the ink using isopropanol as an alternative to dichloromethane, due to its lower surface tension, as shown in Table 5.3. [213]

**Table 5.3** Some physical properties of isopropanol and dichloromethane

| <i>Property</i>  | <i>Solvent</i>                      |                                 |
|--|-------------------------------------|---------------------------------|
|  | <i>Isopropanol</i>                  | <i>Dichloromethane</i>          |
| Molecular formula  | CH <sub>3</sub> CHOHCH <sub>3</sub> | CH <sub>2</sub> Cl <sub>2</sub> |
| Boiling point (°C) at atmospheric pressure,<br>760 mm Hg | 82                                  | 39.8 – 40                       |
| Viscosity (cP) at a temperature of 25°C                  | 2.040                               | 0.413                           |
| Surface tension (mN/ m) at a temperature<br>of 20°C      | 21.74                               | 28.12                           |

Another factor in selecting isopropanol is its higher boiling point compared to that of dichloromethane, and therefore a slower evaporation rate at room temperature which in turn provides improved control of the proportional amounts of the materials in ink formulations. In addition, isopropanol is a significantly less hazardous solvent than dichloromethane. [214]

The investigations of isopropanol-based ink formulation and application to polyester fabric by inkjet printing were carried out using Oxford Blue. In the first attempt, a simple formulation consisting of ethylene glycol 25%, dye 0.1% and isopropanol as required to make up to 100% was used, referred to as ink 1 in Table 5.4. Both the viscosity and surface tension of this ink were lower than the required values, as shown in Table 5.4.

**Table 5.4** Ink formulation of isopropanol-based inks

| <i>Material</i>       | <i>Weight, g per a 100 g of ink</i>                              |   |  |  |   |
|-----------------------|--|---|--|--|---|
|                       | <i>Ink 1</i>   | <i>Ink 2</i>  | <i>Ink 3</i>   | <i>Ink 4</i>   | <i>Ink 5</i>  |
| Ethylene glycol       | 25   | 30  | 35   | 30   | 30  |
| PVP                   | 0  | 0   | 0  | 5  | 5   |
| Polyethylene glycol   | 0  | 0   | 0  | 0  | 5   |
| Dye                   | 0.1  | 0.1   | 0.1  | 0.1  | 0.1   |
| Isopropanol           | As required to make up to 100 g                                  | As required to make up to 100 g                             | As required to make up to 100 g                                | As required to make up to 100 g                                  | As required to make up to 100 g                             |
| <i>Ink Properties</i> | Viscosity = 1.75 cP<br>Surface tension = 27.5 mN m <sup>-1</sup> | Viscosity = 2 cP<br>Surface tension = 28 mN m <sup>-1</sup> | Viscosity = 2.14 cP<br>Surface tension = 27 mN m <sup>-1</sup> | Viscosity = 4.46 cP<br>Surface tension = 27.5 mN m <sup>-1</sup> | Viscosity = 5 cP<br>Surface tension = 29 mN m <sup>-1</sup> |

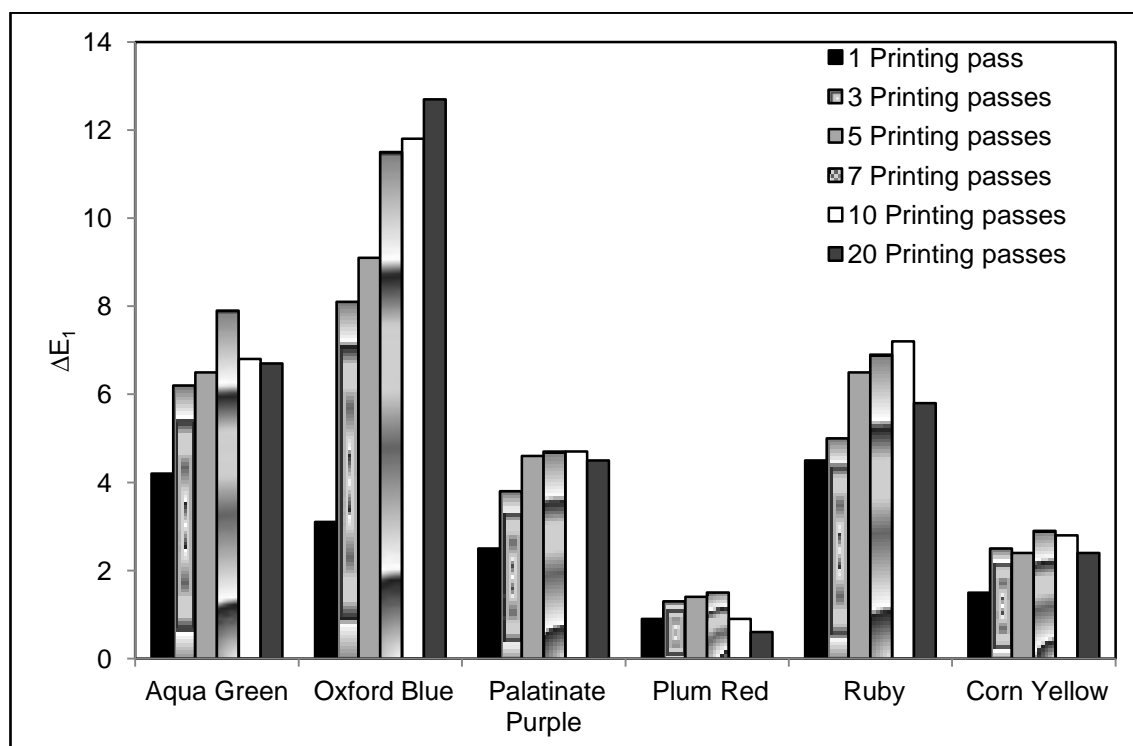
When the amount of ethylene glycol was increased to 30 %, the viscosity and surface tension increased to 2 cP and 28 mN m<sup>-1</sup> respectively, but the viscosity remained lower than the required range, as shown for ink 2 in Table 5.4. Consequently, the amount of ethylene glycol was further increased to 35 % in an attempt to improve the viscosity of the ink, as shown for ink 3 in Table 5.4. The result was a slight increase in the viscosity to 2.14 cP accompanied by a decrease in the surface tension to 27 mN m<sup>-1</sup>. To address the undesirable decrease in the surface tension, the amount of ethylene glycol was fixed at 30 % for further investigations. Thus, ink 4 was formulated using 30 % ethylene glycol, 5 % polyvinylpyrrolidone (PVP), 0.1 % dye and isopropanol as required, as shown in Table 5.4. The formulated ink showed a significant increase in the viscosity to 4.46 cP, which is within the recommended range (4-7) cP, and a slight increase in the surface tension to 27.5 mN m<sup>-1</sup> which is still less than the minimum value recommended for the printhead which is 28 mN m<sup>-1</sup>. Further improvement was achieved by adding 5 % polyethylene glycol to the ink formulation, which resulted in an increase in the

viscosity and surface tension of the ink to levels within the recommended range of values for both parameters, as shown for ink 5 in Table 5.4.

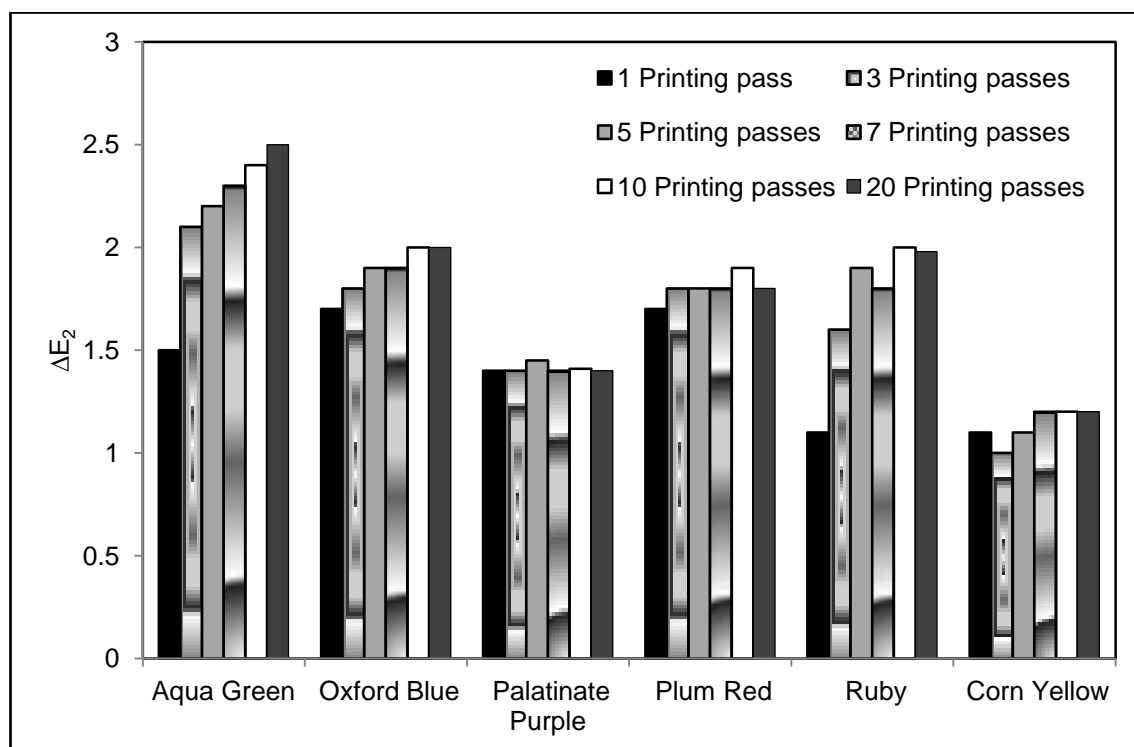
On the basis of the results of this investigation, the ink formulated according to the last recipe, referred to as ink 5 in Table 5.4 was selected as optimum, and was thus used in the investigation of the application of photochromic dyes **1-6** to polyester fabric by inkjet printing. Thus, six inks were prepared according to this formulation using the photochromic dyes **1-6** according to the ink formulation procedure given in section 5.2.3. These inks were applied to polyester fabrics by the inkjet printing method described in section 5.2.4.

### 5.3.2. Degree of photocoloration and background colours of polyester fabric inkjet printed with photochromic dyes with different numbers of printing passes

The degree of photocoloration ( $\Delta E_1$ ) of dyes **1-6** applied to polyester fabric by the digital inkjet printing method optimized for Oxford Blue using ink 5 was measured after 4 minutes of UV light exposure, for fabrics inkjet printed with different numbers of printing passes, as shown in Figures 5.1 and 5.2 illustrates the background colours ( $\Delta E_2$ ) of the same inkjet printed fabrics.



**Figure 5.1** Degree of photocoloration ( $\Delta E_1$ ) of polyester fabric inkjet printed with photochromic dyes **1-6** with different numbers of printing passes



**Figure 5.2** Background colours ( $\Delta E_2$ ) of polyester fabric inkjet printed with photochromic dyes **1-6** with different numbers of printing passes

The degree of photocolouration of dyes **1-6** increased gradually when the number of printing passes increased from 1 to 7. However, the results of further passes were inconsistent except for Oxford Blue which continues to show an increase, as shown in Figure 5.1. A possible explanation for this trend may be the negative effect on the degree of photocolouration brought about by the increase in the background colour of printed fabrics when the number of printing passes increases to 10 or 20, as shown in Figure 5.2. This negative effect may be due to two factors. The first involves minimising the difference between the background colour and developed colour as a result of the increase in the background colour. The second factor is the increase in the number of the ring-opened dye molecules associated with the increase in the background colour, as discussed in section 3.3.5, which in turn leads to a relative decrease in the number of ring-closed molecules which are responsible for the photocolouration process of photochromic dyes under a UV light exposure. As a result of this discussion, the optimum number of printing passes for applying dyes **1-6** was selected as 7 due to the reasonably high degree of photocolouration and reasonable background colours given by samples printed at this number of printing passes, as shown in Figures 5.1 and 5.2. Thus, all further investigations of the application of

photochromic dyes **1-6** to polyester fabric by inkjet printing were carried out using 7 printing passes.

A comparison between the background colours and degree of photocolouration of dyes **1-6** applied to polyester fabric by the inkjet printing method and those of the same dyes applied by the two dyeing methods as discussed in chapters 3 and 4 shows that, in general, both parameters are lower for each dye applied by inkjet printing compared to those of the same dye applied by the dyeing methods, as shown in Table 5.5. The first factor which may be important in determining this trend is the relatively low concentration of the dyes in isopropanol, which was used as the solvent in the ink formulation, due to the low solubility of the dyes in this solvent, which in turn leads to a relatively low amount of the dye delivered to the fabric. A second factor, which may be important in relation to the dyeing from dichloromethane, is the larger difference between the solubility parameter of isopropanol ( $36.8 \text{ J}^{0.5} \text{ cm}^{-1.5}$ ) and polyester ( $45 \text{ J}^{0.5} \text{ cm}^{-1.5}$ ) compared to that between polyester and dichloromethane ( $40.8 \text{ J}^{0.5} \text{ cm}^{-1.5}$ ) [113, 215]. The effect of the match between the solubility parameter of the solvent and fabric on the dyeing process has been discussed in sections 2.7.1 and 2.9. The effect of the relatively significant difference between the solubility parameter of water ( $97.9 \text{ J}^{0.5} \text{ cm}^{-1.5}$ ) and polyester ( $45 \text{ J}^{0.5} \text{ cm}^{-1.5}$ ) was not taken into account in the comparison based on the second possible factor, because the aqueous-based dyeing was carried out at a high temperature and for a relatively long time, as discussed in chapter 3. Thus, isopropanol may be less active than dichloromethane in facilitating dye diffusion into polyester fabric during the dyeing or printing processes. A third factor may be the application of the dyes only on the surface of one side of the fabric in the case of inkjet printing compared to impregnating the fabric completely in the dye solutions in the case of the dyeing methods. Thus, the dye uptake by fabric in the case of inkjet printing may be lower than that in the cases of the dyeing methods due to the application of the dye to only one side of the fabric, and also at the surface so that it is relatively easy to remove dye by the reduction clearing which follows the printing process.

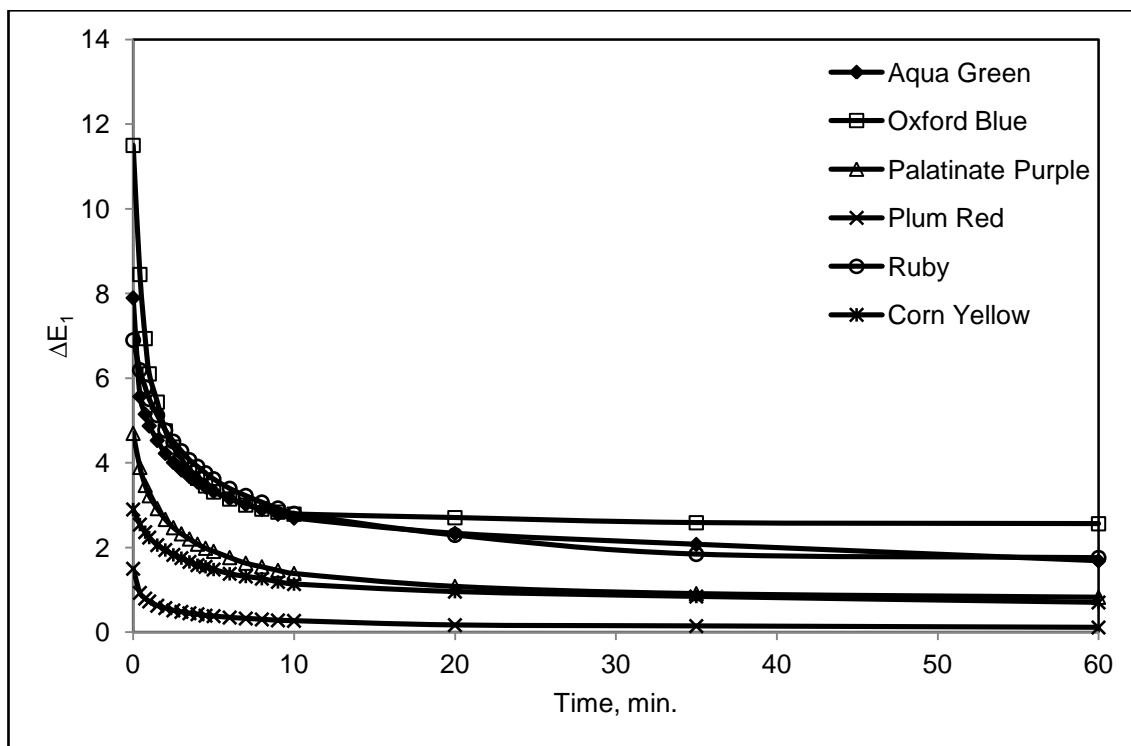
**Table 5.5** Degree of photocolouration and background colours of photochromic dyes **1-6** applied to polyester fabric by different dyeing and inkjet printing methods

| <i>Dye</i>        | $\Delta E_1$           |                             |                             | $\Delta E_2$           |                             |                             |
|-------------------|------------------------|-----------------------------|-----------------------------|------------------------|-----------------------------|-----------------------------|
|                   | <i>Inkjet printing</i> | <i>Aqueous-based dyeing</i> | <i>Solvent-based dyeing</i> | <i>Inkjet printing</i> | <i>Aqueous-based dyeing</i> | <i>Solvent-based dyeing</i> |
| Aqua Green        | 7.9                    | 9.1                         | 12.4                        | 2.3                    | 16.8                        | 9.7                         |
| Oxford Blue       | 11.5                   | 27.1                        | 27.7                        | 1.9                    | 10.0                        | 8.9                         |
| Palatinate Purple | 4.7                    | 3.4                         | 7.1                         | 1.4                    | 32.0                        | 7.0                         |
| Plum Red          | 1.5                    | 3.5                         | 8.0                         | 1.9                    | 8.5                         | 15.3                        |
| Ruby              | 6.9                    | 8.8                         | 8.0                         | 1.8                    | 18.8                        | 11.5                        |
| Corn Yellow       | 2.9                    | 14.7                        | 13.3                        | 1.2                    | 15.5                        | 7.9                         |

### ***5.3.3. Fading time of photochromic dyes applied to polyester fabric by an inkjet printing method***

Samples of polyester fabric inkjet printed with dyes **1-6** at the optimum number of printing passes by using the optimised printing procedure, as described in sections 5.2.4 and 5.3.2, were irradiated with UV light for 4 minutes followed by measuring their degree of photocolouration immediately after irradiation and over 60 minutes of fading in the dark. The fading curves show that the dyes start to fade immediately after removing the UV light source, as shown in Figure 5.3. Although the fading rates were different, they all reached low values at which the fading curves leveled indicating slow fading of all dyes after a relatively long fading time, as shown in Figure 5.3.





**Figure 5.3** Fading curves for photochromic dyes **1-6** applied to polyester fabric by an inkjet printing method

The comparison between the half life of fading, as defined in section 4.3.3, of dyes **1-6** indicates the differences in the fading rates of the dyes applied to polyester fabric. Thus, as shown in Table 5.6, the naphthopyran-based dyes (Ruby and Corn Yellow) showed relatively low fading rates, expressed by higher values of half life of fading, compared to the spironaphthooxazines (Aqua Green, Oxford Blue, Palatinate Purple and Plum Red). In this respect, these results are consistent with the results of half life of fading of the same dyes applied to polyester fabric by the dyeing methods discussed in chapters 3 and 4. This trend has been also observed in a previous study of photochromic dyes applied to polyester fabric by a screen printing method. [103]

**Table 5.6** Half life of fading of dyes **1-6** applied to polyester fabric by different dyeing methods and an inkjet printing method

| <i>Dye</i>        | <i>Half life of fading, min.</i> |                             |                             |
|-------------------|----------------------------------|-----------------------------|-----------------------------|
|                   | <i>Inkjet Printing</i>           | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 2.7                              | 4.5                         | 7.6                         |
| Oxford Blue       | 1.3                              | 3.1                         | 4.2                         |
| Palatinate Purple | 2.9                              | 4.5                         | 7.1                         |
| Plum Red          | 1.0                              | 4.2                         | 3.1                         |
| Ruby              | 5.8                              | 11.5                        | 18.1                        |
| Corn Yellow       | 5.1                              | 14.1                        | 19.8                        |

A notable observation in Table 5.6 is the relatively low values of half life of fading of the dyes applied by inkjet printing compared to those for the same dyes applied by the dyeing methods. This trend may be due to the lower penetration of the dyes into polyester fabric when they are applied by inkjet printing compared with when they are applied by the dyeing methods. Thus, the inkjet printed dyes may have less restriction applied to the molecular ring-closure reaction leading to the colourless ring-closed form due to their presence in an environment close to the surface of the fabric, compared to the more deeply penetrated dyes which may be in a more restricted environment, when applied by the dyeing methods.

In another respect, all inkjet printed fabrics retained residual colours after fading for 60 minutes in the dark. The retained colours were significantly higher in the cases of the naphthopyran-based dyes (Ruby and Corn Yellow) than the other four dyes which are spironaphthooxazines, as shown in Table 5.7. The possible factors that may be causing this phenomenon, which has also been observed when the dyes were applied to polyester fabric by the two dyeing methods investigated in chapters 3 and 4, have been discussed in section 3.3.6.

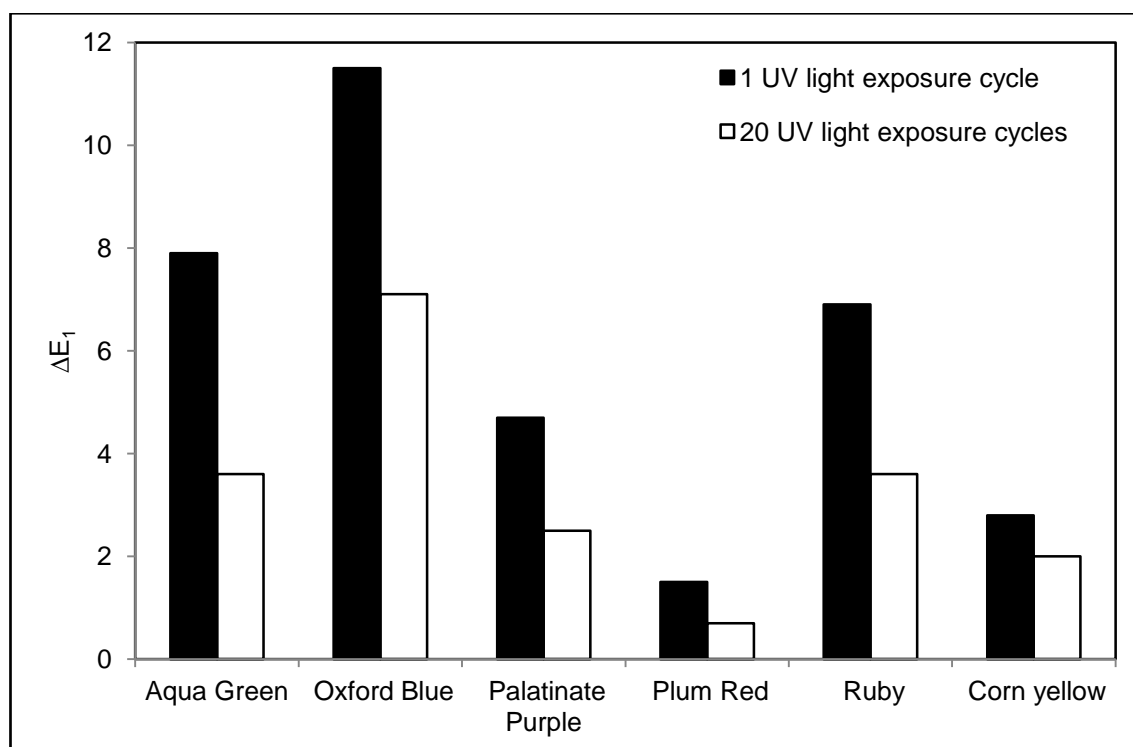
**Table 5.7** Residual colours after fading of photochromic dyes **1-6** applied to polyester fabric by different inkjet printing and dyeing methods

| <i>Dye</i>        | <i>Residual colour after 60 minutes of fading in the dark as a percentage of the degree of photocolouration</i> |                             |                             |
|-------------------|---|-----------------------------|-----------------------------|
|                   | <i>Inkjet printing</i>  | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 21 %  | 18 %                        | 24 %                        |
| Oxford Blue       | 22 %  | 11 %                        | 4 %                         |
| Palatinate Purple | 18 %  | 18 %                        | 21 %                        |
| Plum Red          | 7 %   | 15 %                        | 9 %                         |
| Ruby              | 26 %  | 30 %                        | 32 %                        |
| Corn Yellow       | 24 %  | 37 %                        | 29 %                        |

A comparison between the residual colours retained by photochromic dyes **1-6** applied to polyester fabric by inkjet printing and dyeing methods shows no apparent consistency between the order of magnitude of values of residual colours of dyes applied by the inkjet printing and dyeing methods, although in all cases the naphthopyran dyes, Ruby and Corn Yellow, show the strongest residual colours, as shown in Table 5.7. In addition, the values of the residual colours of each dye applied by the different inkjet printing and dyeing methods vary. These trends are difficult to explain and may be due to differences in the interaction between polyester fabric, the different printing or dyeing solvent at the different application conditions used and the interaction between each dye and the application solvent as determined essentially by the specific chemical structure of the dye.

#### ***5.3.4. Fatigue resistance of photochromic dyes applied to polyester fabric by an inkjet printing method***

The assessment of the fatigue resistance of photochromic dyes applied to polyester fabric by inkjet printing was carried out by repeating the cycle of UV exposure and fading of the optimally printed samples 20 times and comparing the degree of photocolouration of each sample after the first and last UV exposure.



**Figure 5.4** Fatigue resistance of photochromic dyes **1-6** applied to polyester fabric by an inkjet printing method

Results showed that after 20 cycles of UV exposure of fabrics inkjet printed with dyes **1-6**, the dyes retained different proportions of their original degree of photocolouration recorded after the first UV exposure. The retention values ranged between 71% and 46% with the highest value recorded by Corn Yellow and the lowest value given by Aqua Green, as shown in Table 5.8. These values show no obvious correlation with the chemical class of the dye, and may be determined by the specific chemical structure of each dye, possibly also influenced by its interactions with the printing solvent and the fibre under the application conditions.

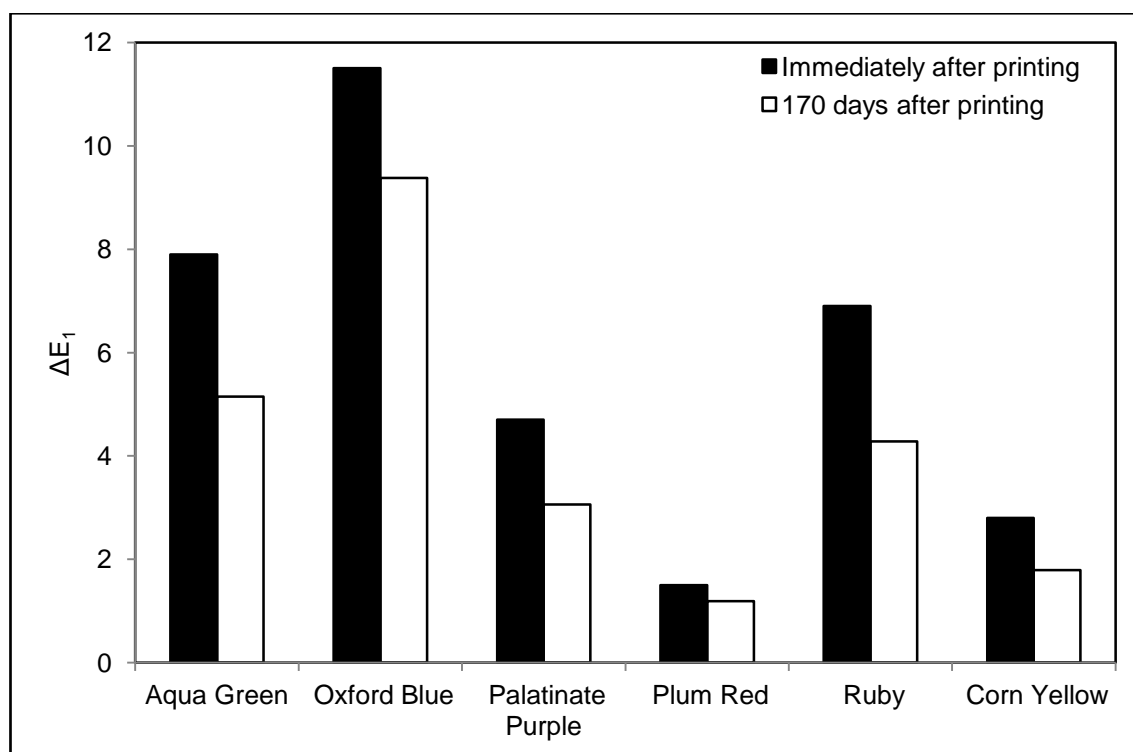
**Table 5.8** Fatigue resistance of photochromic dyes 1-6 applied to polyester fabric by an inkjet printing method

| <i>Dye</i>           | <i>Retention of photochromic response after 20 cycles of UV light exposure</i> |                             |                             |
|----------------------|--|-----------------------------|-----------------------------|
|                      | <i>Inkjet printing</i>   | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green           | 46 %   | 47 %                        | 70 %                        |
| Oxford Blue          | 62 %   | 75 %                        | 92 %                        |
| Palatinate<br>Purple | 53 %   | 60 %                        | 98 %                        |
| Plum Red             | 47 %   | 41 %                        | 28 %                        |
| Ruby                 | 52 %   | 95 %                        | 99 %                        |
| Corn Yellow          | 71 %   | 72 %                        | 78 %                        |

In addition, the fatigue resistance of dyes **1-6** applied to polyester fabric by inkjet printing is mostly lower than that of the same dyes applied by the dyeing methods, as shown in Table 5.8. This trend may be a result of the location of the dyes near the surface of the fabric when they are applied by inkjet printing compared to their penetration deeper in the fabric when they are applied by the dyeing methods. Thus, in the case of the inkjet printed fabrics, the dye will be more susceptible to photodegradation as a result of the effect of the repetitive exposure to UV light

### ***5.3.5. Storage stability of photochromic dyes applied to polyester fabric by an inkjet printing method***

Storage stability of photochromic dyes **1-6** applied to polyester fabric by inkjet printing was assessed by measuring the degree of photocolouration of the optimally printed samples after 170 days of printing and comparing the results with those measured for the same samples on the day of printing.



**Figure 5.5** Storage stability of dyes **1-6** applied to polyester fabric by an inkjet printing method

Figure 5.5 shows that the printed samples retained different levels of their degree of photocolouration after storage for 170 days ranging from 62% in the case of Ruby to 82% in the case of Oxford Blue.

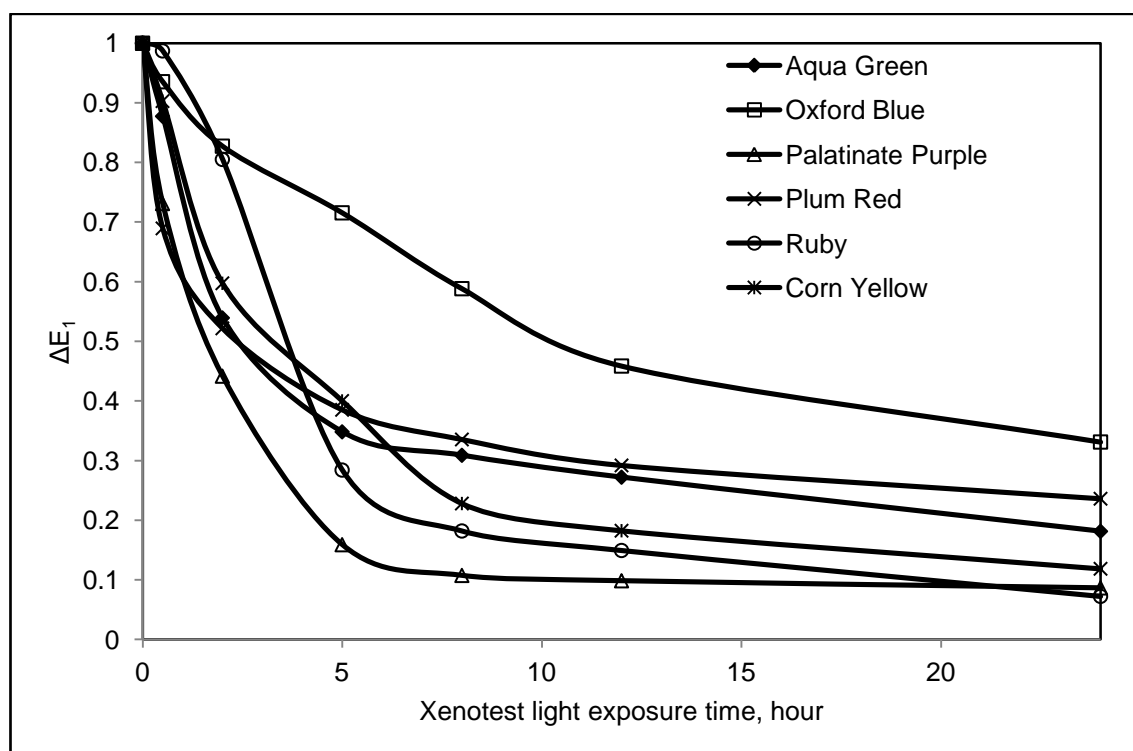
In another respect, it was observed that the storage stability of dyes **1-6** applied to polyester fabric by inkjet printing is mostly lower than that of the same dyes applied by dyeing as described in chapters 3 and 4, as shown in Table 5.9. This trend may be explained by the possibility of the dependence of this property on the interaction between the dye and the printing or dyeing solvent, as discussed in section 4.3.5. Thus, the interaction between photochromic dyes **1-6** and isopropanol, which was used as a printing solvent, may lead to a decrease in the storage stability of the dyes in most cases when this solvent replaces solvents used in the other investigated dyeing methods. In the case of Oxford Blue, the effect on the storage stability of the dye was opposite to its effect on the other dyes, and therefore the specific chemical structure of the dye and the interaction with the solvent may have an effect on its storage stability.

**Table 5.9** Storage stability of photochromic dyes 1-6 applied to polyester fabric by different inkjet printing and dyeing methods

| <i>Dye</i>        | <i>Retention of photochromic response after 170 days of storage in the dark</i> |                             |                             |
|-------------------|---|-----------------------------|-----------------------------|
|                   | <i>Inkjet printing</i>  | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 65 %  | 96 %                        | 84 %                        |
| Oxford Blue       | 82 %  | 71 %                        | 76 %                        |
| Palatinate Purple | 65 %  | 94 %                        | 60 %                        |
| Plum Red          | 79 %  | 86 %                        | 83 %                        |
| Ruby              | 62 %  | 87 %                        | 81 %                        |
| Corn Yellow       | 64 %  | 64 %                        | 73 %                        |

### 5.3.6. Colour fastness to light of polyester fabric inkjet printed with photochromic dyes

The assessment of colour fastness to light was carried out by exposing the printed samples with Xenotest light and measuring the degree of photocoloration of each dye after different periods of the light exposure, as shown in Figure 5.6.



**Figure 5.6** Normalised lightfastness curves of dyes 1-6 applied to polyester fabric by an inkjet printing method

The assessment results showed that all dyes lost a considerable amount of their initial degree of photocolouration at different rates over the same period of time, as shown in Figure 5.6 and Table 5.10 which shows the half life as an indication of the rate of colour fading due to light exposure. The special definition of the half life in this case has been given in section 3.3.9. Table 5.10 shows the variation in the half life of each dye when the dye was applied to polyester fabric by inkjet printing and dyeing methods. There is no real consistency in this trend which in turn indicates the possibility of the effect of the interaction between each dye and the dyeing or printing solvent in determining the lightfastness of the dye depending on the specific chemical structure of the dye.

**Table 5.10** Half life of dyes **1-6** applied to polyester fabric by different inkjet printing and dyeing methods.

| <i>Dye</i>        | <i>Half Life/ Hour</i> |                             |                             |
|-------------------|------------------------|-----------------------------|-----------------------------|
|                   | <i>Inkjet printing</i> | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 2.6                    | 14.5                        | 0.5                         |
| Oxford Blue       | 10.8                   | 1.8                         | 9.4                         |
| Palatinate Purple | 1.7                    | 2.9                         | 1.1                         |
| Plum Red          | 2.5                    | 2.1                         | 1.5                         |
| Ruby              | 3.8                    | 1.1                         | 4.5                         |
| Corn Yellow       | 3.5                    | 1.9                         | 1.5                         |

In another respect, dyes **1-6** applied to polyester fabric by inkjet printing retained different proportions of their degree of photocolouration after 24 hours of Xenotest light exposure, as shown in Table 5.11 which in turn provides a comparison with the same dyes applied by the dyeing methods described in chapters 3 and 4. Thus, consistent with the results of the comparison of the half life of the dyes, Table 5.11 shows that different proportions of light fastness of each dye were retained when the dye was applied to polyester fabric by different inkjet printing and dyeing methods with no common trend of this difference in favor of any of the inkjet printing or dyeing methods, due to a possible certain interaction between each dye and the printing or dyeing solvent.



**Table 5.11** Retention of degree of photocoloration of photochromic dyes **1-6** applied to polyester fabric by different inkjet printing and dyeing methods

| <i>Dye</i>        | <i>Retention of degree of photocoloration after 24 hours of Xenotest light exposure</i> |                             |                             |
|-------------------|---|-----------------------------|-----------------------------|
|                   | <i>Inkjet printing</i>  | <i>Solvent-based dyeing</i> | <i>Aqueous-based dyeing</i> |
| Aqua Green        | 18 %  | 5 %                         | 3 %                         |
| Oxford Blue       | 33 %  | 35 %                        | 21 %                        |
| Palatinate Purple | 9 %   | 11 %                        | 14 %                        |
| Plum Red          | 24 %  | 9 %                         | 1 %                         |
| Ruby              | 7 %   | 2 %                         | 8 %                         |
| Corn Yellow       | 12 %  | 7 %                         | 9 %                         |

**5.3.7. Colour fastness to washing of polyester fabric inkjet printed with photochromic dyes**

Washfastness of the optimally inkjet printed polyester samples was assessed by measuring the degree of photocoloration of each samples after washing and comparing it with the value measured before washing, as discussed in section 3.3.11. On the basis of the discussion given in section 4.3.8, Test 3 of the series of standard washfastness tests described in the British Standard BS 1006:1990 [181] was selected as the initial test applied for measuring washfastness of the inkjet printed fabrics. Thus, the inkjet printed samples were washed under the conditions of Test 3 (a temperature of 60°C and a time of 30 minutes), and their degree of photocoloration were measured and compared to the degree of photocoloration of the unwashed fabrics.

**Table 5.12** Washfastness of photochromic dyes **1-6** applied to polyester fabric by an inkjet printing method

| <i>Dye</i>        | $\Delta E_1$           |                                    |                                    |
|-------------------|------------------------|------------------------------------|------------------------------------|
|                   | <i>Unwashed fabric</i> | <i>Washed at 60°C, for 30 min.</i> | <i>Washed at 95°C, for 30 min.</i> |
| Aqua Green        | 7.9                    | 7.8                                | 7.1                                |
| Oxford Blue       | 11.5                   | 11.5                               | 10.1                               |
| Palatinate Purple | 4.7                    | 4.6                                | 4.2                                |
| Plum Red          | 1.5                    | 1.4                                | 1.3                                |
| Ruby              | 6.9                    | 6.7                                | 6.1                                |
| Corn Yellow       | 2.9                    | 2.8                                | 2.5                                |

Table 5.12 shows that the conditions of Test 3 did not bring about a significant deterioration in the washfastness of the inkjet printed fabrics, represented by only slight differences between the degree of photocolouration of samples washed under these conditions and the unwashed samples. These differences are considered within the limits of experimental variation, similar to the conclusions in section 3.3.11. Consequently, the conditions of Test 4 which are a temperature of 95°C and a time of 30 minutes were then used for washing samples of polyester fabric inkjet printed with dyes **1-6**. Under these conditions, the washed fabrics lost various proportions of their degree of photocolouration compared to the unwashed fabrics, ranging between 10 % and 14 %, as shown in Table 5.12.

**Table 5.13** Proportional deterioration of washfastness, under the conditions of Test 4, of dyes **1-6** applied to polyester fabric by different inkjet printing and dyeing methods

| <i>Dye</i>        | <i>Percentage of deterioration of washfastness of photochromic dyes</i> |                             |
|-------------------|---|-----------------------------|
|                   | <i>Inkjet printing</i>  | <i>Solvent-based dyeing</i> |
| Aqua Green        | 10 %  | 10 %                        |
| Oxford Blue       | 12 %  | 10 %                        |
| Palatinate Purple | 11 %  | 12 %                        |
| Plum Red          | 13 %  | 12 %                        |
| Ruby              | 12 %  | 11 %                        |
| Corn Yellow       | 14 %  | 13 %                        |

These results show similarities between the washfastness of photochromic dyes **1-6** applied to polyester fabric by the inkjet printing method and the solvent-based dyeing method which was investigated in chapter 4, as shown in Table 5.13. However, the washfastness tests of dyes **1-6** applied to polyester fabric by an aqueous-based dyeing method showed that the dyes had lower washfastness by losing considerable proportions of their degree of photocoloration (between 10% and 13 % ) when they were washed under the relatively mild conditions of Test 3, as discussed in section 3.3.11. Thus, the washfastness of photochromic dyes **1-6** applied to polyester fabric by the isopropanol-based inkjet printing or the solvent-based dyeing is higher than that of the same dyes applied to the same fabric by an aqueous-based dyeing method. This result may be explained by the penetration of isopropanol and dichloromethane into regions of the polyester fibres into which the penetration of water is less efficient. Thus, the dyes which diffuse into polyester fibres in the presence of isopropanol or dichloromethane are not easily accessed by the aqueous washing conditions and so do not wash out easily.

#### **5.4. Conclusions**

Six photochromic dyes were successfully applied to polyester fabric by digital inkjet printing using a solvent-based ink. The application process was optimized in terms of ink formulation and the number of printing passes required to achieve the maximum degree of photocoloration ( $\Delta E_1$ ) and minimum background colour ( $\Delta E_2$ ) of printed fabrics. The printed fabrics showed different performance in terms of their degree of photocoloration and background colours. However, the performance was mostly inferior in terms of the degree of photocoloration and superior in the case of background colours compared to that shown by the same dyes applied to polyester fabric by the dyeing methods discussed in chapters 3 and 4.

The investigation of fading characteristics and fatigue resistance of printed fabrics demonstrated mostly the higher rate of fading and lower fatigue resistance of these fabrics compared to the fabrics dyed with the same dyes by the dyeing methods discussed in chapters 3 and 4.

Storage stabilities of photochromic dyes applied to polyester fabric by inkjet printing were variable. In addition, the comparison between storage stability of the photochromic dyes applied by inkjet printing and that of the same dyes applied by the dyeing methods discussed in chapters 3 and 4 showed no consistent effect of the

application method on this property of all dyes probably due to the dependence of this property on the specific chemical structure of each dye.

Colour fastness to light and washing of printed fabrics were assessed by comparing the degree of photocolouration of washed fabrics with those of unwashed fabrics. Results showed different lightfastness of printed fabrics without an apparent effect of the application method on the value of lightfastness of each dye compared to the value measured for the same dye applied by the dyeing methods discussed in chapters 3 and 4. Colour fastness to washing of printed fabrics showed relatively good washfastness of these fabrics which was mostly similar to the wash fastness of fabrics dyed with the same dyes by the solvent-based dyeing method discussed in chapter 4 and higher than that measured for the same dyes applied by an aqueous-based dyeing method.

## **Chapter 6 - The Application of Photochromic Dyes to Cotton Fabric by a Solvent-Based Direct Dyeing Method**

### **6.1. Introduction**

The successful application of photochromic dyes to polyester fabric by the different dyeing and printing methods investigated in chapters 3, 4 and 5 suggests the possibility of investigating the application of these dyes to other textile substrates. Cotton was the choice because it is the most important natural fibre in terms of the quantity used in textile applications. [114, 116, 143] Cotton is normally dyed by different dye classes and dyeing methods. In all of these, the dye is applied to the fibre in a soluble form from an aqueous dyebath, as discussed in section 2.8. The photochromic dyes investigated in this thesis are not soluble in water, and therefore they can not be applied to cotton fabric from an aqueous dyebath. In addition, the disperse dyeing method which is normally used for the application of insoluble disperse dyes to polyester fabric is not suitable for dyeing cotton fibres due to the structural differences between cotton and polyester, as given in sections 2.7 and 2.8. Thus, a solvent-based dyeing method was envisaged to be more appropriate for applying photochromic dyes to cotton fabric due to the high solubility of these dyes in some organic solvents and the successful application of these dyes from solvent-based media to polyester, as discussed in chapters 4 and 5. In this respect, dichloromethane was the solvent of choice due to the good solubility of photochromic dyes in this solvent as an alternative to water which is used for applying traditional direct dyes to cotton fabric by the traditional aqueous-based direct dyeing method. [114] However, in the case of the solvent-based dyeing of cotton it is not appropriate to use the procedure typical of aqueous-based direct dyeing method which involves the exhaustion of direct dyes with a gradual increase in the temperature while adding salt to the dyebath. The reason is the high solubility of photochromic dyes in dichloromethane at its boiling point, and thus the partition coefficient of the dye between solvent and fibre will be low, and consequently dye exhaustion is likely to be lower than a practically acceptable level. [113] The definition of the partition coefficient and its relationship with dye exhaustion have been discussed in section 2.7. This problem may be overcome, in principle, by using a low liquor ratio and dyeing temperature using dyes that are highly soluble in the dyeing solvent in an attempt to increase the partition coefficient, and therefore increase the dye exhaustion. [152] As the boiling point of dichloromethane is relatively low and the solubility of the dyes in the solvent is high even at ambient temperatures, it is envisaged that the

exhaustion of the photochromic dyes may be increased by reducing the liquor ratio which will be referred to in this study as the solvent/fabric ratio. A consequence of the reduction in the solvent/fabric ratio to a low level that achieves the desired increase in the dye exhaustion will be the need to reduce the dyeing time to prevent the evaporation of dichloromethane during dyeing at its boiling point. Another option is using a high temperature similar to that used in the case of typical thermal fixation on polyester with a very low solvent/fabric ratio and a short time of dyeing. In this case, the dyeing process involves impregnating cotton fabric in a dye solution using a low solvent/fabric ratio and then treating the fabric for a short time in an oven preheated to a high temperature. This method is similar to the solvent-based pad dry-heat dyeing method used for applying photochromic dyes to polyester fabric, as discussed in chapter 4, although it is referred to as the solvent-based direct dyeing method. Thus, in the case of polyester dyeing, the high temperature is used for thermal fixation as discussed in section 2.7, while in the case of the solvent-based direct dyeing of cotton discussed in this chapter, the high temperature is used to increase the rate of fabric dyeing, initially from a highly concentrated solution over a short period of time, by increasing the kinetic energy of dye molecules, which is the purpose of heating a dyebath in the traditional direct dyeing method for cotton fabric with direct dyes. [114]

## **6.2. Experimental**

### ***6.2.1. Materials***

The same commercial photochromic dyes **1-6** given in Table 3.1 and used for the investigations described in chapters 3, 4 and 5 were applied to cotton fabric in this chapter. Dichloromethane used as the dyeing medium was of a laboratory grade.

### ***6.2.2. Solvent-based direct dyeing of cotton fabric with photochromic dyes***

The dyeing processes for cotton fabric with different concentrations of dyes **1-6** were carried out by the same method, dyeing concentrations, solvent/fabric ratio and thermal fixation conditions used for the application of the photochromic dyes to polyester fabric by the dyeing method described in section 4.2.4. All dyeing processes were followed by a cold water rinse, washing with an aqueous solution of Synperonic BD100 (1 g l<sup>-1</sup>) for a few minutes, rinsing and then air drying.

### **6.2.3. Colour measurement methodology and conditions**

The specifically–devised methodology described in sections 3.2.1, 3.2.2 and 3.2.3 was used for colour measurement of cotton fabric dyed with photochromic dyes **1-6** by the solvent –based direct dyeing method as investigated in this chapter.

### **6.2.4. Fading characteristics, fatigue resistance and storage stability of dyed fabrics**

These properties were measured for samples of cotton fabric dyed with photochromic dyes **1-6** at their optimum dyeing concentrations by the same methods described in section 3.2.7.

## **6.3. Results and Discussion**

### **6.3.1. The application process of photochromic dyes 1-6 to cotton fabric by a solvent-based direct dyeing method**

The optimum dyeing procedure and conditions used in the application of photochromic dyes **1-6** to polyester fabric by the solvent-based pad dry-heat dyeing method investigated in section 4.3 was used for the application of the same dyes to cotton fabric by the solvent-based direct dyeing method. Thus, six dyeing concentrations of 0.1, 0.2, 0.5, 1, 1.5 and 2 % o.w.f of each dye were applied to cotton fabric under the optimum dyeing conditions as given in Table 6.1.

**Table 6.1** Optimum conditions for applying photochromic dyes **1-6** to cotton fabric

|                      |             |
|----------------------|-------------|
| Solvent/fabric ratio | 2.5:1 o.w.f |
| Dyeing time          | 45 second   |
| Fixation temperature | 190°C       |

It was observed that when cotton samples dyed with the spironaphthooxazine-based photochromic dyes (**1-4**) were transferred to the spectrophotometer for measurement of their degree of photocolouration after UV light exposure, the instrument displayed an error message which expressed the impossibility of measuring the colour of these samples due to the high rate of colour change during measurement which exceeded the tolerance of the instrument. As a result, it was not possible to measure the degree of photocolouration of these dyed samples immediately after UV light exposure. Attempts to carry out this measurement showed that the shortest time of dye fading after UV exposure at which the degree of photocolouration became measurable was 10 seconds. At this time, the rate of colour fading was at an acceptable level for the spectrophotometer

tolerance and consequently allowed measurement of the colour difference between the fabric before and after UV light exposure. However, the measured values of colour difference are not likely to be a sufficiently accurate expression of the degree of photocolouration due to the relatively long time after exposure during which the developed colour faded to a low level, compared with the developed colour that would be recorded either immediately after UV light exposure, or after the minimum practical time of 3 seconds for transferring samples from the UV exposure unit to the spectrophotometer as used for all colour measurements reported in this thesis, as discussed in section 3.2.3. Thus, it was decided to attempt to establish a method to determine a more appropriate value of the degree of photocolouration of cotton fabric dyed with photochromic dyes **1-4** based on the value 10 seconds after removing the UV light source. The method was based on calculating by extrapolation a value for the degree of photocolouration 3 seconds after removing the UV light source, using the measured values after longer periods of colour fading. These measured values were used to derive a mathematical equation which represents the relationship between degree of photocolouration and fading time, as explained in the following example for cotton fabric dyed with Aqua Green at a dyeing concentration of 0.5 %.

The measured values of degree of photocolouration of the UV irradiated sample after 10, 15 and 20 seconds of fading were  $\Delta E_{10} = 13.6$ ,  $\Delta E_{15} = 11.5$  and  $\Delta E_{20} = 10.4$  respectively. The estimation of the value of  $\Delta E_1$  3 seconds after removal of the UV light source is based on deriving the equation which represents the relationship between the degree of photocolouration and fading time. As this relationship has been observed to be non-linear, as discussed in sections 3.3.6, 4.3.3 and 5.3.3, it was decided to represent the relationship discussed by a quadratic equation.

The general formula of the quadratic equation is given as follows:

$$y = ax^2 + bx + c \quad (40)$$

where  $y = \Delta E_1$  and  $x = t$  (fading time).

The measured values of  $\Delta E_1$  at the given fading times are as follows:

$$y = 13.6 \text{ when } t = 10 \text{ seconds}$$

$$y = 11.5 \text{ when } x = 15 \text{ seconds}$$

$$y = 10.4 \text{ when } x = 20 \text{ seconds}$$

By insertion of these values in equation 40, three equations (41, 42 and 43) result:

$$13.6 = 100a + 10b + c \quad (41)$$



$$11.5 = 225a + 15b + c \quad (42)$$

$$10.4 = 400a + 20b + c \quad (43)$$

The solution of simultaneous equations 41, 42 and 43 resulted in the following values of a, b and c:

$$a = 0.02$$

$$b = -0.92$$

$$c = 20.8$$

By inserting these values into the general form of the quadratic equation 40, the fading equation obtained is:

$$y = 0.02x^2 - 0.92x + 20.8 \quad (44)$$

Or

$$\Delta E_1 = 0.02t^2 - 0.92t + 20.8 \quad (45)$$

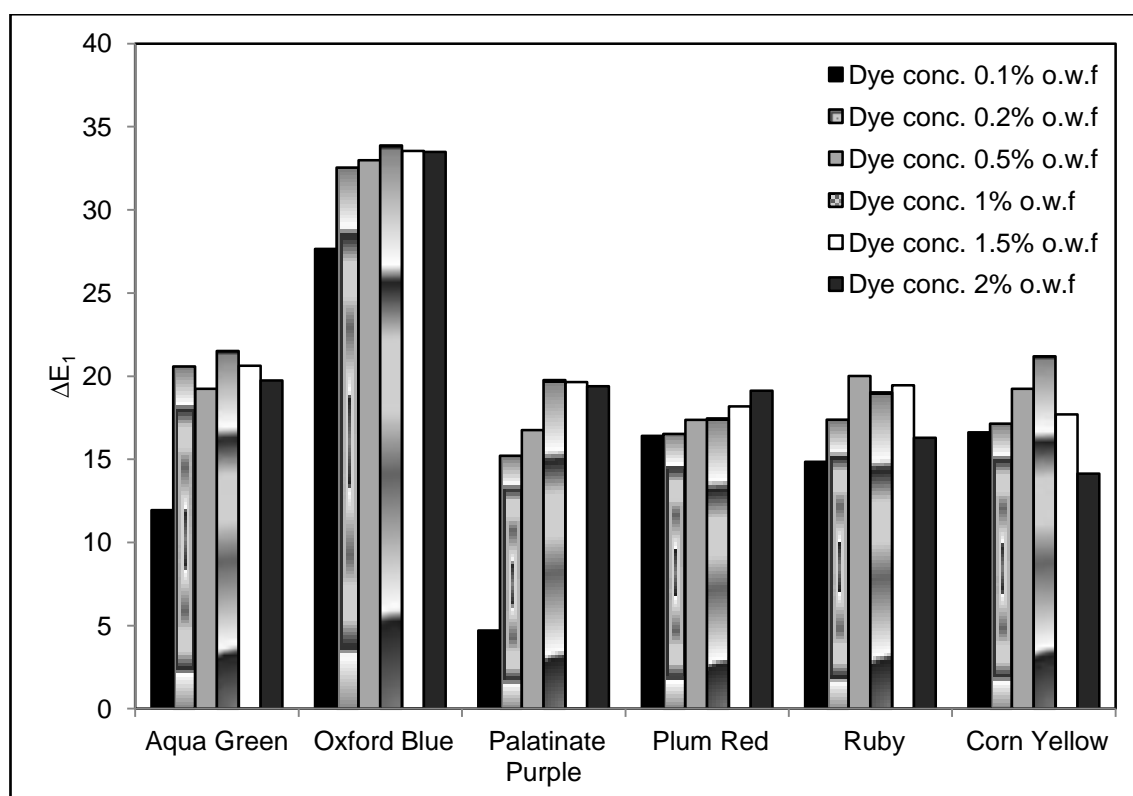
where  $\Delta E_1$  is the degree of photocolouration of Aqua Green at a fading time of t. Thus, the degree of photocolouration of Aqua Green after 3 seconds of fading is given by inserting t = 3 in equation 45 as follows:

$$\Delta E_1 = 0.02 (3)^2 - 0.92 (3) + 20.8 = 18.9$$

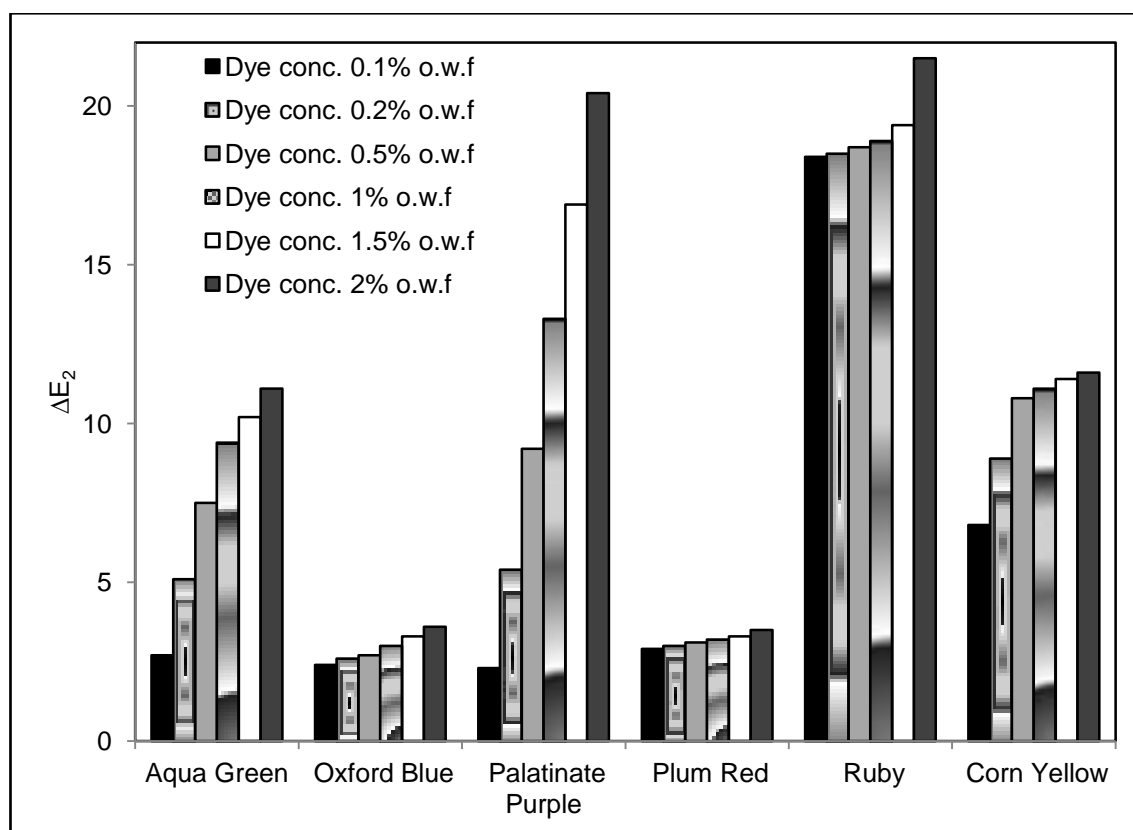
This calculation method is necessarily approximate because of the assumptions made that the degree of photocolouration after 3 seconds of removal of UV light sources locates on the curve represented by the quadratic equation derived using the values of degree of photocolouration 10, 15 and 20 seconds after removal of the UV light. An improved method to address this problem would be to measure the developed colour of dyed samples during UV exposure of these samples. This requires using a special instrument whereby the developed colour is measured during UV exposure which means that there is no colour fading during the colour measurement process, such as that developed at the Technical University of Liberec, Czech Republic. [216, 217] As such an instrument was not available at Heriot-Watt University, the extrapolation method was used to estimate the values of degree of photocolouration of cotton fabrics dyed with the spironaphthooxazine-based photochromic dyes (**1-4**) in such a way that they are consistent with the other measurements described throughout this thesis. In contrast, it was possible to measure the degree of photocolouration of dyes **5** and **6** directly 3 seconds after removal of UV light sources, because these dyes show such a slower rate of fading that did not exceed the ability of the spectrophotometer to measure the colour differences during the first 3 seconds of fading.

### 6.3.2. The degree of photocoloration and background colours of photochromic dyes applied to cotton fabric

Figures 6.1 and 6.2 show the degree of photocoloration and background colours of cotton fabrics dyed with photochromic dyes **1-6** at different dyeing concentrations respectively. Oxford Blue showed the best performance in that it showed the highest degree of photocoloration and a low background colour, while the worst performance was shown by Ruby and Palatiniate Purple which gave the lowest values of  $\Delta E_1$  and highest values of  $\Delta E_2$ .



**Figure 6.1** Degree of photocoloration ( $\Delta E_1$ ) of photochromic dyes **1-6** applied to cotton fabric by a solvent-based direct dyeing method

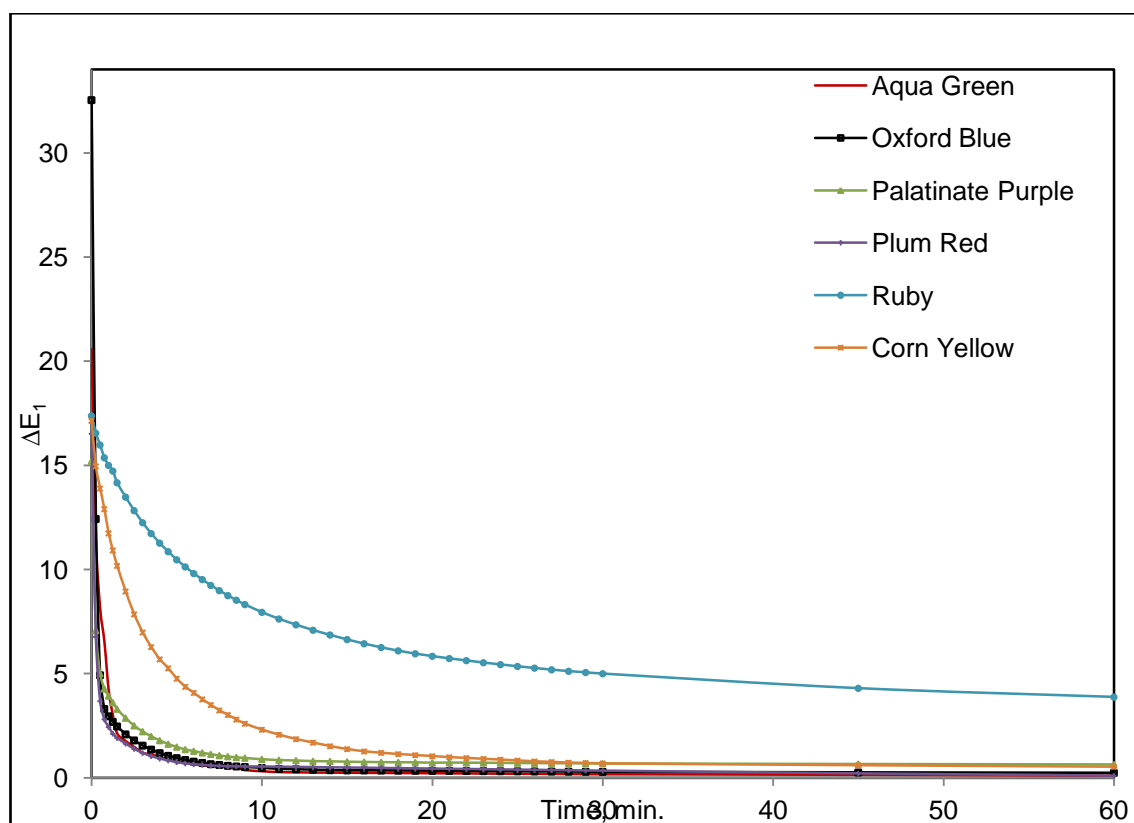


**Figure 6.2** Background colour ( $\Delta E_2$ ) of cotton fabric dyed with photochromic dyes **1-6** by a solvent-based direct dyeing method

In all cases, the background colour of each dye increased steadily with the increase in the dyeing concentration. However, the degree of photocoloration did not vary very significantly with dyeing concentrations especially at higher concentrations. In most cases, a dyeing concentration of 0.2 % showed a relatively high value of  $\Delta E_1$  accompanied by a reasonable value of  $\Delta E_2$ , and therefore this concentration was selected as the optimum and was consequently used for all further investigations on cotton as described in this chapter.

### **6.3.3. Fading time of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method**

The optimally dyed cotton samples were exposed to UV light for 4 minutes, and their degree of photocoloration was measured immediately after UV exposure and at intervals over 60 minutes of fading in the dark.



**Figure 6.3** Fading curves of photochromic dyes **1-6** applied to cotton fabric by a solvent-based direct dyeing method

Figure 6.3 shows that developed colours of dyes **1-6** started to fade to their background colours immediately after removing the UV light source. Fading rates varied from one dye to another. The early periods of fading showed relatively high fading rates compared to the later stages, and a leveling in the curves after a relatively long time of fading, as shown in Figure 6.3. In addition, it was observed that the spironaphthooxazine-based dyes (**1-4**) showed higher fading rates than the naphthopyrans **5** and **6**. This trend was confirmed by the measured half lives of fading, with dyes **1-4** giving values between 0.2 and 0.3 minutes, compared to values of 2.1 and 8 minutes for dyes **6** and **5** respectively, as shown in Table 6.2.

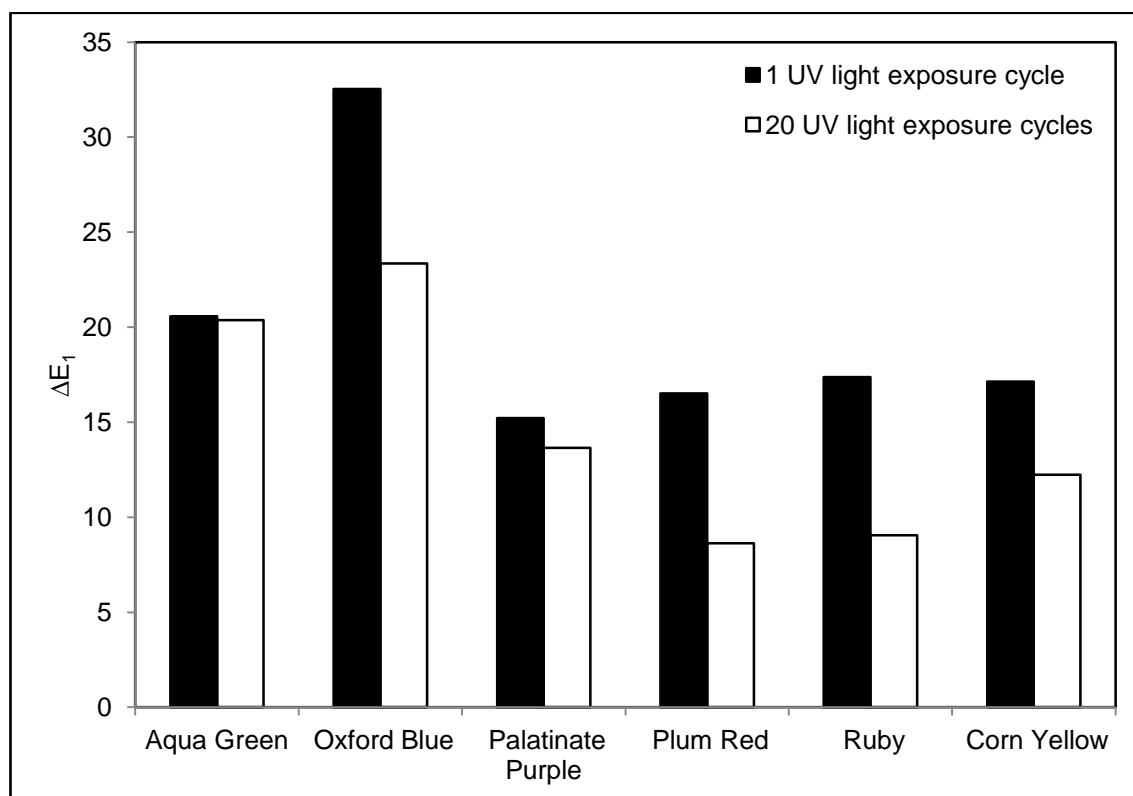
**Table 6.2** Half life of fading of photochromic dyes **1-6** applied to cotton fabric by a solvent-based direct dyeing method

| <i>Dye</i>        | <i>Half life of fading, min</i> |
|-------------------|---------------------------------|
| Aqua Green        | 0.3                             |
| Oxford Blue       | 0.2                             |
| Palatinate Purple | 0.2                             |
| Plum Red          | 0.2                             |
| Ruby              | 8.2                             |
| Corn Yellow       | 2.1                             |

The relatively slow fading of naphthopyran-based dyes compared to that of the spironaphthooxazine-based dyes has been observed in previous studies of the photochromic dyes applied to polyester fabrics by the dyeing and printing methods as discussed in chapters 3, 4 and 5. However, the fading rate of each dye applied to cotton fabric by the solvent-based direct dyeing method is higher than that of the same dye applied to polyester fabric by dyeing and printing. This feature led to the difficulties in measuring the degree of photocolouration of the dyes on cotton fabrics, as explained in section 6.3.1. This observation may be due to the more open structure of cotton fibres compared with polyester and thus the dyes are located in a less restricted environment on cotton compared to polyester. This favours the ring closure reaction of dye molecules on cotton compared to the situation on polyester. This difference in the restriction applied of the dye molecules may be a result of the different location of dye molecules on the fibre depending on the fibre structure and the dye application method. Description of the structures of polyester and cotton are given in sections 2.7 and 2.8 respectively. In the case of polyester, dye molecules are finally located between the molecular chains within the compact structure of the fibre as explained in section 2.7. In the case of cotton fabric dyed by the direct dyeing method, the association of the dye with the fibre is attributed only to weak intermolecular forces between the dye and the fibre due to the possible presence of dye molecules in the numerous channels between the cellulosic fibrils of cotton fibres with no presence of any chemical bonding or trapping of dye molecules between molecular chains of cotton, as explained in sections, 2.8 and 2.8.1.

#### 6.3.4. Fatigue resistance of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method

Fatigue resistance was investigated by comparing the degree of photocolouration of each dyed fabric after 20 cycles of UV light exposure with that after the first UV exposure. Dyes 1-6 retained different proportions of their degree of photocolouration after 20 cycles of UV exposure, as shown in Figure 6.4.

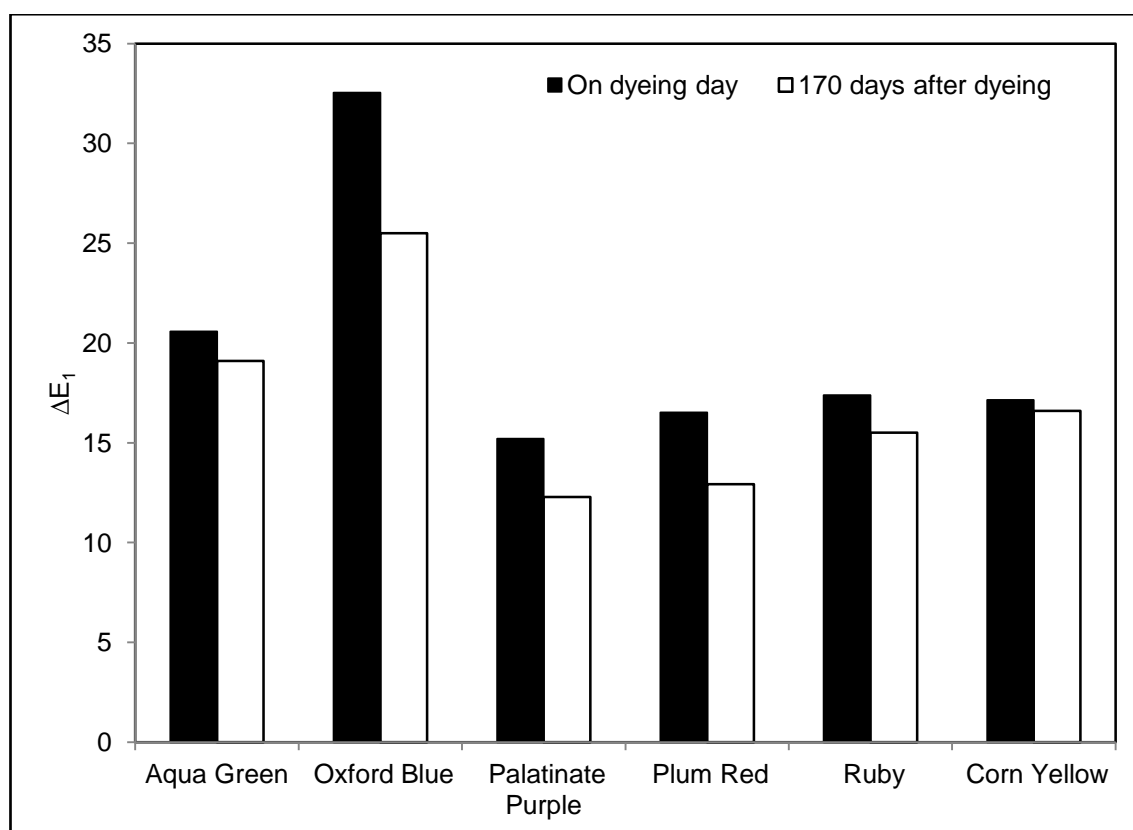


**Figure 6.4** Fatigue resistance of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method

In this respect Aqua Green showed the best performance by retaining more than 99% of its degree of photocolouration after the UV exposure cycles. In contrast, the worst performance was shown by Plum Red and Ruby which each retained only 52% of their degree of photocolouration. Palatinate Purple retained 90% of its degree of photocolouration followed by Oxford Blue and Corn Yellow which retained 72% and 71% respectively. Thus, the fatigue resistance of the photochromic dyes applied to cotton does not appear to be related to the general chemical class of the dyes; however it may be associated with the specific chemical structure of each dye and its susceptibility to photodegradation under repetitive UV exposure.

### 6.3.5. Storage stabilities of photochromic dyes applied to cotton fabric by a solvent-based direct dyeing method

For storage stability measurements of cotton fabric dyed with photochromic dyes 1-6 the optimally dyed samples were kept in the dark for 170 days after which their degree of photocolouration was measured and compared to that on the day of dyeing. The dyed samples showed various levels of deterioration in their ability to develop colours on UV light exposure after the period of storage in the dark, as shown in Figure 6.5.



**Figure 6.5** Storage stabilities of photochromic dyes 1-6 applied to cotton fabric by a solvent-based direct dyeing method

The highest storage stability was shown by Corn Yellow followed by Aqua Green which retained 96% and 93% of their degree of photocolouration after 170 days of storage respectively compared to their original degree of photocolouration. Oxford Blue and Plum Red showed the lowest level of 78% of retention of their degree of photocolouration. Palatinate Purple came next retaining 81 % followed by Ruby which retained 89%. The results show that storage stability may be determined by the specific chemical structure of each dye rather than its general chemical class.

#### **6.4. Conclusions**

An investigation of a solvent-based dyeing of cotton fabric using a series of photochromic dyes showed that they can be applied to cotton with different levels of success. The dyes exhausted on cotton from highly concentrated dye solutions in dichloromethane which was explored as an alternative to water due to the low aqueous solubility of the photochromic dyes investigated. A notable observation was the high rate of fading of the spironaphthooxazine-based dyes on cotton during the first few seconds after removal of the UV light source. This high fading rate exceeded the ability of the spectrophotometer to tolerate the change in colour, and therefore the degree of photocoloration of these dyes was not directly measurable. This feature necessitated using a method for estimating the degree of photocoloration of the spironaphthooxazine-based dyes by applying a mathematical extrapolation.

Another general observation was the higher fading rate of each dye applied to cotton fabric compared to the fading rate of the same dye applied to polyester fabric by the different dyeing and printing methods described in chapters 3, 4 and 5. This observation was explained by lower restriction in the polymeric environment of the ring closure reaction of photochromic dyes on cotton compared to that on polyester due to the differences in the structures of the two fibres.

Fatigue resistance and storage stability of photochromic dyes applied to cotton fabric, expressed by the retention of the degree of photocoloration after 20 cycles of UV light exposure in the case of fatigue resistance and after 170 days of storage in the dark in the case of storage stability, showed variation with the nature of the dye. Fatigue resistance ranged between 99% and 52% and storage stability ranged between 96% and 78% with no obvious relation between either of these properties with the general chemical classes of the dyes.



## **Chapter 7 - Photochromism and Absorption Spectra of Photochromic Dyes in Different Solvents**

### **7.1. Introduction**

In all of the dyeing processes investigated as discussed in chapters 3, 4, 5 and 6, there was a common drawback represented by the permanent background colours of the dyed fabrics. In the case of the aqueous dispersion dyeing method, discussed in chapter 3, permanent colours of dye solutions were generated immediately after dissolving the photochromic dyes in acetone prior to adding to the dyebath, as explained in section 3.2.6. In the case of the solvent-based dyeing methods discussed in chapters 4 and 6, it was observed that all dye solutions in dichloromethane were permanently coloured prior to impregnating the fabric in these solutions, as explained in sections 4.2.4 and 6.2.2. The same trend, i.e. of the presence of permanent colours of dye solutions and printed fabrics, was observed in the case of the inkjet printing method as discussed in chapter 5 where isopropanol was used as the main printing solvent. In all dyeing and printing cases, the permanent colours proved to be transferred to fabrics during the dyeing and printing processes and formed permanent background colours on the dyed and printed fabrics. These permanent background colours were considered as a common drawback of all the photochromic fabrics produced by different dyeing and printing methods due to the possible negative effect of this property on the degree of photocoloration of the photochromic fabrics. In addition, the background colour may become an obstacle to the use of photochromic fabrics in some proposed applications where a white background is required.

It was also observed that the background colour, expressed by  $\Delta E_2$ , gave different values when different solvents were used as media for applying photochromic dyes to fabrics, as discussed in chapters 3, 4, 5 and 6 and shown in Table 7.1 for the optimally dyed samples using the different dyeing and printing methods.

**Table 7.1** Permanent background colours of fabrics dyed or printed with photochromic dyes **1-6** by different dyeing and printing methods

| <i>Dye</i>        | <i>Background colour (<math>\Delta E_2</math>)</i> |   |   |                                      |
|-------------------|--|---|---|--------------------------------------|
|                   | <i>Inkjet printing (polyester)</i>                 | <i>Aqueous-based dyeing (polyester)</i> | <i>Solvent-based dyeing (polyester)</i> | <i>Solvent based dyeing (cotton)</i> |
| Aqua Green        | 2.3  | 16.8                                    | 9.7                                     | 5.1                                  |
| Oxford Blue       | 1.9  | 10.0                                    | 8.9                                     | 2.6                                  |
| Palatinate Purple | 1.4  | 32.0                                    | 7.0                                     | 5.4                                  |
| Plum Red          | 1.9  | 8.5                                     | 15.3                                    | 3.0                                  |
| Ruby              | 1.8  | 18.8                                    | 11.5                                    | 18.5                                 |
| Corn Yellow       | 1.2  | 15.5                                    | 7.9                                     | 8.9                                  |

This observation raised questions as to whether the photochromic dyes show the same photochromic behaviour in all solvents, and whether the solvent has an effect on the permanent background colour transferred to the dyed fabric. To answer these questions, an investigation of solutions of photochromic dyes in different solvents was performed, as discussed in this chapter.

## 7.2. Experimental

### 7.2.1. Colour measurements of dye solutions

Solutions of dyes **1-6** in dichloromethane, toluene, diethyl acetate, acetone and DMSO, were prepared at two different concentrations: a low concentration of  $2 \times 10^{-4} \text{ g.l}^{-1}$ , and a high concentration of  $5 \text{ g.l}^{-1}$ . The latter concentration is equal to the dyeing concentration of 1% o.w.f when 0.04 g of the dye is dissolved in 10 g of the solvent to be applied to 4 g of fabric. For colour measurement of dye solutions of concentration  $5 \text{ g.l}^{-1}$  in different solvent, 10 ml of each dye solution was filled in a silica gel cell prior to transferring the samples to a Lambda 2 UV-visible Spectrophotometer. In the spectrophotometer, absorption spectra of dye solutions between 400 – 700 nm were recorded.

### **7.2.2. Materials**

A series of commercial photochromic dyes was used as given in Table 3.1. Solvents used for dyeing and measuring absorption spectra of dye solutions (Dichloromethane, toluene, diethyl acetate, acetone and DMSO) were of a laboratory grade as supplied by Sigma-Aldrich, UK, in the case of dichloromethane stabilized with amylene. For dyeing applications woven twill, heat-set polyester (Toray Textiles) was used.

### **7.2.3. Application of photochromic dyes to polyester fabric from different solvents by the Solvent-based pad dry-heat dyeing method**

Photochromic dyes **1-6** were applied to polyester fabric by the solvent-based pad dry-heat dyeing method discussed in chapter 4 by following the procedure described in section 4.2.4. This procedure was repeated for application of the dyes to the fabric from toluene and ethyl acetate at the optimum dyeing concentrations which are 1 % o.w.f in the case of Oxford Blue, and 0.2 % o.w.f in the cases of the other dyes, as discussed in section 4.3.2.

### **7.2.4. Colour measurements of polyester fabric dyed with photochromic dyes by the solvent-based pad dry-heat dyeing method from different solvents**

For colour measurements, the same calibration conditions of the spectrophotometer, the measurements conditions and time variations described in sections 3.2.1, 3.2.2, and 3.2.3 respectively were used.  $\Delta E_1$  and  $\Delta E_2$ , as defined in section 3.2.5, were used to express the degree of photocolouration and background colours of dyed fabrics respectively.

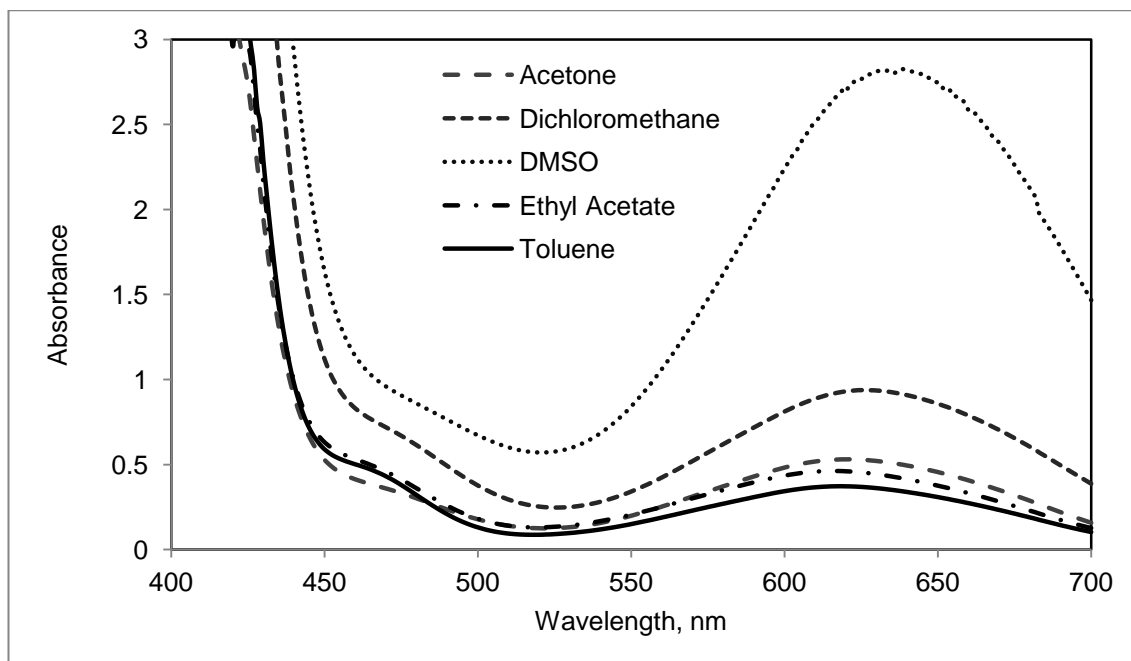
## **7.3. Results and Discussion**

A significant observation in the investigations of the dyeing of polyester using photochromic dyes, is that the dyed fabrics inevitably develop a permanent background colour, which may be an undesirable feature for certain applications. It was thus of interest to explore this issue further and, in the particular context of the focus, to investigate the behaviour of the photochromic dyes in a wider range of solvents, as given in Table 7.2.

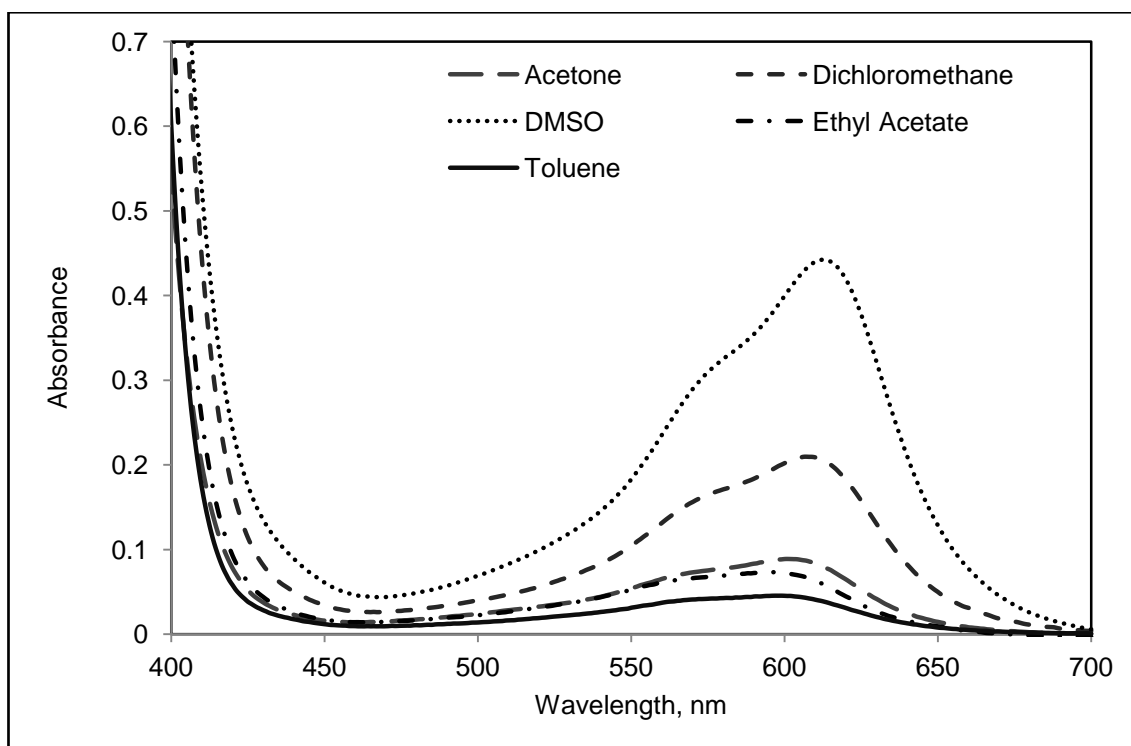
**Table 7.2** Solvent polarity indexes [147]

| <i>Solvent</i>  | <i>Polarity Index</i> |
|-----------------|-----------------------|
| DMSO            | 7.2                   |
| Acetone         | 5.1                   |
| Ethyl Acetate   | 4.4                   |
| Dichloromethane | 3.1                   |
| Toluene         | 2.4                   |

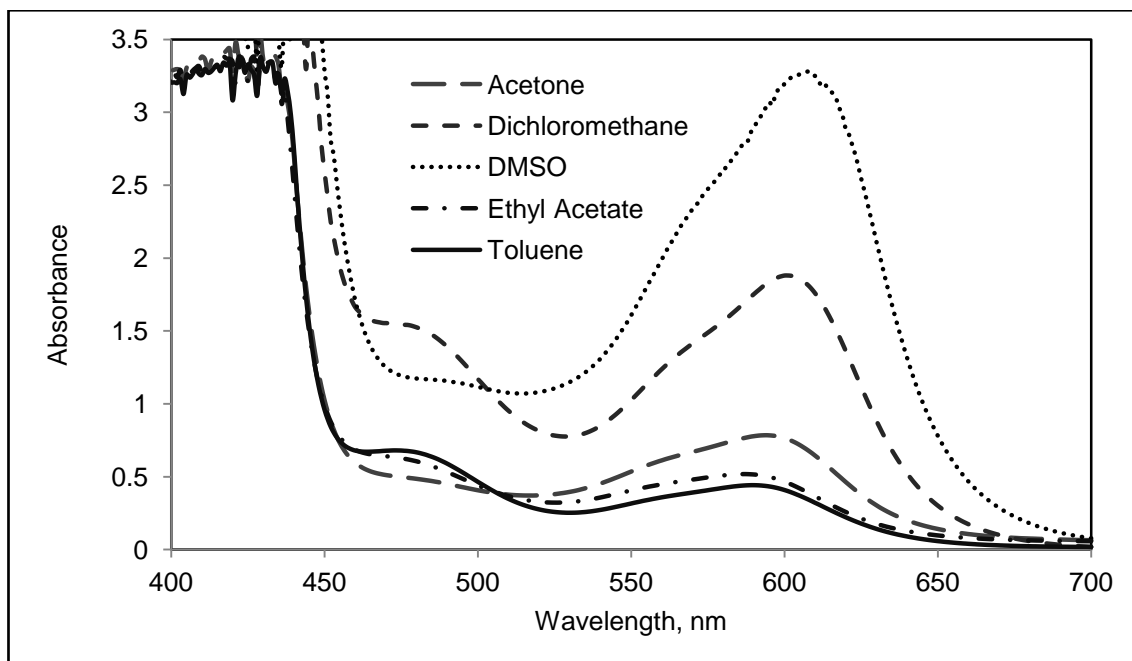
Solutions of dyes **1-6** at low concentration ( $2 \times 10^{-4} \text{ g l}^{-1}$ ) in the range of solvents shown in Table 7.2 [218, 219] selected to provide a range of solvent types and polarities, were colourless and acquired colour after UV irradiation. The solutions reverted to colourless rapidly when the UV light source was removed. In contrast, solutions of dyes **1-6** at high concentration ( $5 \text{ g l}^{-1}$ ), which is typical of the concentration at which they were applied to the fabric, were coloured. The colour persisted even when the solutions were stored in the dark for prolonged periods, demonstrating that the colour is not induced by extraneous light. Absorption spectra of these more concentrated dye solutions, as shown in Figures 7.1 – 7.6, show significant visible absorption. Thus, under these conditions, there appears to be a thermal equilibrium involving the coloured and colourless forms. If dichloromethane is excluded from the argument, the spectra show, in general, that the concentration of the coloured ring-opened species increases with solvent polarity (Table 7.2). This is explained by the stabilisation of the more polar ring-opened form (**Ia** and **IIa** in Schemes 3.1 and 3.2) in solvents of higher polarity, compared with the much less polar ring-closed form, (**I** and **II** in Schemes 3.1 and 3.2). This solvent effect is observed consistently in the case of the spectra of the spironaphthoxazines **1-4**, while there are a few exceptions in the case of the naphthopyrans **5** and **6**. The effect of dichloromethane cannot be explained in this way, and so it is evident that this particular solvent provides a more pronounced stabilising effect on the ring-opened form than would be expected on the basis of polarity arguments alone. There is a notable contrast between the spironaphthoxazine-based dyes **1-4**, where DMSO, the most polar solvent in the series, provides the strongest visible absorption while in the cases of the naphthopyran-based dyes **5** and **6**, the strongest visible absorption is observed in dichloromethane.



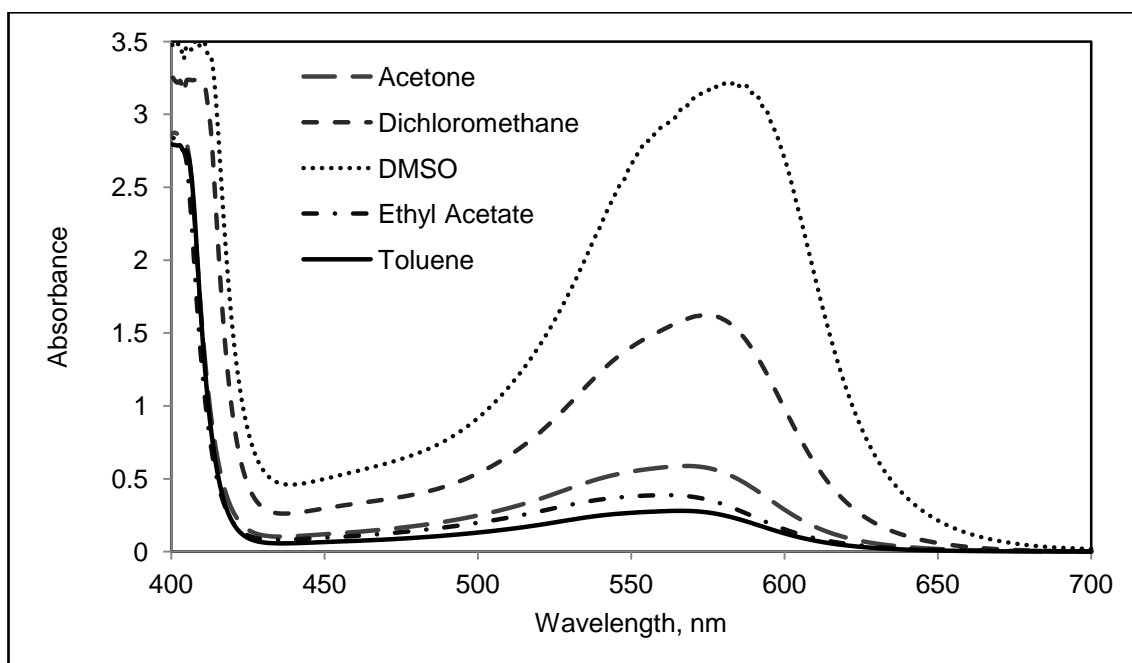
**Figure 7.1** Absorption spectra of Aqua Green (5 g/l) in different solvents



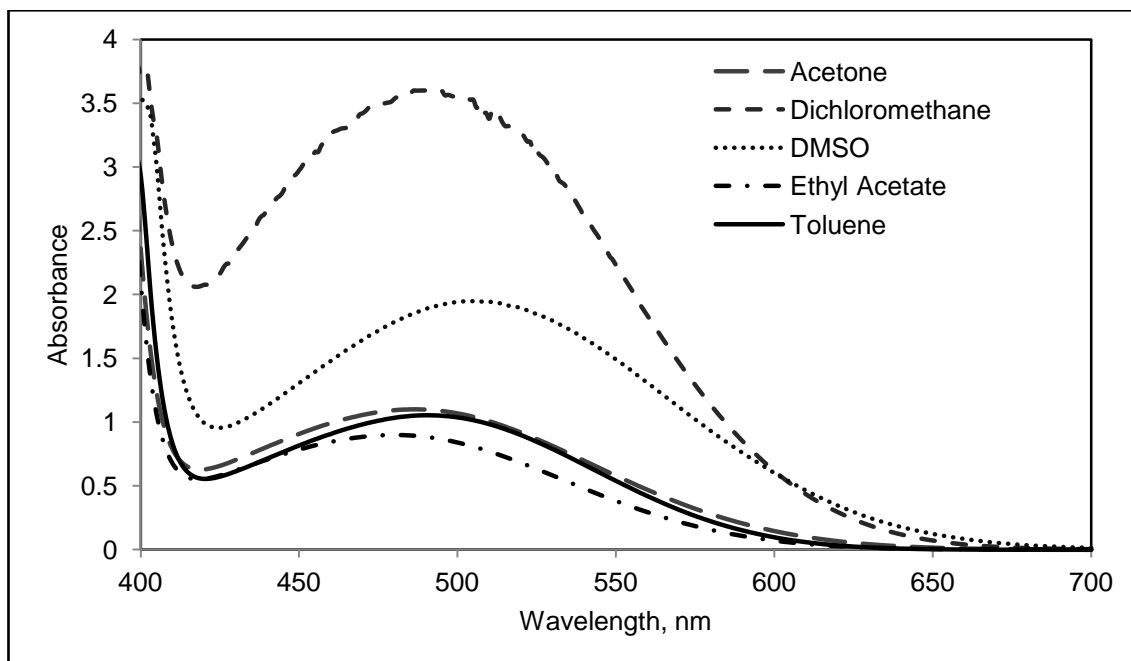
**Figure 7.2** Absorption spectra of Oxford Blue (5 g/l) in different solvents



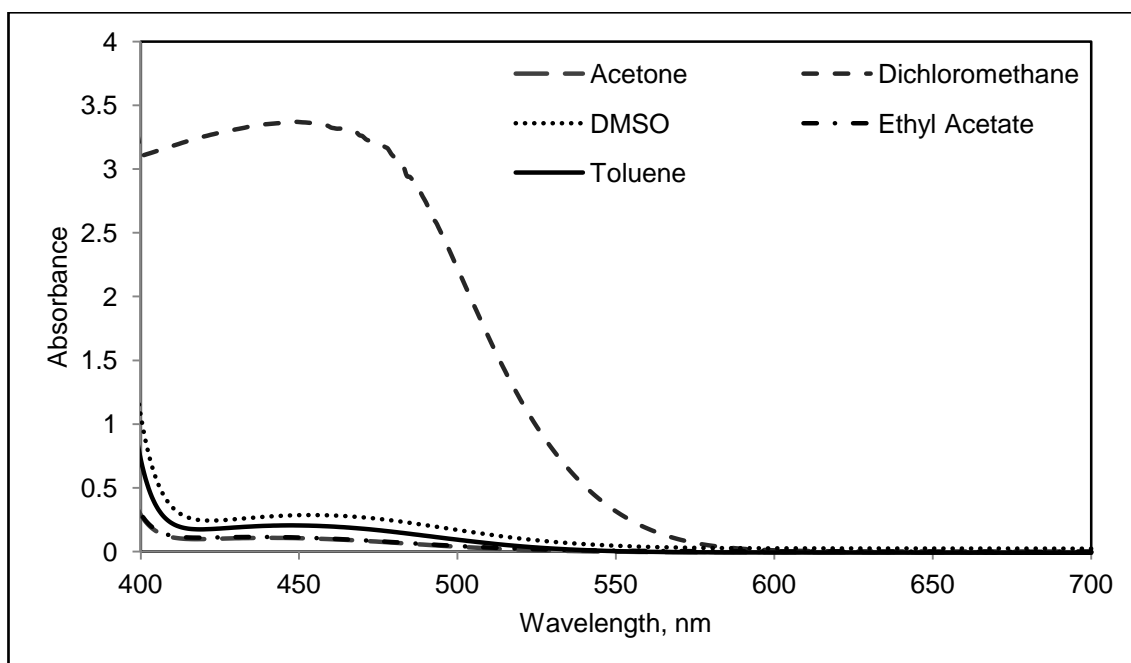
**Figure 7.3** Absorption spectra of Palatinat Purple (5 g/l) in different solvents



**Figure 7.4** Absorption spectra of Plum Red (5 g/l) in different solvents



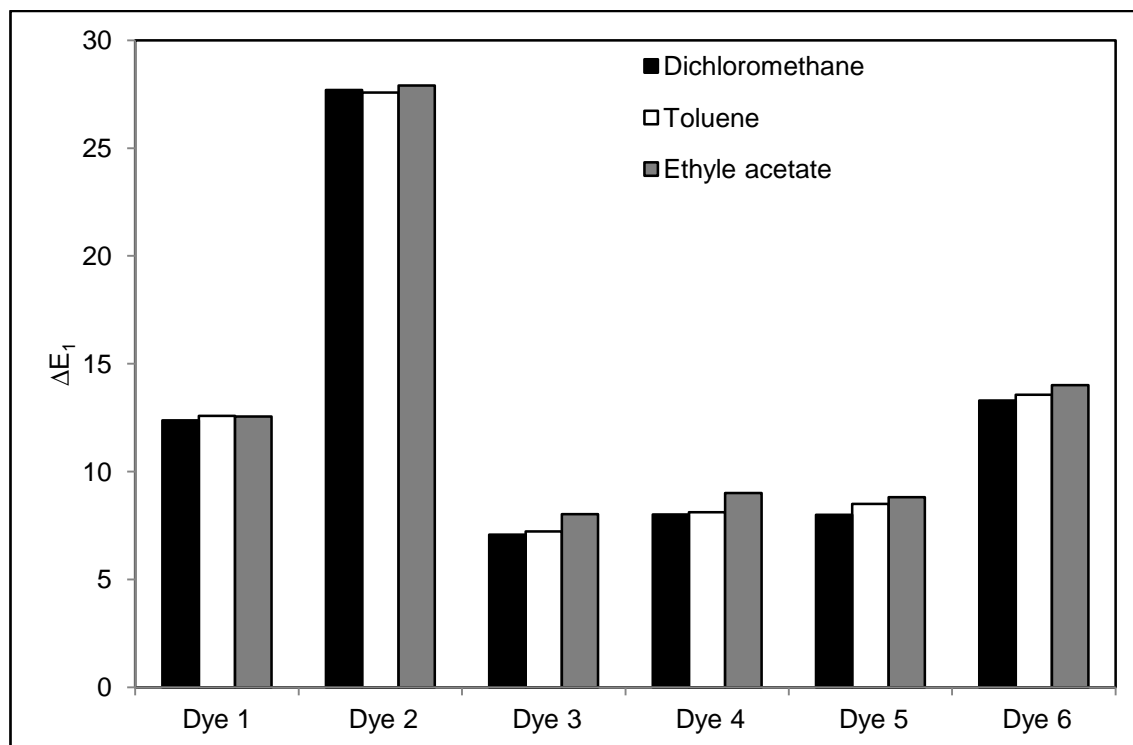
**Figure 7.5** Absorption spectra of Ruby (5 g/l) in different solvents



**Figure 7.6** Absorption spectra of Corn Yellow (5 g/l) in different solvents

A consistent feature, however, is that solutions of the dyes in toluene and ethyl acetate showed the lowest visible absorption. Thus, in order to investigate whether dyeing from these solvents might offer the potential to minimize the permanent background colours, dyes **1-6** were applied to polyester fabric from toluene and ethyl acetate by the solvent-

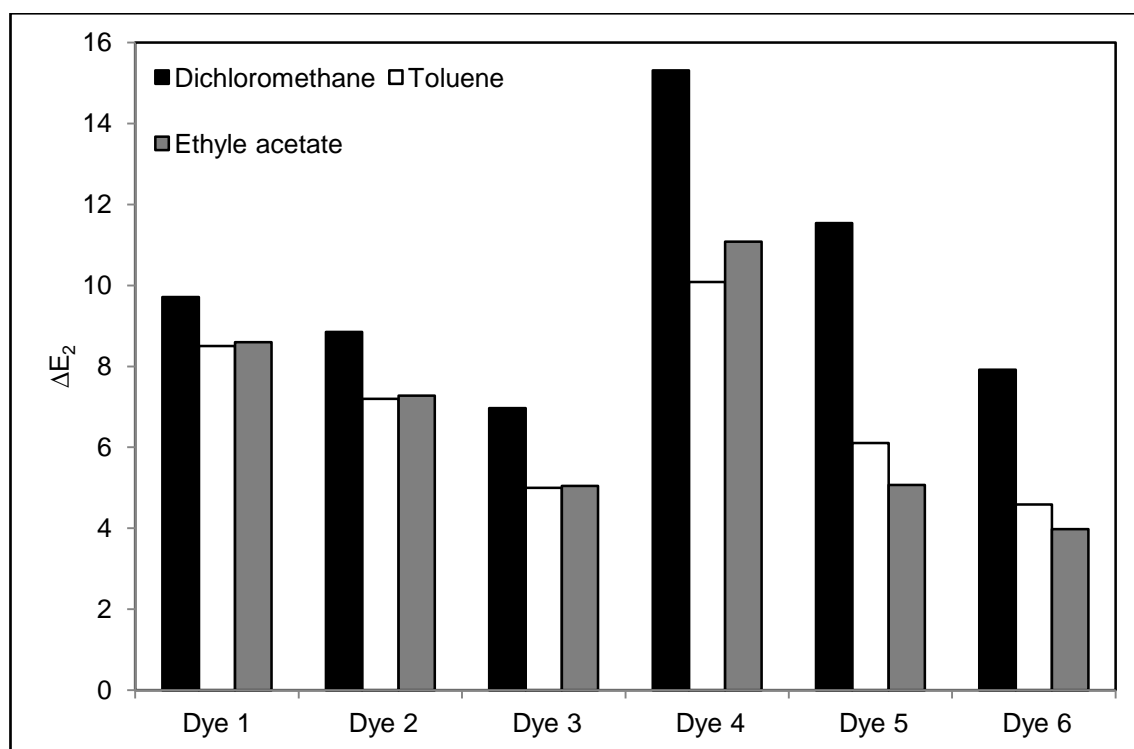
based pad dry-heat dyeing method under the optimised conditions which have been given in sections 4.2.4 and 4.3.1.



**Figure 7.7** Photocoloration of dyes **1-6** applied to polyester from different solvents

Figure 7.7 shows that there is a consistent slight improvement in the degree of photocoloration (higher  $\Delta E_1$ ) of dyed fabric when dichloromethane was replaced by either toluene or ethyl acetate. Additionally, there is a pronounced decrease in the background colours ( $\Delta E_2$ ) of photochromic fabrics dyed using toluene or ethyl acetate compared to those obtained when the fabrics were dyed using dichloromethane, as shown in Figure 7.8.





**Figure 7.8** Background colours of dyes 1-6 applied to polyester from different solvents

There is a strong qualitative correlation between the values of  $\Delta E_2$  for the dyed fabrics and the magnitude of the visible absorption of the dyes in solution. In all cases, the highest  $\Delta E_2$  value is given by dyeing from dichloromethane. In the cases of spironaphthooxazine-based dyes **1-4**, the lowest  $\Delta E_2$  value is given by dyeing from toluene while with the naphthopyran-based dyes **5** and **6** the lowest  $\Delta E_2$  value is given by dyeing from ethyl acetate, in complete agreement with the observations that those solvents give the lowest visible absorption with the particular dyes.

This provides evidence that direct transfer of the coloured ring-opened form of the dye from solution to the fabric may be playing an important part in the mechanism of formation of the background colours.

#### 7.4. Conclusions

Photochromism of solutions of dyes **1-6** in various solvents was investigated. An investigation of the visible spectra of concentrated solutions of the dyes in a series of solvents demonstrated, in general, a correlation between the magnitude of the visible absorption, due to the presence of an equilibrium concentration of the ring-opened form of the dyes, and solvent polarity. However, in the case of dichloromethane, a more pronounced stabilising effect was exerted on the ring-opened form than would be expected on the basis of polarity arguments alone. Interestingly, a strong qualitative correlation was established between the level of the permanent background colour on

the photochromic fabrics and the magnitude of the visible absorption of the dyes in solution when each of the dyes was applied to the polyester from dichloromethane, toluene and ethyl acetate.

## **Chapter 8 – An Investigation of an Instrumental-Based Method for Assessment of Colour Fastness to Light of Textiles**

### **8.1. Introduction**

Colour fastness to light is a routinely investigated property of dyed and printed textiles due to its importance in determining the resistance of the colour of textiles to the action of daylight, which in turn contributes towards the possible uses of coloured textiles. The standard procedure for assessing colour fastness to light of textiles in the most popular lightfastness standard methods involves exposing an area of a specimen of the textile material to simulated daylight under prescribed conditions along with areas of eight samples of dyed wool as references. [180, 220, 221] According to these methods, colour fastness is assessed by comparing the change in colour between exposed and unexposed areas of the specimen with that of the references. The blue wool references are designated by either the numbers 1-8 or the letter L followed by the numbers 2-9. In both cases each higher-numbered reference possesses higher fastness to light compared to the preceding reference. Thus, colour fastness to light of a specimen is given as a numerical rating which represents the number of the reference that showed the same change in colour between exposed and unexposed areas as observed by visual inspection of the specimen or references after controlled periods of light exposure. Thus, visual inspection of the colour change brought about by light exposure is a critical stage in determining the lightfastness of textiles in the traditional system of lightfastness testing. This stage is carried out under standard lighting conditions. However, the assessment depends to an extent on the vision and judgment of the human observer which may vary from one observer to another. The dependence of the evaluation of lightfastness on the visual assessment of the observer may cause a degree of suspicion on the accuracy of this assessment compared to whether this inspection is performed instrumentally.

The reliance on visual assessment highlights another drawback of the traditional method of lightfastness assessment when assessing textiles dyed with photochromic dyes, due to the dynamic nature of the colours produced by these dyes. This drawback of the traditional method of lightfastness measurement has led to the search described in this chapter for a method for lightfastness assessment which is based on instrumental measurement of colour changes after light exposure of specimens and blue wool references. This method which was investigated especially to overcome the difficulties associated with lightfastness assessment of photochromic fabrics may have the potential

to establish a replacement for the conventional method which uses the blue wool references and human observation with a more accurate and reliable instrumental method. The performance of the blue wool references and their fading rates have been examined since the 1950s [222-225] However, there have been no reports about using the results of the investigations of fading rates of the references in assessment of lightfastness of textiles.

## **8.2. Experimental**

### ***8.2.1. Materials***

Polyester fabrics as described in section 3.2.4 dyed with photochromic dyes **1-6**, given in Table 3.1, by the optimum exhaust dyeing method described in sections 3.2.6 and 3.3 at their optimum dyeing concentration, as given in section 3.3.5 were used to test their colour fastness to light. Blue wool references supplied by SDC, UK and identified by the numerical designation 1-8 were used. The references, which are used according to the British standard BS 1006:1990, range from 1 (very low lightfastness) to 8 (very high lightfastness). [180] Undyed Wool fabric supplied from Whaleys and classified as wool serge natural (dyeing) was used for evaluation of colour difference between the Blue wool references and undyed wool fabric.

### ***8.2.2. Instrumental methods***

Exposure of blue wool references and polyester fabric dyed with photochromic dyes **1-6** was carried out using a Heraeus Xenotest 150S instrument equipped with a xenon arc lamp. Samples were cut into a size of 2×4 cm, attached to cards and exposed to light in the Xenotest for increasing periods of time with parts of the fabric covered to prevent exposure. The blue wool references were removed after specific time intervals and the colour differences between the exposed and unexposed areas were measured on the Datacolor Spectraflash SF600 spectrophotometer. The degree of photocolouration of polyester samples dyed with photochromic dyes **1-6** was measured on the spectrophotometer after 4 minutes of UV exposure. The UV light sources, calibration conditions of the spectrophotometer, the temperature control and the time lapse described in sections 3.2.1, 3.2.2 and 3.2.3 were used except for the aperture which was changed from small to ultra small due to the small size of samples. The polyester samples were exposed to Xenotest light for a controlled period of time and then left in the dark for 2 hours to ensure that colours developed by the Xenotest light exposure faded to their background colours. After that, the degree of photocolouration of polyester

samples exposed to Xenotest light was measured. The degree of photocolouration ( $\Delta E_1$ ) of fabrics dyed with photochromic dyes was assessed as defined in section 3.2.5. The lightfastness of polyester samples dyed with photochromic dyes **1-6** was assessed by comparing the percentage decrease in the degree of photocolouration of the tested samples with the percentage decrease in colours of the blue wool references exposed to Xenotest light for the same period of time.

### **8.3. Results and Discussion**

#### ***8.3.1. Principles of the instrumental-based method of lightfastness measurement***

The principle of the method developed in this research was based on exposing parts of the blue wool references to Xenotest light for increasing periods of time, measuring differences between the exposed and unexposed areas instrumentally and calculating the percentage differences in colours of the blue wool references, compared to their original colours without exposure. These assessments were used as a scale of lightfastness of the blue wool references which represents their resistance to photodegradation by light exposure. Thus, the lightfastness of a textile material coloured with photochromic dyes was estimated by exposing an area of a sample of this textile to light for a period of time and then measuring the colour difference between the exposed and unexposed areas of the sample. As the colour of textile material dyed with photochromic dyes is not developed until it is exposed to UV light, the measurement of colour difference after Xenotest light exposure was carried out immediately after UV light exposure. The colour difference was converted to a percentage decrease in the colour of the sample relative to its colour before exposure. This percentage decrease in colour was compared to the percentage decreases in colours of blue wool references brought about by light exposure for the same period of time.

Table 8.1 shows the colour differences brought about by exposing the blue wool references 1-8 to Xenotest light for increasing periods of time.

**Table 8.1** Colour differences between blue wool references exposed to xenotest light and unexposed areas

| <i>Xenotest light exposure time, h.</i> | <i>Colour difference (<math>\Delta E</math>) between exposed and unexposed parts of blue wool references <math>R_1 - R_8</math></i> |       |       |       |       |       |       |       |
|---|---|-------|-------|-------|-------|-------|-------|-------|
|   | $R_1$   | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | $R_7$ | $R_8$ |
| <b>0</b>                                | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   | 0.0   |
| <b>0.5</b>                              | 3.2   | 2.5   | 1.6   | 0.4   | 0.0   | 0.0   | 0.0   | 0.0   |
| <b>1</b>                                | 7.1   | 4.7   | 2.6   | 0.4   | 0.1   | 0.0   | 0.0   | 0.0   |
| <b>1.5</b>                              | 9.2   | 5.4   | 3.4   | 0.5   | 0.2   | 0.1   | 0.0   | 0.0   |
| <b>2</b>                                | 11.0  | 6.7   | 4.0   | 0.6   | 0.3   | 0.1   | 0.0   | 0.0   |
| <b>2.5</b>                              | 12.2  | 8.4   | 4.1   | 0.6   | 0.4   | 0.2   | 0.0   | 0.0   |
| <b>3</b>                                | 13.5  | 9.6   | 4.7   | 0.6   | 0.4   | 0.2   | 0.0   | 0.0   |
| <b>3.5</b>                              | 14.3  | 10.3  | 5.1   | 0.7   | 0.5   | 0.3   | 0.0   | 0.0   |
| <b>4</b>                                | 15.6  | 10.9  | 5.6   | 0.7   | 0.6   | 0.3   | 0.1   | 0.0   |
| <b>4.5</b>                              | 16.2  | 12.0  | 5.7   | 0.7   | 0.6   | 0.4   | 0.1   | 0.0   |
| <b>5</b>                                | 17.5  | 12.9  | 6.2   | 1.0   | 0.7   | 0.4   | 0.1   | 0.0   |
| <b>5.5</b>                              | 18.7  | 13.7  | 6.7   | 1.1   | 0.8   | 0.5   | 0.1   | 0.0   |
| <b>6</b>                                | 19.4  | 14.4  | 6.9   | 1.2   | 0.8   | 0.5   | 0.1   | 0.0   |
| <b>6.5</b>                              | 20.2  | 15.0  | 7.0   | 1.2   | 0.9   | 0.6   | 0.2   | 0.0   |
| <b>7</b>                                | 20.9  | 15.8  | 7.6   | 1.3   | 0.9   | 0.6   | 0.2   | 0.0   |
| <b>7.5</b>                              | 21.4  | 16.4  | 8.0   | 1.4   | 1.0   | 0.7   | 0.2   | 0.0   |
| <b>8</b>                                | 21.9  | 17.0  | 8.4   | 1.4   | 1.1   | 0.7   | 0.2   | 0.0   |
| <b>8.5</b>                              | 22.3  | 17.6  | 8.7   | 1.4   | 1.1   | 0.7   | 0.2   | 0.0   |
| <b>9</b>                                | 23.0  | 18.1  | 8.7   | 1.4   | 1.2   | 0.7   | 0.3   | 0.0   |
| <b>9.5</b>                              | 23.6  | 18.5  | 8.8   | 1.4   | 1.2   | 0.7   | 0.3   | 0.0   |
| <b>10</b>                               | 24.2  | 18.9  | 8.9   | 1.4   | 1.3   | 0.7   | 0.3   | 0.1   |
| <b>10.5</b>                             | 24.7  | 19.4  | 8.9   | 1.4   | 1.3   | 0.8   | 0.3   | 0.1   |
| <b>11</b>                               | 25.2  | 19.8  | 9.3   | 1.5   | 1.3   | 0.8   | 0.3   | 0.1   |
| <b>11.5</b>                             | 25.6  | 20.1  | 9.7   | 1.5   | 1.4   | 0.8   | 0.4   | 0.1   |
| <b>12</b>                               | 26.0  | 20.6  | 10.0  | 1.6   | 1.4   | 0.8   | 0.4   | 0.1   |
| <b>12.5</b>                             | 26.4  | 20.9  | 10.4  | 1.6   | 1.5   | 0.8   | 0.4   | 0.1   |
| <b>13</b>                               | 26.9  | 21.2  | 10.5  | 1.6   | 1.5   | 0.8   | 0.4   | 0.1   |
| <b>13.5</b>                             | 27.3  | 21.5  | 10.6  | 1.7   | 1.6   | 0.8   | 0.4   | 0.1   |

|             |      |      |      |     |     |     |     |     |
|-------------|------|------|------|-----|-----|-----|-----|-----|
| <b>14</b>   | 27.7 | 21.8 | 10.7 | 1.7 | 1.6 | 0.8 | 0.5 | 0.1 |
| <b>14.5</b> | 28.2 | 22.2 | 10.8 | 1.7 | 1.6 | 0.9 | 0.5 | 0.1 |
| <b>15</b>   | 28.6 | 22.5 | 11.2 | 1.8 | 1.7 | 0.9 | 0.5 | 0.2 |
| <b>15.5</b> | 29.0 | 22.8 | 11.5 | 1.8 | 1.7 | 0.9 | 0.5 | 0.2 |
| <b>16</b>   | 29.4 | 23.2 | 11.8 | 1.8 | 1.7 | 0.9 | 0.5 | 0.2 |
| <b>16.5</b> | 29.8 | 23.5 | 12.1 | 1.9 | 1.8 | 1.0 | 0.5 | 0.2 |
| <b>17</b>   | 30.5 | 24.0 | 12.4 | 2.1 | 1.9 | 1.1 | 0.5 | 0.2 |
| <b>17.5</b> | 31.1 | 24.5 | 12.7 | 2.2 | 2.0 | 1.2 | 0.5 | 0.2 |
| <b>18</b>   | 31.8 | 25.0 | 13.0 | 2.4 | 2.1 | 1.2 | 0.5 | 0.2 |
| <b>18.5</b> | 32.4 | 25.4 | 13.3 | 2.5 | 2.2 | 1.2 | 0.6 | 0.2 |
| <b>19</b>   | 32.8 | 25.7 | 13.4 | 2.5 | 2.4 | 1.3 | 0.6 | 0.2 |
| <b>20</b>   | 33.6 | 26.1 | 13.7 | 2.8 | 2.7 | 1.3 | 0.6 | 0.2 |
| <b>21</b>   | 34.4 | 26.7 | 14.0 | 3.0 | 2.7 | 1.3 | 0.6 | 0.3 |
| <b>22</b>   | 35.0 | 27.5 | 14.6 | 3.2 | 2.8 | 1.4 | 0.6 | 0.3 |
| <b>23</b>   | 35.7 | 28.6 | 15.2 | 3.4 | 2.8 | 1.4 | 0.7 | 0.3 |
| <b>24</b>   | 36.2 | 29.0 | 15.5 | 3.6 | 2.8 | 1.5 | 0.7 | 0.3 |

The values of colour differences in Table 8.1 were converted to the percentage decreases in colour difference between the undyed blue wool references and the light exposed references compared to the initial colour differences before light exposure. The purpose is converting the measured values for colour fading of blue wool references to percentages which can be compared to the percentages of colour fading of tested photochromic samples. For this purpose, the colour differences ( $\Delta E'$ ) between the undyed wool and each reference were measured on the spectrophotometer and results are given in Table 8.2.

**Table 8.2** Colour difference between undyed wool and blue wool references

| <i>Blue wool reference</i> | <i>Colour difference (<math>\Delta E^*</math>) between undyed wool and blue wool references</i> |
|----------------------------|---|
| R <sub>1</sub>             | 68  |
| R <sub>2</sub>             | 73  |
| R <sub>3</sub>             | 82  |
| R <sub>4</sub>             | 64  |
| R <sub>5</sub>             | 64  |
| R <sub>6</sub>             | 61  |
| R <sub>7</sub>             | 67  |
| R <sub>8</sub>             | 60  |

Thus, the percentage decrease in colour differences between undyed wool and each blue wool reference ( $\Delta E^*$ ) after different periods of Xenotest light exposure were calculated, as given in Table 8.3.

**Table 8.3** Percentage decreases in the colour difference between undyed wool and blue wool references after Xenotest light exposure for different periods of time

| <i>Xenotest light exposure time, h.</i> | <i>Percentage decrease in the colour difference between undyed wool and blue wool references after Xenotest light exposure (<math>\Delta E^*</math>)</i> |                      |                      |                      |                      |                      |                      |                      |
|---|--|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
|   | <i>R<sub>1</sub></i>   | <i>R<sub>2</sub></i> | <i>R<sub>3</sub></i> | <i>R<sub>4</sub></i> | <i>R<sub>5</sub></i> | <i>R<sub>6</sub></i> | <i>R<sub>7</sub></i> | <i>R<sub>8</sub></i> |
| <b>0</b>                                | 0%   | 0%                   | 0%                   | 0%                   | 0%                   | 0%                   | 0%                   | 0%                   |
| <b>0.5</b>                              | 5%   | 3%                   | 2%                   | 1%                   | 0%                   | 0%                   | 0%                   | 0%                   |
| <b>1</b>                                | 10%  | 6%                   | 3%                   | 1%                   | 0%                   | 0%                   | 0%                   | 0%                   |
| <b>1.5</b>                              | 13%  | 7%                   | 4%                   | 1%                   | 0%                   | 0%                   | 0%                   | 0%                   |
| <b>2</b>                                | 16%  | 9%                   | 5%                   | 1%                   | 0%                   | 0%                   | 0%                   | 0%                   |
| <b>2.5</b>                              | 18%  | 11%                  | 5%                   | 1%                   | 1%                   | 0%                   | 0%                   | 0%                   |
| <b>3</b>                                | 20%  | 13%                  | 6%                   | 1%                   | 1%                   | 0%                   | 0%                   | 0%                   |
| <b>3.5</b>                              | 21%  | 14%                  | 6%                   | 1%                   | 1%                   | 0%                   | 0%                   | 0%                   |
| <b>4</b>                                | 23%  | 15%                  | 7%                   | 1%                   | 1%                   | 1%                   | 0%                   | 0%                   |
| <b>4.5</b>                              | 24%  | 16%                  | 7%                   | 1%                   | 1%                   | 1%                   | 0%                   | 0%                   |
| <b>5</b>                                | 26%  | 18%                  | 8%                   | 2%                   | 1%                   | 1%                   | 0%                   | 0%                   |



|             |     |     |     |    |    |    |    |    |
|-------------|-----|-----|-----|----|----|----|----|----|
| <b>5.5</b>  | 28% | 19% | 8%  | 2% | 1% | 1% | 0% | 0% |
| <b>6</b>    | 29% | 20% | 8%  | 2% | 1% | 1% | 0% | 0% |
| <b>6.5</b>  | 30% | 21% | 9%  | 2% | 1% | 1% | 0% | 0% |
| <b>7</b>    | 31% | 22% | 9%  | 2% | 1% | 1% | 0% | 0% |
| <b>7.5</b>  | 31% | 22% | 10% | 2% | 2% | 1% | 0% | 0% |
| <b>8</b>    | 32% | 23% | 10% | 2% | 2% | 1% | 0% | 0% |
| <b>8.5</b>  | 33% | 24% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>9</b>    | 34% | 25% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>9.5</b>  | 35% | 25% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>10</b>   | 36% | 26% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>10.5</b> | 36% | 27% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>11</b>   | 37% | 27% | 11% | 2% | 2% | 1% | 0% | 0% |
| <b>11.5</b> | 38% | 28% | 12% | 2% | 2% | 1% | 1% | 0% |
| <b>12</b>   | 38% | 28% | 12% | 2% | 2% | 1% | 1% | 0% |
| <b>12.5</b> | 39% | 29% | 13% | 2% | 2% | 1% | 1% | 0% |
| <b>13</b>   | 39% | 29% | 13% | 2% | 2% | 1% | 1% | 0% |
| <b>13.5</b> | 40% | 29% | 13% | 3% | 2% | 1% | 1% | 0% |
| <b>14</b>   | 41% | 30% | 13% | 3% | 2% | 1% | 1% | 0% |
| <b>14.5</b> | 41% | 30% | 13% | 3% | 2% | 1% | 1% | 0% |
| <b>15</b>   | 42% | 31% | 14% | 3% | 3% | 1% | 1% | 0% |
| <b>15.5</b> | 43% | 31% | 14% | 3% | 3% | 2% | 1% | 0% |
| <b>16</b>   | 43% | 32% | 14% | 3% | 3% | 2% | 1% | 0% |
| <b>16.5</b> | 44% | 32% | 15% | 3% | 3% | 2% | 1% | 0% |
| <b>17</b>   | 45% | 33% | 15% | 3% | 3% | 2% | 1% | 0% |
| <b>17.5</b> | 46% | 34% | 15% | 3% | 3% | 2% | 1% | 0% |
| <b>18</b>   | 47% | 34% | 16% | 4% | 3% | 2% | 1% | 0% |
| <b>18.5</b> | 48% | 35% | 16% | 4% | 3% | 2% | 1% | 0% |
| <b>19</b>   | 48% | 35% | 16% | 4% | 4% | 2% | 1% | 0% |
| <b>20</b>   | 49% | 36% | 17% | 4% | 4% | 2% | 1% | 0% |
| <b>21</b>   | 51% | 37% | 17% | 5% | 4% | 2% | 1% | 0% |
| <b>22</b>   | 51% | 38% | 18% | 5% | 4% | 2% | 1% | 0% |
| <b>23</b>   | 52% | 39% | 19% | 5% | 4% | 2% | 1% | 0% |
| <b>24</b>   | 53% | 40% | 19% | 6% | 4% | 2% | 1% | 1% |

An example of the method used for calculating the values in Table 8.3 is given as follows. The colour difference between exposed and unexposed parts of blue wool reference 1 after 0.5 hour of light exposure was  $\Delta E = 3.2$ , as given in Table 8.1. The colour difference between undyed wool and blue wool reference 1 is  $\Delta E' = 68$ , as given in Table 8.2. As a result, the percentage decrease in the colour difference between undyed wool and blue wool reference 1 after 0.5 hour of Xenotest light exposure is given by  $\Delta E'' = \left( \frac{\Delta E}{\Delta E'} \right) \times 100\% = \left( \frac{3.2}{68} \right) \times 100\% = 5\%$ .

### ***8.3.2. Assessment of colour fastness to light of polyester fabric dyed with photochromic dyes by the exhaust dyeing method***

An example of using  $\Delta E''$  values in Table 8.3 for photochromic textiles is given by measuring the lightfastness of polyester fabrics dyed with photochromic dyes **1-6** at their optimum dyeing concentrations by the exhaust dyeing method discussed in Chapter 3. Degrees of photocoloration ( $\Delta E_1$ ) of the optimally dyed samples were measured before and after 30 minutes of Xenotest light exposure and the decreases in the degree of photocoloration were calculated as percentages of the original values, as given in Table 8.4.

**Table 8.4** Percentage decrease in the degree of photocoloration of photochromic dyes after Xenotest light exposure for different periods of time.

| <i>Dye</i>        | $\Delta E_1$                    |   | <i>Percentage decrease in <math>\Delta E_1</math></i> |
|-------------------|---------------------------------|---|---|
|                   | <i>Before Xenotest exposure</i> | <i>After 0.5 h of Xenotest exposure</i> |   |
| Aqua Green        | 9.1                             | 4.1                                     | 55 %  |
| Oxford Blue       | 27.1                            | 24.4                                    | 10 %  |
| Palatinate Purple | 3.6                             | 2.3                                     | 36 %  |
| Plum Red          | 3.5                             | 1.9                                     | 46 %  |
| Ruby              | 8.8                             | 7.7                                     | 12 %  |
| Corn Yellow       | 14.7                            | 10.3                                    | 30 %  |

By comparing the percentage decrease in the degree of photocoloration of each dye in Table 8.4 with the percentage decreases in the colour difference between undyed wool and each blue wool reference after Xenotest light exposure for 30 minutes as given in Table 8.3, it was observed that all polyester samples dyed with photochromic dyes **1-6** lost a higher percentage of their degree of photocoloration than the percentage lost by

the blue wool reference 1. As a result, the lightfastness of photochromic dyes **1-6** applied to polyester fabric by the exhaust dyeing method may be given the rate 1 although the colours of these samples are more fugitive than that of the blue wool reference 1, and therefore their lightfastness is classified as very low.

#### **8.4. Conclusions**

The establishment of a new method for measurement of colour fastness to light of textiles dyed with photochromic dyes was investigated. This method, which uses the blue wool scale, may be closer to the standard methods used for lightfastness measurements compared to the method used for testing lightfastness of photochromic dyes which was given in section 3.3.9.

This method is based on replacing the visual assessment of colour difference between exposed and unexposed areas of textile samples, which is used in the traditional method of assessment of lightfastness, by an instrumental measurement of the colour difference. According to this method, the percentage decreases in the degree of photocolouration of tested samples are compared to the percentage decreases in the colour difference between undyed wool and each blue wool reference after light exposure for increasing periods of time. This method may be more accurate than the traditional method of lightfastness assessment of traditional dyes due to using an instrumental method for measuring changes in colour for both blue wool references and tested textiles. Another advantage associated with this method is that a set of values of percentage decreases in colour difference between undyed wool and blue wool references may be used for assessment of lightfastness of tested textiles as long as the light exposure of blue wool references is carried out on a similar instrument to that used for light exposure of tested samples. However, other factors related to the similarity of light exposure conditions, such as the lifetime of light exposure bulbs, should be considered when this method is used for lightfastness assessment of textiles dyed with either photochromic or traditional dyes.

With taking all these factors into account, the application of the lightfastness test method may be extended to include testing colour fastness to light of traditional dyes applied to textiles. For this purpose, the blue wool references are exposed at the same time with the tested samples. After light exposure to a fixed period, the percentage increases in colour differences between exposed and unexposed parts of the blue wool references and the tested samples are measured on the spectrophotometer and compared. The lightfastness of the sample is rated by the number of the blue wool references that

showed the closest value of the percentage increase in the colour difference after the same period of exposure.

## Chapter 9 - Development of New Photochromic Systems for Evaluation in Textile Applications

### 9.1. Introduction

The application of a set of commercial photochromic dyes to textiles by various dyeing and printing methods was investigated as discussed in chapters 3, 4, 5 and 6. In general, the applications were successful, but to different extents depending on the substrate type, the dyeing or printing methods used and the chemical structure of the photochromic dyes. The performance of different dyes applied by the same method varied widely probably due to differences in the chemical structures of each dye, the extent to which it penetrates into the fibre and its final location, and conceivably influenced by the interaction with the application solvent. The selection of dyes with chemical structures appropriate for textile coloration is mainly determined by the type of textile material, the application method and the required technical properties of the coloured textiles. [114] Textile colorants are classified into chemical classes according to certain common chemical structural features, and belong mainly to the azo, carbonyl, phthalocyanine, arylcarbonium ion, sulphur, methine and nitro chemical classes. [147] In this respect, azo dyes are the most important and also most intensively investigated chemical class of dyes. [147, 226] The importance of azo colorants is derived from their capability to give a wide range of colours of high intensity and brightness, and the fact that they are relatively inexpensive. [147] These dyes contain at least one azo group (-N=N-), which is principally responsible for the colour of the molecule (the chromophore), attached to two groups at least one of which is aromatic. Certain other functional groups that may be required to constitute a dye molecule are referred to as auxochromes, such as hydroxyl (OH) and amino (NR<sub>2</sub>) groups, whose role is to increase the intensity of colour and shift the absorption to longer wavelengths of visible light. In addition to the chromophores and auxochromes, a system of alternate double and single bonds, referred to as a conjugated system, is incorporated in the azo dye molecule. This conjugated system, which is an essential feature of all dye and organic pigment molecules, as it confers stability, normally contains aromatic rings. The general synthesis route to azo dyes starts with diazotization of a primary aromatic amine followed by coupling of the resulting diazonium salt with an electron-rich nucleophile referred to as the coupling component. The relative simplicity of the synthesis means that a large number of these colorants can be prepared by linking various pairs of organic components.

In this chapter, a study of the conversion of a particular photochromic compound of known chemical structure to azospirooxazine dyes by azo coupling with various diazonium salts is reported. The photochromism in different solvents of the synthesized azospirooxazine dyes, which may be appropriate for textile applications, is investigated.

## 9.2. Experimental

### 9.2.1. Starting materials

The chemicals used in this study (2,7-dihydroxynaphthalene, sodium hydroxide, sodium nitrite, sulphuric acid, 1,3,3-trimethyl-2-methyleneindoline (Fischer's base), *p*-nitroaniline, *m*-nitroaniline, *o*-nitroaniline, anhydrous sodium acetate, sulphamic acid, ethanol, dichloromethane, methanol, acetone and toluene) were of laboratory grade as supplied by Sigma-Aldrich, UK.

### 9.2.2. Instrumental methods

Melting points were determined as peak temperatures using a Mettler DSC 12E at a heating rate of 10°C min<sup>-1</sup> from 30 to 400°C. Fourier Transform Infrared (FTIR) spectra were recorded as KBr discs with a Nicolet Protégé 460 Fourier Transform Spectrophotometer. The software used for the spectrophotometer was EZ OMNiC. <sup>1</sup>H NMR spectra were recorded for dye solutions in d-DMSO on a Bruker AC 200 instrument at 200 MHz. Microanalysis for C, H and N was carried out on an Exeter Analytical CE440 analyser with the industry standard error of +/- 0.3% on each of the three elements analysed. UV-Visible spectra were recorded on a Perkin-Elmer UV-VIS Lambda 2 spectrophotometer.

### 9.2.3. Synthesis of azospirooxazine dyes

#### a) Synthesis of 2,7-dihydroxy-1-nitrosophthalene [227, 228]

2,7-Dihydroxynaphthalene (13.9 g, 0.087 mol) and 150 ml of 0.6 M sodium hydroxide solution were added to a 250 cm<sup>3</sup> three-necked flask equipped with a mechanical stirrer. The mixture was cooled to 0°C with an ice-salt bath, and then sodium nitrite (6 g, 0.087 mol) was added. With stirring, concentrated sulphuric acid (10 cm<sup>3</sup>, 0.18 mol) was slowly added to the mixture such that the temperature was maintained at 0°C. 2,7-dihydroxy-1-nitrosophthalene precipitated out during the addition as a dark brownish precipitate. The mixture was allowed to stir for 1 hour at the low temperature after all the sulphuric acid was added. The precipitate was suction-filtered, thoroughly washed with water and allowed to air dry for 2-3 days. 2,7-dihydroxy-1-nitrosophthalene (

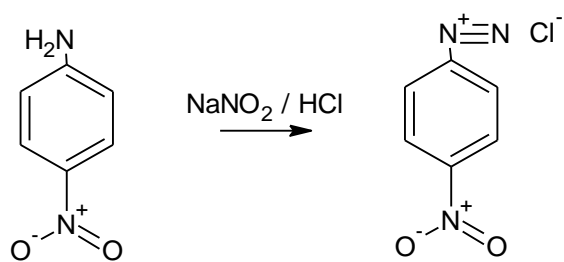
22g, 90% ), m.p. 285°C [228], KBr (IR): 407, 418, 837, 1229, 1306, 1558, 1651, 1694, 2359, 3180, 3646, 3668, 3743, 3814, 3851 cm<sup>-1</sup>, was obtained.

*b) Synthesis of spironaphtho[2,1-b]oxazine (I) [229, 230]*

2,7-Dihydroxy-1-nitrosonaphthalene (8 g, 0.044 mol) and ethanol 96% (83 cm<sup>3</sup>) were added to a 100 cm<sup>3</sup> round bottom flask equipped with a condenser and stirred while a solution of 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (14 g, 0.044 mol) in ethanol 96% (50 cm<sup>3</sup>) was added over a period of 30 minutes. The mixture was refluxed for 3 hours and then rotary evaporated to approximately 50% of its original volume. The dark viscous material was allowed to stand overnight, the precipitate which was formed suction filtered and the residue was rinsed with cold ethanol to give the crude spirooxazine. Two recrystallizations from ethanol gave 7.88 g (47%) of a light pink product characterized by m.p. 223°C [229] and KBr (IR): 606, 744, 754, 830, 844, 967, 1015, 1031, 1068, 1084, 1135, 1167, 1197, 1218, 1247, 1303, 1361, 1384, 1451, 1486, 1526, 1607, 1632, 2968, 3063, 3321 cm<sup>-1</sup>.

*c) Preparation of diazonium salts by diazotization of p-nitroaniline, m-nitroaniline and o-nitroaniline*

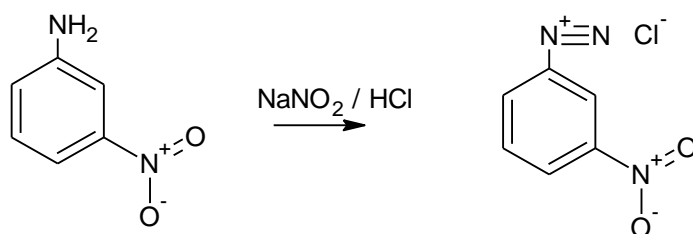
The nitroaniline, either *p*-nitroaniline, *m*-nitroaniline or *o*-nitroaniline (0.52 g, 0.00375 mol), was stirred with concentrated hydrochloric acid (3.75 cm<sup>3</sup>). With stirring over 2 minutes, a solution of sodium nitrite (0.265 g, 0.00375 mol) in water (3.4 cm<sup>3</sup>) was added while keeping the temperature below 5°C by the addition of ice, because diazonium salts are unstable at higher temperatures. An excess of nitrous acid was demonstrated by a positive reaction with starch/KI paper. The mixture was stirred for 20 minutes at 5°C until the suspensions converted into solutions. Just before coupling, a few drops of sulphamic acid solution were added to the diazonium salt solutions to remove the excess of nitrous acid. Diazotization reactions are illustrated in Schemes 9.1 – 9.3.



*p*-nitroaniline

Diazotized *p*-nitroaniline

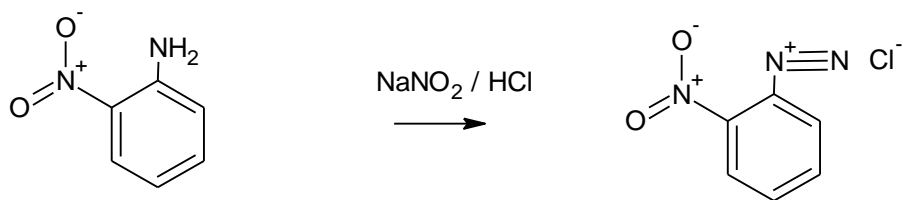
**Scheme 9.1** Diazotization of *p*-nitroaniline



*m*-nitroaniline

Diazotized *m*-nitroaniline

**Scheme 9.2** Diazotization of *m*-nitroaniline



*o*-nitroaniline

Diazotized *o*-nitroaniline

**Scheme 9.3** Diazotization of *o*-nitroaniline

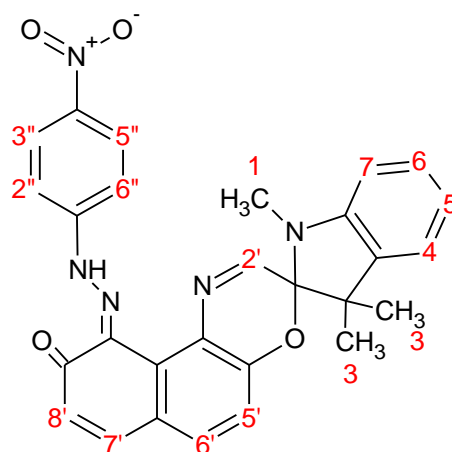


d) *Synthesis of azospirooxazine dyes 2 and 3*

Spirooxazine **1** (2.55 g, 0.0075 mol) was added to ethanol 96% (195 ml) and heated gently at 40°C for 2-3 minutes to dissolve the compound, and then the solution was cooled to room temperature. A solution of sodium hydroxide (4.5 g, 0.1125 mol) in water (24 ml) was added and the mixture was stirred for 20 minutes. Anhydrous sodium acetate (18.9 g) was added and the mixture stirred for 30 minutes. One third of the spirooxazine **1** (coupling component) solution was used for coupling with each diazonium salt. The diazonium salt solutions (diazotized *p*-nitroaniline, *m*-nitroaniline and *o*-nitroaniline) were added to the coupling component solutions over 30 minutes. After addition was completed, the pH was 8, and this dropped further to 7.5 after stirring overnight. It was then adjusted to 6 by adding dilute acetic acid. The precipitate was suction filtered and dried. An orange-brown product (1.17 g) and a yellowish brown product (1.17 g) were obtained in the case of diazotized *p*-nitroaniline and *m*-nitroaniline respectively. In the case of diazotized *o*-nitroaniline, the azo coupling reaction resulted in a mixture of two compounds, as indicated by TLC. Instability of the dye was demonstrated by a 2-dimensional TLC test which showed a brown and a blue spots after first elution. After the second elution an orange spot was observed together with some of the original brown material showing the decomposition of the dye. The decomposition indicates that the two compounds could not be purified by the column chromatography, as was experienced in a similar study carried out on azospirooxazine dye **2**. [231] Hence, no further work was carried out on this compound.

After recrystallization from ethanol, azospirooxazine dye **2** was obtained as orange-brown crystals (0.59 g, 47 %). M.p. 192°C; (C<sub>28</sub>H<sub>23</sub>N<sub>5</sub>O<sub>4</sub>: microanalysis found C,67.61;H,4.58;N,13.89 % requires:C,68.14;H,4.70;N,14.19 %). KBr (IR): 745, 790, 844, 974, 1003, 1032, 1069, 1106,, 1128, 1159, 1205, 1234, 1333, 1360, 1382, 1400, 1425, 1487,1545, 1572, 1595, 2959, 3067, 3568, 3630, 3651, 3677, 3737, 3745, 3753, 3803, 3823, 3855 cm<sup>-1</sup>.

Analyses of the <sup>1</sup>H NMR spectrum gave further confirmation of the structure, as shown in Figure 9.1 and Table 9.1.



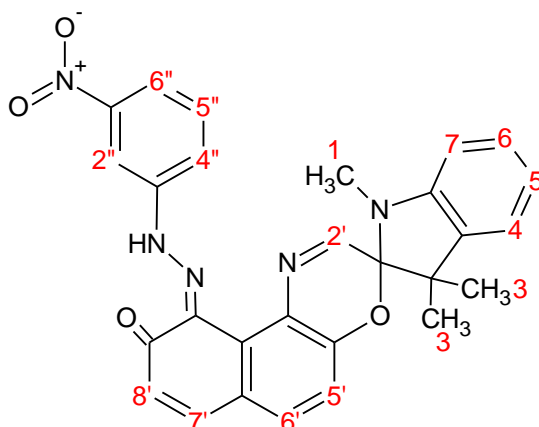
**Figure 9.1** Molecular structure of azospirooxazine dye 2

**Table 9.1** Analysis of  $^1\text{H}$  NMR (200 MHz) spectrum of azospirooxazine dye 2

| <i>Hydrogen atoms</i>                  | <i>Signal/Chemical shift <math>\delta</math> (ppm)</i> |
|--|--|
| $\text{C}(\text{CH}_3)_2$              | $\delta$ 1.12(s, 3H), $\delta$ 1.33(s, 3H)             |
| N- $\text{CH}_3$                       | $\delta$ 2.79 (s, 3H)                                  |
| $\text{H}_7'$                          | $\delta$ 6.57 (d, J= 9.16, 1H)                         |
| $\text{H}_7$                           | $\delta$ 6.69 (d, J= 7.50, 1H)                         |
| $\text{H}_5$                           | $\delta$ 6.83 (m, 1H)                                  |
| $\text{H}_5'$                          | $\delta$ 7.04 (d, J= 8.33 , 1H)                        |
| $\text{H}_6, \text{H}_4$ (overlapping) | $\delta$ 7.07-7.23 ( m, 2H)                            |
| $\text{H}_6'$                          | $\delta$ 7.58 (d, J= 8.33, 1H)                         |
| $\text{H}_8'$                          | $\delta$ 7.85 (d, J= 9.16, 1H)                         |
| $\text{H}_2'', \text{H}_6''$           | $\delta$ 7.94 (d, J= 9.16, 2H)                         |
| $\text{H}_2'$                          | $\delta$ 8.12 (s, 1H)                                  |
| $\text{H}_3'', \text{H}_5''$           | $\delta$ 8.34 (d, J= 9.16, 2H)                         |

After recrystallization from ethanol, azospirooxazine dye 3, a new compound, was obtained as yellow-brown crystals (0.65 g, 52 %). M.p. 188 °C; ( $\text{C}_{28}\text{H}_{23}\text{N}_5\text{O}_4$ : microanalysis found C, 66.21; H, 4.63; N, 15.43%. requires: C,68.14;H,4.7;N,14.19% ). KBr (IR): 520, 548, 635, 649, 708, 745, 790, 844, 975, 1004, 1033, 1070, 1107, 1128, 1160, 1206, 1234, 1306, 1334, 1361, 1401, 1425, 1488, 1545, 1572, 1595, 2926, 2961, 3068, 3448, 3630, 3651, 3677, 3691, 3713, 3737, 3746, 3753, 3803, 3823, 3855, 3871  $\text{cm}^{-1}$ .

Analysis of the  $^1\text{H}$  NMR spectrum gave further confirmation of the structure, as shown in Figure 9.2 and Table 9.2.



**Figure 9.2** Molecular structure of azospirooxazine dye **3**

**Table 9.2** Analysis of  $^1\text{H}$  NMR (200 MHz) spectrum of azospirooxazine dye **3**

| <i>Hydrogen atoms</i>                   | <i>Signal/Chemical shift <math>\delta</math> (ppm)</i> |
|---|--|
| $\text{C}(\text{CH}_3)_2$               | $\delta 1.28$ (s, 3H), $\delta 1.33$ (s, 3H)           |
| N- $\text{CH}_3$                        | $\delta 2.80$ (s, 3H)                                  |
| $\text{H}_7, \text{H}_7'$ (overlapping) | $\delta 6.65$ - $6.70$ (m, 1H)                         |
| $\text{H}_5$                            | $\delta 6.82$ (m, 1H)                                  |
| $\text{H}_5'$                           | $\delta 7.01$ (d, $J = 8.57$ , 1H)                     |
| $\text{H}_6, \text{H}_4$                | $\delta 7.10$ - $7.21$ (m, 2H)                         |
| $\text{H}_6'$                           | $\delta 7.62$ (d, $J = 8.57$ , 1H)                     |
| $\text{H}_4''$                          | $\delta 7.76$ (d, $J = 8.57$ , 1H)                     |
| $\text{H}_8'$                           | $\delta 7.85$ (d, $J = 9.99$ , 1H)                     |
| $\text{H}_2'$                           | $\delta 7.99$ (s, 1H)                                  |
| $\text{H}_5''$                          | $\delta 8.07$ (m, 1H)                                  |
| $\text{H}_6''$                          | $\delta 8.18$ (d, $J = 8.57$ , 1H)                     |
| $\text{H}_2''$                          | $\delta 8.83$ (s, 1H)                                  |

#### ***9.2.4. Molecular modelling of spirooxazine 1 and azospirooxazine dyes 2 and 3***

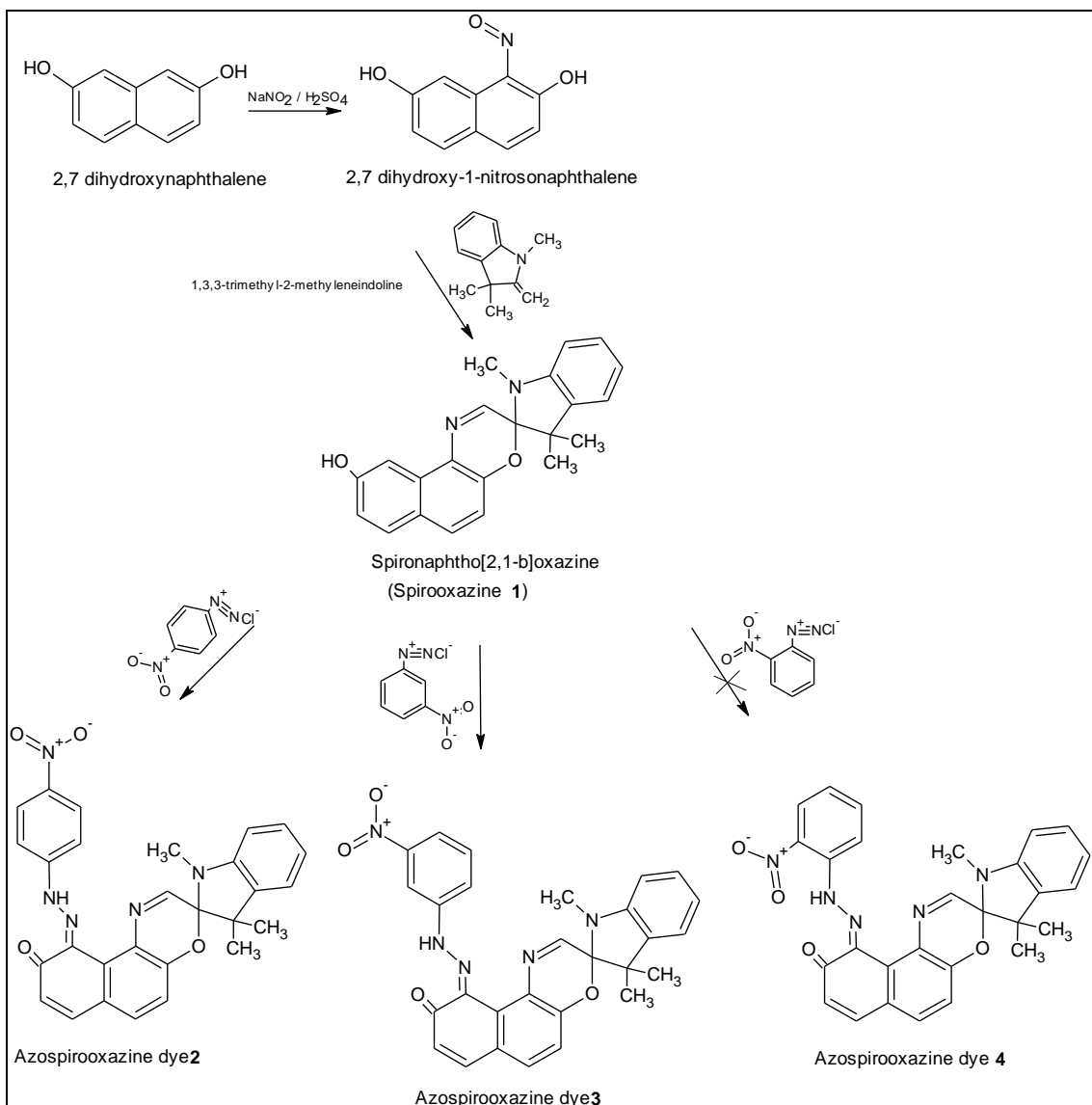
The molecular geometries of azospirooxazine dyes **2** and **3** and of the transoid isomers of the ring opened forms (photomerocyanines) were calculated using standard augmented MM2 and AM1 within a computer-aided application system referred to as CaChe, with a fine convergence limit of  $1e^{-5}$  used in the minimizations.

#### ***9.2.5. Photochromism of spirooxazine 1 and azospirooxazine dyes 2 and 3 in different solvents***

Solutions of spirooxazine **1** and azospirooxazine dyes **2** and **3** ( $2 \times 10^{-5}$  mol/l) in various solvents were prepared and irradiated for an appropriate time using a Philips TL20W/05 UVA bulb (emission maximum 365 nm). The UV light source was set up horizontally, below which samples were mounted at a distance of 4.5 cm. For spectroscopic measurements, 10 ml of each solution was filled into a silica cell prior to transferring the samples to a Lambda 2 UV/visible Spectrophotometer, and absorption spectra were recorded from 400 – 700 nm.

### **9.3. Results and Discussion**

The synthesis routes to spirooxazine **1** and azospirooxazine dyes **2**, **3** and **4** are shown in Scheme 9.4.



**Scheme 9.4** Synthesis routes of spirooxazine **1** and azospirooxazine dyes **2**, **3**, and **4**

The ideal properties required from a chemical class of organic photochromic compounds for most traditional applications are as follows. [1]

- A rapid development of a strong colour on UV light exposure.
- A controllable rate of colour fading reaction to colourless state.
- A wide range of colours available to cover parts of the visible spectrum.
- Long life to insure constant response to UV exposure through many coloration cycles.
- Colourless or minimum colour of the rest state.

The absorption spectra of spirooxazine **1** and azospirooxazine dyes **2** and **3** were obtained for  $2 \times 10^{-5}$  mol/l solutions in various solvents at ambient temperature. Solvents were selected to cover a range of polarities, as shown in Table 9.3, to

investigate a possible correlation between solvent polarity and the equilibrium between ring-closed and ring-opened forms, as might be expected from the investigation of the absorption spectra of commercial photochromic dyes as described in section 7.3.

**Table 9.3** Polarity indices of solvents used [219]

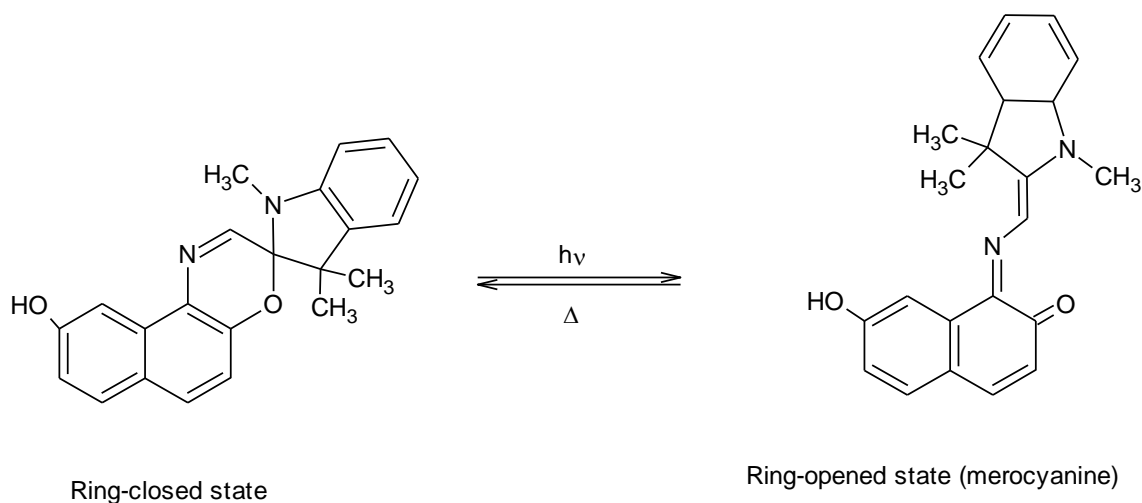
| <i>Solvent</i>  | <i>Polarity index</i> |
|-----------------|-----------------------|
| Toluene         | 2.4                   |
| Dichloromethane | 3.1                   |
| Acetone         | 5.1                   |
| Methanol        | 5.1                   |
| Ethanol         | 5.2                   |

### 9.3.1. Investigations of Photochromism of spirooxazine 1 in different solvents

UV/visible spectra of solutions of spirooxazine **1** ( $2 \times 10^{-5}$  mol/l) in various solvents were obtained by exposing the solutions to UV light for increasing exposure times.

#### a) General mechanism of photochromism of spirooxazine 1

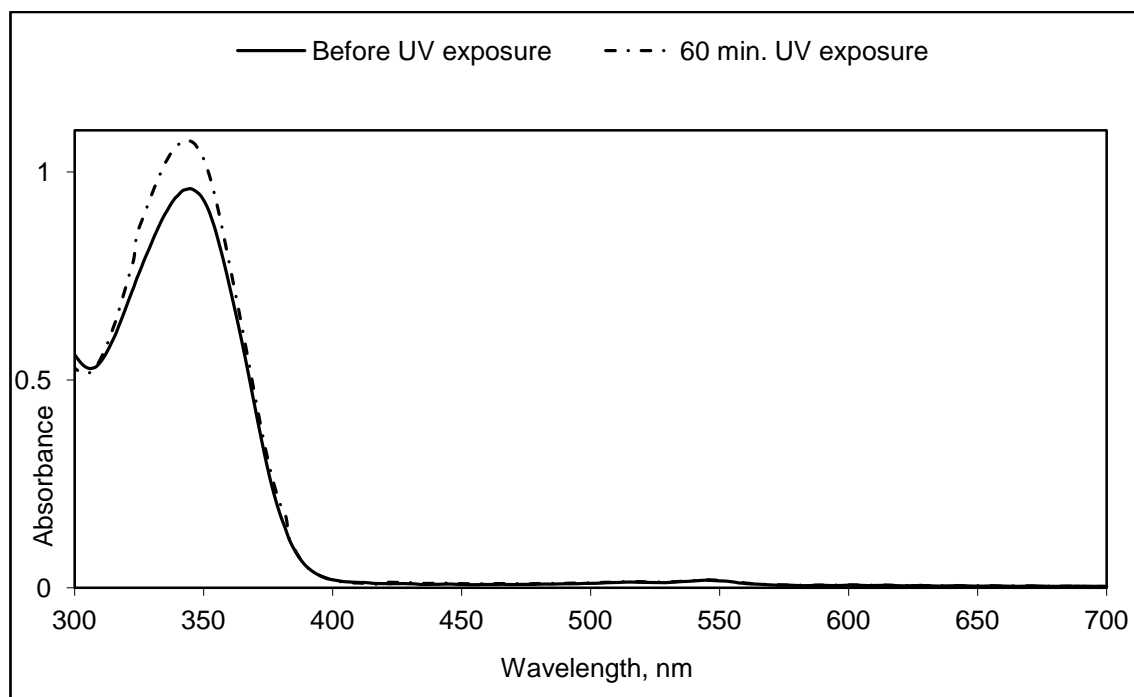
The general mechanism proposed for the anticipated reversible photochromism of spirooxazine **1** is given in Scheme 9.5, involving conversion of the spirooxazine to its ring-opened merocyanine structure under the effect of UV exposure. Cleavage of the C-O bond leads to the formation of the ring-opened merocyanine which absorbs at a longer wavelength compared to the ring-closed form due to the more coplanar structure and extended  $\pi$ -conjugation.



**Scheme 9.5** Photochromism of spirooxazine **1**

*b) Investigation of photochromism of spirooxazine 1 in ethanol*

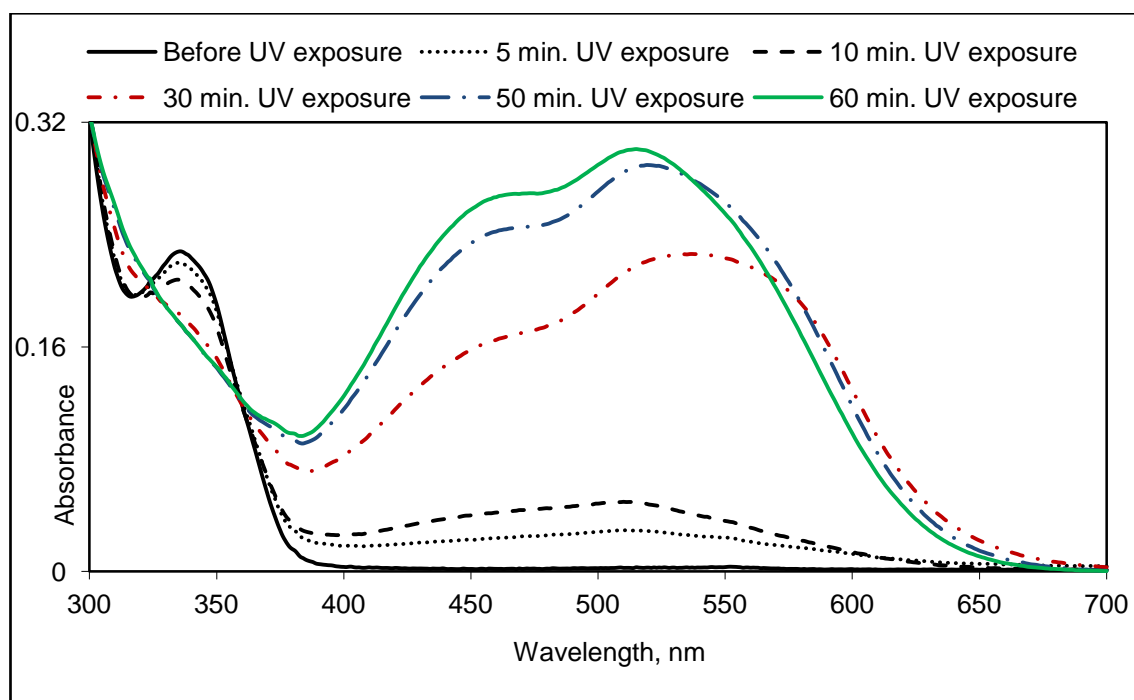
Continuous UV exposure of the colourless ethanolic solution of spirooxazine **1** did not lead to visual change of its colour. This observation was confirmed by comparing absorption spectra of the solution before and after UV exposure which showed no absorption in the visible region in both cases, as shown in Figure 9.3. Thus, spirooxazine **1** is not photochromic in an ethanolic solution under the conditions employed.



**Figure 9.3** Absorption spectra of spirooxazine **1** in ethanol before and after UV exposure

*c) Investigation of photochromism of spirooxazine 1 in dichloromethane*

A solution of spirooxazine **1** in dichloromethane was colourless ( $\lambda_{\text{max}} = 343 \text{ nm}$ ), with no absorption bands in the visible region, as shown in Figure 9.4. Continuous UV exposure of the solution resulted in a gradual conversion from colourless to purple, and the spectrum after 5 minutes of UV exposure showed that a broad visible absorption band ( $\lambda_{\text{max}} = 517 \text{ nm}$ ) was starting to develop which indicates the initiation of conversion from the colourless ring-closed form to the coloured ring-opened (merocyanine) form.

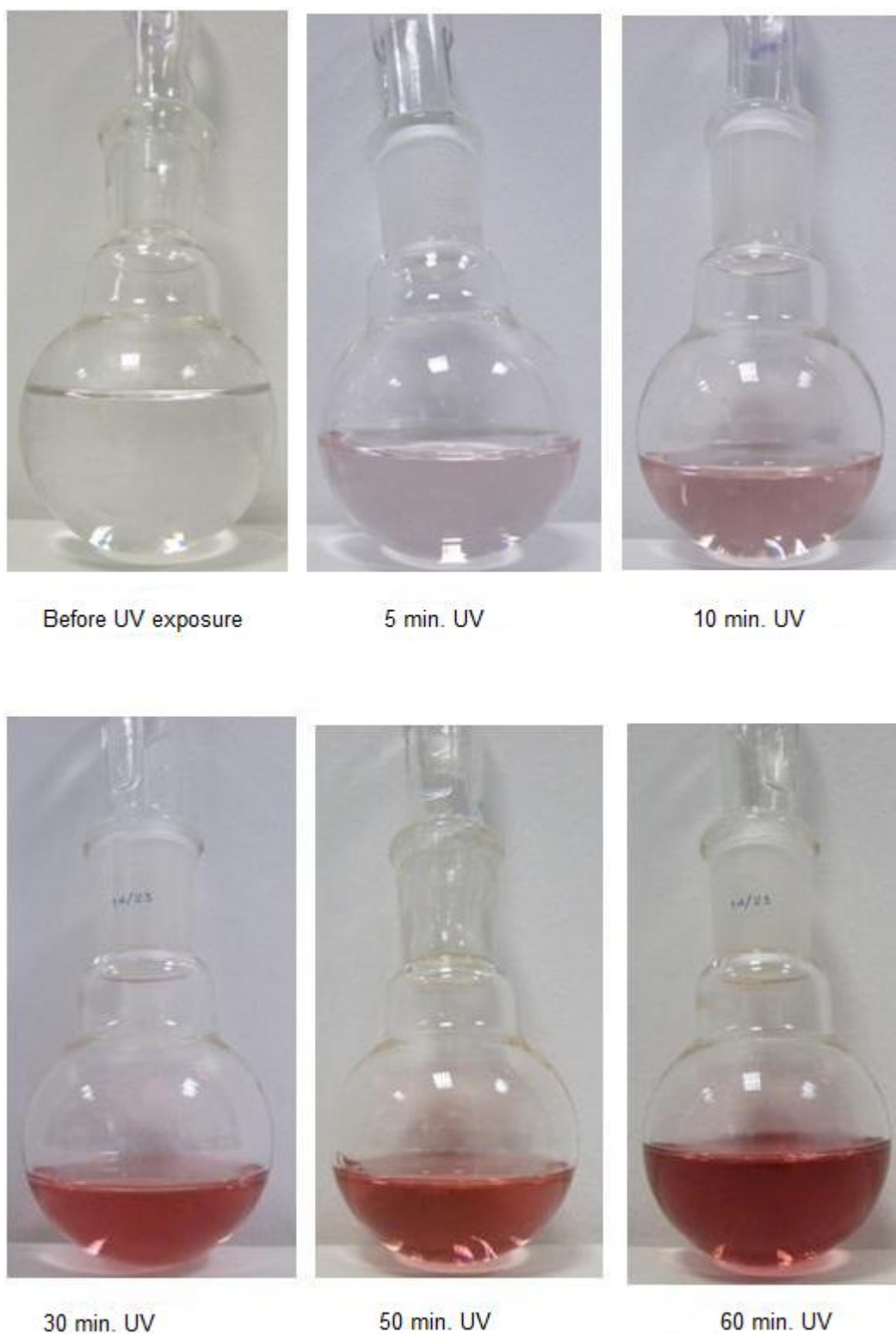


**Figure 9.4** Absorption spectra of solutions of spirooxazine **1** in dichloromethane upon UV light exposure for increasing periods of time up to 60 min.

Curves in Figure 9.4 apparently show isosbestic behaviour under UV exposure over 50 minutes. This behaviour is characterised by an isosbestic point at a wavelength of 360 nm which provides evidence that only two principal species are present in the solution during the early period of UV exposure. [232, 233] Isosbestic points represent particular locations in absorption spectra at which the species in solution absorb light with equal strength at a particular wavelength. [234, 235] Isosbestic points are generated as a result of a conversion of one absorbing species to another. If the spectra cross a single wavelength during the transformation, this is referred to as an isosbestic point. The net absorption of the solution at that wavelength is not affected by the relative proportions of the species in solution. In the case of the solution of spirooxazine **1** in dichloromethane, the isosbestic point was generated at 360 nm by UV exposure which shifted the equilibria between the ring-opened and ring-closed forms without altering their intrinsic absorbance, as shown in Figure 9.4. Absorption spectra of the spirooxazine solution exposed to UV light for 60 minutes showed a departure from the isosbestic behaviour, as shown in Figure 9.4, due possibly to formation of new species as a result of photodegradation of spirooxazine **1** under prolonged exposure to UV light. The new species may result from irreversible photodegradation of the spirooxazine **1**, for example by the oxidation and free radical mechanisms which have been described in



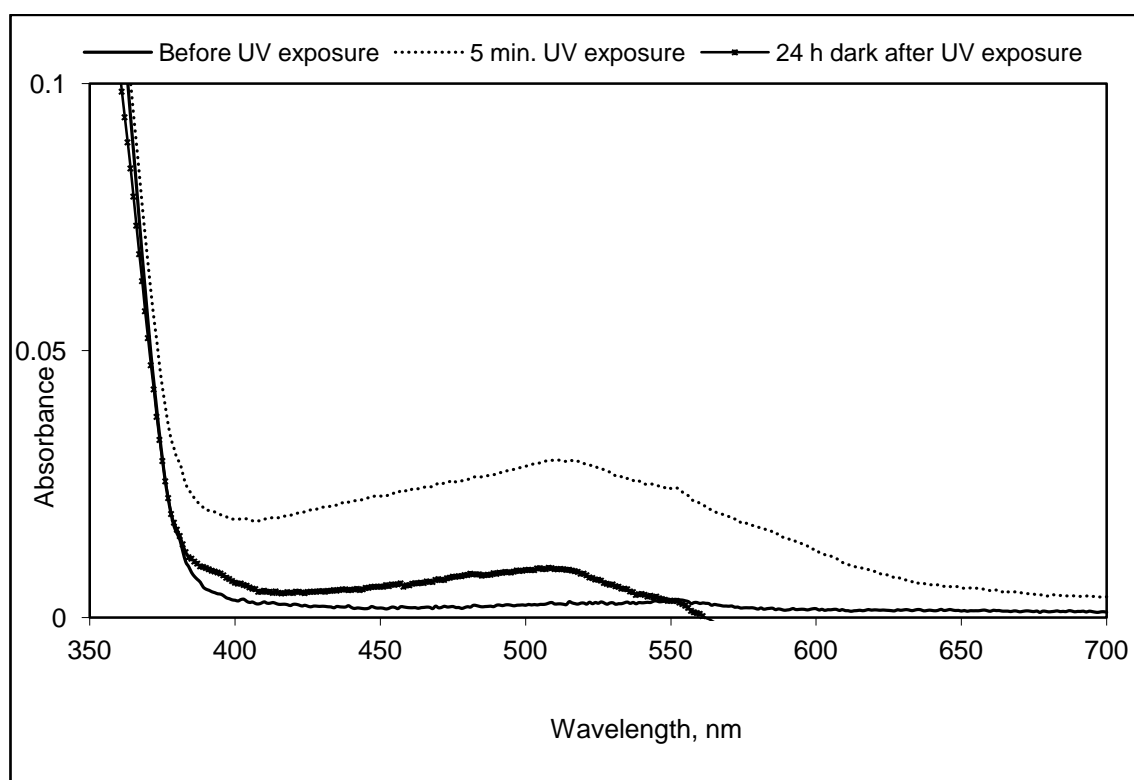
section 2.5. [236, 237] In fact, there is evidence from changes in other regions of the spectra shown in Figure 9.4 that the decomposition may be occurring sooner than this. In an attempt to provide visual evidence for the colour development and the possible photodegradation of spirooxazine **1** in dichloromethane during UV exposure, photographs of the solution were taken after different periods of UV exposure, as shown in Figure 9.5.



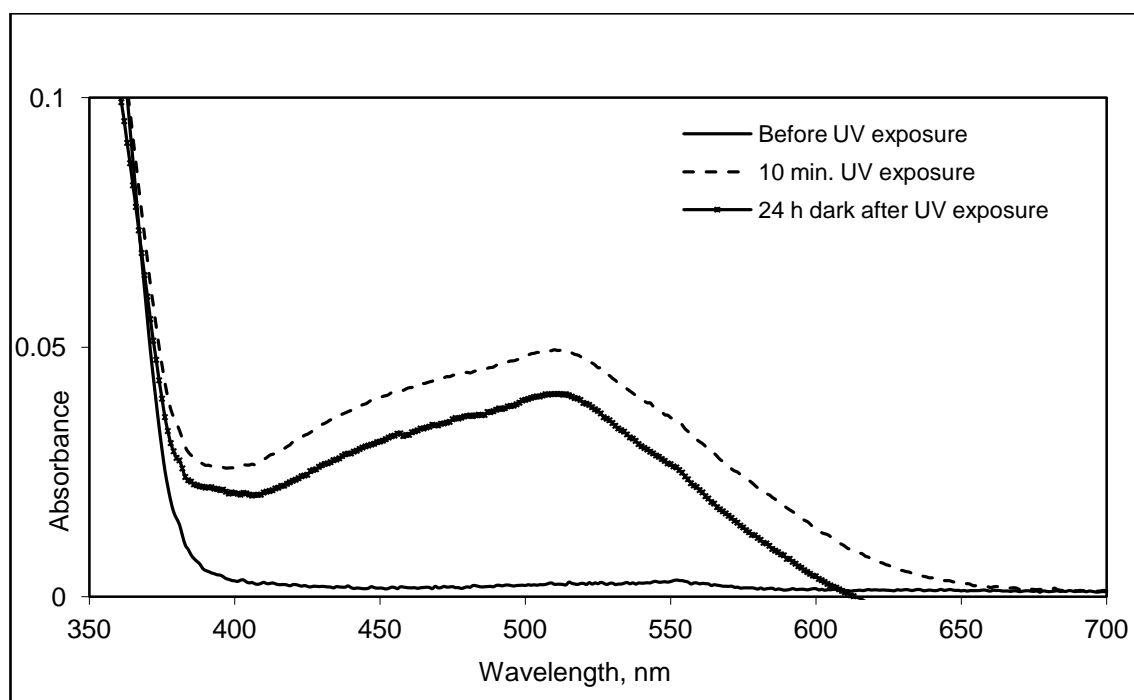
**Figure 9.5** Colour development on UV exposure of a solution of spirooxazine **1** in dichloromethane

Figure 9.5 shows that the solution was colourless before UV exposure, and a purple colour started to develop after 5 minutes of UV exposure with increasing intensity over a UV exposure period of 50 minutes. Exposure for longer than 50 minutes brought

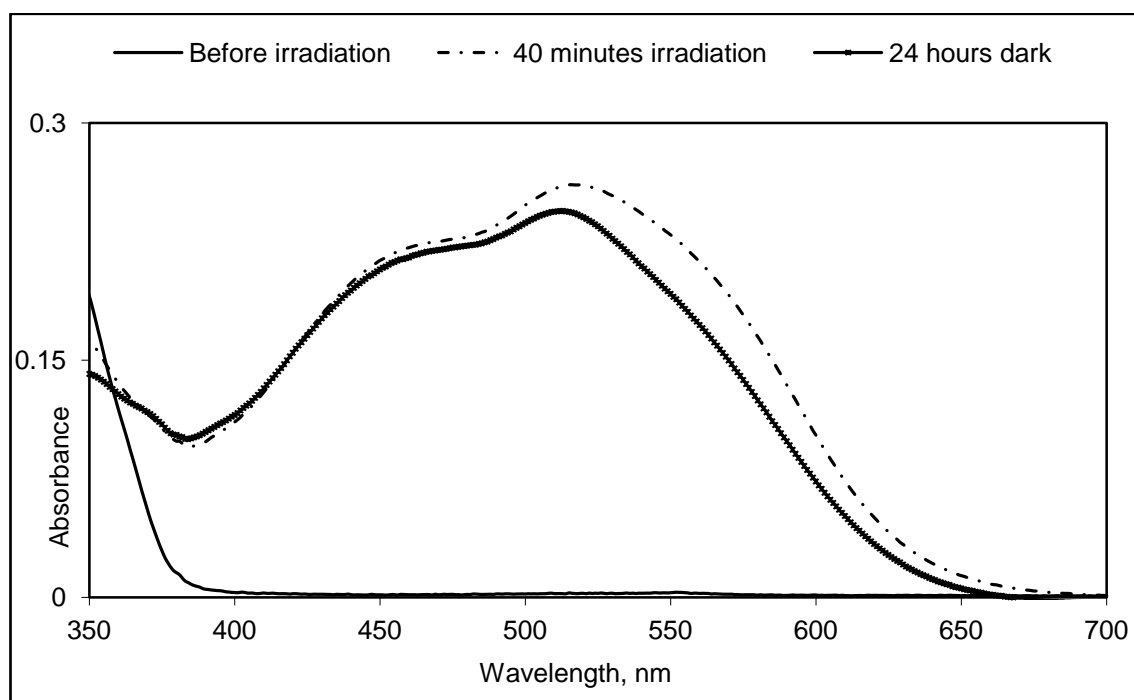
about a significant increase in the colour intensity, which may be a result of photodegradation for example by a free radical mechanism. It has been reported that free radicals can react with merocyanines to give deeply coloured adducts that are devoid of photochromic activity and can no longer revert to the ring-closed colourless form of the spirooxazine. [237] It has been reported that these adducts absorb in the 510-560 nm region, which would be consistent with changes in this region in the spectra of solutions of spirooxazine **1** after prolonged UV exposure, as shown in Figure 9.4. Further investigation of photochromic behaviour involved obtaining the UV/visible spectra of the exposed solutions after fading in the dark. As the exposed solutions did not show fast visible change to the colourless state, they were left for 24 hours in the dark at room temperature, and their absorption spectra were then measured.



**Figure 9.6** Absorption spectra of spirooxazine **1** in dichloromethane after 5 min. of UV exposure and fading for 24 hours



**Figure 9.7** Absorption spectra of spirooxazine **1** in dichloromethane after 10 min. of UV exposure and fading for 24 hours



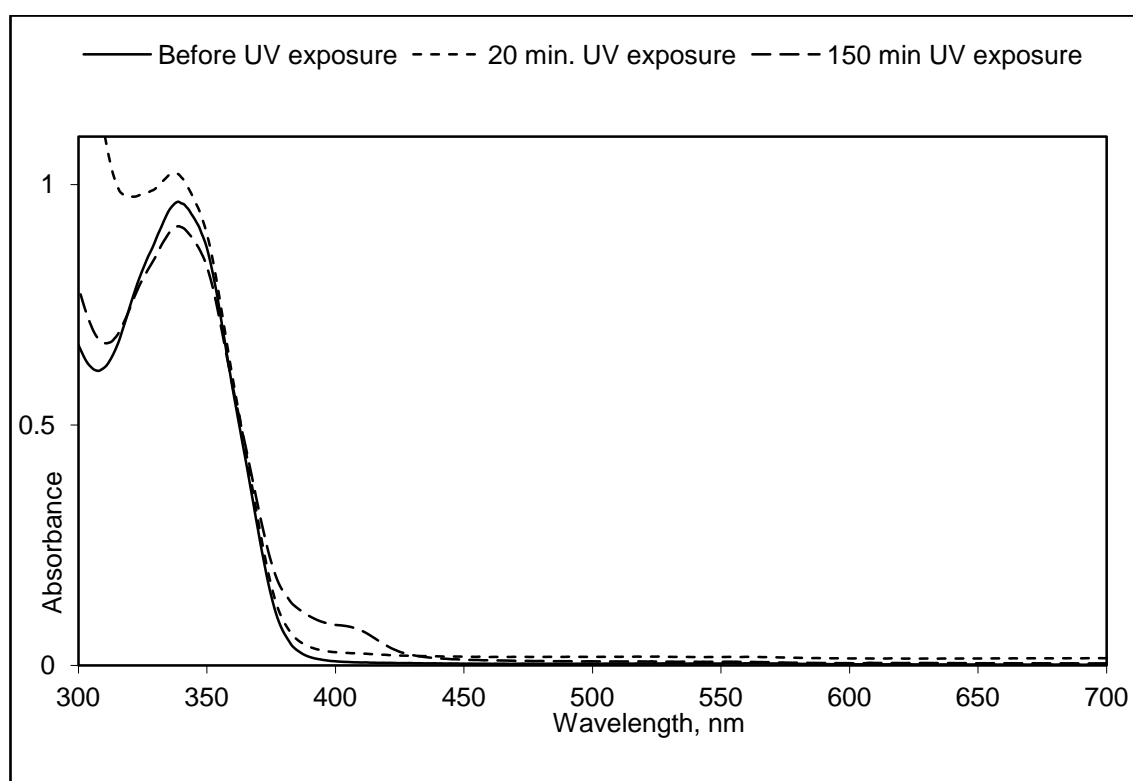
**Figure 9.8** Absorption spectra of spirooxazine **1** in dichloromethane after 40 min. of UV exposure and fading for 24 hours

Figures 9.6 – 9.8 show that the exposed solutions returned only partially towards their initial colourless state. The change was not pronounced with a short exposure time of 5 minutes. The incomplete coloured-to-colourless reaction may be a result of the

formation of photodegradation products, which do not possess photochromic properties, and therefore do not undergo reverse reaction to the colourless state. This inference is supported by the significantly lower relative reversibility shown by the sample exposed to UV light for 40 minutes compared to that shown by the sample exposed for 5 minutes which may be a result of the higher proportion of the non photochromic products in the former sample comparing to the latter, as shown by comparing Figures 9.6 and 9.8.

*d) Investigation of photochromism of spirooxazine 1 in toluene*

The spirooxazine **1** solution in toluene was colourless before UV exposure showing no absorption bands in the visible region, as shown in Figure 9.9. Continuous UV exposure did not lead to a significant colour change; however a light yellow colour appeared after UV exposure for a relatively long period of 150 minutes. The UV/visible spectra of the dye solution after UV exposure showed a small absorption band in the visible region at a wavelength of 400 nm which accounts for the light yellow colour after UV exposure, as shown in Figure 9.9.

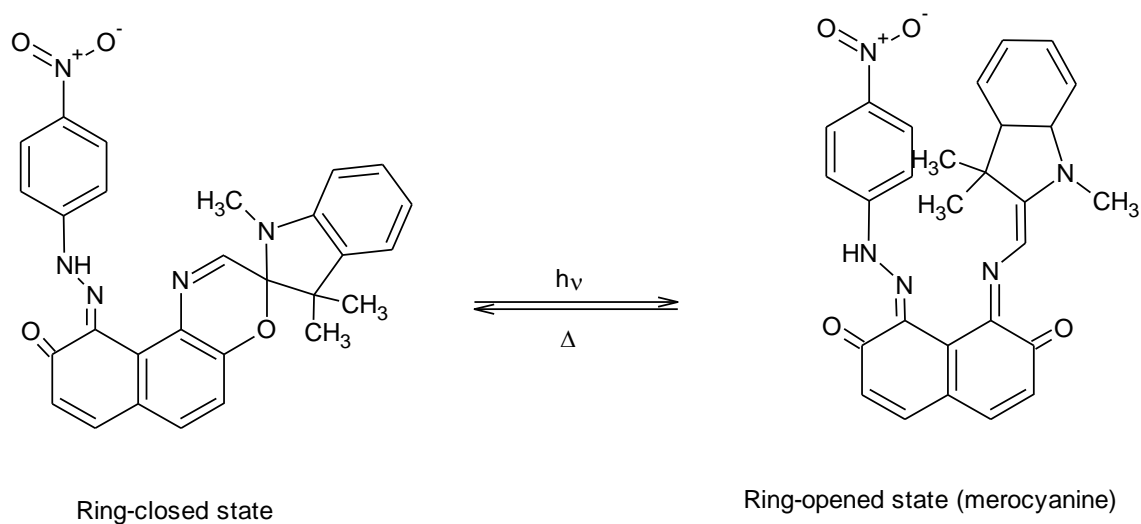


**Figure 9.9** Absorption spectra of spirooxazine **1** in toluene before and after UV exposure

### 9.3.2. Investigation of the photochromism of azospirooxazine dye 2

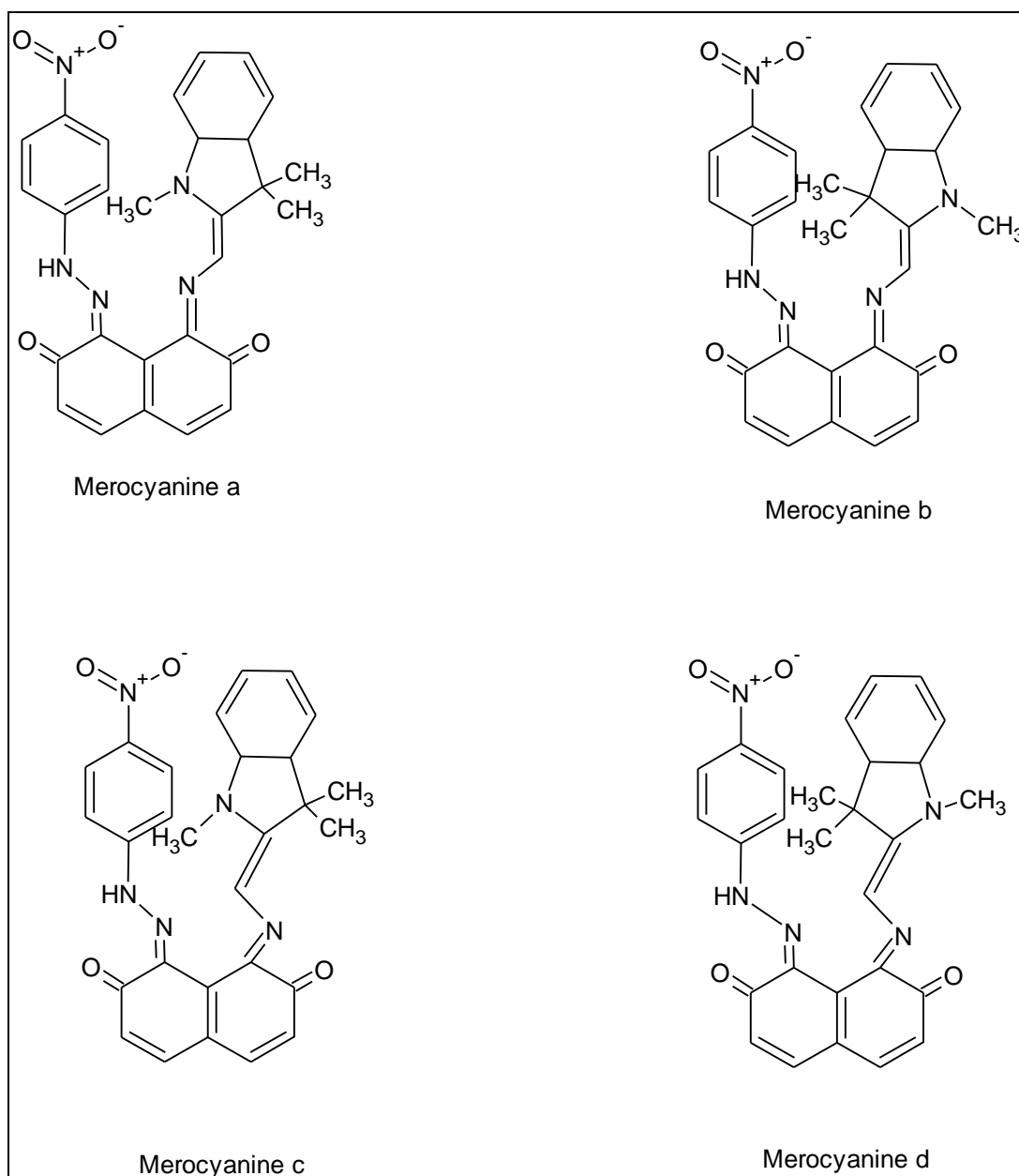
#### a) Mechanism of photochromism of azospirooxazine dye 2

A probable mechanism that might be expected for the photochromism of azospirooxazine dye **2** is given in Scheme 9.6.



**Scheme 9.6** Photochromism of azospirooxazine dye **2**

Scheme 9.6 shows only one of several possible isomers of the merocyanine forms. The ring-opening of spirooxazines is believed initially to proceed through metastable cisoid isomers which subsequently rearrange to one or more of the more stable transoid isomers, such as that illustrated in Scheme 9.6. The four possible transoid isomers of the merocyanine form of azospirooxazine dye **2** are given in Figure 9.10.



**Figure 9.10** Transoid isomers of the ring-opened form of azospirooxazine dye **2**

*b) Molecular modeling of azospirooxazine dye 2*

Computer-aided molecular modeling may be applied to provide a prediction of features of the photochromic behaviour of spironaphthooxazine-based compounds. [27] According to a reported methodology [27], heats of formation, calculated using AM1, and MM2 geometry optimization for ring-closed and ring-opened forms of spironaphthooxazines have been used to assess the ability of a spirooxazine to show photochromic behaviour. Thus, molecular geometries of spirooxazines and their transoid isomers of their merocyanines were calculated using standard augmented MM2 within the CaChe software to optimize molecular geometry by providing a structure that

corresponds to a minimum steric energy. A reasonable assumption that can be made from the comparison of steric energy values is that the lower the value, the more stable is the merocyanine isomer. [231, 238] Heat of formation values calculated from quantum mechanics (AM1) were employed to predict the potential photochromic behaviour of the molecule by a comparison of heat of formation values of the ring-closed form with those of the merocyanine forms. If the heat of formation of the ring closed form is lower than heats of formation of all merocyanine forms then the compound is predicted to have the potential to show photochromism.

Molecular modeling of azospirooxazine dye **2** showed that the calculated steric energies and heat of formation of the ring-closed form were lower than those of the four ring-opened isomers a-d, as shown in Table 9.4. On the basis of these results, azospirooxazine dye **2** was predicted to have the potential to show photochromic behaviour by converting to the higher energy merocyanines as a result of absorbing UV light, and to revert thermally to the more stable ring-closed form when the light source is removed. [27]

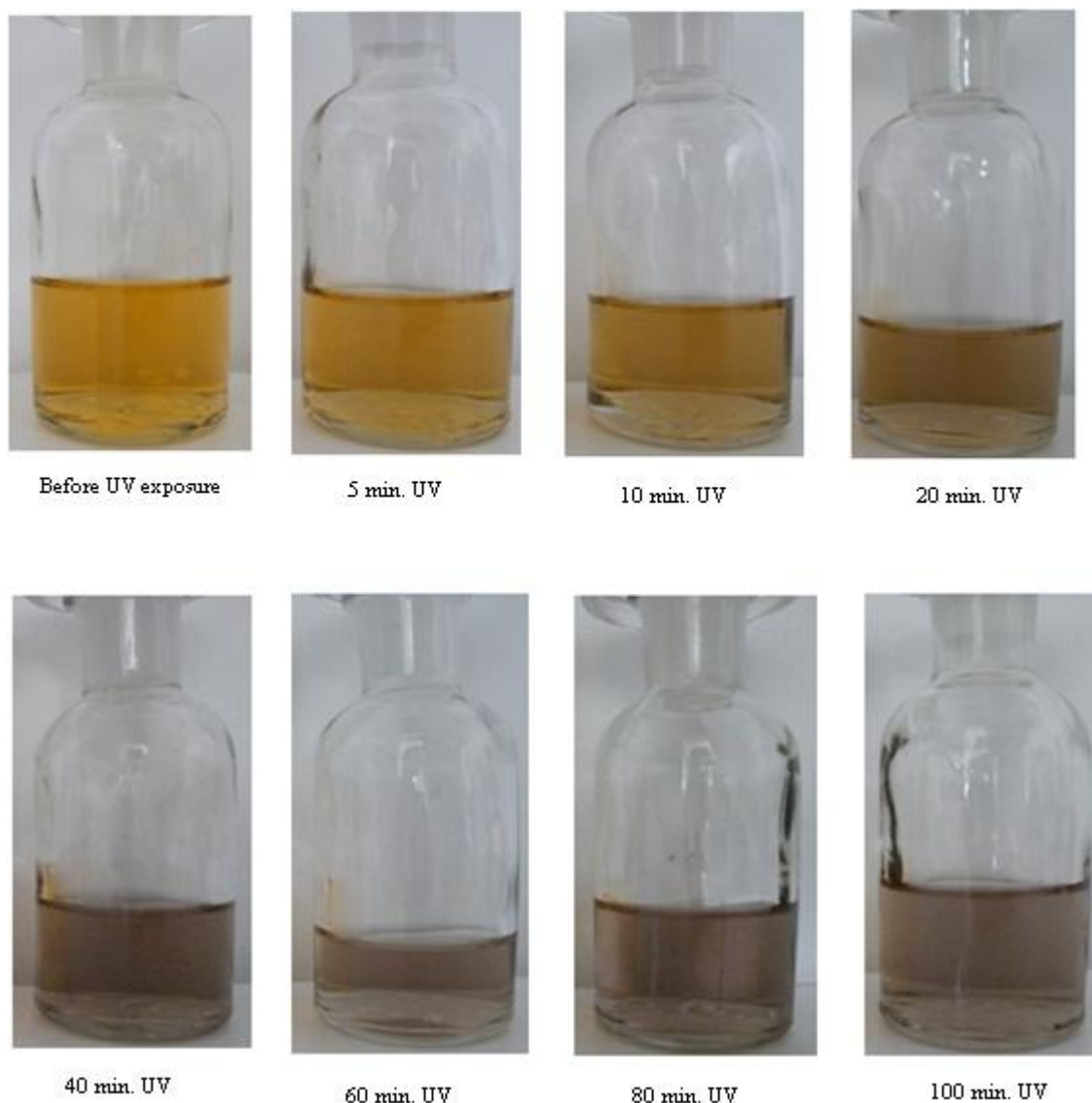
**Table 9.4** Calculated energy data for azospirooxazine dye **2** and isomers of the ring-opened forms

| <i>Azospirooxazine dye</i><br><b>2</b> | <i>Final energy (Kcal/mol)</i><br>(MM2) | <i>Heat of formation (Kcal/mol)</i><br>(AMI) |
|--|---|--|
| Ring-closed form                       | -1.47                                   | 126.89                                       |
| Merocyanine a                          | 16.46                                   | 135.8  |
| Merocyanine b                          | 24.99                                   | 139.43                                       |
| Merocyanine c                          | 24.70                                   | 141.87                                       |
| Merocyanine d                          | 30.19                                   | 139.07                                       |

*c) Photochromism of azospirooxazine dye 2 in ethanol*

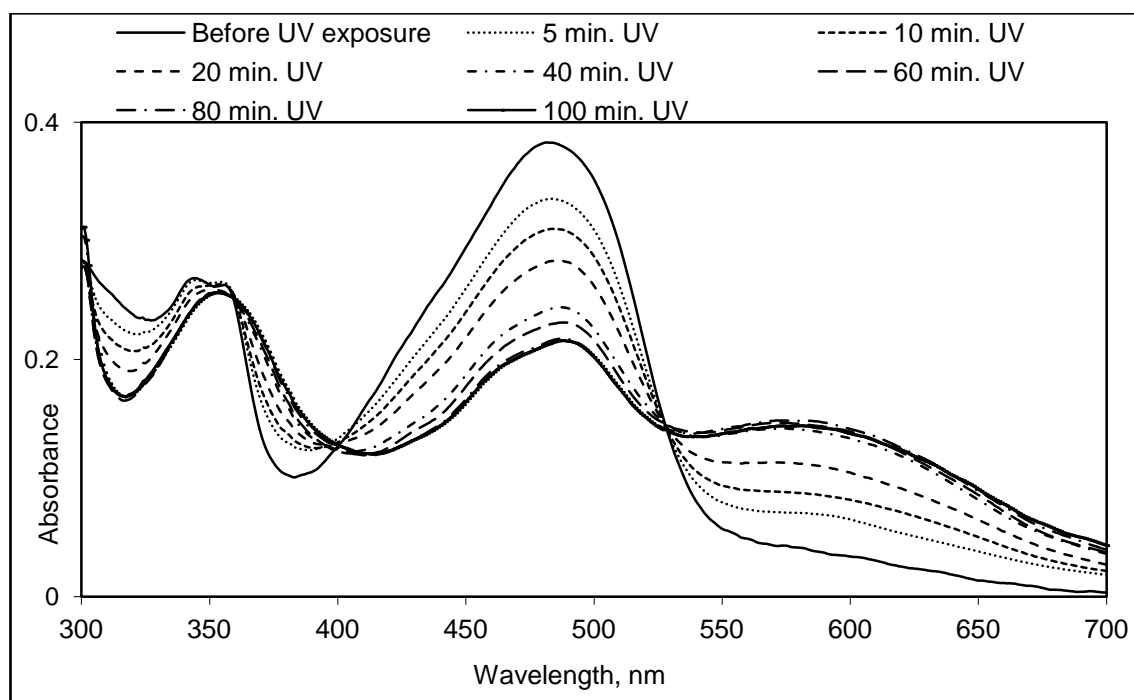
The solution of azospirooxazine dye **2** in ethanol was orange before UV exposure and gradually converted to grey after UV exposure for increasing periods of time, as shown in Figure 9.11.





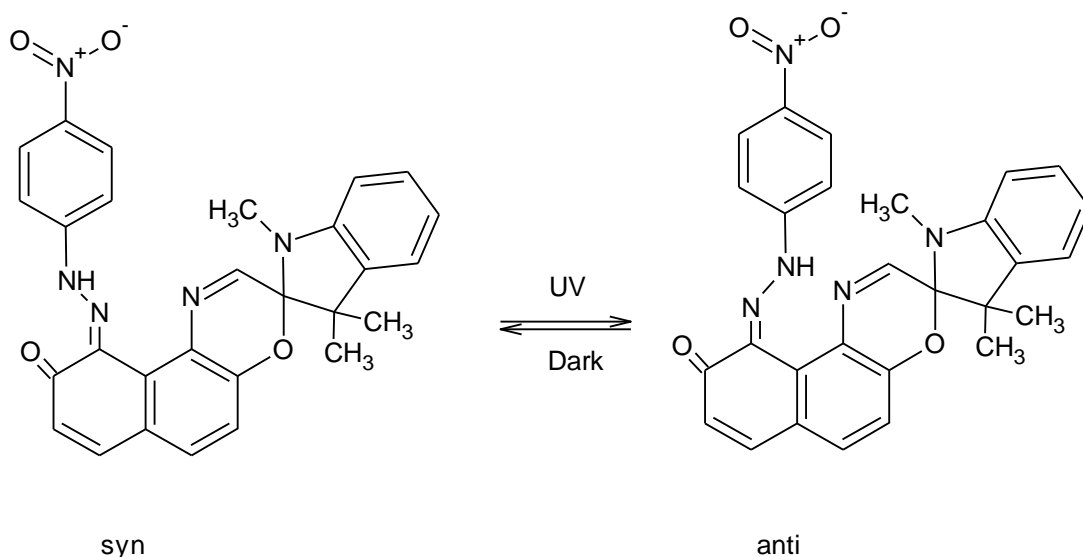
**Figure 9.11** Colour development on UV exposure of a solution of azospirooxazine dye **2** in ethanol

Figure 9.12 shows the UV/visible spectra of the dye solution before and after UV exposure for increasing periods of time. Before UV exposure the dye solution showed a single absorption band in the visible region at a wavelength of  $\lambda_{\text{max}} = 483 \text{ nm}$  which accounts for its orange colour. The spectrum of the photomerocyanine after 80 minutes of UV exposure showed two weaker absorption bands in the visible region,  $\lambda_{\text{max}} = 487 \text{ nm}$  and a broad band,  $\lambda_{\text{max}} = 571 \text{ nm}$ , the resulting broad absorption accounting for the observed grey colour.



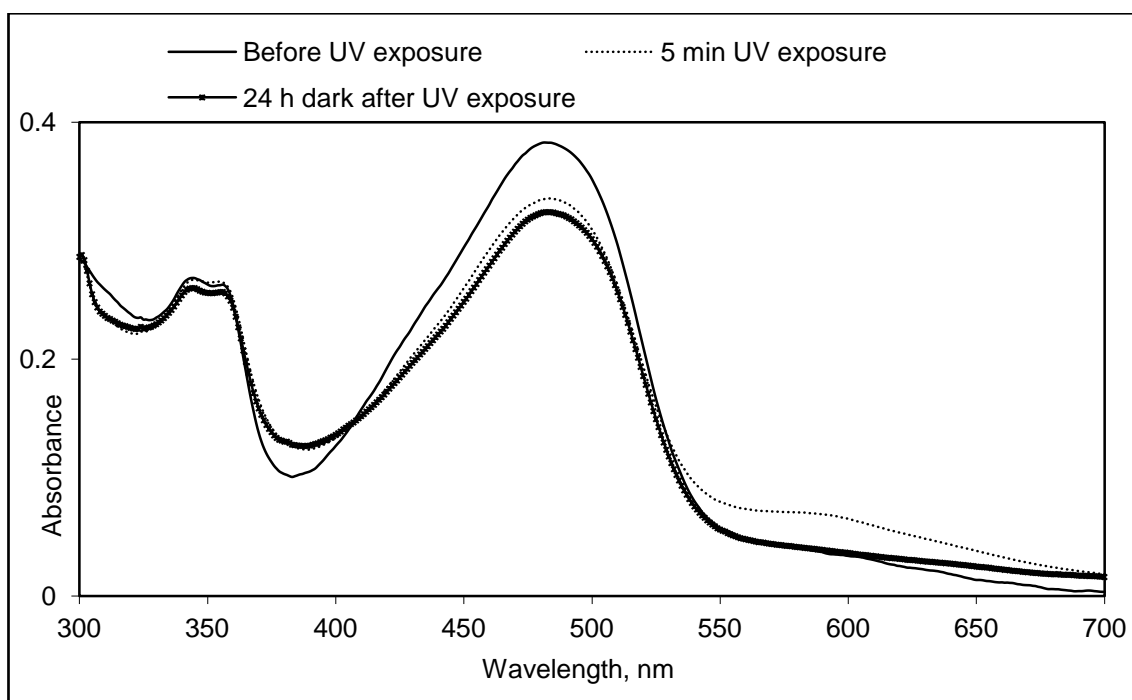
**Figure 9.12** Absorption spectra of solutions of azospirooxazine dye **2** in ethanol upon UV exposure for increasing periods of time up to 100 min.

Figure 9.12 shows the presence of isosbestic points at wavelengths 528, 392 and 353 nm which is consistent with photochromic behaviour of dye **2** in ethanol involving photochemical conversion of the ring-closed form to the merocyanine isomers. A further possibility that requires consideration is that there may be photo-induced isomerisation involving syn-anti isomers of the hydrazone group, as shown in Scheme 9.7, during UV exposure. Investigations of the syn-anti isomerisation of hydrazone groups have shown photochromic properties due to this phenomenon. [239, 240] The hydrazone group is principally responsible for the absorption band at  $\lambda_{\text{max}} = 485$  nm, The decrease in the absorbance at this wavelength after UV exposure is consistent with a photo-induced conversion from a strongly coloured syn-isomer, due to its planarity, to a less strongly coloured non-planar anti-isomer, in a similar way to the E- to Z-isomerization of an azo group, as discussed in section 2.2.6., (e).

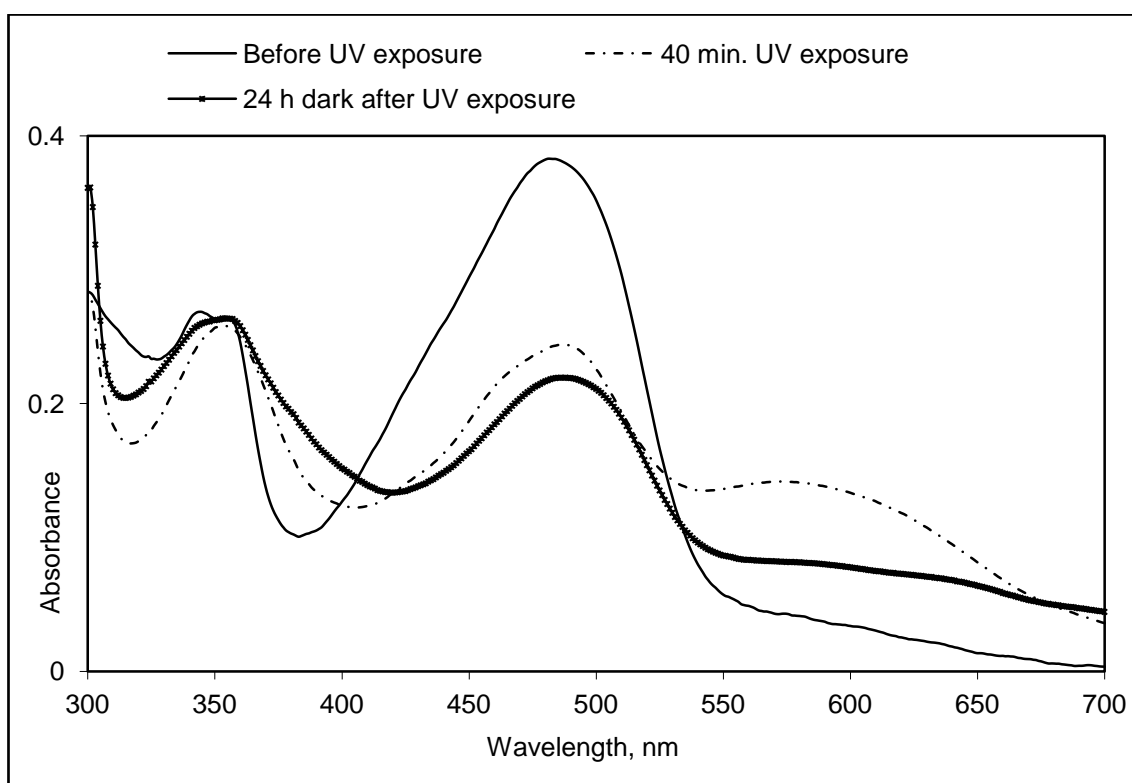


**Scheme 9.7** Potential syn-anti isomerisation involving the hydrazone group of azospirooxazine dye **2**

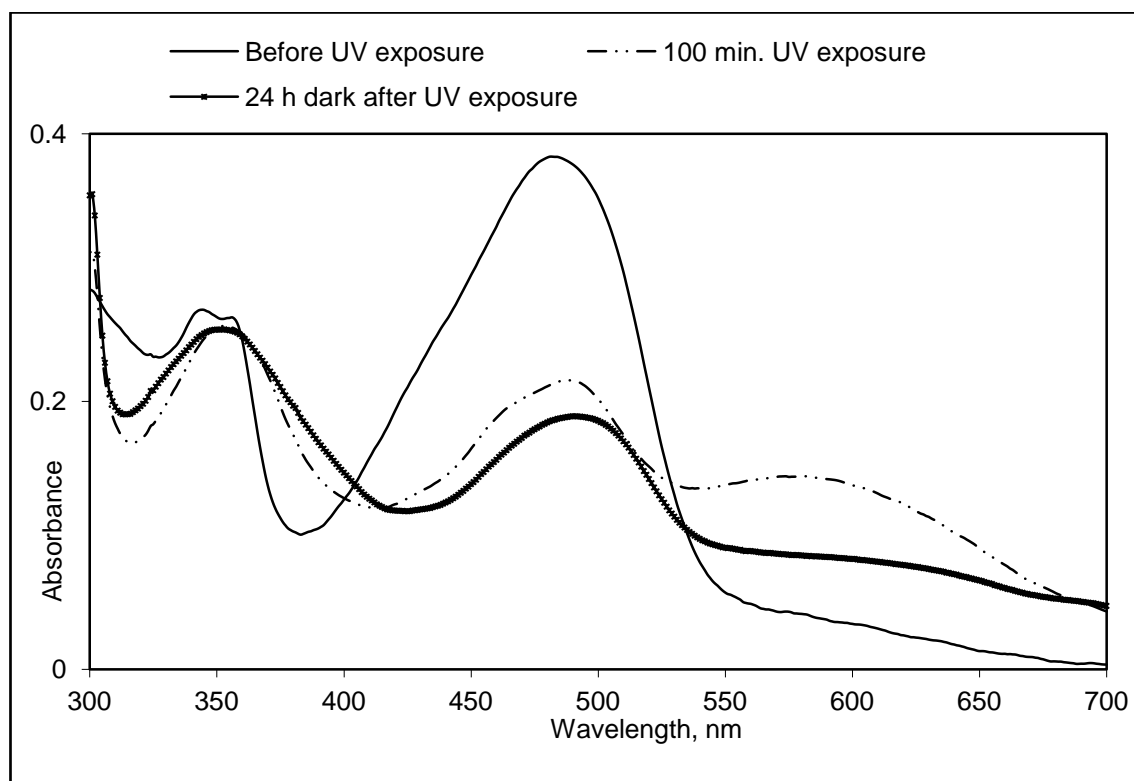
In addition, it was observed that the absorption spectrum after 100 minutes of exposure did not pass through the isobestic points, as shown in Figure 9.12. This observation indicates formation of new species in the solution, due possibly to photodegradation of the dye as a result of prolonged exposure to UV light. Another indication of photodegradation is the decrease in the absorbance after 100 minutes in the region between 527 and 700 nm, which contrasts with the trend of the spectra measured during exposure periods up to 80 minutes, as shown in Figure 9.12. This observation may be a result of different light absorption characteristics of photodegradation products compared with the ring-closed and merocyanine forms of the dye.



**Figure 9.13** Absorption spectra of azospirooxazine dye **2** in ethanol after 5 min. of UV exposure and fading for 24 hours

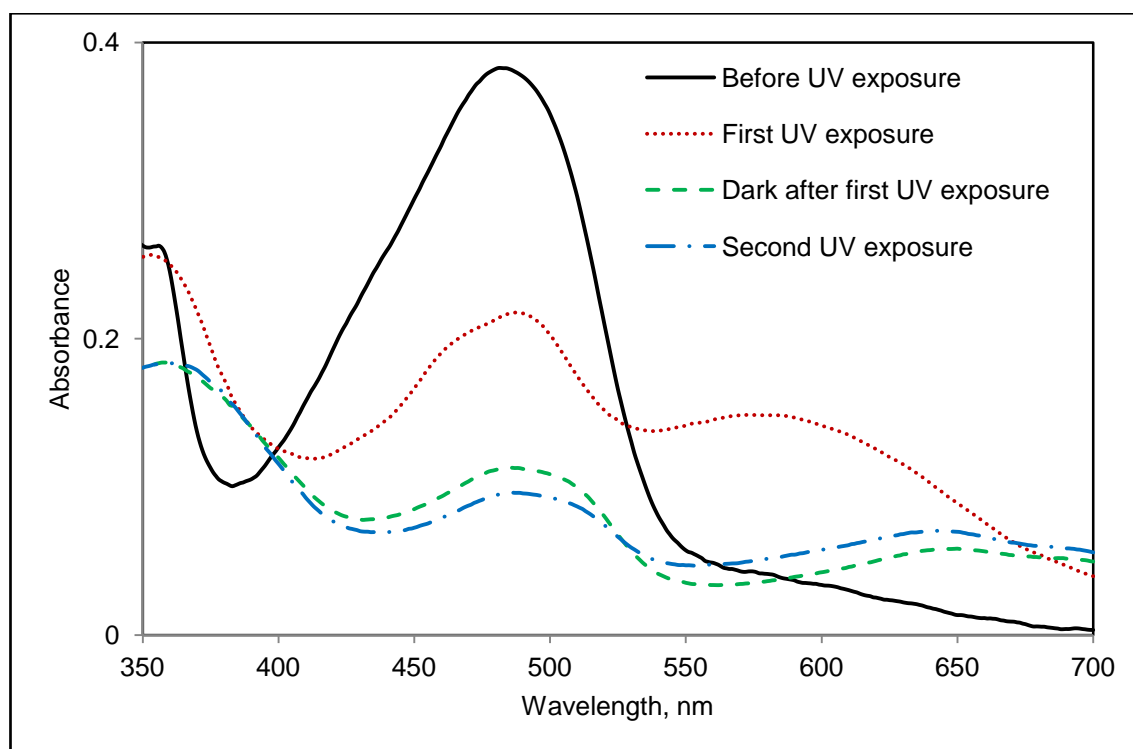


**Figure 9.14** Absorption spectra of azospirooxazine dye **2** in ethanol after 40 min. of UV exposure and fading for 24 hours



**Figure 9.15** Absorption spectra of azospirooxazine dye **2** in ethanol after 100 min. of UV exposure and fading for 24 hours

Removal of the UV light source after exposure resulted in a change which is consistent with a partial reverse reaction from the merocyanine to the ring-closed form on the basis of the spectra of exposed samples after 24 hours in the dark, as shown in Figures 9.13 – 9.15 which provide examples of a range of exposure periods. However, standing in the dark for 24 hours did not result in a visible reverse colour change of exposed samples from grey to orange. The incomplete reverse change may be a result of the presence of non-photochromic species which may be products of thermal or chemical degradation of the dye in solution during the fading time, and photodegradation products formed during UV exposure. This inference is supported by the observation that the relative reversibility of the sample exposed to UV for 100 minutes was lower than that of the sample exposed for 5 minutes, as shown by comparing Figure 9.13 with Figure 9.15. In agreement with this inference, longer exposure to UV light may have resulted in more pronounced formation of non-photochromic photodegradation products which do not undergo the reverse reaction.

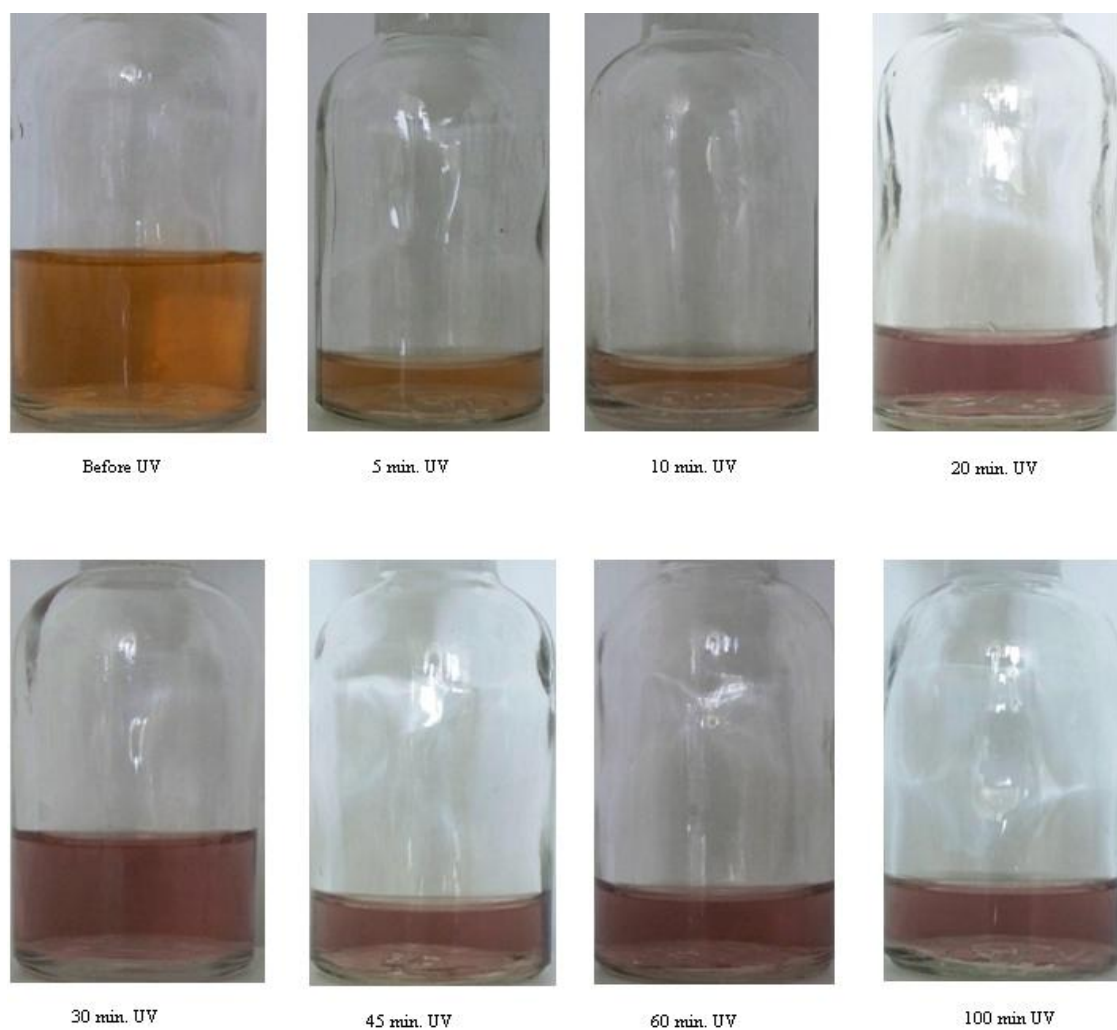


**Figure 9.16** UV/visible spectra of azospirooxazine dye **2** in ethanol after two 80 min. cycles of UV exposure with an intervening period of 24 hours of darkness

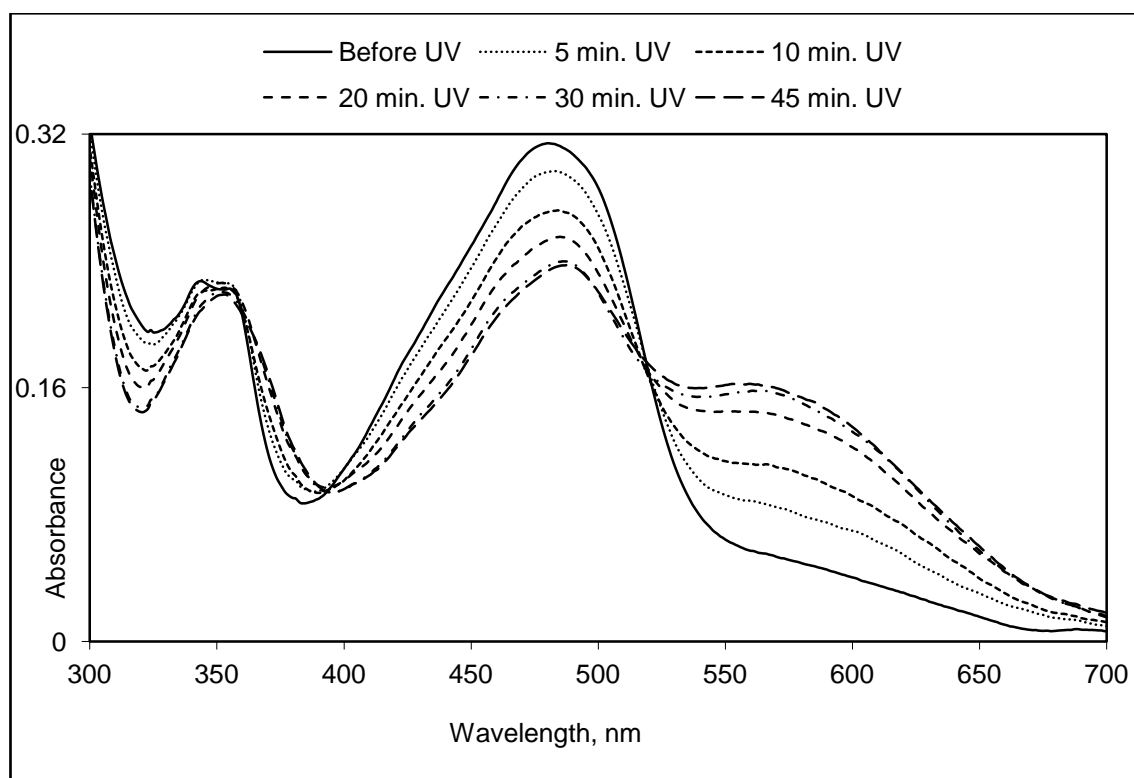
Further evidence of thermal or chemical degradation of the dye during the period in the dark was given by exposing a sample to a second cycle of UV exposure after first exposure and storage in the dark or 24 hours. Figure 9.16 shows that the second UV exposure did not reproduce an absorption spectrum similar to that measured after first UV exposure. Thus, the dye solution after 24 hours in darkness contains species which do not undergo a photocolouration reaction on UV exposure.

*d) Investigation of photochromism of azospirooxazine dye 2 in methanol*

UV exposure of a solution of azospirooxazine dye **2** in methanol resulted in a gradual photochromic colour change confirmed by photographs of the solutions taken after increasing periods of time, as shown in Figure 9.17, and the isosbestic points on the UV/visible spectra of the exposed solution, as shown in Figure 9.18.



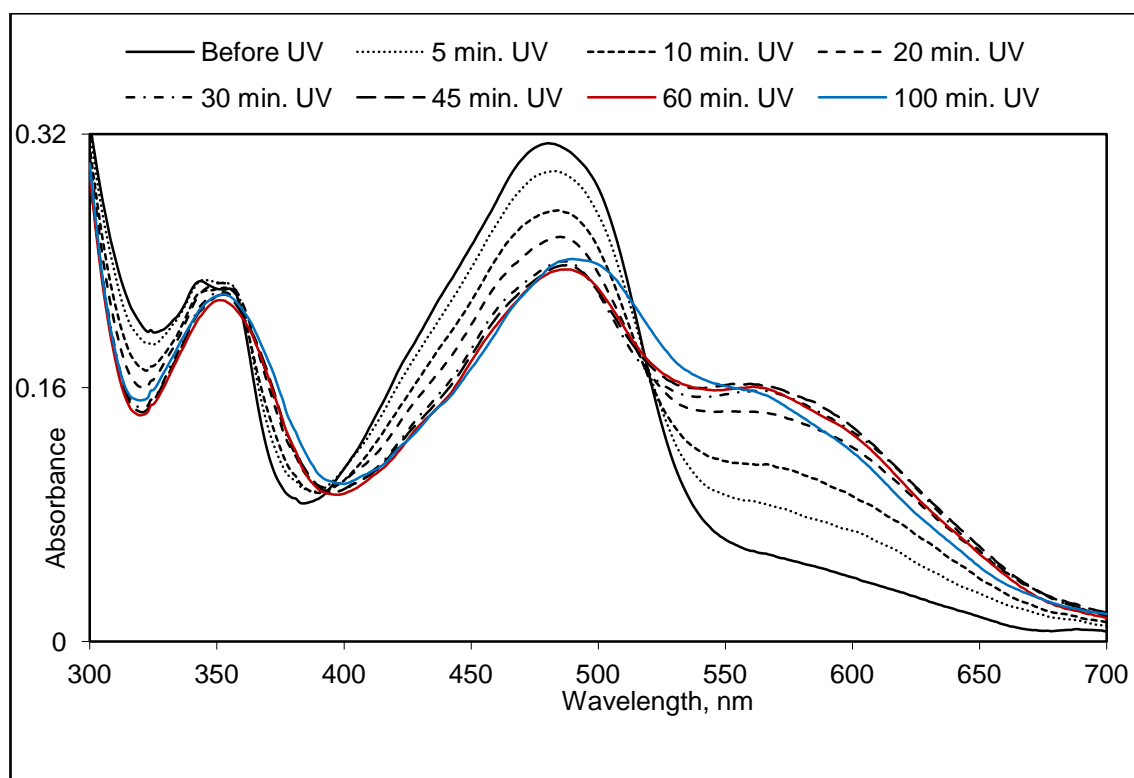
**Figure 9.17** Colour development on UV exposure of a solution of azospirooxazine dye **2** in methanol



**Figure 9.18** Absorption spectra of solutions of azospirooxazine dye **2** in methanol upon UV exposure with time up to 45 min.

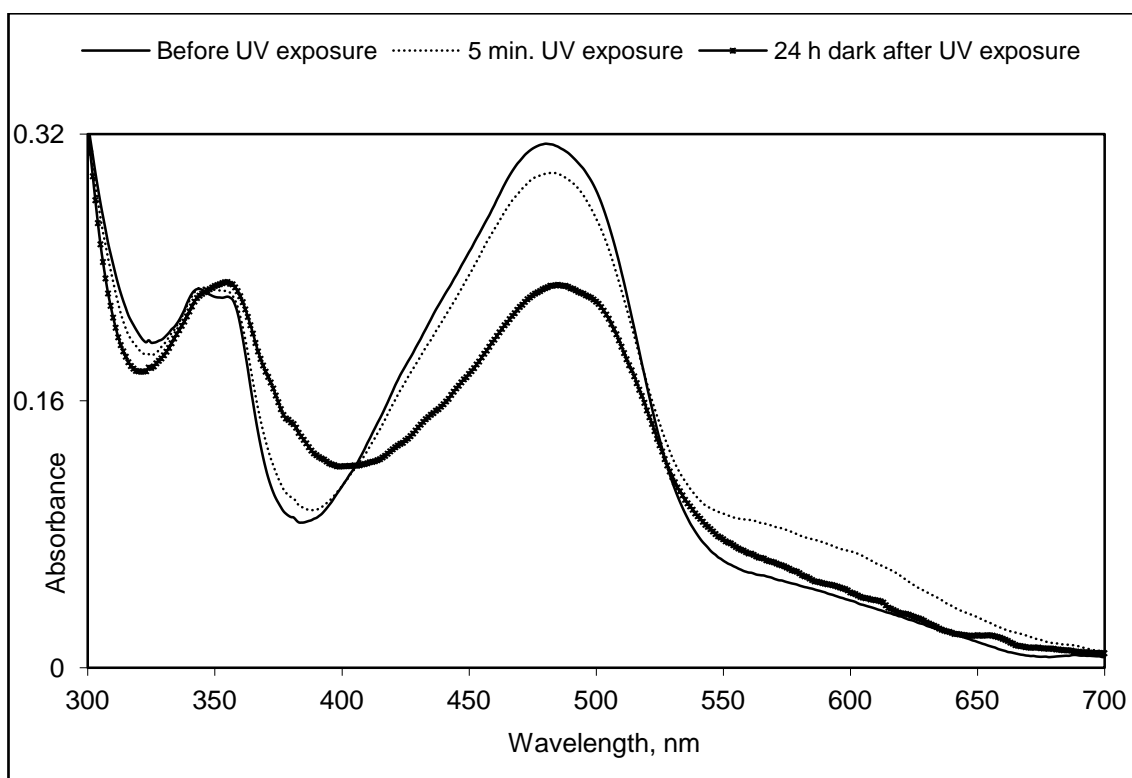
UV exposure for 60 minutes or longer resulted in departure from the isosbestic behaviour, as shown in Figure 9.19, which indicates formation of new species, as described in section 9.3.1., (b), possibly due to photodegradation of the dye with prolonged UV exposure.



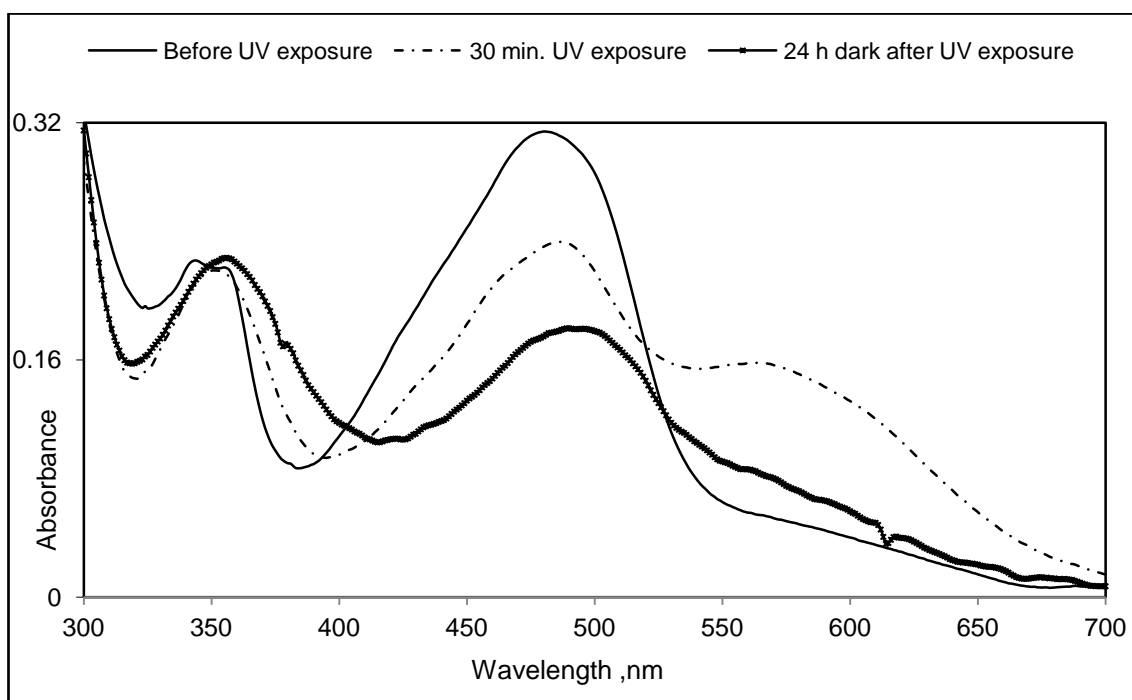


**Figure 9.19** Absorption spectra of solutions of azospirooxazine dye **2** in methanol upon UV exposure with time up to 100 min.

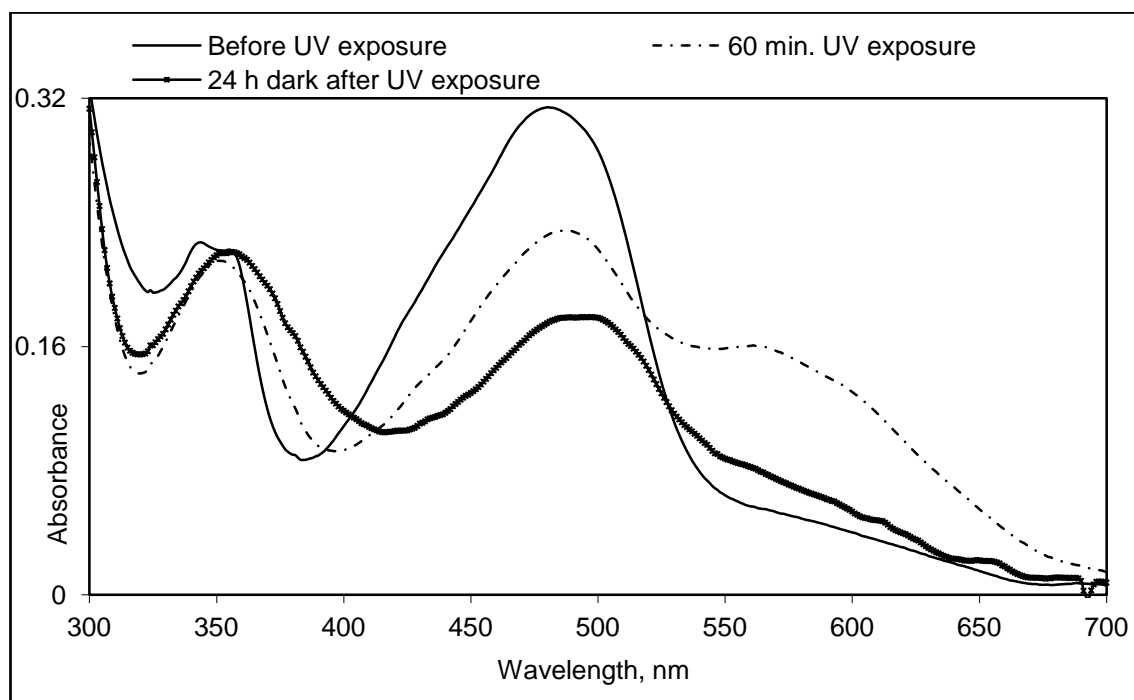
Colour reversal of the exposed samples was investigated by allowing them to stand in the dark for 24 hours followed by spectral measurements and visual inspection. Visual inspection of the samples did not show the reverse colour change. This observation was confirmed by the UV/visible spectra of the exposed samples after standing in the dark which show that they did not return to their original states before UV exposure, as shown in the examples given in Figures 9.20 – 9.22.



**Figure 9.20** Absorption spectra of azospirooxazine dye **2** in methanol after 5 min. of UV exposure and storing in the dark for 24 hours



**Figure 9.21** Absorption spectra of azospirooxazine dye **2** in methanol after 30 min. of UV exposure and storing in the dark for 24 hours

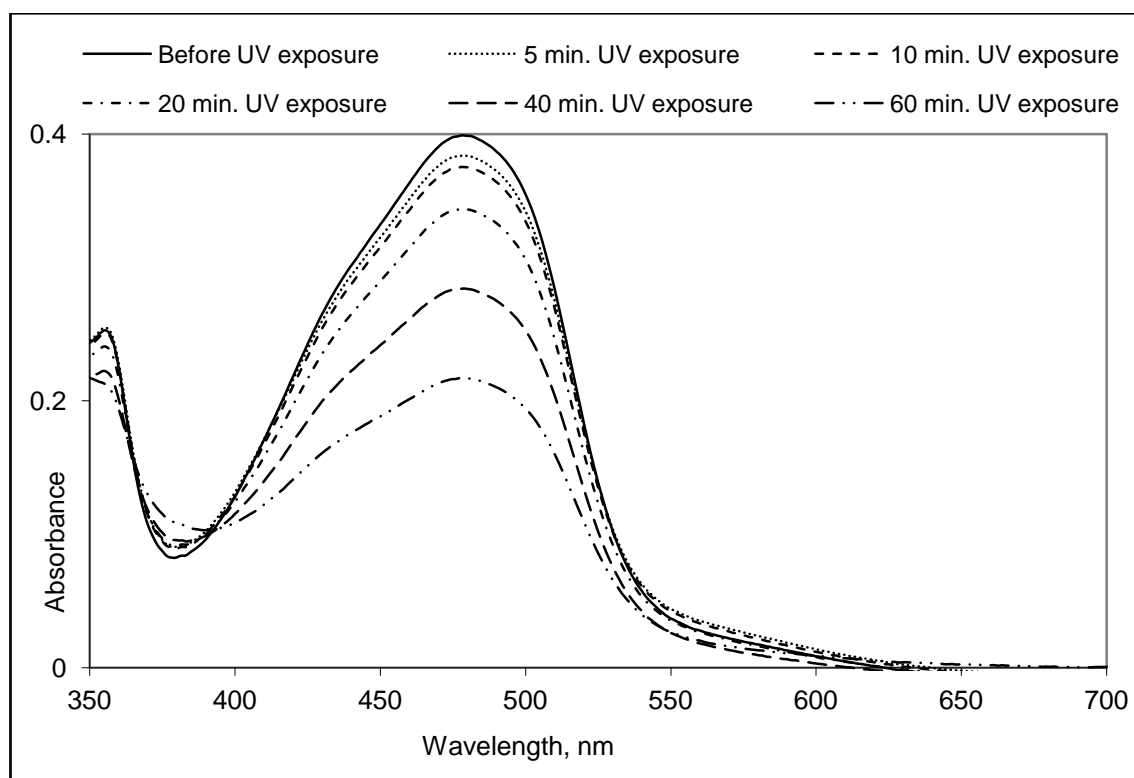


**Figure 9.22** Absorption spectra of azospirooxazine dye **2** in methanol after 60 min. of UV exposure and fading for 24 hours

Evidence for the incomplete reverse colour change shown in Figures 9.20 – 9.22, is that the absorption decreased in the long wavelength region 530-700 nm close to but not the same as the original absorption before irradiation. In the 350-530 nm region, the absorption spectra moved slightly bathochromically from the original absorption spectrum, possibly due to degradation of the dye in solution during the 24 hours in the dark.

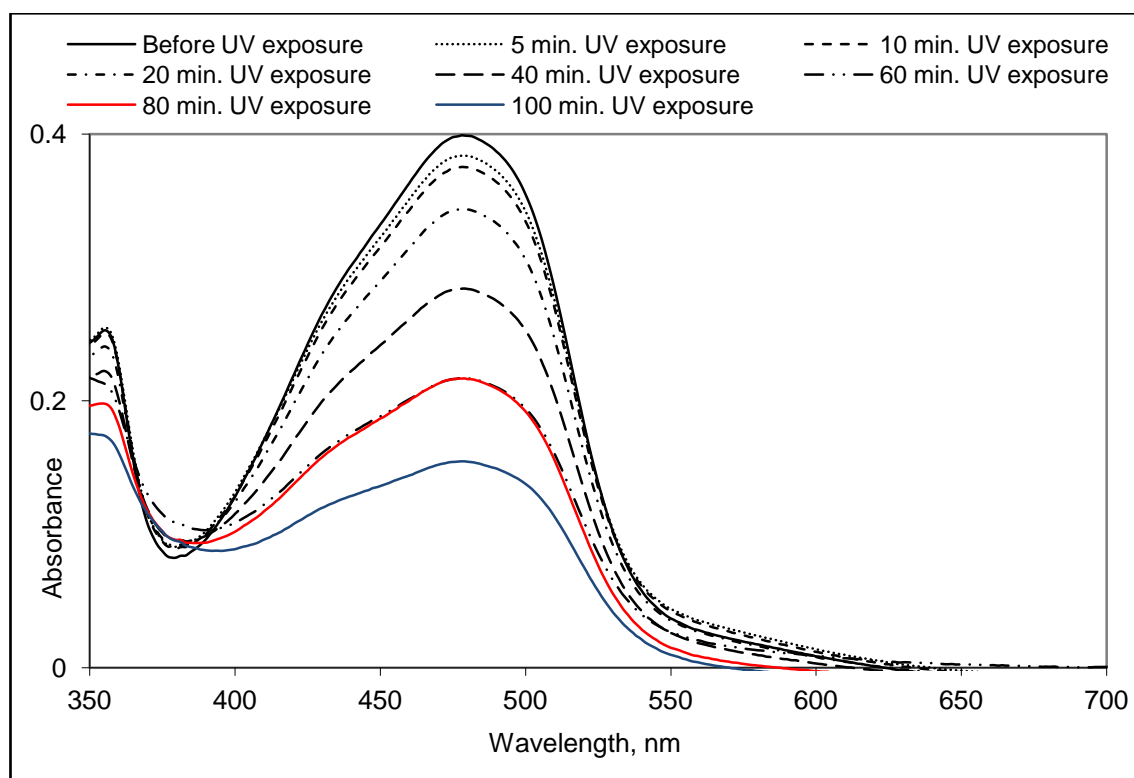
*e) Investigation of the photochromism of azospirooxazine dye 2 in acetone*

UV exposure of a solution of azospirooxazine dye **2** in acetone initiated a decrease in the intensity of its orange colour represented by a gradual decrease in the absorbance at  $\lambda_{\text{max}} = 478 \text{ nm.}$ , as shown in Figure 9.23. As this colour change is confined to a decrease in its intensity, it is proposed that this may be a result of photochromic isomerisation of the hydrazone group which is responsible for the orange colour of the dye solution. The decrease in the colour intensity may result from the conversion of the thermally stable syn- isomer to the less intensely coloured non-planar anti- isomer.



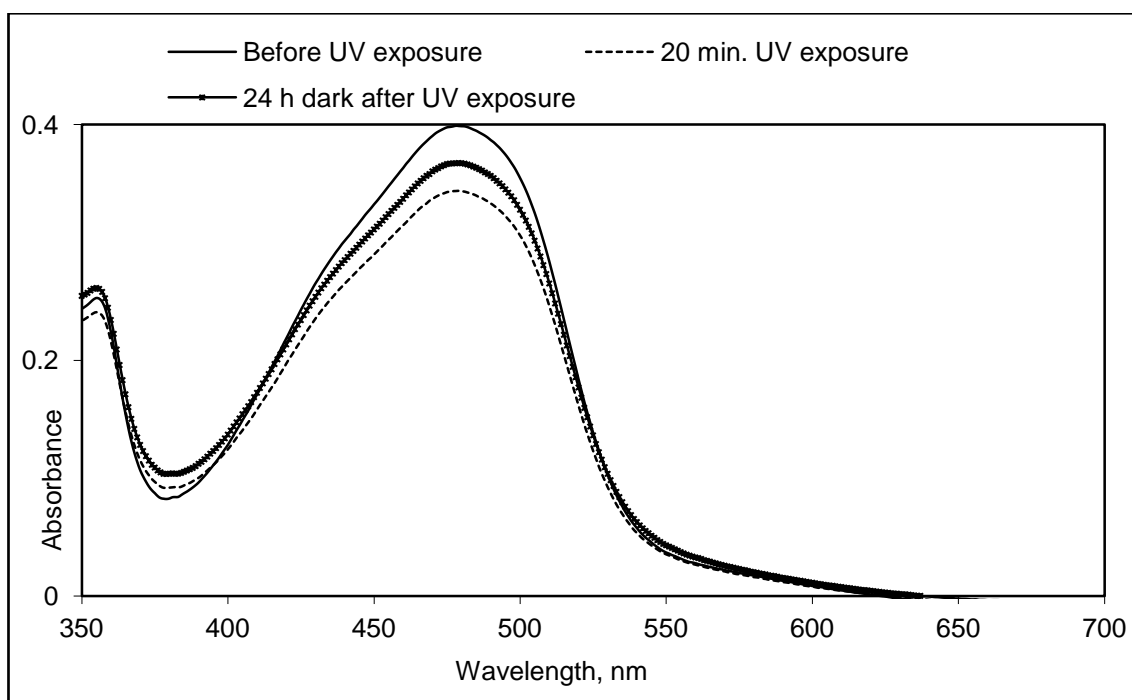
**Figure 9.23** Absorption spectra of solutions of azospirooxazine dye **2** in acetone upon UV exposure for increasing periods of time up to 60 min

UV exposure of the dye solution for 80 minutes and longer resulted in a gradual departure from the isosbestic behaviour with no significant change in absorbance, as shown in Figure 9.24. This indicates that the photochromic isomerisation no longer occurs at some point between 60 and 80 minutes of UV exposure, and that possible formation of new species due to photodegradation of the dye was initiated with prolonged UV exposure.

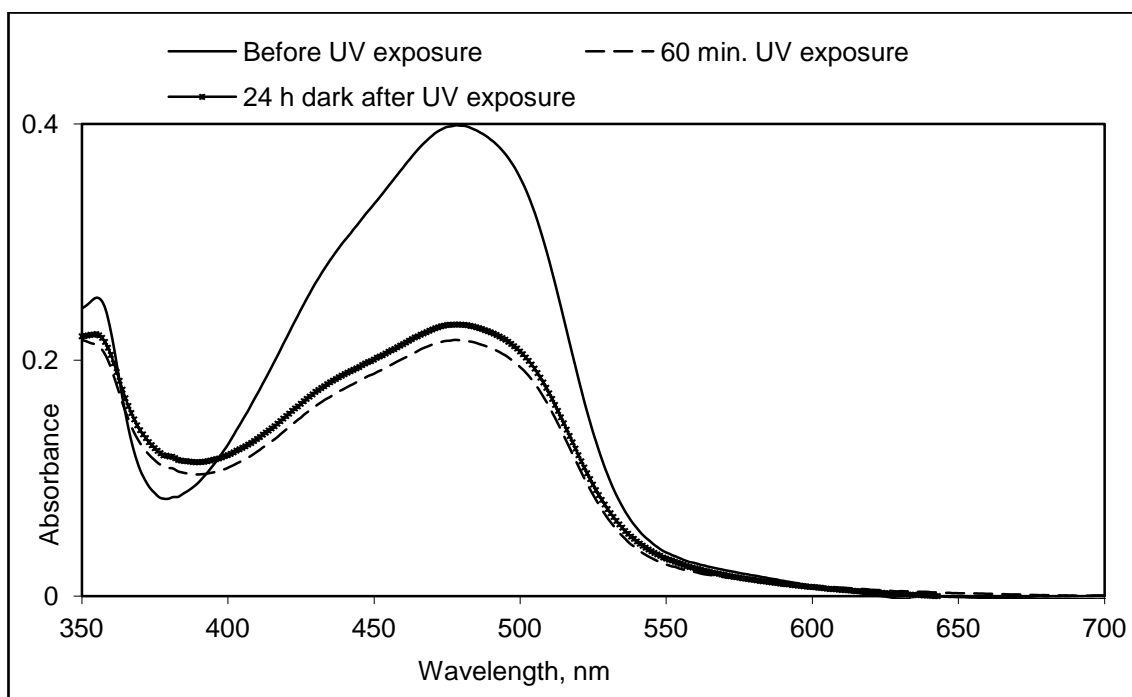


**Figure 9.24** Absorption spectra of solutions of azospirooxazine dye **2** in acetone upon UV exposure for increasing periods of time up to 100 min.

After removal of the UV light source, a reverse colour change initiated; however this colour change towards the unexposed state was not complete even after standing the exposed samples in the dark for 24 hours, as shown in Figures 9.25 and 9.26. This observation may be due to partial thermal or chemical degradation in solution during the period in the dark. This explanation is supported by the non-isosbestic nature of the reverse colour change, as shown in Figures 9.25 and 9.26, due to the possible presence of the non-photochromic thermal degradation products in the dye solution, as discussed in section 9.3.1, (b).



**Figure 9.25** Absorption spectra of azospirooxazine dye **2** in acetone after 20 min. of UV exposure and fading for 24 hours



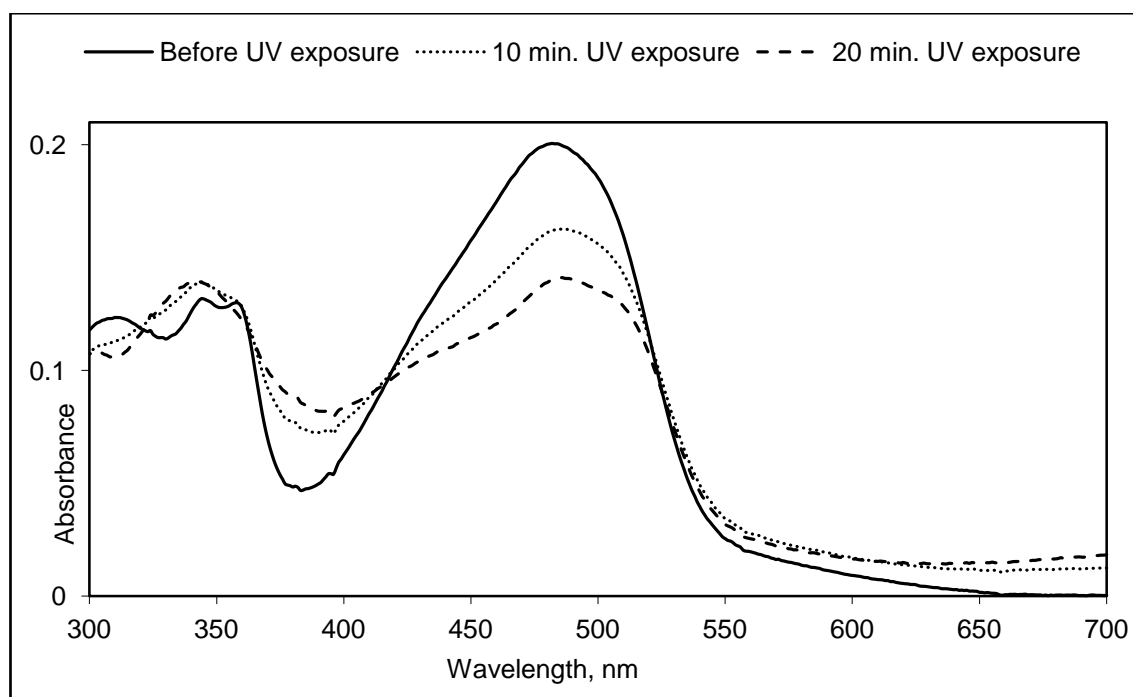
**Figure 9.26** Absorption spectra of azospirooxazine dye **2** in acetone after 60 min. of UV exposure and fading for 24 hours

f) Investigation of photochromism of azospirooxazine dye **2** in dichloromethane

UV exposure of a solution of azo spirooxazine dye **2** in dichloromethane brought about only a slight decrease in the intensity of the orange colour of the dye solution with no visually perceptible changes in the hue of the dye solution, as shown in Figure 9.27.



**Figure 9.27** Colour development on UV exposure of a solution of azospirooxazine dye **2** in dichloromethane

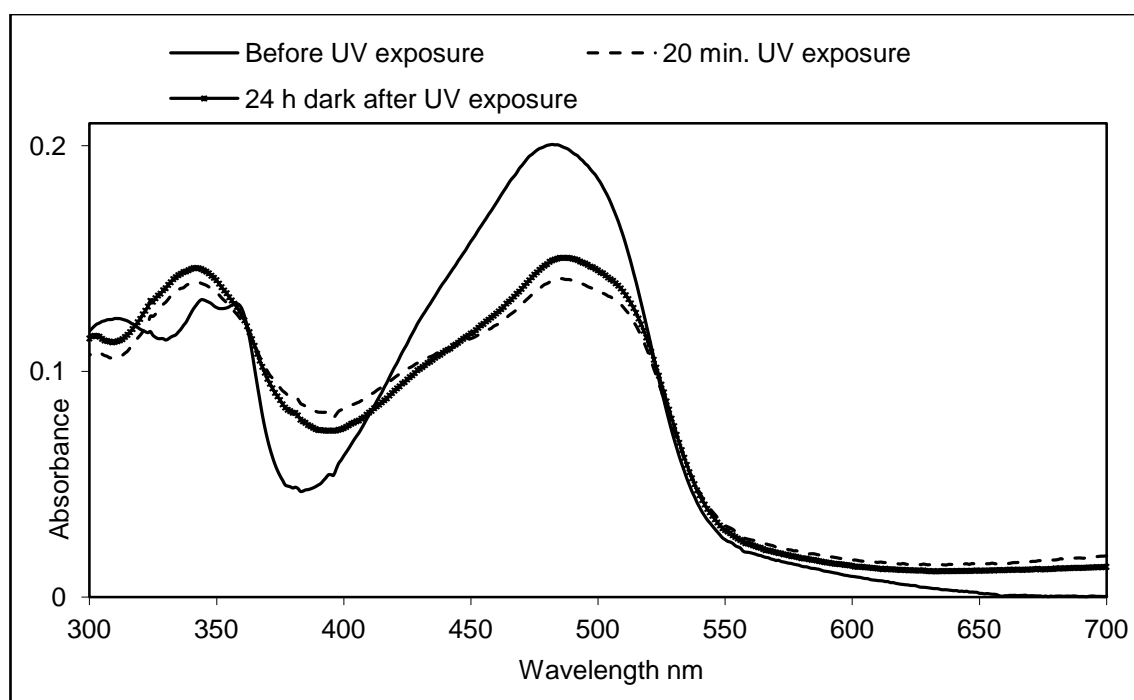


**Figure 9.28** Absorption spectra of solutions of azospirooxazine dye **2** in dichloromethane upon UV exposure for increasing periods of time up to 20 min.

Figure 9.28 shows that continuous UV exposure of the azospirooxazine dye **2** in dichloromethane for 20 minutes resulted in a significant decrease in absorbance at  $\lambda_{\max} = 479$  nm and a slight increase in absorbance at wavelengths longer than 550 nm. The colour change was associated with the presence of isosbestic points at 360, 415 and 524 nm, as shown in Figure 9.28, which provides evidence of photochromic colour change,

as described in section 9.3.1, b. However, this colour change may be mostly due to syn- and anti- isomerism about the hydrazone group, as discussed in section 9.3.2., (e). There is only tentative evidence for photochromic colour change brought about by the ring-opening of the dye molecule represented by the slight increase in the absorbance at longer wavelengths.

After UV exposure for 20 minutes, the sample was stored in the dark for 24 hours, and then its UV/visible spectrum was measured. Figure 9.29 shows that the absorption spectrum of the dye solution after storage in the dark is mostly located between the absorption spectra measured before and after UV exposure with no isosbestic points. This observation indicates that the reverse colour change of the dye during 24 hours in the dark did not only produce the original form of the dye, but also produced other species which may be products of degradation during the fading time.



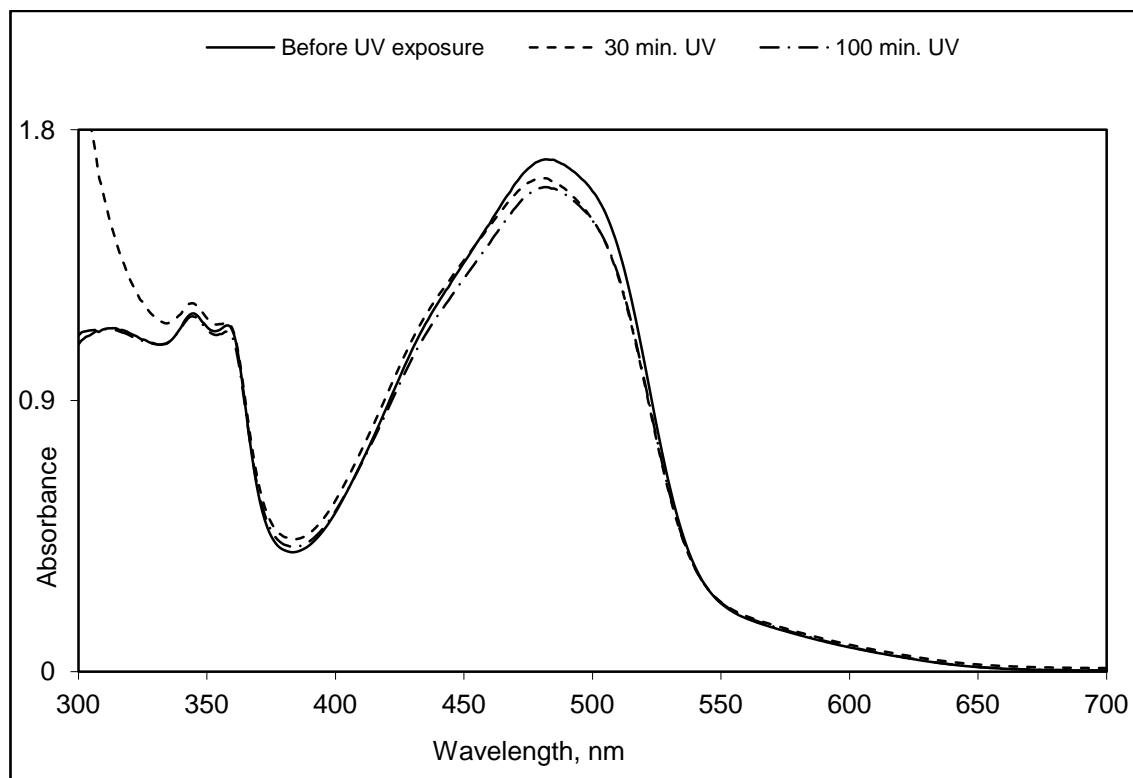
**Figure 9.29** Absorption spectra of azospirooxazine dye **2** in dichloromethane after 20 min. of UV exposure and fading for 24 hours

*g) Photochromism of azospirooxazine dye 2 in toluene*

UV exposure of azospirooxazine dye **2** solution in toluene did not bring about a notable colour change. This observation was confirmed by measuring the UV/visible spectra of the dye solution before and after UV exposure for increasing periods of time. This showed that UV exposure for the long time of 100 minutes caused only a slight



difference in the absorption spectrum of the dye compared to that measured before UV exposure, as shown in Figure 9.30.

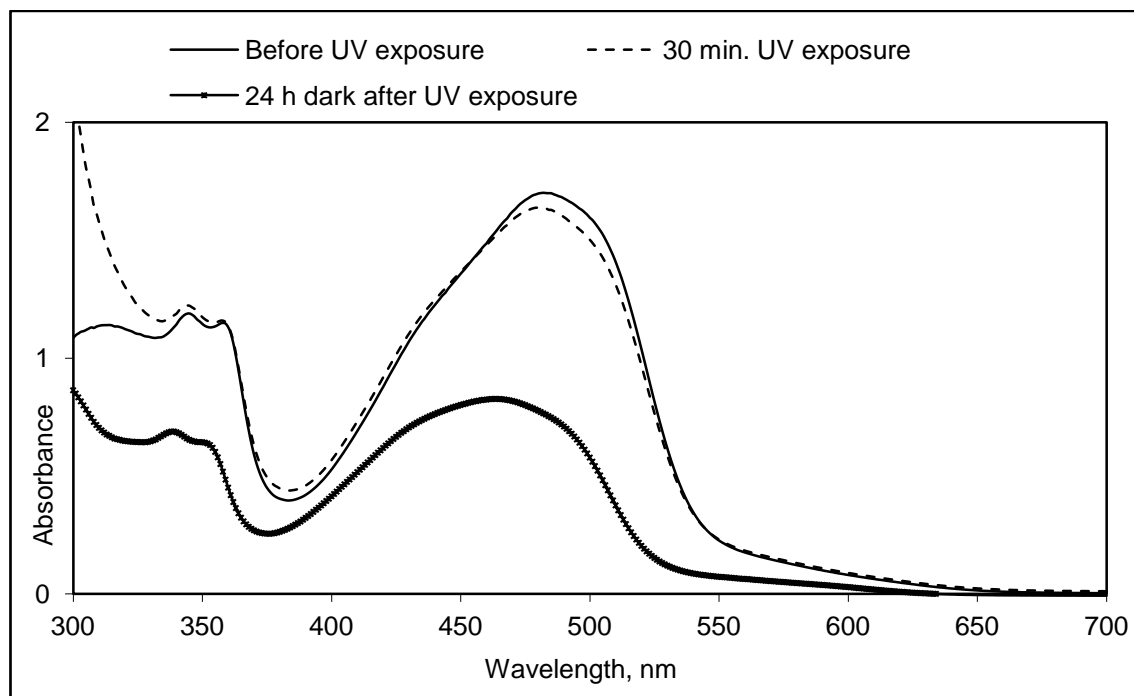


**Figure 9.30** Absorption spectra of solutions of azospirooxazine dye **2** in toluene upon UV exposure for increasing periods of time up to 100 min.

The decrease in the single absorption band ( $\lambda_{\text{max}} = 485 \text{ nm}$ ) may be due to a limited amount of photo-induced syn- to anti- isomerisation about the hydrazone group, as discussed in section 9.3.2., (e). This trend may be due to the relatively low level of stabilization of the high polarity ring-opened form of the dye in the low polarity solvent, toluene, and therefore the ring-opening reaction was restricted in this solvent. In addition, the relatively limited change brought about by the syn- and anti- isomerisation, as shown in Figure 9.30, is consistent with the rotation mechanism proposed for hydrazone isomerisation which is facilitated by polar solvents due to the involvement of charge separation in the transition state. [241]

In an attempt to investigate the behaviour of exposed samples after removal of the UV light source, exposed samples were stored in the dark, and their absorption spectra were re-measured. In this respect, Figure 9.31 shows that dark storage for 24 hours of an exposed sample led to a significant change in its absorption spectrum compared to that measured immediately after UV exposure for 30 minutes. This difference between the

absorption spectra, which dempnstrates non-photochromic change, may be a result of formation of thermal or chemical degradation products.

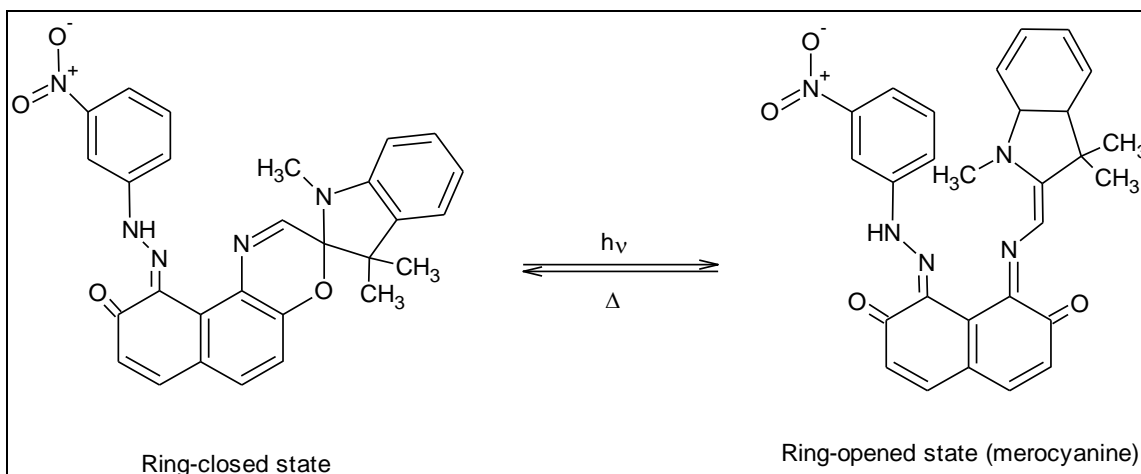


**Figure 9.31** Absorption spectra of azospirooxazine dye **2** in toluene after 30 min. of UV exposure and fading for 24 hours

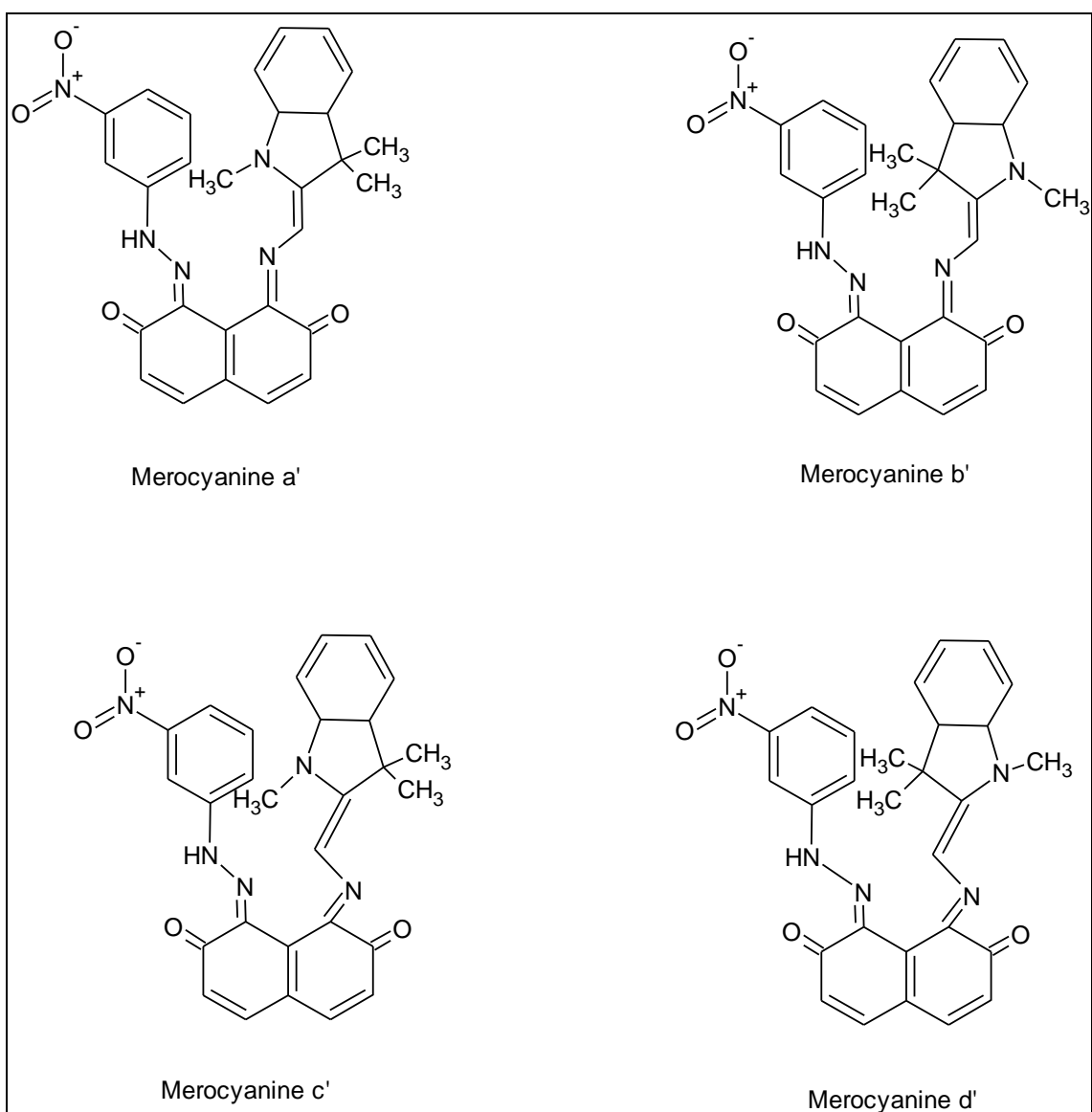
### 9.3.3. Investigation of photochromism of azospirooxazine dye **3**

#### a) Mechanism of photochromism of azospirooxazine dye **3**

A possible mechanism for the photochromism of azospirooxazine dye **3** is given in Scheme 9.8, which shows only one of several possible isomers of the merocyanine forms as explained in section 9.3.2, a. The four possible transoid isomers of the merocyanine of azospirooxazine dye **3** are given in Figure 9.32.



**Scheme 9.8** Photochromism of azospirooxazine dye **3**



**Figure 9.32** Transoid isomers of the ring-opened form of azospirooxazine dye **3**

There are eight possible isomers of the photomerocyanines, four of them considered to be cisoid and four as transoid. The focus of the investigation was on the transoid isomers (a'-d'), shown in Figure 9.32, because of the high instability due to steric constraints in the cisoid isomers.

*b) Molecular modeling of azospirooxazine dye 3*

Molecular modeling of azospirooxazine dye **3** shows that the calculated steric energies and heat of formation of the ring-closed form are lower than the corresponding values of the four ring-opened isomers a'-d', as shown in Table 9.5, and therefore azospirooxazine dye **3** has the potential to show photochromic behaviour by converting to the higher energy merocyanines as a result of absorbing UV light and to revert thermally to the more stable ring-closed form when the light source is removed. The concepts on which this inference is based were given in section 9.3.2, b.

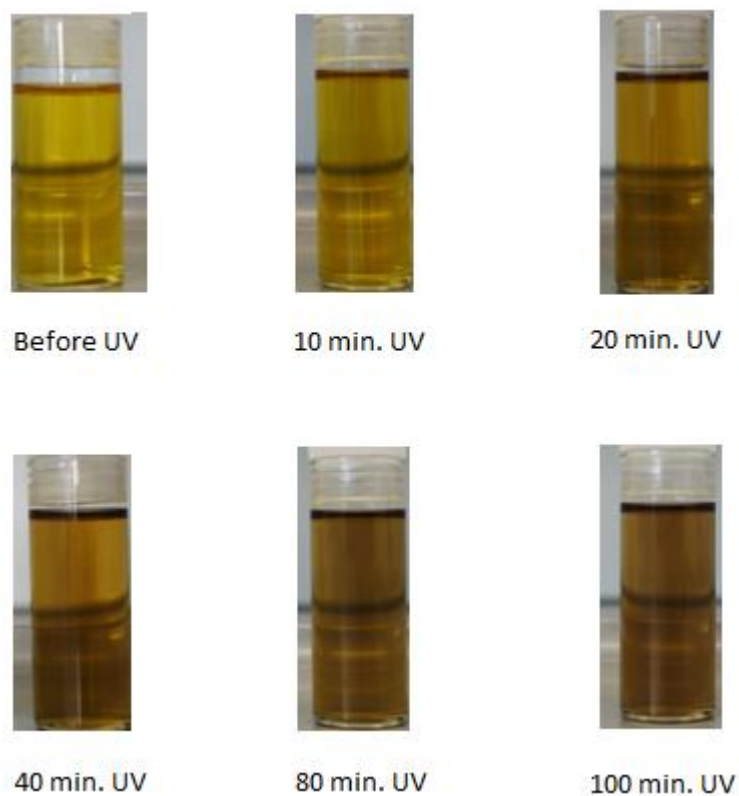
**Table 9.5** Calculated energy data for azospirooxazine dye **3** and isomers of the ring-opened forms

| <i>Azospirooxazine dye</i><br><b>3</b> | <i>Final energy (Kcal/mol)</i><br><i>(MM2)</i> | <i>Heat of formation (Kcal/mol)</i><br><i>(AM1)</i> |
|--|--|---|
| Ring-closed form                       | - 1.6  | 128.6   |
| Merocyanine a'                         | 5.3  | 141.6   |
| Merocyanine b'                         | 10   | 142.1   |
| Merocyanine c'                         | 4  | 144.3   |
| Merocyanine d'                         | 69.1   | 141.6   |

The investigation of UV/visible spectra of azospirooxazine dye **3** was confined to the dye solutions in ethanol, dichloromethane and toluene which cover the same range of polarities as the study of azospirooxazine dye **2**.

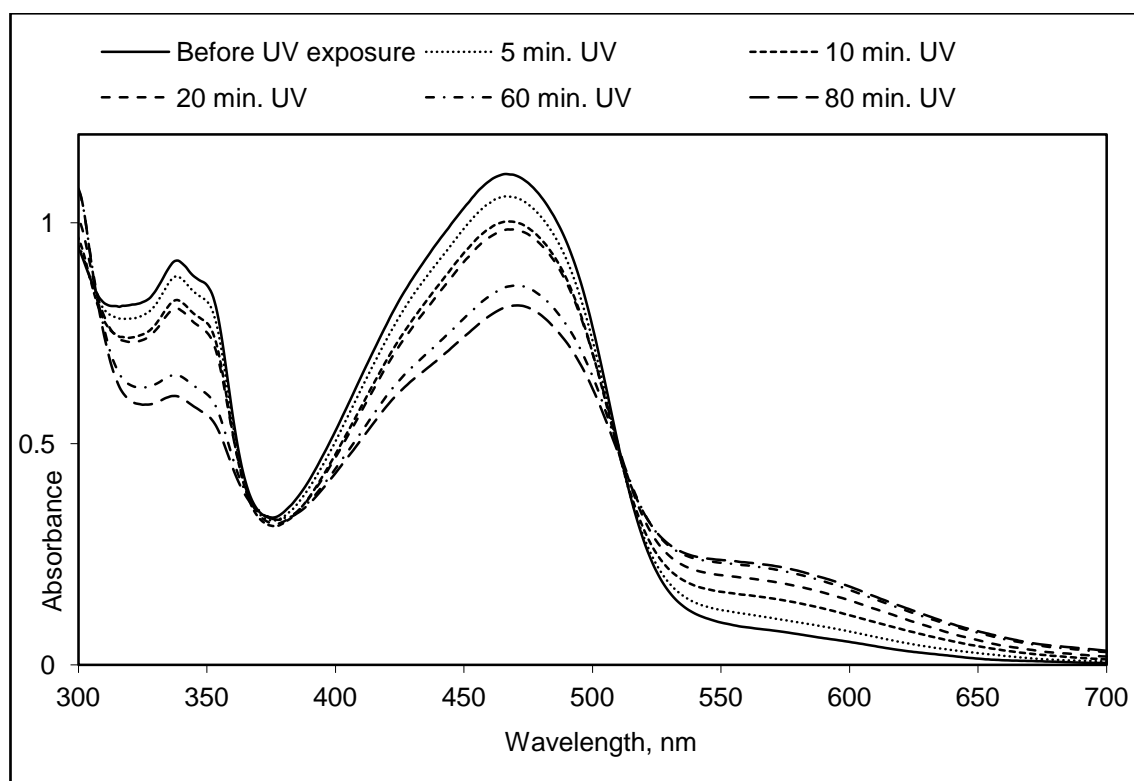
*c) Photochromism of azospirooxazine dye 3 in ethanol*

UV exposure of the dye solution in ethanol caused a gradual photochromic color change from yellow to yellowish grey, as shown in Figure 9.33.



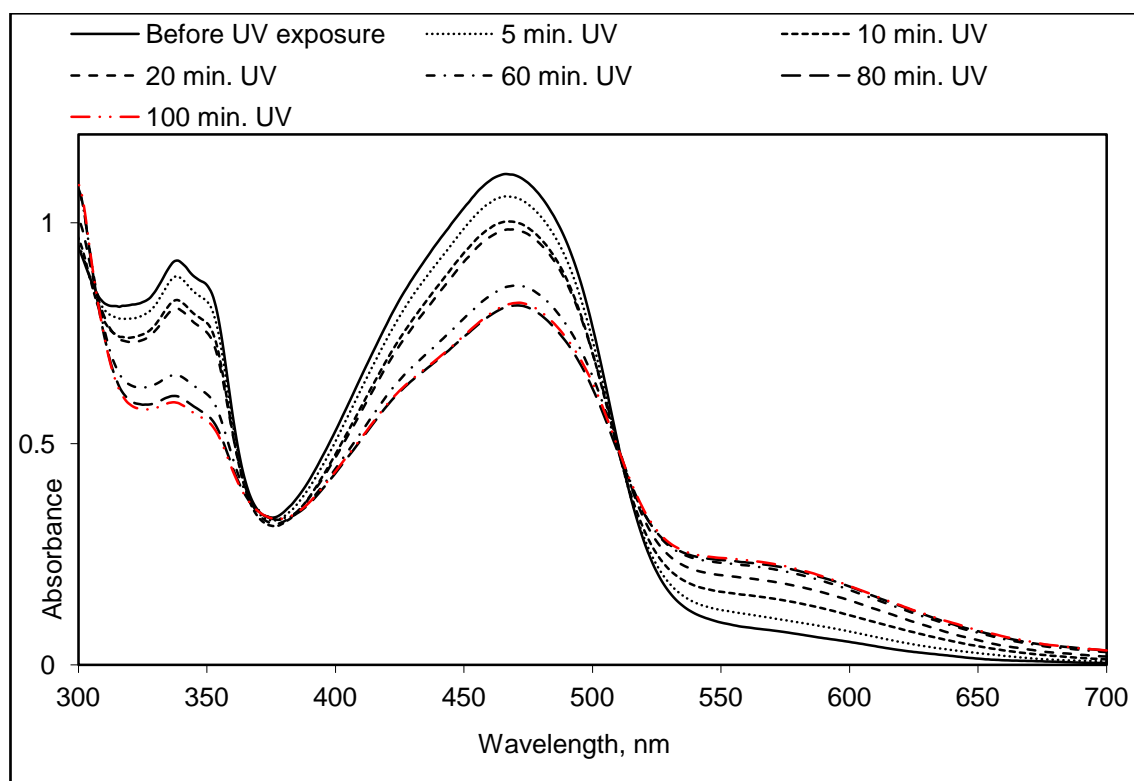
**Figure 9.33** Colour development on UV exposure of a solution of azospirooxazine dye **3** in ethanol

The photochromic nature of the colour change of azospirooxazine dye **3** was observed by measuring UV/visible spectra of the dye solution before and after UV exposure for increasing periods of time of up to 80 minutes, as shown in Figure 9.34, which shows isosbestic points at 511 and 381 nm.



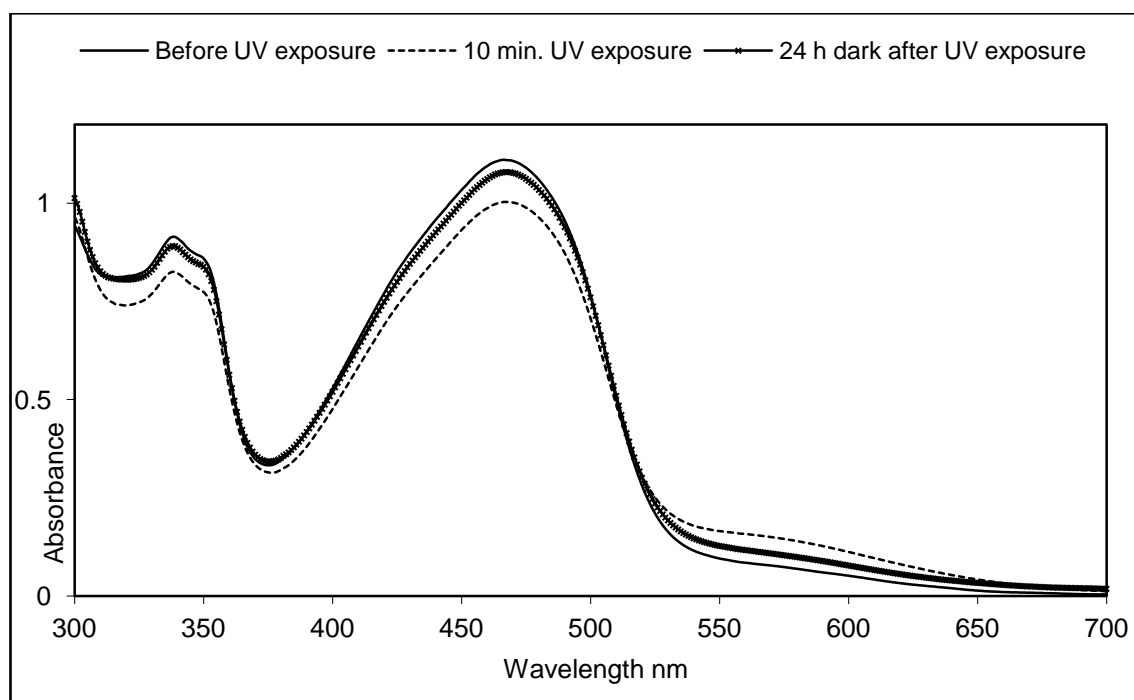
**Figure 9.34** Absorption spectra of solutions of azospirooxazine dye **3** in ethanol upon UV exposure for increasing periods of time up to 80 min.

Further UV exposure of the dye solution resulted in only a slight colour change, compared to the change occurring within the first 80 minutes of exposure, accompanied by initiating a departure from the isosbestic behaviour measured after 100 minutes of UV exposure, as shown in Figure 9.35. These trends are consistent with no further photochromic colour change and dye photodegradation due to the prolonged exposure to UV light. The relation between the isosbestic behaviour and photochromism has been discussed in section 9.3.1., (b) in the context of azospirooxazine dye **2**.



**Figure 9.35** Absorption spectra of solutions of azospirooxazine dye **3** in ethanol upon UV exposure for increasing periods of time up to 100 min.

The possibility of reverse colour change of azospirooxazine dye **3** solution in ethanol was investigated by measuring the UV/visible spectrum of an exposed sample after storing in the dark for 24 hours. The spectrum shows that the dye underwent only partial reverse change towards the unexposed state, as shown in Figure 9.36.



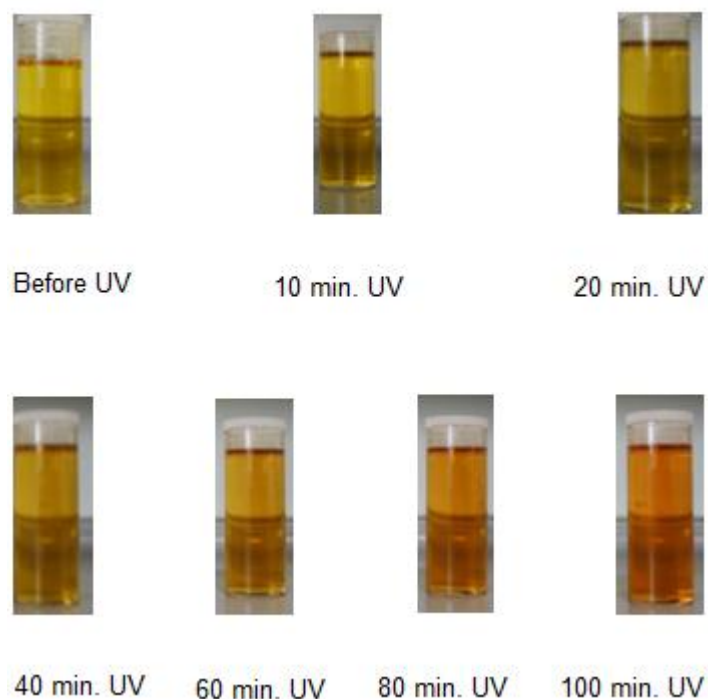
**Figure 9.36** Absorption spectra of azospirooxazine dye **3** in ethanol after 10 min. of UV exposure and fading for 24 hours

The possible initiation of ring closure reaction after removal of the UV source was observed in Figure 9.36 by the direction of movement of the absorption spectrum measured after the dark period. The incompleteness of the reverse change may be a result of formation of products of thermal or chemical degradation of the dye during the period in the dark, as discussed in section 9.3.2, (e).

*d) Investigation of photochromism of azospirooxazine dye 3 in dichloromethane*

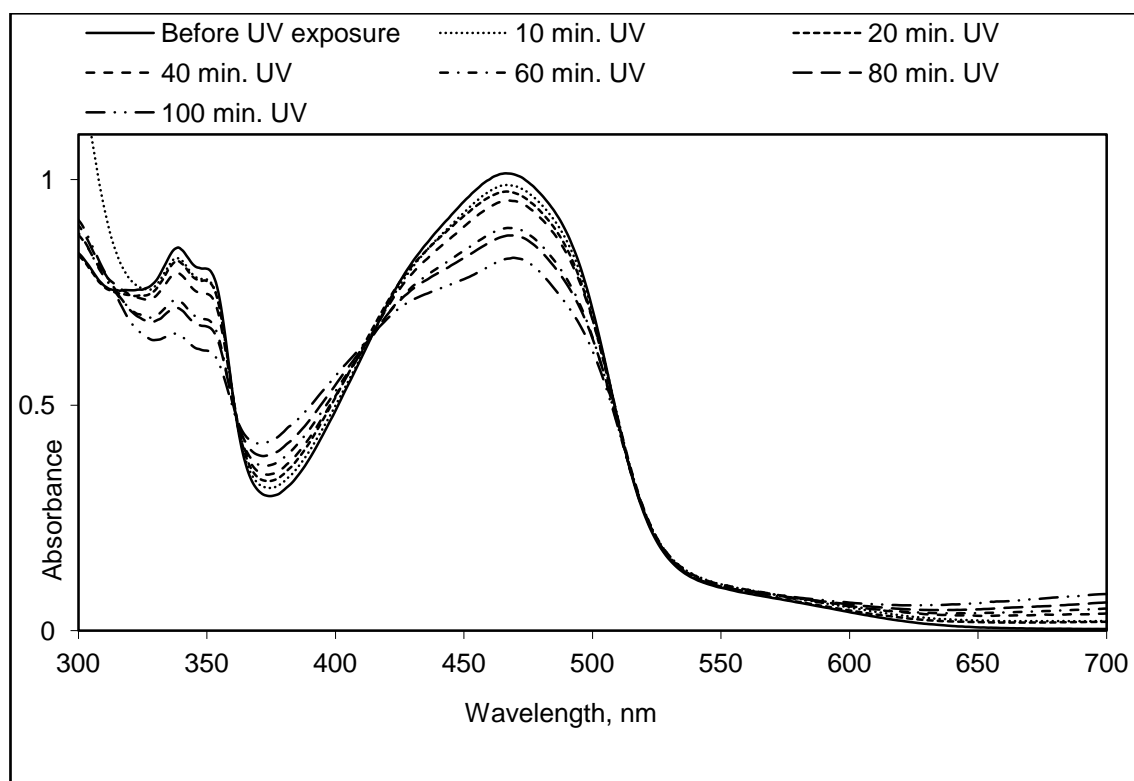
UV exposure of azospirooxazine dye **3** in dichloromethane brought about a gradual colour change from yellow to orange, as shown in Figure 9.37.





**Figure 9.37** Colour development on UV exposure of a solution of azospirooxazine dye **3** in dichloromethane

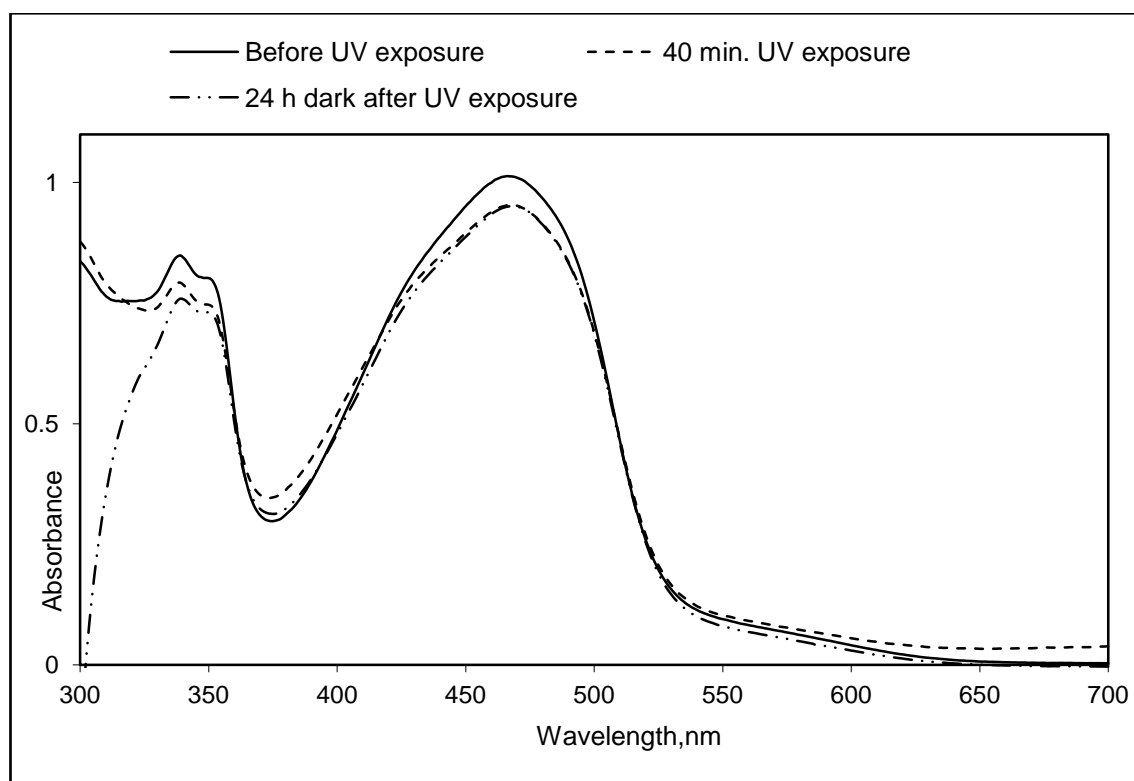
Investigation of the colour change of azospirooxazine dye **3** in dichloromethane suggests a possible photochromic change, due to the presence of isosbestic points at 360, 413 and 510 nm for dye samples exposed for periods up to 100 minutes, as shown in Figure 9.38. This colour change may result from the photo-induced isomerisation about the hydrazone group, as discussed in section 9.3.2., (f) in the context of azospirooxazine dye **2**.



**Figure 9.38** Absorption spectra of solutions of azospirooxazine dye **3** in dichloromethane upon UV exposure for increasing periods of time up to 100 min.

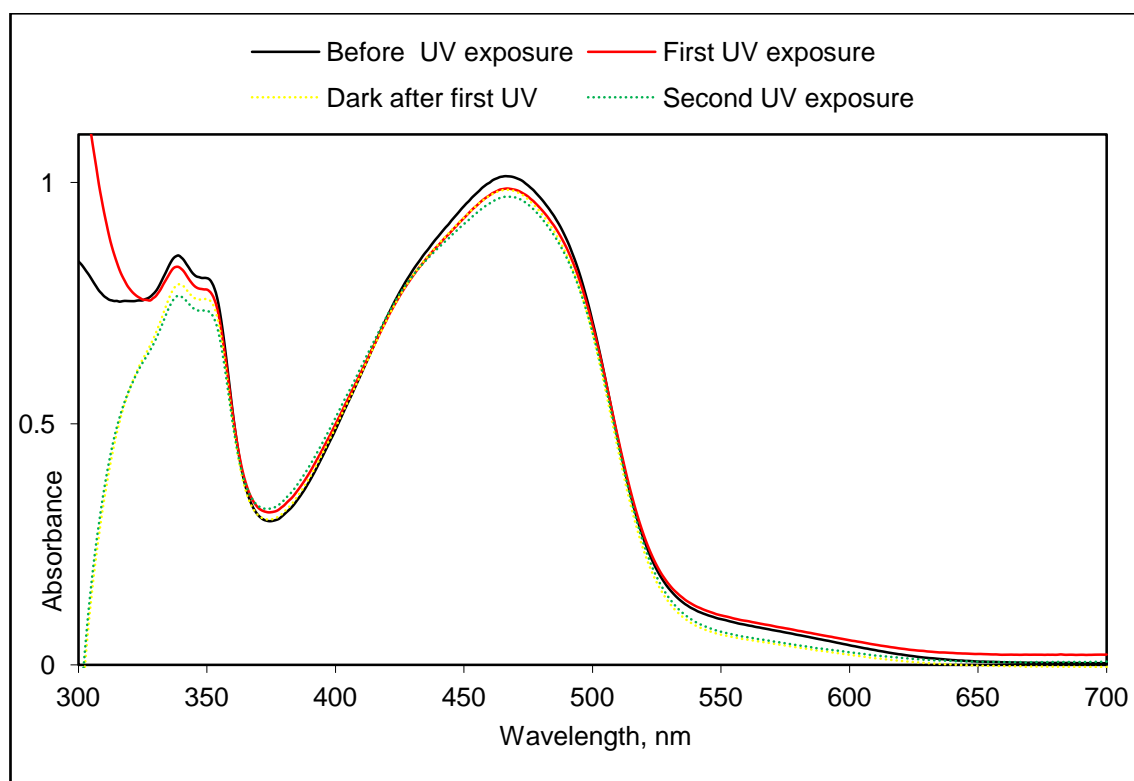
It was observed that UV exposure of the dye solution in dichloromethane for 100 minutes resulted in a departure from the isosbestic behaviour, as shown in Figure 9.38, which may be a result of photodegradation after prolonged exposure to UV light. As a result of this observation, the dye solution was not exposed to UV light for more than 100 minutes, as this was judged to be the appropriate time for maximum colour change with minimum dye photodegradation.

Reversibility of the photochromic colour change was investigated by storing an exposed sample in the dark for 24 hours, measuring its UV/visible spectrum and comparing it to the spectra measured before and after UV exposure. The spectra showed that the dye did not return to the original state, as shown in Figure 9.39, due to possible degradation in the dark, as described in section 9.3.3., c.



**Figure 9.39** Absorption spectra of azospirooxazine dye **3** in dichloromethane after 40 min. of UV exposure and fading for 24 hours

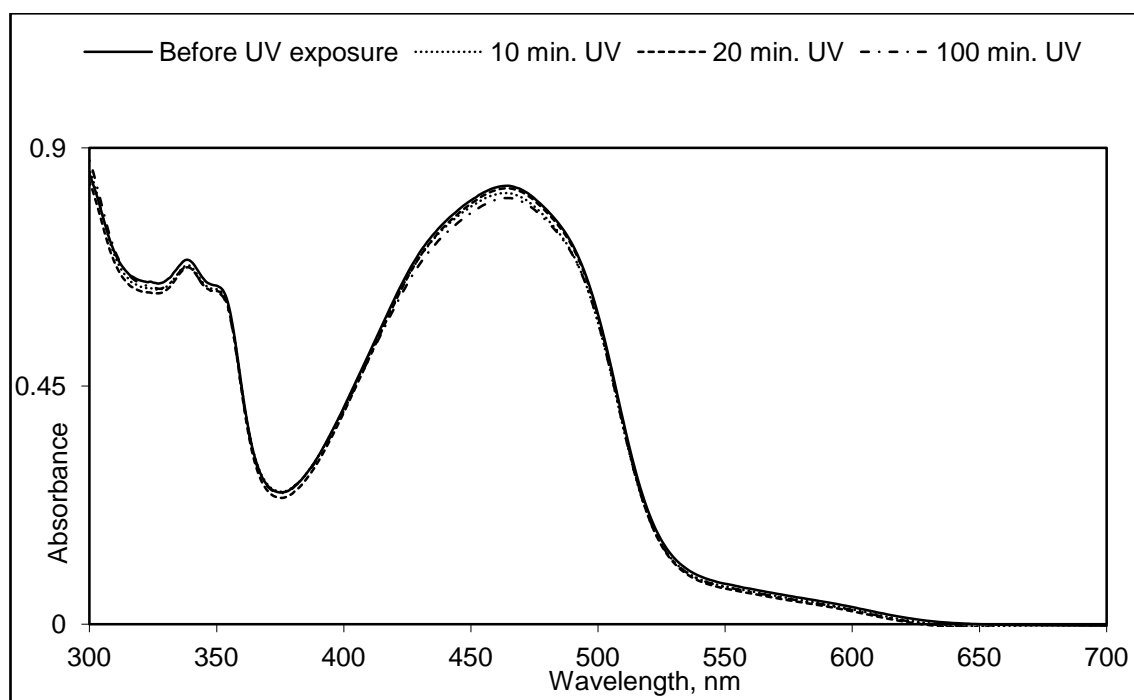
The possibility of degradation was investigated by re-exposing the dye sample to UV light after the period of storage in the dark. The measured spectrum after a second UV exposure was different from that after the first UV exposure, as shown in Figure 9.40. It was therefore concluded that there were other species in the dye solution, other than the ring-opened and ring-closed forms, which may be non-photochromic products of degradation.



**Figure 9.40** Absorption spectra of azospirooxazine dye **3** in dichloromethane over two cycles of UV exposure

*e) Investigation of photochromism of azospirooxazine dye 3 in toluene*

UV exposure of the dye solution in toluene did not show a perceptible colour change, and this trend was confirmed by measuring the UV/visible spectra of the dye solution before and after UV exposure for increasing periods of time, as shown in Figure 9.41.



**Figure 9.41** Absorption spectra of solutions of azospirooxazine dye **3** in toluene upon UV exposure for increasing periods of time up to 100 min.

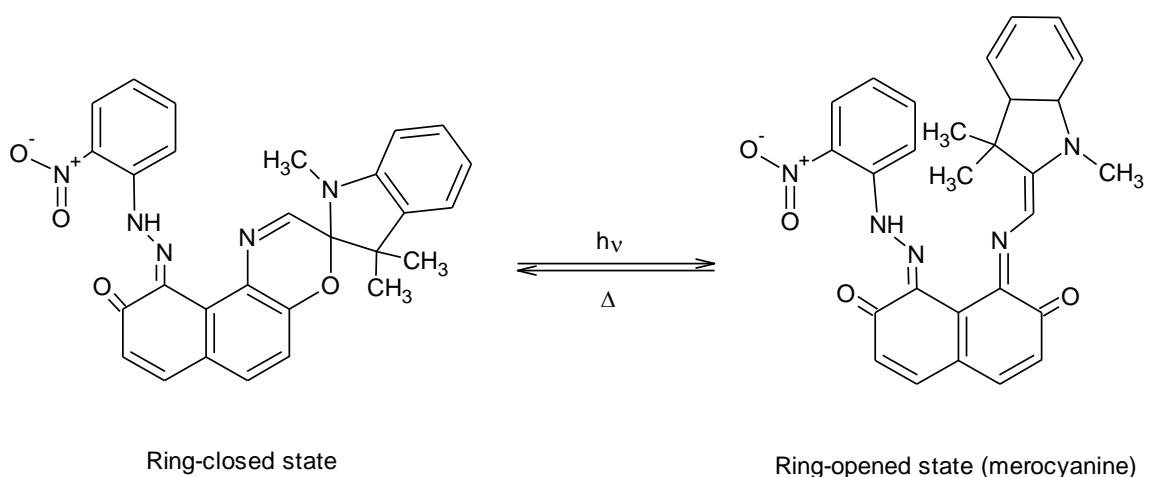
Figure 9.41 shows that there is no significant difference in the spectra even after 100 minutes exposure. The slight decrease in the single absorption band at  $\lambda_{\text{max}} = 466$  is possibly due to the photo-induced isomerisation about the hydrazone group, as discussed in section 9.3.2., (g).

#### **9.3.4. Investigation of photochromism of the ortho-derivative of azospirooxazine dyes (azospirooxazine dye 4)**

As the synthesis of this compound was unsuccessful, due to the reasons discussed in section 9.2.1., (d), the investigation of this dye was confined to molecular modelling and investigating the possible photochromism of the dye theoretically.

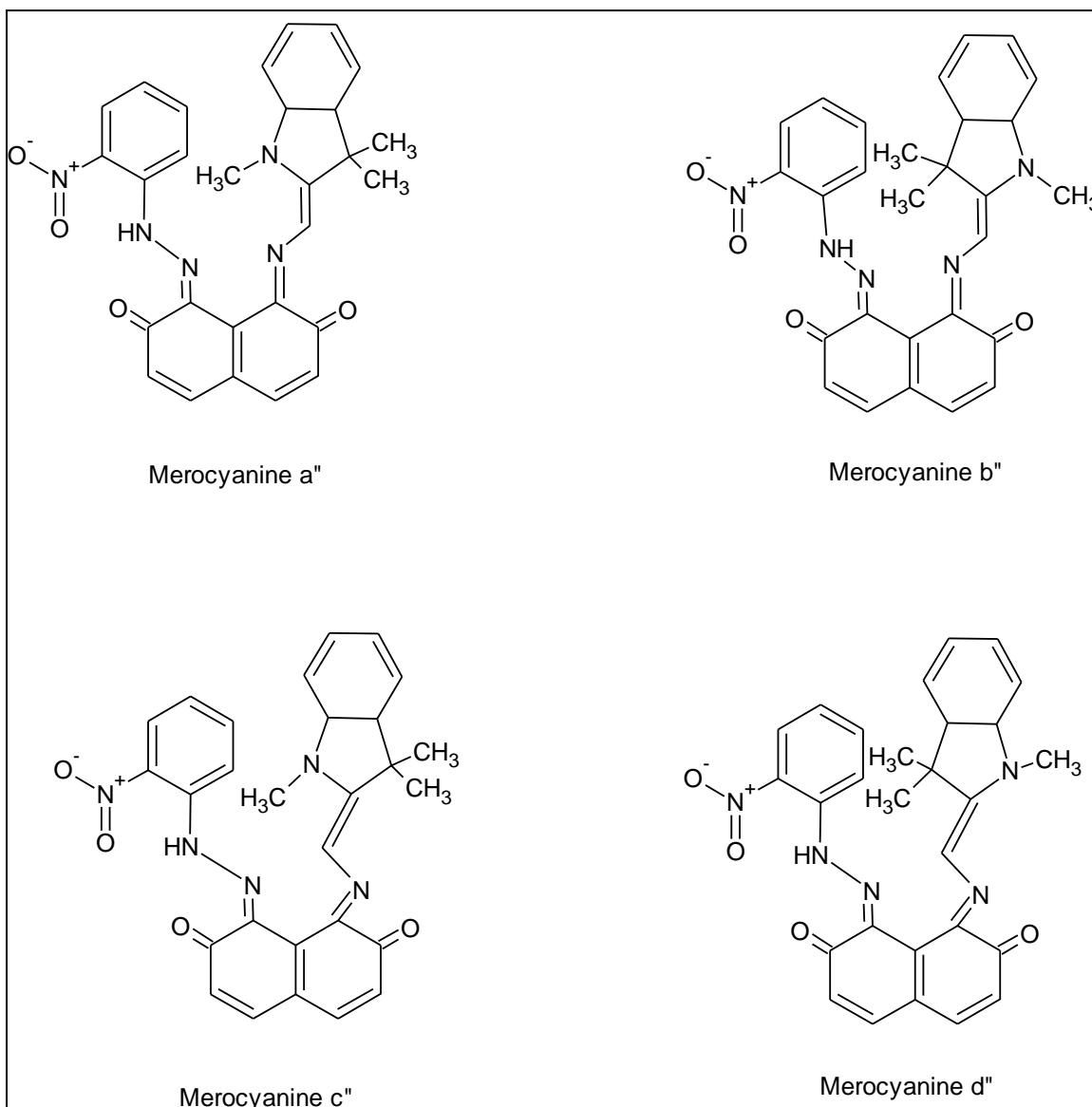
##### *a) Mechanism of photochromism of the azospirooxazine dye 4*

The general mechanism suggested for reversible photochromism of azospirooxazine dye **4** is given in Scheme 9.9, which shows only one of several possible isomers of the merocyanine forms as explained in section 9.3.2., (a).



**Scheme 9.9** Photochromism of azospirooxazine dye **4**

The four possible transoid isomers of the merocyanine of azospirooxazine dye **4** are given in Figure 9.42.



**Figure 9.42** Transoid isomers of the ring-opened form of the orto-derivative of azospirooxazine dye

*b) Molecular modeling of azospirooxazine dye 4*

Molecular modeling of azospirooxazine dye **4** shows that the calculated steric energies and heats of formation of the ring-closed form are lower than those of the four ring-opened isomers a''-d'', as shown in Table 9.6, and therefore the dye might be expected to show photochromic behaviour by converting to the higher energy merocyanines as a result of absorbing UV light and to revert thermally to the more stable ring-closed form when the light source is removed. The concepts on which this inference is based are given in section 9.3.2, b.

**Table 9.6** Calculated energy data for the ortho azospirooxazine dye **4** and isomers of the ring-opened forms

| <i>orto-derivative of azospirooxazine dye</i> | <i>Final energy (Kcal/mol) (MM2)</i> | <i>Heat of formation (Kcal/mol) (AM1)</i> |
|---|--------------------------------------|---|
| Ring-closed form                              | -10.1                                | 129.3                                     |
| Merocyanine a''                               | 13.4                                 | 149.1                                     |
| Merocyanine b''                               | 8.8                                  | 142.3                                     |
| Merocyanine c''                               | 97.4                                 | 154.7                                     |
| Merocyanine d''                               | 14.6                                 | 151.3                                     |

#### 9.4. Conclusions

In an attempt to produce photochromic dyes appropriate for textile coloration applications, two azospirooxazine dyes were successfully synthesized and their photochromic properties were investigated. The synthesis was based on a spironaphtho[2,1-b]oxazine, which is photochromic, as a coupling component which, by azo coupling with diazotised *p*- and *m*-nitroanilines produced the azospirooxazine dyes **2** and **3** respectively. Computer-aided molecular modelling using MM2 and AM1 calculations of the dyes showed that both dyes were predicted to have the potential to show photochromism.

The investigation of photochromism of the azospirooxazine dyes showed that the dyes possessed different properties in different solvents in terms of their colours, colour intensities, photocoloration on UV exposure, rate and reversibility of photochromic colour change. In general, the dye solutions in all solvents investigated showed incomplete reversibility to different extents; however the forward colour change on UV exposure varied according to the solvent used. In this respect, the solutions of azospirooxazine dyes **2** and **3** in ethanol showed photochromic colour change on UV exposure for times up to 80 minutes. This colour change was represented by changes in two absorption bands in the visible region which probably represent photochemical conversion of the ring-closed form to the merocyanine isomers, and there is a possibility of a photo-induced isomerisation from syn- to anti- isomers about the hydrazone group. UV exposure for prolonged periods resulted in the formation of non-photochromic products, due to a possible photodegradation.



Solutions of the dyes in toluene did not show significant photochromism; this result may be due to the fact that the low polarity ring-closed form (unexposed state) form is stabilised in a solvent of low polarity such as toluene.

The solutions of azospirooxazine dyes **2** and **3** in dichloromethane required different periods of time for maximum photocolouration on UV exposure to be reached before dye photodegradation becomes significant. The main absorbance and colour change of the dye solutions in dichloromethane may have resulted from the photo-induced isomerisation between syn- and anti- isomers involving the hydrazone group.

Investigations of the reverse colour change of the azospirooxazine dyes in various solvents suggest instability of the dyes during fading at room temperature leading to formation of non-photochromic thermal or chemical degradation products which in turn prevented complete reverse colour changes. This observation suggests the possibility that performing these investigations at low temperatures may lead to improved reversibility by minimizing thermal degradation of the photochromic dyes.

## Chapter 10 – Conclusions

### 10.1. General Conclusions

The application of a set of commercial photochromic dyes (**1-6**) to polyester and cotton fabrics by different dyeing and printing methods was investigated as described in this thesis. The photochromic performance of dyed and printed fabrics was investigated and optimised, using the degree of photocolouration ( $\Delta E_1$ ) and background colour ( $\Delta E_2$ ), defined in chapter 3, as optimisation criteria. In addition, UV/visible spectra of solutions of dyes **1-6** in a range of solvents were measured and comparisons made in an attempt to understand the photochromic properties of the dyes in different media and consequently to optimise the selection of solvents used as media for applying photochromic dyes to textiles.

On the basis of the results of the investigations as described in this thesis, it was concluded that the solvent-based dyeing is more appropriate for applying the photochromic dyes to polyester than the aqueous-based dyeing method. The advantages of the solvent-based dyeing method over the aqueous-based method are the generally better performance characteristics of dyed fabrics, shorter dyeing time, easier dyeing procedure and avoidance of effluent issues because there is the possibility of solvent recovery of dyeing solvents when this method is applied in industry.

A significant issue which was minimised but not overcome in the research described in this thesis, and may adversely affect the performance of photochromic polyester fabrics, is their low colour fastness to light. Thus, an investigation into improving this technical property of photochromic dyes is suggested for any study aiming at further optimisation of the performance of photochromic polyester fabrics.

The six commercial photochromic dyes (**1-6**) showed different performance characteristics when they were applied to polyester fabric by the different dyeing and printing methods investigated. On the basis of the optimization criteria used to assess the photochromic performance of the dyed fabrics, Oxford Blue, a spironaphthoxazine photochromic dye showed the best performance, compared to the other photochromic dyes, on the basis of a relatively low background colour and the highest degree of photocolouration after UV light exposure for 4 minutes. In all dyeing and printing methods, the naphthopyran dyes (**5** and **6**) took longer to fade to their unexposed state and retained higher residual colours after fading for a fixed period of time compared to spironaphthoxazine dyes (**1-4**) applied by the same method.

The solvent-based dyeing method brought about an improvement in the performance of most of the photochromic dyes applied to polyester fabric compared to the same dyes applied to the same fabric by the aqueous-based dyeing method. This improvement was characterised by an increase in the degree of photocolouration and a decrease in the background colour in the cases of polyester fabrics dyed with Aqua Green, Oxford Blue and Palatinate Purple and a significant decrease in the background colour, with only a slight decrease in the degree of photocolouration in the cases of the fabrics dyed with Ruby and Corn Yellow.

The performance of photochromic dyes **1-6** applied to polyester fabric by inkjet printing was generally inferior in terms of the degree of photocolouration and superior in the case of background colours compared to that shown by the same dyes applied by the aqueous-based and solvent-based dyeing methods as described in chapters 3 and 4. In addition, it was observed that the inkjet printed fabrics showed a higher rate of fading and lower fatigue resistance.

The fatigue resistance of dyes **1-6** applied to polyester fabric by inkjet printing was mostly lower than that of the same dyes applied by the dyeing methods. The fatigue resistance of the dyes applied to polyester fabric by the solvent-based dyeing method was variable, but lower than that shown by the dyes applied by the aqueous-based disperse dyeing method.

It was observed that the storage stabilities of dyes **1-6** applied to polyester fabric by inkjet printing were mostly lower than those of the same dyes applied by the dyeing methods.

The investigations of the fastness properties of polyester fabric dyed with photochromic dyes **1-6** showed that the dyed fabrics generally possessed low lightfastness but high washfastness. In addition, the solvent-based dyeing method brought about an improvement in both of these properties of polyester fabrics dyed by most of the dyes compared to the aqueous-based dyeing method.

With regard to lightfastness of dyed and printed polyester fabrics, there was no general trend in this property favoured by the inkjet printing or either of the dyeing methods.

The washfastness of polyester fabric dyed or printed with the photochromic dyes showed similarities when applied by the inkjet printing method and the solvent-based dyeing method and were higher than the washfastness of the dyes applied by the aqueous-based dyeing method.

Cotton fabrics dyed with the spironaphthooxazine-based dyes **1-4** showed a common feature represented by the higher rate of fading of these dyes after removal of the UV

light sources compared to the rates of fading of the same dyes applied to polyester fabric by the dyeing and printing methods investigated, due possibly to the lower restriction applied to the ring closure reaction of photochromic dyes on cotton compared to that experienced by the dyes on polyester due to the differences between the structures of the two fibres.

The investigation of photochromic performance of photochromic dyes **1-6** in different solvents and the application of these dyes to polyester fabric from different solvents demonstrated that toluene and ethyl acetate led to improved performance of the dyes applied to polyester fabric by the solvent-based dyeing method in terms of minimizing the permanent background colour of dyed fabrics compared to that of the fabrics dyed from dichloromethane.

In an attempt to improve the accuracy of lightfastness assessment of photochromic textiles, and to allow a meaningful comparison with traditionally dyed textiles, a new instrumental-based method for assessment of the colour fastness to light of these textiles was investigated. According to this method, replacement of the visual assessment of colour difference between exposed and unexposed areas of textile samples by an instrumental measurement of the colour difference was made successfully. The main advantages that may be achieved using this method are accuracy, compared to the traditional method of lightfastness assessment of normal dyes, and the possibility of using a set of values of percentage decrease in colour difference between undyed wool and blue wool references for assessment of lightfastness of coloured textiles as long as the light exposure of blue wool references is carried out on a similar instrument and similar conditions to that used for light exposure of tested samples.

In an attempt to synthesise new photochromic systems for evaluation in textile applications, two azospirooxazine dyes, **2** and **3**, were successfully synthesised by azo coupling of a spironaphtho[2,1-b]oxazine with diazotized *p*-nitroaniline and *m*-nitroaniline respectively. Computer-aided molecular modelling using MM2 and AM1 calculations of the dyes suggested that both dyes were predicted to have the potential to show photochromism. In general, the dye solutions in all solvents investigated showed incomplete reversibility to different extents; however the colour change with UV exposure varied according to the solvent used. In this respect, the solutions of azospirooxazine dyes **2** and **3** in ethanol showed photochromic colour change with UV exposure up to 80 minutes. UV exposure for more than 80 minutes resulted in non-photochromic change, due possibly to photodegradation of the dyes under prolonged UV exposure. Solutions of the dyes in toluene did not show photochromism; this

observation was explained by the fact that the low polarity ring-closed (unexposed state) form is stabilised in a solvent of low polarity such as toluene relative to the more polar ring-opened form. The solutions of azospirooxazine dyes **2** and **3** in dichloromethane required different periods of time for maximum degree of photo-induced colour change on UV exposure to be reached before initiating dye photodegradation. Investigations of the reverse colour change of the azospirooxazine dyes in various solvents suggested instability of the dyes during fading at room temperature leading to formation of non-photochromic thermal degradation products which in turn prevented complete reverse colour changes. This observation suggests the possibility that performing these investigations at low temperatures may lead to improved reversibility by minimizing thermal degradation of photochromic dyes.

## **10.2. Future Work**

On the basis of the results of the research described in this thesis, further research can be envisaged in a variety of directions aiming at further optimisation of technical methods for applying the photochromic dyes and extending a number of final uses based on the methods investigated, as given in the examples below.

The investigation of UV-visible spectra of the commercial photochromic dyes in various solvents which was described in chapter 7 suggests the possibility that other solvents may introduce further improvement in the photochromic performance of photochromic dyes in terms of minimising the intensity of the colours of the dye solutions before UV exposure. Hence, further investigations of the media of application of photochromic dyes to textiles by the solvent-based dyeing method would be of value aiming at producing photochromic fabrics with minimum background colours. The optimum solvents may also offer advantages as solvents for formulation of photochromic inks for application by the digital inkjet printing method.

The successful application of the commercial photochromic dyes **1-6** to polyester fabric by the solvent-based dyeing method as discussed in chapter 4, and the improvement delivered in the photochromic performance of photochromic fabrics by applying these dyes to polyester fabric using toluene or ethyl acetate as application media, suggests the possibility that azospirooxazine dyes **2** and **3** may be successfully applied to polyester fabric by this dyeing method. Investigation of this process would involve following the application procedure given in section 4.2.4 but using ethyl acetate or toluene instead of dichloromethane. Further optimisation of the procedure may be envisaged depending on the investigations with a wider range of solvents. The photochromic fabrics produced by

this method may have the potential to show photochromic colour changes between two states of different hues, opening the door to new fields of applications of the photochromic phenomenon in textiles.

In another respect, and in a similar way to the development of the lightfastness test method which is described in chapter 8, a new method for testing washfastness of photochromic and traditional dyes applied to textiles may be developed. For this purpose, in principle, the colour difference between each pair of colours of the grey scale, which is used for evaluation of washfastness of textiles according to the traditional method, is measured instrumentally and compared to the colour difference between washed and unwashed samples. The new method may have the potential to replace the conventional method of washfastness testing by a more accurate and less subjective instrumentally-based method. However, a detailed investigation and optimisation of this method would be required to evaluate the possibility of its application as a standard method of test for colour fastness to washing of textiles.

## Appendix

### Published Papers

1. Mohanad Aldib and Robert M Christie, *Textile applications of photochromic dyes. Part 4: Application of commercial photochromic dyes as disperse dyes to polyester by exhaust dyeing*, *Coloration Technology*, **127**, 5, 282-287 (2011).
2. Mohanad Aldib and Robert M Christie, *Textile applications of photochromic dyes. Part 5: Application of commercial photochromic dyes to polyester fabric by a solvent-based dyeing method*, *Coloration Technology*, **129**, 2, 131–143 (2013)
3. Robert M. Christie, Keith M Morgan, Ayesha Rasheed, Mohanad Aldib, Georgina Rosair, *The molecular design, synthesis and photochromic properties of spirooxazines containing a permanent azo (hydrazone) chromophore*, *Dyes and Pigments*, **98**, 1, 263-272, (2013)

## Chapter 11 - References

- [1] P. Bamfield, *Chromic phenomena: technological applications of colour chemistry*, [Royal Society of Chemistry, Cambridge, 2001].
- [2] V. Pimienta, C. Froute, M.H. Deniel, D. Lavabre, R. Guglielmetti, J.C. Micheau, *Kinetic modeling of the photochromism and photodegradation of a spiro [indolinaphthoxazine]*, *Journal of Photochemistry and Photobiology A: Chemistry*, **122**, 3, 199-204 (1999).
- [3] C.J.C. Crano, R.J. Gugliemetti, *Organic photochromic and thermochromic compounds*, [Kluwer Academic/ Plenum Publishers, New York, 1999].
- [4] B.L. Feringa, *Molecular switches*, [Wiley-VCH, Weinheim, 2001].
- [5] H. Bouas-Laurent, H. Durr, *Organic photochromism (IUPAC technical report)*, *Pure and Applied Chemistry*, **73**, 4, 639-665 (2001).
- [6] M. Fritzsche, *Note sur les carbures d'hyfogene solides, tires du goudron de houille*, *Comptes Rendus de l'Academic des Sciences*, **64**, 1053 (1867).
- [7] E.t. Meer, *Ueber dinitroverbindungen der fettreihe*, *European Journal of Organic Chemistry*, **181**, 1, 1-22 (1876).
- [8] G.H. Brown, *Photochromism*, [Wiley, New York, 1971].
- [9] S.M. Burkinshaw, J. Griffiths, A.D. Towns, *Colour science '98. Vol. 1: Dye and pigment chemistry*, [University of Leeds, department of colour chemistry, Leeds, 1999].
- [10] P.M.S. Monk, *The viologens: Physiochemical properties, synthesis and applications of the salts of 4,4'-bipyridine*, [Wiley, Chichester, 1998].
- [11] X.D. Sun, M.G. Fan, X.J. Meng, E.T. Knobbe, *Acidichromic effects in spiro(1,3,3-trimethylindolo-2,3'-naphth[1,2-b]-1,4-oxazine)*, *Journal of Photochemistry and Photobiology A: Chemistry*, **102**, 2-3, 213-216 (1997).
- [12] V.C. Goncalves, D.T. Balogh, *Synthesis and characterization of a dye-functionalized polythiophene with different chromic properties*, *European Polymer Journal*, **42**, 12, 3303-3310 (2006).
- [13] M. Zagorska, I.K. Bajer, A. Pron, P. Raimond, F. Kajzar, A.J. Attias, *Polythiophenes functionalized with disperse red 1 chromophore*, *Synthetic Metals*, **102**, 1-3, 1141-1142 (1999).
- [14] G. Dufresne, J. Bouchard, M. Belletete, G. Durocher, M. Leclerc, *Thermochromic and solvatochromic conjugated polymers by design*, *Macromolecules*, **33**, 22, 8252-8257 (2000).



- [15] M. Leclerc, *Optical and electrochemical transducers based on functionalized conjugated polymers*, *Advanced Materials*, **11**, 18, 1491-1498 (1999).
- [16] Y.A. Son, Y.M. Park, M.S. Choi, S.H. Kim, *Synthesis of hetero-bi-functional dye having photochromism and electrochromism. part 1: Characteristics and its sensing properties*, *Dyes and Pigments*, **75**, 2, 279-282 (2007).
- [17] Y.A. Son, B.S. Kim, M.S. Choi, S.h. Kim, *Synthesis of hetero-bi-functional dye having photochromism and electrochromism*, *Dyes and Pigments*, **75**, 2, 283-286 (2007).
- [18] A.F. Acebes, J.M. Lehn, *Optical switching and fluorescence modulation in photochromic metal complexes*, *Advanced Materials*, **10**, 18, 1519-1522 (1998).
- [19] S. Fraysse, C. Coudret, J.P. Launay, *Synthesis and properties of dinuclear complexes with a photochromic bridge: an intervalence electron transfer switching "on" and "off"*, *European Journal of Inorganic Chemistry*, **2000**, 7, 1581-1590 (2000).
- [20] V.W.W. Yam, C.C. Ko, N. Zhu, *Photochromism and luminescence switching properties of a versatile diarylethene-containing 1,10-phenanthroline ligand and its rhenium(I) complex*, *Journal of American Chemical Society*, **126**, 40, 12734-12735 (2004).
- [21] P.J. Coelho, L.M. Carvalho, A. Mauricio, C. Fonseca, M. Manuela, M. Raposo, *Photochromic properties of thienylpyrrole azo dyes in solution*, *Tetrahedron Letters*, **47**, 22, 3711-3714 (2006).
- [22] V.Z. Shirinian, S.O. Besugliy, A.V. Metelitsa, M.M. Krayushkin, D.M. Nikalin, V.I. Minkin, *Novel photochromic spirocyclic compounds of thienopyrroline series: 1: Spiropyrans*, *Journal of Photochemistry and Photobiology A: Chemistry*, **189**, 2-3, 161-166 (2007).
- [23] I. Casades, S. Constantine, D. Cardin, H. Carcia, A. Gilbert, F. Marquez, *'Ship-in-a-bottle' synthesis and photochromism of spiropyrans encapsulated within zeolite Y supercages*, *Tetrahedron*, **56**, 36, 6951-6956 (2000).
- [24] C. Lee, J. Wang, A.T. Hu, *Microwave-assisted synthesis of photochromic spirooxazinr dyes under solvent-free condition*, *Materials Letters*, **58**, 3-4, 535-538 (2004).
- [25] T.F. Tan, P.L. Chen, H.M. Huang, J.B. Meng, *Synthesis, characterization and photochromic studies in film of heterocycle-containing spirooxaine*, *Tetrahedron*, **61**, 34, 8192-8198 (2005).

- [26] Y.A. Son, Y.M. Park, S.Y. Park, C.J. Shin, S.H. Kim, *Exhaustion studies of spiroxazine dye having reactive anchor on polyamide fibres and its photochromic properties*, *Dyes and Pigments*, **73**, 1, 76-80 (2007).
- [27] R.M. Christie, L.J. Chi, R.A. Spark, K.m. Morgan, A.S.F. Boyd, A. Lycka, *The application of molecular modeling techniques in the prediction of the photochromic behaviour of spiroindolinonaphthoxazines*, *Journal of Photochemistry and Photobiology A: Chemistry*, **169**, 1, 37-45 (2005).
- [28] H. Durr, H.B. Laurent, *Photochromism: molecules and systems*, [Elsevier, Amsterdam, 1990].
- [29] V.I. Minkin, *Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic compounds*, *Chemical Reviews*, **104**, 5, 2751 (2004).
- [30] S.O. Besugliy, A.V. Metelisa, V.Z. Shirinian, M.M. Krayushkin, D.M. Nikalin, V.I. Minkin, *Novel photochromic spirocyclic compounds of thienopyrroline series: 2. Spirooxazines*, *Journal of Photochemistry and Photobiology A: Chemistry*, **206**, 2-3, 116-123 (2009).
- [31] G. Berkovic, V. Krongauz, V. Weiss, *Spiropyrans and spirooxazines for memories and switches*, *Chemical Reviews*, **100**, 5, 1741-1754 (2000).
- [32] S.N. Corns, S.M. Partington, A.D. Towns, *Industrial organic photochromic dyes*, *Coloration Technology*, **125**, 5, 249-261 (2009).
- [33] V.G. Luchina, I.Y. Sychev, A.I. Shienok, N.L. Zaichenko, V.S. Marevtsev, *Photochromism of spironaphthooxazines having electron-donor substituents*, *Journal of Photochemistry and Photobiology A: Chemistry*, **93**, 2-3, 173-178 (1996).
- [34] K. Kurihara, K. Suzuki, *Theoretical understanding of an absorption-based surface plasmon resonance sensor based on Kretschmann's theory*, *Analytical Chemistry*, **74**, 3, 696-701 (2002).
- [35] H. Jir, *Surface plasmon resonance sensors: review*, *Sensors and Actuators B: Chemical*, **54**, 1-2, 3-15 (1999).
- [36] I. Pockrand, J.D. Swalen, J.G.G. II, M.R. Philpott, *Surface plasmon spectroscopy of organic monolayer assemblies*, *Surface Science*, **74**, 1, 237-244 (1978).
- [37] J. Biteau, F. Chaput, J.P. Boilot, *Photochromism of spiroxazine-doped gels*, *The Journal of Physical Chemistry*, **100**, 21, 9024-9031 (1996).
- [38] G. Park, S.W. Choi, J.H. Kim, S.H. Kim, S.P. Keum, K. Koh, *Formation of photo-functional spiroxazine monolayers and their dielectric constant determination using surface plasmon resonance*, *Microchemical Journal*, **80**, 2, 207-211 (2005).

- [39] R.S. Becker, J. Michl, *Photochromism of synthetic and naturally occurring 2H-Chromenes and 2H-pyrans*, Journal of American Chemical Society, **88**, 24, 5931-5933 (1966).
- [40] C. Lenoble, R.S. Becker, *Photophysics, photochemistry and kinetics of photochromic 2H-pyran and chromenes*, Journal of Photochemistry and Photobiology A: Chemistry, **33**, 2, 187-197 (1986).
- [41] B.V. Gemert, A. Kumar, D.B. Knowles, *Naphthopyrans. Structural features and photochromic properties*, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, **297**, 1, 131-138 (1997).
- [42] A. Kumar, *The relationship between the structure and the absorption spectra of naphtho[2, 1-B] pyran*, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, **297**, 1, 139-145 (1997).
- [43] B.V. Gemert, M.P. Bergomi. Photochromic naphthopyran compounds. Patent. United States. 5,066,818. (1991).
- [44] D.B. Knowles. Photochromic naphthopyrans. Patent. United States. 5,238,981. (1993).
- [45] L. Chen, G. Wang, X. Zhao, *A fluorescence switch based on a controllable photochromic naphthopyran group*, Journal of Luminescence, **131**, 8, 1617-1620 (2011).
- [46] J.C. Crano, T. Flood, D. Knowles, A. Kumar, B.V. Gemert, *Photochromic compounds: Chemistry and application in ophthalmic lenses*, Pure and Applied Chemistry, **68**, 7, 1395-1398 (1996).
- [47] H. Durr, H. Bouas-Laurent, *Photochromism: molecules and systems*, [Elsevier, Amsterdam, 1990].
- [48] M. Irie, *Diarylethenes for memories and switches*, Chemical Reviews, **100**, 5, 1685-1716 (2000).
- [49] H. Stobbe, *A product of the action of light on diphenylfulgide and the polymerization of phenylpropionic acid*, European Journal of Inorganic Chemistry, **40**, 3, 3372-3382 (1907).
- [50] D. Chem, G. Hauck, H. Durr, *1,8a-dihydroindolizines as compounds of novel photochromic systems*, Angewandte Chemie International Edition, **18**, 12, 945-946 (1979).

- [51] D.H. Waldeck, *Photoisomerization dynamics of stilbenes*, Chemical Reviews, **91**, 3, 415-436 (1991).
- [52] G.S. Kumar, *Photochemistry of azobenzene-containing polymers*, Chemical Reviews, **89**, 8, 1915-1925 (1989).
- [53] H.G. Heller, S. Oliver, *Photochromic heterocyclic fulgides. Part 1. Rearrangement reactions of (E)- $\alpha$ -3-furylethylidene(isopropylidene)succinnic anhydride*, Journal of the Chemical Society: Perkin Transactions 1, 197-201 (1981).
- [54] Y. Yokoyama, *Fulgides for memories and switches*, Chemical Reviews, **100**, 5, 1717-1740 (2000).
- [55] M.V. Alfimov, O.A. Fedorova, S.P. Gromov, *Photoswitchable molecular receptors*, Journal of Photochemistry and Photobiology A: Chemistry, **158**, 2-3, 183-198 (2003).
- [56] R. Ramos-Garcia, R. Delgado-Macuil, D. Iturbe-Castillo, E.G.D.L. Santos, F.S. Corral, *Polarization dependance on the holographic recording in spiropyran-doped polymers*, Optical and Quantum Electronics, **35**, 6, 641-650 (2003).
- [57] Y. Huang, W. Liang, J.K.S. Poon, Y. Xu, R.K. lee, A. Yariv, *Spiro-oxazine photochromic fibre optical switch*, Applied Physics Letters, **88**, 18, 1102- (2006).
- [58] D.A. Foucher, R.D. Patel, N. Chopra, P.M. Kazmaier, J. Wojtyk, E. Buncel. *Photochromic electrophoretic ink display*. Patent. United States. 6,517,618. (2003).
- [59] <http://www.orionprint.com/SecurityFeatures/>. 03/10/2011.
- [60] <http://www.securityprinting.co.uk/security-inks.php>. 03-10-2011.
- [61] S. Kawata, Y. Kawata, *Three-dimensional optical data storage using photochromic materials*, Chemical Reviews, **100**, 5, 1777-1788 (2000).
- [62] J. Chaiken, R.R. Birge. *Photochromic materials suitable for cosmetic and sunblocking effects*. Patent. United States. 6,461,594. (2002).
- [63] R. Kolodziej, N. Soistier, J.C. Simon. *Cosmetic composition containing a photochromic colouring agent and its use for skin and/or skin appendage make-up and/or care*. Patent. United States. 7,776,316. (2010).
- [64] L. Theisen. *Thermochromic/photochromic cosmetic compositions*. Patent. United States. 7,022,331. (2006).
- [65] A.J. Myles, N.R. Branda, *1,2-Dithienylethene photochromes and non-destructive erasable memory*, Advanced Functional Materials, **12**, 3, 167-173 (2002).
- [66] M. Irie, *Diarylethenes for memories and swithes*, Chemical Reviews, **100**, 5, 1685-1716 (2000).

- [67] F.M. Raymo, M. Tomasulo, *Electron and energy transfer modulation with photochromic switches*, Chemical Society Reviews, **34**, 4, 327-336 (2005).
- [68] G. Zou, H. Jiang, H. Kohn, T. Manaka, M. Iwamoto, *Control and modulation of chirality for azobenzene-substituted polydiacetylene LB film with circularly polarized light*, Chemical Communications, 37, 5627-5629 (2009).
- [69] C.W. Lee, Y.H. Song, Y. Lee, K.S. Ryu, K.W. Chi, *Reversible photochromic switch ensemble and its photoimaging using H\* transfer between spyropyrans and fluorescein in a polymer matrix*, Chemical Communications, 17, 6282-6284 (2009).
- [70] J.D. Winkler, C.M. Bowen, V. Michelet, *Photodynamic fluorescent metal ion sensors with parts per billion sensitivity*, Journal of American Chemical Society, **120**, 13, 3237-3242 (1998).
- [71] C.J. Barrett, J.I. Mamiya, K.G. Yager, T. Ikeda, *Photo-mechanical effects in azobenzene-containing soft materials*, Soft Matter, **3**, 10, 1249-1261 (2007).
- [72] Y. Zhao, J. He, *Azobenzene-containing block copolymers: the interplay of light and morphology enables new functions*, Soft Matter, **5**, 14, 2686-2693 (2009).
- [73] S. Kumar, D.L. Watkins, T. Fujiwara, *A tailored spirooxazine dimer as a photoswitchable binding tool*, Chemical Communications, 29, 4369-4371 (2009).
- [74] S. Wang, W. Shen, Y. Feng, H. Tian, *A multiple switching bisthiénylene and its photochromic fluorescent organogelator*, Chemical Communications, 14, 1497-1499 (2006).
- [75] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Organic chemistry: A digital fluorescent molecular photoswitch*, Nature, **420**, 6917, 759-760 (2002).
- [76] S.J. Lim, B.K. An, S.Y. Park, *Bistable photoswitching in the film of fluorescent photochromic polymer: enhanced fluorescence emission and its high contrast switching* Macromolecules, **38**, 15, 6236-6239 (2005).
- [77] M. Bossi, V. Belov, S. Polyakova, S.W. Hell, *Reversible red fluorescent molecular switches*, Angewandte Chemie International Edition, **45**, 44, 7462-7465 (2006).
- [78] T.A. Golovkova, D.V. Kozlov, D.C. Neckers, *Synthesis and properties of novel fluorescent switches*, Journal of Organic Chemistry, **70**, 14, 5545-5549 (2005).
- [79] E.J. Harbron, D.A. Vicente, D.H. Hadley, M.R. Imm, *Phototriggered fluorescence color changes in azobenzene-functionalized conjugated polymers*, Journal of Physics Chemistry A, **109**, 48, 10846-10853 (2005).
- [80] I.S. Park, E.J. Heo, J.M. Kim, *A photochromic phenoxyquinone based cyanide ion sensor*, Tetrahedron Letters, **52**, 19, 2454-2457 (2011).

- [81] A. Zahavy, S. Rubin, I. willner, *Conformational dynamics associated with photoswitchable binding of spiropyran-modified concanavalin a*, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals **246**, 1, 195-199 (1994).
- [82] T.B. Norsten, N.R. Branda, *Axially coordinated porphyrinic photochromes for non-destructive information processing*, Advanced Materials, **13**, 5, 347-349 (2001).
- [83] G.M. Tsivgoulis, J.M. Lehn, *Photonic molecular devices: reversibly photoswitchable fluorophores for nondestructive readout for optical memory*, Angewandte Chemie International Edition in English, **34**, 10, 1119-1122 (1995).
- [84] L. Giordano, T.M. Jovin, M. Irie, E.A.J. Erijman, *Diheteroarylethenes as thermally stable photoswitchable acceptors in photochromic fluorescence resonance energy transfer (pcFRET)*, Journal of American Chemical Society, **124**, 25, 7481-7489 (2002).
- [85] Z. Hu, Q. Zhang, M. Xue, Q. Sheng, Y. Liu, *Spirobenzopyran-based photochromic nanohybrids with photoswitchable fluorescence*, Optical Materials, **30**, 6, 851-856 (2008).
- [86] M. Irie, *Photochromism: memories and switches introduction*, Chemical Reviews, **100**, 5, 1683-1684 (2000).
- [87] S. Kawata, Y. kawata, *Three-dmensional optical data storage using photochromic materials*, Chemical Reviews, **100**, 5, 1777-1788 (2000).
- [88] C.Q. Huang, Y. Wang, C.Y. Hong, C.Y. Pan, *Spiropyran-based polymeric vesicles: Preparation and photochromic properties*, Macromolecular Rapid Communications, **32**, 15, 1174-1179 (2011).
- [89] M. Irie, S. Kobatake, M. Horichi, *Reversible surface morphology changes of a photochromic diarylethene single crystal by photoirradiation*, Science, **291**, 5509, 1769-1772 (2001).
- [90] H. Tian, S. Wang, *Photochromic bisthenylethene as multi-function switches*, Chemical Communications, 8, 781-792 (2007).
- [91] Q. Zou, J. Jin, B. Xu, L. Ding, H. Tian, *New photochromic chemosensors for Hg<sup>2+</sup> and F<sup>-</sup>*, Tetrahedron, **67**, 5, 915-921 (2011).
- [92] C.C. Corredor, Z.L. Huang, K.D. Felfield, *Two-photon 3D optical data storage via fluorescence modulation of an efficient fluorene dye by photochromic diarylethene*, Advanced Materials, **18**, 21, 2910-2914 (2006).
- [93] K. Matsuda, *Photochromic diarylethene as an information processing unit: Magnetic and electric switching*, Pure and Applied Chemistry, **80**, 3, 555-561 (2008).

- [94] Z. Walsh, S. Scarmagnani, F.B. Lopez, S. Abele, F.Q. Nie, C. Slater, R. Byrne, D. Diamond, B. Paull, M. Macka, *Photochromic spiropyran monolithic polymer: Molecular Photo-controllable electroosmotic pumps for micro-fluidic devices*, *Sensors and Actuators B: Chemical*, **148**, 2, 569-576 (2010).
- [95] K. Ock, N. Jo, S. Kim, K. Koh, *Thin film optical waveguide type sensor using a photochromic molecule device, spirooxazine*, *Synthetic Metals*, **117**, 1-3, 131-133 (2001).
- [96] S. Wang, M.S. Choi, S.H. Kim, *Multiple switching photochromic poly(N-isopropylacrylamide) with spironaphthoxazine hydrogel*, *Dyes and Pigments*, **78**, 1, 8-14 (2008).
- [97] S. Wang, M.S. Choi, S.H. Kim, *Bistable photoswitching in poly(N-isopropylacrylamide) with spironaphthoxazine hydrogel for optical data storage*, *Journal of Photochemistry and Photobiology A: Chemistry*, **198**, 1, 150-155 (2008).
- [98] P.Y. Wang, C.J. Wu, *Photochromic behaviour of some phenoxanthraquinone dyes in solution and on polyester substrate*, *Dyes and Pigments*, **35**, 3, 279-288 (1997).
- [99] S.J. Lee, Y.A. Son, H.J. Suh, D.N. Lee, S.H. Kim, *Preliminary exhaustion studies of spiroxazine dyes on polyamide fibers and their photochromic properties*, *Dyes and Pigments*, **69**, 1-2, 18-21 (2006).
- [100] S.M.R. Billah, R.M. Christie, K.M. Morgan, *Direct coloration of textiles with photochromic dyes. Part 2: The effect of solvents on the colour change of photochromic textiles*, *Coloration Technology*, **124**, 4, 229-233 (2008).
- [101] S.M.R. Billah, R.M. Christie, R. Shamey, *Direct coloration of textiles with photochromic dyes. Part 1: Application of spiroindolinonaphthoxazines as disperse dyes to polyester, nylon and acrylic fabrics*, *Coloration Technology*, **124**, 4, 223-228 (2008).
- [102] A.F. Little, R.M. Christie, *Textile applications of photochromic dyes. Part 2: factors affecting the photocolouration of textiles screen-printed with commercial photochromic dyes*, *Coloration Technology*, **126**, 3, 164-170 (2010).
- [103] A.F. Little, R.M. Christie, *Textiles application of photochromic dyes. Part 1: Establishment of a methodology for evaluation of photochromic textiles using traditional colour measurement instrumentation*, *Coloration Technology*, **126**, 3, 157-163 (2010).
- [104] A.F. Little, R.M. Christie, *Textile applications of photochromic dyes. Part 3: factors affecting the technical performance of textiles screen-printed with commercial photochromic dyes*, *Coloration Technology*, **127**, 5, 275-281 (2011).

- [105] Y.-r.H.-C. Hwu, TW), Bai, Chi-chung (Hsin-Chu, TW), Tao, Li-chang (Hsin-Chu, TW), Luo, Der-guey (Hsin-Chu, TW), Hu, Andrew T. (Hsin-Chu, TW). Method of making synthetic fibers containing photochromic pigment. United States. (1993).
- [106] J. Oakes, *Photofading of textile dyes*, Review of Progress in Coloration and Related Topics, **31**, 1, 21-28 (2001).
- [107] S.N. Batchelor, D. Carr, C.E. Coleman, L. Fairclough, A. Jarvis, *The photofading mechanism of commercial reactive dyes on cotton*, Dyes and Pigments, **59**, 3, 269-275 (2003).
- [108] G. Baillet, M. Campredon, R. Guglielmetti, G. Giusti, C. Aubert, *Dealkylation of N-substituted indolinospironaphthoxazine photochromic compounds under UV irradiation*, Journal of Photochemistry and Photobiology A: Chemistry, **83**, 2, 147-151 (1994).
- [109] G. Baillet, G. Giusti, R. Guglielmetti, *Comparative photodegradation study between spiro[indolin-oxazine] and spiro[indoline-pyran] derivatives in solution*, Journal of Photochemistry and Photobiology A: Chemistry, **70**, 2, 157-161 (1993).
- [110] V. Malatesta, M. Milosa, R. Millini, L. Lanzini, P. Bortolus, S. Monti, *Oxidative degradation of organic photochromes*, Molecular Crystals and Liquid Crystals, **246**, 1, 303-310 (1994).
- [111] C. Salemi, G. Giusti, R. Guglielmetti, *DABCO effect on the photodegradation of photochromic compounds in spiro[indoline-pyran] and spiro[indoline-oxazine] series*, Journal of Photochemistry and Photobiology A: Chemistry, **86**, 1-3, 247-252 (1995).
- [112] X.L. Jinliang, L.Y. Wang, T. Matsuura, J. Meng, *Synthesis of functionalized spiropyran and spirooxazine derivatives and their photochromic properties*, Journal of Photochemistry and Photobiology A: Chemistry, **161**, 2-3, 201-213 (2004).
- [113] A. Johnson, *The theory of coloration of textiles*, [Society of Dyers and Colourists, Bradford, 1989].
- [114] A.D. Broadbent, *Basic principles of Textiles Coloration*, [Society of Dyers and Colourists, Bradford, 2001].
- [115] E.R. Trotman, *Dyeing and chemical technology of textile fibres* 6th ed, [Charles Griffin & Company LTD, Nottingham, 1984].
- [116] S. Rosenbaum, *Temperature dependance of dye diffusion*, Journal of Polymer Science Part A: Polymer Chemistry, **3**, 5, 1949-1958 (1965).
- [117] W. Ingamells, R.H. Peters, S.R. Thornton, *The mechanism of carrier dyeing*, Journal of Applied Polymer Science, **17**, 12, 3733-3746 (1973).
- [118] R. Knight, *Intoductory physical chemistry*, [Prentice Hall, London, 1970].



- [119] R.H. Peters, *Textile chemistry*, [Elsevier, New York, 1975].
- [120] G.E. Krichevskii, *Chemical engineering of textile materials*, [Ros. Zaoch. In-t Tekst. Leg. Prom-sti, Moscow, 2001].
- [121] O.V. Romankevich, Y.V. Red'ko, *Adsorption isotherm of a disperse dye*, *Fibre Chemistry*, **38**, 2, 155-157 (2006).
- [122] D. Patterson, R.P. Sheldon, *The dyeing of polyester fibres with disperse dyes. Mechanism and kinetics of the process for purified dyes*, *Transactions of the Faraday Society*, **55**, 1254-1264 (1959).
- [123] A.S. Fern, H.R. Hadfield, *The dyeing of mixture of terylene polyester fibre and wool*, *Journal of The Society of Dyers and Colourists*, **71**, 6, 277-282 (1955).
- [124] D. Balmforth, C.A. Bowers, J.W. Bullington, T.H. Guion, T.S. Roberts, *Equilibrium studies on the dyeing of polyester fibre with disperse dyes in the presence of carriers*, *Journal of The Society of Dyers and Colourists*, **82**, 11, 405-409 (1966).
- [125] W.C. Ingamells, *Important concepts in the dyeing and finishing of man-made fibres*, *Journal of The Society of Dyers and Colourists*, **96**, 9, 466-474 (1980).
- [126] <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>.  
07/09/2011.
- [127] F.M. Rawicz, D.M. Cates, H.A. Rutherford, *The swelling action of carriers in dyeing polyethylene terephthalate fibre*, *American dyestuff Reporter*, **50**, 320-323 (1961).
- [128] H. Fujita, A. Kishimoto, *Diffusion-controlled stress relaxation in polymers.II. Stress relaxation in swollen polymers*, *Journal of Polymer Science Part A: Polymer Chemistry*, **28**, 118, 547-567 (1958).
- [129] M.K. Gokhale, L. petees, C.B. Stevens, *Dyeing hydrophobic fibres in solutions of solvents*, *Journal of The Society of Dyers and colourists*, **74**, 4, 236-241 (1958).
- [130] S.R. Shukla, R.V. Hundekar, A.N. Saligram, *Solvent assisted dyeing of acrylic fibres. Part 2-dyeing with disperse and cationic dyes*, *Journal of The Society of Dyers and Colourists*, **107**, 12, 463-465 (1991).
- [131] O. Glenz, W. Beckmann, W. Wulder, *The mechanism of the dyeing of polyester fibres with disperse dyes*, *Journal of The Society of Dyers and Colourists*, **75**, 3, 141-147 (1959).
- [132] W. Ingamells, A. Yabani, *The swelling and plasticization of poly(ethylene terephthalate) during carrier dyeing*, *Journal of The Society of Dyers and Colourists*, **93**, 11, 417-423 (1977).

- [133] Z. Gur-Arieh, W. Ingamells, R.H. Peters, *The effect of plasticizing compounds on acrylic fibres*, Journal of Applied Polymer Science, **20**, 1, 41-54 (1976).
- [134] D. Brunnschweiler, *Polyester: 50 years of achievement: tomorrow's ideas and profits* [Textile Institute, Manchester, 1993].
- [135] A. Murray, K. Mortimer, *Carrier dyeing*, Review of Progress in Coloration and Related Topics, **2**, 1, 67-72 (1971).
- [136] D. Aitken, S.M. Burkinshaw, *The effect of carrier on the dyeing of courtell S*, Journal of The Society of Dyers and colourists, **108**, 4, 219-225 (1992).
- [137] W. Ingamells, K.V. Narasimham, *The effect of benzyl alcohol on the physical and dyeing properties of poly(ethylene terephthalate) filaments*, Journal of The Society of Dyers and Colurists, **93**, 8, 306-312 (1977).
- [138] W. Ingamells, A. Yabani, *The swelling and plesticization of poly(ethylene terephthalate) during carrier dyeing*, Journal of The Society of Dyers and Colurists, **93**, 11, (1977).
- [139] S.R. Shukla, M.R. Mathur, *Dyeing of solvent-pretreated polyesters*, Journal of The Society of Dyers and colourists, **113**, 5-6, 178-181 (1997).
- [140] S.M. Burkinshaw, *Chemical principles of synthetic fibre dyeing*, [Blackie Academic & Professional, Glasgow, 1995].
- [141] E. Merian, J. Carbonell, U. Lerch, V. Sanahuja, *The saturation values, rates of dyeing, rates of diffusion, and migration of disperse dyes on heat-set polyester fibres*, Journal of The Society of Dyers and Colourists, **79**, 11, 505-515 (1963).
- [142] S.V. Kulkarni, A.L. Blackard, C.D. Blackwell, C.W. Stackhouse, M.W. Alexander, *Textile dyeing operations: chemistry, equipment, procedures, and environmental aspects*, Acta Polymerica, **38**, 2, 160 (1987).
- [143] J. Shore, *Cellulosic Dyeing*, [Society of Dyers and Colourists, Bradford, 1995].
- [144] BASF, *Manual: Sizing, pretreatment and dyeing of cellulosic fibres*, [B.A.S.F, Ludwigshafen, 1979].
- [145] J. Bouloton, T.H. Morton, *The dyeing of cellulosic materials: A review of the physics and chemistry of the dyeing process*, Journal of The Society of Dyers and Colourists, **56**, 4, 145-159 (1940).
- [146] <http://list.emich.edu/~dyers/pdfs/dyeglossary.PDF>. 14/09/2011.
- [147] R.M. Christie, R.R. Mather, R.H. Wardman, *The chemistry of colour application*, [Blackwell Science, Oxford, 2000].
- [148] R.M. Christie, *Colour Chemistry*, [Royal Society of Chemistry, London, 2001].

- [149] J. Hubner, H.B. Avery, *Dyeing from different solvents*, Journal of The Society of Dyers and Colourists, **28**, 9, 280-286 (1912).
- [150] W. Furness, J. Rayment, *Some practical experiences in solvent dyeing*, Journal of The Society of Dyers and Colourists, **87**, 12, 514-520 (1971).
- [151] Z. Morita, R. Kobayashi, K. Uchimura, H. Motomura, *Fundamental studies on solvent dyeing with tetrachloroethylene. I. Diffusion of disperse dyes in poly(ethylene terephthalate)*, Journal of Applied Polymer Science, **19**, 4, 1095-1102 (1975).
- [152] W. Kothe, *Textile solvent technology update*, AACTT Symposium, **73**, 127-134 (1973).
- [153] K. Gerbert, *The dyeing of polyester textile fabric in perchloroethylene by the exhaust process*, Journal of The Society of Dyers and Colourists, **87**, 12, 509-513 (1971).
- [154] R.B. Love, *The use of Non-aqueous solvent in dyeing I - Dyeing polyester fibre by the dacsol process*, Journal of The Society of Dyers and Colourists, **94**, 10, 440-447 (1978).
- [155] W.C. Ingamells, M.N. Thomas, *The mechanism of carrier dyeing*, Textile Chemist and Colorist, **16**, 3, 55-60 (1984).
- [156] F.O. Harris, T.H. Guion, *A new approach to solvent dyeing with non-ionic dyes*, Textile Research Journal, **42**, 10, 626-627 (1972).
- [157] R.F. Blanks, J.M. Prausnitz, *Thermodynamics of polymer solubility in polar and nonpolar systems*, Industrial and Engineering Chemistry Fundamentals, **3**, 1, 1-8 (1964).
- [158] C.J. Bent, T.D. Flynn, H.H. Sumner, *A new insight into the thermofix dyeing of polyester-cellulose blends. I-investigation of mechanism of transfer of disperse dyes*, Journal of The Society of Dyers and Colourists, **85**, 12, 606-613 (1969).
- [159] G. Wolfrum, R. Neef, W. Kruckenberg. Continuous dyeing of polyester fibres with azo dyestuffs soluble in water-immiscible halogenated hydrocarbons. Patent. United states. 3,775,049. (1973).
- [160] L.W.C. Miles, *Textile printing*, Revised second edition ed, [Society of Dyers and Colourists, Manchester, 2003].
- [161] J.W. Blease, R.P. Szajewski. Glycerol derivatives for inkjet inks. Patent. United States. 7,442,245. (2008).
- [162] H. Ujiie, *Digital printing of textiles*, [Woodhead, Cambridge, 2006].
- [163] L. Rayleigh, *On the instability of jets*, London Mathematical Society, **s1-10**, 1, 4-13 (1878).
- [164] C.W. Hansell. Recorder. United States. (1933).

- [165] T.L. Dawson, *Ink jet printing of textiles - An overview of its development and the principles behind ink drop formation and deposition*, Journal of The Society of Dyers and Colourists, **51**, 10, 75-82 (2004).
- [166] M. Taniguchi. Method for ink jet printing, ink jet printing ink, and pretreatment agent. Patent. Japan. 2004162247. (2004).
- [167] H. Yanagihara. Ink composition for ink-jet printing, printing method and printed fabric. Patent. Japan. 2004210806. (2004).
- [168] K. Siemensmeyer, J.R. Provost, F.W. Raulfs, J. Weiser, Thermodynamics of the digital transfer printing process, Image Science & Technology NIP 17 Digital Printing Conference, The Society for Imaging Science and Technology, Fort Lauderdale, Florida, 2001, pp. 426-430.
- [169] S.N. Chevli. Disperse dye black ink. Patent. United States. 7,211,130. (2007).
- [170] S.N. Chevli. Inkjet ink set. Patent. United States. 7,223,300. (2007).
- [171] S. Saibara, S. aoyama, T. Taki. Dispersion ink. Patent. United States. 6,099,627. (2000).
- [172] J.H. Xim, *Total colour management in textiles*, [Woodhead, Cambridge, 2006].
- [173] R. McDonald, *Colour physics for industry*, second ed, [Society of Dyers and Colourists, Bradford, 1997].
- [174] D. Dilaura, K. Houser, R. Mistrick, G. Staffy, *The IES lighting handbook*, 10<sup>th</sup> ed, [Illuminating Engineering Society, New York, 2011].
- [175] J. Schanda, *Colorimetry: understanding the CIE system*, [John Wiley & Sons, New Jersey, 2007].
- [176] K. Nassau, *The physics and chemistry of color*, [John Wiley & Sons, New York, 1983].
- [177] G.T. Yonemura, *Opponent-color-theory treatment of the CIE 1960 (u,v) diagram: chromaticness difference and constant hue loci*, Journal of the Optical Society of America, **60**, 10, 1407-1409 (1970).
- [178] <http://www.cie.co.at/>. 03-11-2011.
- [179] S.R. Cockett, *Dyeing and Printing*, [Pitman, London, 1964].
- [180] British Standard 1006: 1990, "British standard methods of test for colour fastness of textiles and leather", Group B02 Colour fastness to artificial light: Xenon arc fading lamp test, British Standard Institution, Milton Keynes, UK, 1990.
- [181] British Standard 1006: 1990, "British standard methods of test for colour fastness of textiles and leather", Group C Colour fastness to washing and laundering, British Standard Institution, Milton Keynes, UK, 1990.

- [182] <http://www.dyes.co.uk/disperse-dyes-application.html>. 20-02-2013.
- [183] S. Delbaere, B. Luccioni-Houze, C. Bochu, Y. Teral, M. Campredon, G. Vermeesch, *Kinetic and structural studies of the photochromic process of 3H-naphthopyrans by UV and NMR spectroscopy*, Journal of Chemical Society, Perkin Transactions, **2**, (1998).
- [184] S. Delbaere, J. Micheau, G. Vermeesch, *NMR Kinetic investigations of the photochemical and thermal reactions of a photochromic chromene*, Journal of Organic Chemistry, **68**, 23, 8968-8973 (2003).
- [185] S. Delbaere, G. Vermeesch, *NMR characterization of allenyl-naphthol in photochromic process of 3, 3-diphenyl-[3H]-naphthol[2-1,b]pyran*, Journal of Photochemistry and Photobiology A: Chemistry, **159**, 3, 227-232 (2003).
- [186] A.F. Little, *An investigation into textile applications of photochromic dyes*. PhD Thesis. School of Textiles and Design. Heriot-Watt University. Edinburgh. 2008.
- [187] <http://www.specialchem4adhesives.com/tc/uv-light-stabilizers/index.aspx?id=hals>. 23-02-2013.
- [188] M. McCusker, *A UVA/HALS primer: Everything you've ever wanted to know about light stabilizers-part II*, Metal Finishing, **97**, 6, 83-86 (1999).
- [189] J. Pospisil, S. Nespurek, *Photostabilization of coatings. Mechanisms and performance*, Progress in Polymer Science, **25**, 9, 1261-1335 (2000).
- [190] W. Ingamells, A.M. Yabani, *The effect of carriers on drawn poly(ethylene terephthalate) filaments*, Journal of Applied Polymer Science, **22**, 6, 1583-1592 (1978).
- [191] C.D. Shah, D.K. Jain, *Solvent (perchloroethylene) dyeing of disperse dyes on polyester*, Textile Research Journal, **55**, 1, 23-27 (1985).
- [192] S.A. Siddiqui, H.L. Needles, *Studies of solvent dyeing part II: solvent dyeing behavior of new disperse dyes on polyethylene terephthalate fiber*, Textile Research Journal, **52**, 6, 403-411 (1982).
- [193] W.S. Pkmkins, D.M. Hall, *A fundamental study of the sorption from trichloroethelene of three disperse dyes on polyester*, Textile Research Journal, **43**, 2, 115-120 (1973).
- [194] L.E. Fletcher, *Potential replacements for solvents that are ozone depleting substances*, [DSTO Aeronautical and Maritime Research Laboratory, Melbourne Victoria, 1994].
- [195] C.M. Hansen, *Hansen solubility parameters, A user's Handbook*, 2nd ed, [CRC Press, Boca Raton, 2007].

- [196] B. Mangovska, D. Burevski, G. Petrov, *Mechanism of dye diffusion in polyester yarns treated in mixtures of solvents*, Bulletin of the Chemists and Technologists of Macedonia, **14**, 1, 7-12 (1995).
- [197] H.C. Alexander, W.M. McCarty, E.A. Bartlett, *Toxicity of perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride to fathead minnows*, Bulletin of Environmental Contamination and Toxicology, **20**, 1, 344-353 (1978).
- [198] G. Such, R.A. Evans, L.H. Yee, T.P. Davis, *Factors influencing photochromism of spiro-compounds within polymeric matrices*, Journal of Macromolecular Science, Part C, **43**, 4, 547-579 (2003).
- [199] A. Dehghani, F. Jahanshah, D. Borman, K. Dennis, J. Wang, *Design and engineering challenges for digital ink-jet printing on textiles*, International Journal of Clothing Science and Technology, **16**, 1-2, 262-273 (2004).
- [200] T.L. Dawson, H. Ellis, *Will ink jets ever replace screens for textile printing?*, Journal of The Society of Dyers and colourists, **110**, 10, 331-337 (1994).
- [201] A.L. Eckman, S. Writer, *Developments in textile inkjet printing*, AATCC Review, **4**, 8, 12-15 (2004).
- [202] C. Zhang, K. Fang, *Surface modification of polyester fabrics for inkjet printing with atmospheric-pressure Air/Ar plasma*, Surface & Coatings Technology, **203**, 2058-2063 (2009).
- [203] C.H. Xue, M.M. Shi, H.Z. Chen, G. Wu, M. Wang, *Preparation and application of nanoscale microemulsion as binder for fabric inkjet printing*, Colloids and Surfaces, **287**, 1-3, 147-152 (2006).
- [204] S. Noppakundilokrat, P. Buranagul, W. Graisuwan, C. Koopipat, S. Kiatkamjornwong, *Modified chitosan pretreatment of polyester fabric for printing by ink jet ink*, Carbohydrate Polymers, **82**, 4, 1124-1135 (2010).
- [205] S. Leelajariyakul, H. Noguchi, S. Kiatkamjornwong, *Surface-modified and micro-encapsulates pigmented inkf for ink jet printing on textile fabrics*, Progress in Organic Coatings, **62**, 2, 145-161 (2008).
- [206] [http://www.wolframalpha.com/entities/chemicals/dowanol\\_dpm/iy/kp/wo/](http://www.wolframalpha.com/entities/chemicals/dowanol_dpm/iy/kp/wo/). 28-12-2011.
- [207] [http://www.wolframalpha.com/entities/chemicals/triethylene\\_glycol\\_monomethyl\\_ether/le/dh/9k/](http://www.wolframalpha.com/entities/chemicals/triethylene_glycol_monomethyl_ether/le/dh/9k/). 28-12-2011.
- [208] M.S. Cruz, L.D.A. Chumpitaz, J. Guilherme, *Kinematic viscosities of poly(ethylene glycols)*, Journal of Chemical and Engineering Data, **45**, 1, 61-63 (1999).

- [209] A.G. Abuin, D.G. Diaz, J.M. Navaza, I.V. Tato, *Surface tension of aqueous solutions of short n-alkyl-2-pyrrolidinones*, Journal of Chemical and Engineering Data, **53**, 11, 2671-2674 (2008).
- [210] <http://www.epa.gov/dfepubs/pwb/ctsa/appc/appc-2.pdf>. 17-12-2011.
- [211] <http://www.sigmaaldrich.com/chemistry/solvents/2propanol-center.html>. 17-12-2011.
- [212] G. Vazquez, E. Alvarez, J.M. Navaza, *Surface tension of Alcohol water + water from 20 to 50 .degree. C*, Journal of Chemical and Engineering Data, **40**, 3, 611-614 (1995).
- [213] <http://www.sigmaaldrich.com/chemistry/solvents/dichloromethane-center/physical-properties.html>. 17-12-2011.
- [214] E.G. Lee, M. Harper, R.B. Bowen, J. Slaven, *Evaluation of COSHH essentials: methylene chloride, Isopropanol and acetone exposures in a small printing plant*, The Annals of Occupational Hygiene, **53**, 5, 463-474 (2009).
- [215] [http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/General\\_Information/polymer\\_solutions.Par.0001.File.tmp/polymer\\_solutions.pdf](http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/General_Information/polymer_solutions.Par.0001.File.tmp/polymer_solutions.pdf). 27-01-2012.
- [216] M. Vikova, *Photochromic Textiles*. PhD thesis. School of Textiles and Design. Heriot-Watt University. Edinburgh. 2011.
- [217] M. Vik, M. Vikova. Equipment for monitoring of dynamism of irradiation and decay phase of photochromic substances. Patent. Czech Republic. PV 2007/858 PS3546CZ. (2007).
- [218] L.G. Torres, A. Velasquez, M.A. Brito-Arias, *Ca-alginate spheres behavior in presence of some solvents and water-solvent mixtures*, Advances in Bioscience and Biotechnology, **2**, 8-12 (2011).
- [219] <http://www.chemical-ecology.net/java/solvents.htm>. 12-04-2012.
- [220] AATCC Test Method, Colourfastness to light: AATCC technical manual, 2000.
- [221] Japanese Industrial Standard L0841: "Test Methods for colour fastness to daylight", Japanese Industrial Standard Association, Tokyo, Japan, 2004.
- [222] R.H. Ricketts, *The rates of fading of the S.D.C. light fastness standards (B. S. 1006)*, Journal of the Society of Dyers and Colourists, **68**, 6, 200-203 (1952).
- [223] S.M. Jaeckel, C.D. Ward, D.M. Hutchings, *Variations in assessment of light fastness and in rates of fading and spacing of the blue standards*, Journal of the Society of Dyers and Colourists, **79**, 12, 702-722 (1963).



- [224] F.W. Lindley, M.P. Harris, *Rate of fading of British dyed-wool light fastness standards in daylight*, Journal of the Society of Dyers and Colourists, **78**, 5, 231-233 (1961).
- [225] H. Hattori, K. Yoshizumi, P.C. Crews, *Wavelength sensitivity of AATCC blue wool lightfastness standards under light radiation*, Dyes and Pigments, **92**, 3, 936-941 (2012).
- [226] K. Hunger, *Industrial dyes. Chemistry, properties, applications*, [WILEY-VCH, Kelkheim, 2003].
- [227] C.S. Marvel, P.K. Porter, *2-naphthol, 1-nitroso-*, Organic Synthesis Collective, **1**, 411 (1941).
- [228] B. Osterby, R.B. McKelvey, L. Hill, *Photochromic sunglasses: A patent-based advanced organic and demonstration*, Journal of Chemical Education, **86**, 5, 424-425 (1991).
- [229] Y. Liu, M. Fan, C. Zhang, W. Yang, L. Zhu, G. Zhang, Z. Shuai, J. Zhou, W. Yan, H. Fu, J. Yao, *Waterchromism of protonated photomerocyanine dye*, Dyes and Pigments, **76**, 1, 264-269 (2008).
- [230] N.Y.C. Chu, *Photochromism of spiroindolinonaphthoxazine. I. Photophysical properties*, Canadian Journal of Chemistry, **61**, 2, 300-305 (1983).
- [231] A. Rasheed, *Molecular modelling aided design and synthesis of photochromic dyes containing a permanent chromophore*. PhD thesis. School of Textiles and Design. Heriot-Watt University. Edinburgh. 2007.
- [232] S.K. Lower, *Thermal physics (and some chemistry) of the atmosphere*, Journal of Chemical Education, **75**, 7, 837- 840 (1998).
- [233] W.C. Troglor, *The environmental chemistry of trace atmospheric gases*, Journal of Chemical Education, **72**, 11, 973-976 (1995).
- [234] D.C. Harris, *Quantitative chemical analysis*, seventh ed, [W. H. Freeman and Company, New York, 2003].
- [235] P.L. Geissler, *Temperature dependence of inhomogeneous broadening: on the meaning of isosbestic points*, Journal of the American Chemical Society, **127**, 42, 14930-14935 (2005).
- [236] V. Malatesta, R. Millini, L. Montanari, *Key intermediate product of oxidative degradation of photochromic spirooxazines. X-ray crystal structure and electron spin resonance analysis of its 7,7,8,8-tetracyanoquinodimethane ion-radical salt*, Journal of the American Chemical Society, **117**, 23, 6258-6264 (1995).



- [237] V. Malatesta, F. Renzi, M.L. Wis, L. Montanari, M. Milosa, D. Scotti, *Reductive degradation of photochromic spiro-oxazines. Reaction of the merocyanine forms with free radicals*, *The Journal of Organic Chemistry*, **60**, 17, 5446-5448 (1995).
- [238] A.R. Leach, *Molecular modelling: Principles and applicationd*, 2nd ed, [Pearson Education Limites, Essex, 2001].
- [239] J.L. Wong, M.F. Zady, *Photochromism of quinolyhydrazones. III. The mechanism of isomerization of the photocolored  $\alpha$ -quinolyimino-(Z)-hydrazone to the  $\alpha$ -quinolyamino-(E)-hydrazone*, *Journal of Organic Chemistry*, **40**, 17, 2512-2516 (1975).
- [240] R.S. Becker, F. Chagneau, *Comprehensive investigation of the photophysics, photochemistry, and kinetics of a wide variety of photochromic hydrazones in various solvents*, *Journal of American Chemical Society*, **114**, 4, 1373-1381 (1992).
- [241] J.C. Tobin, A.F. Hegarty, F.L. Scott, *The mechanism of bromination of heterocyclic hydrazones. syn-anti- isomerisation of 5-(Arylmethylenehydrazino)-1- and -2-benzyltetrazoles*, *Journal of the Chemical Society B: Physical Orgaric*, 2198-2202 (1971).