

**Technical University of Liberec**

**Faculty of Textile Engineering**



# **DIPLOMA THESIS**

**2012**

**Lindelani Archie Ndlovu**

Technical University of Liberec  
Faculty of Textile Engineering  
Chemical Technology of Textile  
Department of Textile Chemistry

**Warning clothing – Study of fluorescence fading in UV irradiation**

By  
Lindelani Archie Ndlovu

Supervisor: Ing. Martina Viková, Ph.D.

Consultant: Assoc. Prof. Michal Vik. MSc., Ph.D.

Number of text pages: 100

Number of tables: 6

Number of figures: 32

Number of appendices: 3

## STATEMENT

I have been informed that on my thesis is fully applicable the Act No. 121/2000 Coll. about copyright, especially §60 - school work.

I acknowledge that Technical University of Liberec (TUL) does not breach my copyright when using my thesis for internal need of TUL.

Shall I use my thesis or shall I award a licence for its utilisation I acknowledge that I am obliged to inform TUL about this fact, TUL has right to claim expenses incurred for this thesis up to amount of actual full expenses.

I have elaborate the thesis alone utilising listed and on basis of consultations with supervisor.

Date:

Signature:

## ACKNOWLEDGEMENTS

I would like to express my gratitude to the KwaZulu Natal Department of Economic Development for financial support of my studies.

A special thanks to my supervisor and consultant, Ing. Martina Vikova, PhD and Assoc. Prof. Michal Vik, Ph.D. respectively, who greatly enriched my knowledge and constantly inspired me. They have been able to skillfully manage this research without forgetting the essential human being relationship. From deep inside, thank you.

I am thankful to Ing. Pavlína Munzarová in Textile Materials for providing the practical support and help allowing me use of their laboratories and facilities for some parts of my experiments. Also, I extend my thanks to my friends and laboratory members for the help, friendliness and other discussions about work.

Finally, I would like to thank my family for the love, support and patience they have shown to me and thus I would like to dedicate my whole work to them. Overall, I thank God Almighty for the opportunity as well as strength to accomplish this work with success.

*“Ukwanda kwaliwa wumthakathi”*. Ngiyabonga.

## ABSTRACT

Most of the textile materials made for outdoor application purposes undergo photolytic and photo-oxidative reactions during exposure to solar UV radiation. These reactions which result in colour loss (or fading) are also problematic for warning clothes (highly visible clothes). Photostability of warning clothes (fluorescent materials) is essential for their practical application. Warning clothes are used to ensure the visibility of a person wearing them under limited visibility like firemen, policemen, road workers and pedestrians. An understanding of the durability and degradation of dye molecule in the fibre within specific environments such as under UV radiation is required to assist the warning clothes manufacturers and consumers in making correct decisions on materials. Performing such tests as colourfastness to light provides information on how much studied textiles are fading or degrading and allow one to determine if it is needed to use another material.

The main goal of this study was to investigate the standard test methods for colourfastness to light, originally developed for non-fluorescent samples, if they are applicable or valid for fluorescent materials. This was done by studying the degradation behavior of fluorescent textile materials under accelerated ageing using ultramed UV metal halide lamp. The results of this study evaluated by the use of kinetic model, CIE colour difference calculations and curves showing fading confirm the validity of the standard methods used for fluorescent materials. Visual inspections were performed through comparison of change in colour of a test specimen with unexposed reference sample.

## TABLE OF CONTENTS

LIST OF TABLES.....	7
LIST OF FIGURES .....	8
CHAPTER 1: INTRODUCTION.....	10
CHAPTER 2: LITERATURE REVIEW.....	12
2.1 Theory of irradiation and interaction of light with materials.....	12
2.2 Luminescent materials .....	17
2.3 Fluorescence .....	21
2.4 Jablonski Diagram & Stokes shift description.....	27
2.5 Colorimetry: Lab color space and visibility of light.....	32
2.6 Measuring methods: Radiometry and Fluorometry .....	36
2.7 Definitions of terms .....	41
Chapter 3: Experimental Section.....	43
3.1 Materials .....	43
3.2 Reflectance measurements (spectrophotometer) and materials analysis .....	44
3.3 Exposure to light.....	45
CHAPTER 4: Results and Discussion.....	49
CHAPTER 5: Conclusion and recommendations for future research .....	68
REFERENCES .....	70
APPENDICES .....	73
Appendix A.....	73
Appendix B .....	83
Appendix C .....	92

**LIST OF TABLES**

Table 1.	shows the measured and calculated basic parameters of fabric pieces that are used in results and discussion section .....	43
Table 2.	The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester) ....	49
Table 3.	The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester) ....	50
Table 4.	The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester) ....	51
Table 5.	The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyamide/elastane). .....	52
Table 6.	Calculated half-lives of the tested materials. ....	64

## LIST OF FIGURES

Fig. 2-1: Electromagnetic spectrum with light highlighted .....	13
Fig. 2-2: Absorption and emission.....	14
Fig. 2-3 Reflection of light onto the surface.....	15
Fig. 2-4 Schematic energy diagram for phosphorescence and fluorescence. ....	22
Fig. 2-5 Jablonski diagram .....	28
Fig. 2-6: Diagram illustrating Stokes shift .....	31
Fig. 2-7: Practical display of fluorescence lifetime .....	32
Fig. 2-8. The CIE LAB color space.....	34
Fig. 2-9: CIE L*a*b* color system (CIE, 1976) .....	35
Fig. 3-1 Melting point meter.....	44
Fig. 3-2: ELREPHO 3000 spectrophotometer, Datacolor .....	45
Fig. 3-3: Left is a picture of the whole lamp taken in the laboratory .....	46
Fig. 3-4: Spectral Power Distribution of Ultramed 400 Lamp .....	46
Fig. 3-5: Laboratory pictures of the whole light exposure equipment/set up.....	47
Fig. 3-6 Reflectance measurements performed on the spectrophotometer.....	48
Fig. 4-1 A photograph showing visual inspection of samples. Comparison of UV exposed samples (left) and unexposed samples (right).....	53
Fig. 4-2 Colour change of a dyed textile material on exposure to light over a period of time. Typical for fading resistant materials. ....	54
Fig. 4-3 Colour change of a dyed textile material on exposure to light over a period of time. Typical curve for colour change weak materials. ....	55
Fig. 4-4 Color difference graph showing fading of a resistant textile material Green 4B .....	56



Fig. 4-5 Color difference graph showing fading of a resistant textile material Orange M3. Correlation, $R = 0.99686$ .....	56
Fig. 4-6 Color difference graph showing fading of weakly colour changing textile material Green 4A. Correlation, $R = 0.99339$ .....	57
Fig. 4-7 Color difference graph showing fading of weakly colour changing textile material Orange 6. Correlation, $R = 0.98979$ .....	57
Fig. 4-8 Reflectance as a function of wavelength plotted from the spectrophotometer data (1) .....	58
Fig. 4-9 Reflectance as a function of wavelength plotted from the spectrophotometer data (2). .....	59
Fig. 4-10 Reflectance as a function of wavelength plotted from the spectrophotometer data (3). .....	60
Fig. 4-11 Reflectance as a function of wavelength plotted from the spectrophotometer data (4) .....	61
Fig. 4-12 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (1). .....	62
Fig. 4-13 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (2). .....	62
Fig. 4-14 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (3). .....	63
Fig. 4-15 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (4). .....	63
Fig. 4-16 Temperature increase inside the chamber as a function of time .....	65
Fig. 4-17 Comparison of results for three different devices used to measure same sample. <i>Left:</i> E3000 and SF600 had setup with no cut-off filter (100%UV). <i>Right:</i> 400 nm cut-off filters used for E3000 and SF600 devices.....	66

## CHAPTER 1: INTRODUCTION

High-visibility materials are used to make an object to stand out from the surrounding environment. For example, firemen must be readily visible in dangerous conditions. Policemen and road workers, working in the roadway, use vests with fluorescent materials which ensure that they are visible during bad atmospheric conditions. The use of warning clothes is believed to have the ability to increase the visibility of pedestrians under conditions of limited visibility.

There are standards specifying the requirements for high visibility clothing which is capable of signaling the users presence visually intended to provide conspicuity of the user in high-risk situations under any light conditions by day and under illumination by vehicle headlights in the dark. The European standard EN 471 defines fabrics that have inherently high daylight visibility as ‘background material’ and other material generally in the form of a tape with night-time reflective properties, as ‘retroreflective material’ [29]. Some of the in-use test requirements for retroreflective and fluorescent materials in EN 471 include brightness after: UV exposure, washing, dry cleaning, colour fastness, rainfall performance, etc... EN 471 is split into three sections:

- Design – one of the aspects regarding this is the encouragement that high luminance colours include fluorescent colours to distinguish the colours of intended environments. [30]
- Background material – According to SATRA Spotlight (November 2006), the background material consist of coloured fluorescent fabric intended to be highly conspicuous during daylight conditions (fluorescent material give off light when light is shown onto them) E471 details the specific colour requirements – ‘yellow’, ‘orange-red’ and ‘red’. These are defined by colour ‘coordinates’ measured using a spectrophotometer both before and after a treatment intended to assess the durability of the material to fading when exposed to sunlight. Other treatments include colour fastness to rubbing and perspiration, washing, hot pressing and bleaching.
- Retroreflective material

There are challenges associated with the design of safety apparel for workers, as an example. A field study by James R. Sayer and Mary Lynn Mefford revealed that these

include providing comfortable materials that are light weight and do not trap much heat or moisture. Garments that permit worker flexibility and durable materials that stand up to prolonged ultraviolet exposure yet can be easily laundered.

Herein, the theory of irradiation and interaction of light with materials will be discussed. This will be followed by the discussion of the theory of luminescent materials. Fluorescent concept and Jablonski diagram and Stokes shift will be described. Finally, colorimetry will be briefly discussed (information on lab colour space and the visibility of light) and measuring methods/instruments, radiometry and fluorimetry, will be described in details.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 Theory of irradiation and interaction of light with materials

We, as human beings, normally experience colour as a result of the interaction of light and materials. Our eyes and brains are of course involved or participate in the process. Light has been viewed in many different ways which, according to Kurt Nassan (2001), include the Greek philosophers' view of light as a stream of particles, although they were not certain whether the particles were emitted by the eye or by the source of light. "Although Newton worked widely on sound and water waves, he chose not to view light as consisting of waves. His theory treated light as a stream of corpuscles, particles emitted by the light source, reflected by objects, and detected upon entering the eye" (Kurt Nassan 2001: pg. 24). With time, quantum theory was required after the experimental results were found not being able to be explained as a pure wave picture. The first step towards a formulation of the theory was made in 1900 by Max Planck, the German physicist of which it was developed further in 1905 by Albert Einstein. Light consists of a certain kind of electromagnetic radiation. The quantum theory is therefore said to be a detailed mathematical formulation that can be used to explain all observed electromagnetic phenomena. In 1900, Max Planck made a profound discovery showing that light must be emitted and absorbed in discrete amounts if it was to correctly describe observed phenomena (Blackbody radiation). Albert Einstein (1905) used Planck's relationship to explain the results of the photoelectric effect which showed that the energy  $E$  of ejected electrons was dependent upon the frequency  $f$  of incident light as described in the equation  $E = hf$  (where  $h$  is Planck's constant). His work on the photoelectric effect confirmed that light energy was only emitted and absorbed by electrons in discrete amounts or quanta. This quanta of light soon became known as the 'photon' (that is, discrete like a particle) and led to the paradox that light behave both as continuous wave as well as a discrete particle/photon. Hence, from the discoveries discussed above, it is clear that wave theory of light could not yield a satisfactory account of the ejection of electrons from the material's surface when irradiated by light. The reason being the energy of a wave is spread over the entire surface. Light quanta, on the other hand, acting like little particles, could easily eject electrons, since the electron absorbs the entire quantum of energy on impact.

Furthermore, light can be produced from light of a different wavelength, from the electromagnetic radiation, or from energetic particles as in fluorescence.

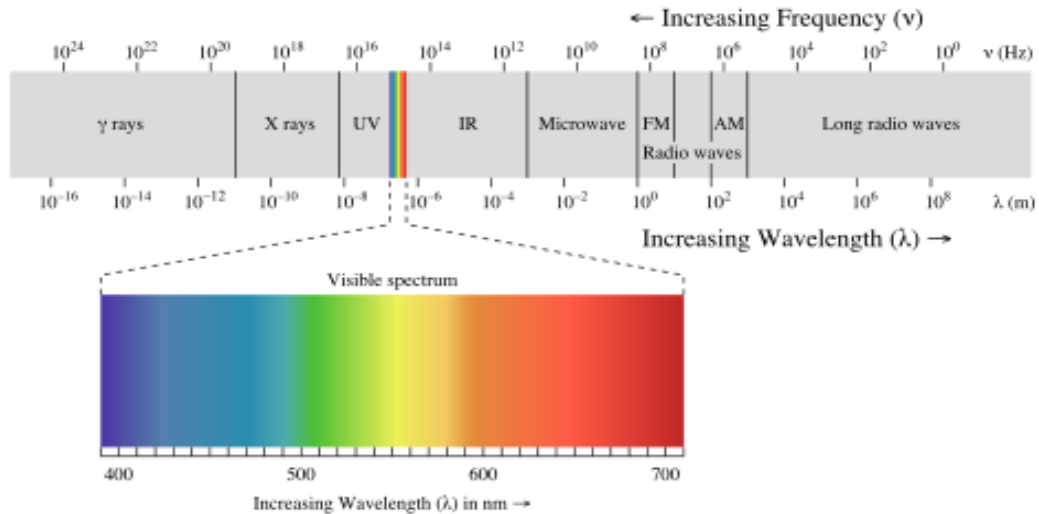


Fig. 2-1: Electromagnetic spectrum with light highlighted. <sup>[19]</sup>

Electromagnetic radiation with a wavelength between approximately 400 nm and 700 nm is directly detected by the human eye and perceived as visible light. Other wavelengths, especially nearby infrared (longer than 700 nm) and ultraviolet (shorter than 400 nm) are also sometimes referred to as light. If radiation having a frequency in the visible region of the electromagnetic spectrum reflects off of an object and then strikes our eyes, this results in our visual perception of the object. Our brain's visual system processes the multitude of reflected frequencies into different shades and hues, and through this psychological phenomenon, we perceive the object. According to Kurt Nassau (2001), from all different ways or forms from which light can be produced, there is an intermediate step where an atom or molecule is converted into an excited state and then becomes de-excited, often with the appearance of some heat as by-product.

When we are viewing an object or a surface, it is the light reaching our eyes that conveys the appearance of the surface to us. The appearance is our interpretation of the characteristics of the light, characteristics that arise from the interactions of the light incident on the object with the material of the object. The interaction of light with matter can occur in a number of forms. The object may absorb, scatter or reflect the light to mention few of the most common effects. The

reaction of the object on the light struck on it will of course depend on the properties of the object. Some types of interaction are wavelength dependent, for example some wavelengths of light may be absorbed more strongly than other wavelengths. Other types of interaction may be occurring giving rise to effects such as interference or luminescence.

**Absorption** is said to be the ultimate fate of light; that is, photons of the light beam interact with atoms or molecules that can respond to their energy level, and are absorbed by them. This causes the outer electrons of the absorbing substance to be raised on the energy ladder. As the electrons fall back to their normal state, energy is emitted as photons of a lower energy level in form of infrared radiation.

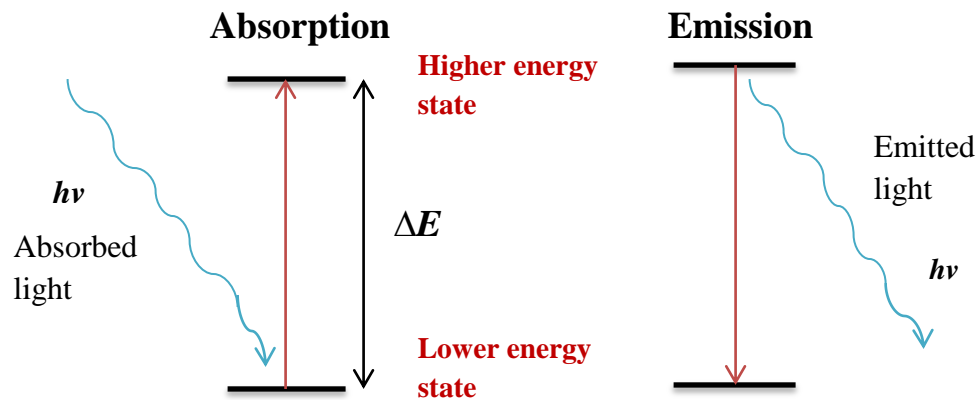


Fig. 2-2: Absorption and emission.

An atom in a lower energy state can absorb light of frequency  $\nu$  and thereby be promoted to a higher energy state, provided  $h\nu = \Delta E$ , where  $\Delta E$  is the difference in energy between the two states of the atom. Emission is the reverse of this process.

Excluding the black body which is regarded as the most efficient absorber (by definition), real objects are often selective absorbers. They can absorb a little light, they can absorb a lot, or they can absorb amounts in between. “The selective absorption of wavelengths from white light is probably the most common cause of the creation of colour; it occurs in almost all conventional dyes or pigments” H21: colour4free. Dyed fabrics are amongst the examples of the use of light absorption in colour creation. Absorption implies that the light absorbed is lost as visible light; it may be converted to heat or other forms of energy. This conversion of light may be made in several ways; the most common involves absorption of light energy by

molecules to excite electrons into a less stable (higher energy) arrangement within the molecule. The electrons quickly fall back to their original, stable arrangement, the molecule dissipating the extra energy as heat. See fig. 2-2 above. A system will only absorb light of particular wavelengths which correspond exactly to the amount of energy needed to promote the electrons involved. The absorption band may be wide, however, due to the constantly changing vibrational energy of the molecules involved changing the amount of energy needed for promotion. Only those substances that absorb light, radiation in the visible region of the electromagnetic spectrum, (380 to 760 nm) appear to be coloured. Since real objects do not absorb all the light energy falling on them, some photons have another fate: they are scattered or reflected.

**Reflection** is a special form of scattering. It is the process by which photons arriving at the surface of the material with a smooth surface change their direction of travel on impact and is returned. The ray of light which strikes the surface is called the incident ray. The ray of light which leaves the surface is called the reflected ray. A line perpendicular to the surface is imagined at the point of reflection. This line is called a normal. (as can be observed in figure 2-3). Angle of incidence is equal to the angle of reflection. The amount of light reflected by an object, and how it is reflected, is highly dependent upon the degree of smoothness or texture of the surface. However, in the real world most objects have convoluted surfaces that exhibit a diffuse reflection (produced by rough surfaces that tend to reflect light in all directions).

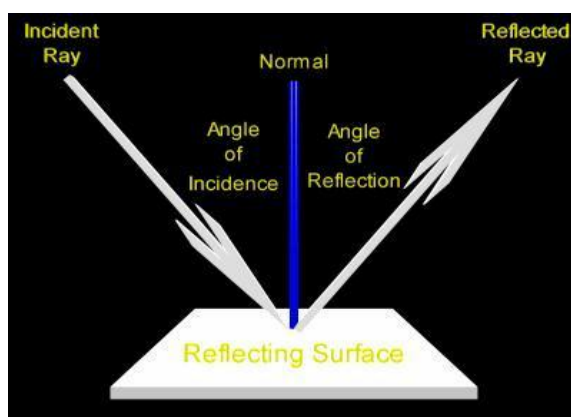


Fig. 2-3 Reflection of light onto the surface. [21]

**Scattering** refers to the change in direction imparted by a rough-surfaced material or by fine particles. Textile fibers are amongst the representative scattering materials. The appearance of a material is said to depend on the extent of scattering of the light and adjectives such as transparent, translucent, turbid and opaque are associated with the perceived degree of scattering.

The larger the difference between the refractive indices of the particles and the surrounding medium then the stronger is the scattering effect. For this reason, inorganic pigments, which are said to often have high refractive indices tend to scatter light much more effectively than organic pigments. The scattering of light gives rise to one of the most common colours in the natural world – the blue of the sky.

Furthermore, there exists no perfectly reflecting or scattering material [10]. Most colours we encounter are created by the wavelength-specific absorption and reflection. The material involved generally has properties causing it to absorb and reflect some photons of all energy levels, but those of some energy levels are absorbed or reflected to a greater degree than others.

The four major things that are said to possible happen to light when it encounters an object are:

- 1) Specular reflection at the first surface of the object.
- 2) Scattering within the material (associated with diffuse reflection and sometimes with diffuse transmission).
- 3) Absorption within the material (largely responsible for colour)
- 4) Regular transmission directly through the object, if it is more or less transparent (associated with clarity).

The processes of reflection and absorption in combination with the features of object construction are responsible for the appearance of almost all objects. Under product classification by optical sub-mode, most textile materials fall under opaque objects (non-metallic) and some fall under light-transmitting objects (translucent objects) i.e. colour is seen by diffuse reflection and by diffuse transmission respectively. The same classification goes for pigments and dyes [7]. The interaction of the matter or of a molecule with the light (i.e. photo-physical process) is said to be always the starting point for any other processes including chemical reactions. Photo-chemical processes can be observed when the electromagnetic



radiation falls in the ultraviolet (UV) or visible region (VIS) which is sufficient to promote electrons to excited states of either atoms or molecules. In such reactions, photo-chemical, light interacts with electrons ( $\sigma$  and  $\pi$  electrons and lone pairs). So, when photons interact with the electrons of a molecule or an atom, a higher energy state is produced which is the state pictured as the transition state of a photo-chemical reaction. As it has been mentioned on this document above that light is represented as electromagnetic radiation, the electric and magnetic components of light have been said to tend to set the electrons of a molecule or atom into oscillation from their natural motion around nuclei. In simpler terms, this implies that light consists of oscillating electric and magnetic fields. Moreover, since nuclei and electrons are charged particles, their motions in atoms and molecules generate oscillating electric fields. An atom or molecule is said to possibly absorb energy from light only if the frequency of the light oscillation and the frequency of the electron match. In other words, there will be absorption of light by matter if the energy of light matches with the difference in energy between occupied and unoccupied atomic orbitals. If this is not the case, light absorption cannot occur. A photo-physical process is described as a transition that exchanges an excited state with another or an excited state with the ground state and always occurs before chemical transformation [13]. Such processes are further classified as radiative (absorption or emission takes place here) and radiationless which is not applicable in this particular piece of work. Fluorescence falls under radiative physical process as an allowed or singlet-singlet emission ( $S_1 \rightarrow S_0 + h\nu$ ) and is characterized by the radiative rate constant  $k_F$  which will be described later on in this paper work.

## 2.2 Luminescent materials

Luminescent materials have a long history, in which chemistry is said to play an important role. These materials, also called phosphors, can be found in a broad range of everyday applications such as cathode ray tubes, projection televisions, fluorescent tubes, and X-ray detectors. Even though the search and development of synthetic phosphors began in the 1930s, according to Chen R. and Lockwood D. (2002), it was in 1949 where there appeared in a journal: a paper which characterizes phosphors that made white fluorescent lamps possible; silver and copper activated phosphors which are said to be still used today in colour television and display tubes; halophosphate phosphors discovered which became the standard white emitting phosphors for

fluorescent lamps; a paper that presented mechanisms of phosphor degradation in lamps. When it was generally believed that phosphors were as efficient as possible following the symposium held in 1940s by electrochemical society as well as papers published as far as they are concerned, Verstegen *et al.* announced in 1970s a new set of rare-earth activated aluminate compounds, which were reported to have improved both the color rendition and efficiency of fluorescent lamps. The pursuit of more phosphors emitting different visible wavelength light continued in 1954. The papers based on this were published for different kinds of luminescence and also for different types of dopants. In short, the journal has been a leading vehicle for publication on luminescence and display materials. Over 1000 papers on different aspects of luminescence in a wide variety of materials have been published in the 100 years of existence of the journal. In addition, practically every important aspect of the science of luminescence has been covered in the journal, reported by thousands of scientists from all over the world.

The following groups of luminescent materials have been reported to be of current interest: phosphors for luminescent lighting, where the classic halophosphate is replaced by mixtures of rare-earth-metal activated phosphors; X-ray phosphors for X-ray intensifying screens; X-ray storage phosphors for digital radiography; broad-band emitting crystals for use in tunable lasers; luminescent glasses and glass ceramics for lasers, fiber optics, solar concentrators, and lighting; electroluminescent thin films; cathode-ray phosphors that can withstand high excitation density (projection television); scintillator materials; the use of luminescent lanthanide ions as a probe for the structure of biological macromolecules [3].

In luminescence, some energy source kicks an electron of an atom out of its lowest energy level (ground state) into a higher energy level (excited state); then the electron returns the energy in the form of light so it can fall back to its ground state. More formally, luminescence is due to the excitation of the system to a higher energy state characteristic to the material which is followed by radiative transition to a lower state. Luminescence materials such as phosphors are materials that emit light (infrared to ultraviolet) under external energy excitation. The incident energy, in the form of high energy electron, photons, or electric field, can then be re-emitted in the form of electromagnetic radiation. The role of the phosphor is to convert the incoming radiation into visible light. It has been revealed that the vast majority of commercially important luminescent phosphors or pigments are inorganic. When used commercially, the

luminescent materials are said to be often called phosphorescent pigments. Such inorganic phosphors are crystalline compounds, which comprise a host lattice designed to hold tightly to the dopant ions, which are called activators. The presence of additional sensitizer ions in the materials is also reported. The basic processes involved in the luminescence behavior of these phosphor materials are:

- a) Absorption and excitation. The energy of the exciting radiation, from photons, electrons or X-rays, is absorbed by the activator, which is raised to an excited state. The exact mechanism of excitation depends on which type energy involved.
- b) Emission. Loss of energy from the excited triplet state of the excited luminescent centre produces radiant light which, whilst dependent on the excitation energy, is usually of a lower energy as some is also lost to the matrix in the form of heat, i.e. non-radiative energy.
- c) Energy transfer. Energy transfer involves getting the absorbed energy from the excited luminescent centre to another before emission occurs. Sensitizers present in the crystal lattice are used to transfer energy to the activator [2].

Furthermore, the phosphors can be divided into inorganic and organic. Inorganic compounds doped with rare earth ions have been said to form important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency and flexible emission colors with different activators. There are different kinds of inorganic phosphors and, based on composition, they are industrially used to obtain emissions of different colours. For example, there are sulfides and oxysulfides phosphors which include ZnS:Ag phosphor industrially used to obtain blue emissions. Also, there are oxygen-dominant phosphors which include aluminates, oxides silicates and halophosphates. Apart from halophosphates, the above mentioned oxygen phosphors are said to be of most interest from a colour standpoint.

Moreover, it is wise to say that a deep understanding of the interaction of light and matter is the key to both improved and new luminescent materials. In this case we talk of the interaction of an electron or a photon with the lattice of a solid like a phosphor. A photon is regarded as a “force carrier” while an electron is regarded as a “matter-consistent”. Also, an overview on the chemistry of phosphors will provide a basic explanation on how chemistry plays role in

luminescent materials. The rare earth materials exhibit excellent sharp-emission luminescence properties with suitable sensitization and effectively used in designing of white light emitting materials. Classical inorganic phosphors usually consist of a host lattice with activator ions doped into it in small concentrations. The activator ions possess energy levels that can be populated by direct excitation or indirectly by energy transfer, and are responsible for the luminescence. Generally, two types of activator ions can be distinguished. In the first type the energy levels of the activator ion involved in the emission process show only weak interactions with the host lattice. Typical examples are many of the lanthanide ions  $\text{Ln}^{3+}$ , where the optical transitions take place solely between 4f terms that are well shielded from their chemical environment by outer electrons. As a consequence characteristic line emission spectra can be observed.

The second type of activator ions strongly interact with the host lattice. This is the case when d electrons are involved, for example, in  $\text{Mn}^{2+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Ce}^{2+}$ , as well as for  $s^2$  ions like  $\text{Pb}^{2+}$  or  $\text{Sb}^{3+}$ , or for complex anions such as  $\text{MoO}_4^{2-}$  or  $\text{NbO}_4^{3-}$ . The strong coupling of the electronic states with vibrational modes of the lattice mainly leads to more or less broad bands in the spectrum. Phosphors that show an emission with a large Stokes shift (this will be dealt with later in this paper) usually exhibit a low quenching-temperature, which is disadvantageous for many applications. Luminescent materials based on lanthanide ions circumvent this problem because the actual luminescent process is largely independent of its environment, a fact that makes them unique in the luminescence world. Energy absorption need not necessarily take place at the activator ion itself but can occur at a random place in the lattice. This implies that energy transfer of the absorbed energy to the luminescent center takes place before emission can occur. The migration of the energy absorbed by the lattice can take place through one of the following processes:

- migration of electric charge (electrons, holes),
- migration of excitons
- resonance between atoms with sufficient overlap integrals,
- reabsorption of photons emitted by another activator ion or sensitizer.

Overall, it is clear that the search for new phosphors for the conversion of the near UV or blue emission into visible light is indeed an exciting development in the field of luminescent materials. The efficient shielding of the  $4f^n$  ( $n: 1-14$ ) electrons by the  $5s^2$  and  $5p^6$  electrons has been reported to result in similar chemical properties of the lanthanides with a few exceptions. They show characteristic intraconfigurational 4f luminescence which is almost independent of the selected host lattice since their absorption and emission energies are only weakly affected by the external electric field. The lanthanide ions are usually employed in the trivalent form in the luminescent materials [11].

### **2.3 Fluorescence**

Fluorescence from organic materials is a very important phenomenon that is reported to have been exploited in a broad range of application areas. These include their use in the dyeing of synthetic textile fibres, as daylight fluorescent pigments in a wide variety of media, including inks, paints and plastics, in detection of flaws in materials, in dye lasers, as solar collectors, in many very important analytical methodologies and in biological and medical applications in both detection and diagnosis of diseases, in assays and in display applications such as electroluminescence. Chemical compounds described as fluorescent substances have been known for a long time. In 1971, Bayer designated the fluorescent dye he discovered as 'fluorescine'. Since this time, several dozen dyeing substances showing fluorescent ability have been recognized. For example, the acridine and xanthene dyes, and the rhodamine and phthalein derivatives can be included into this group. Many chemical structures which are characterised by the phenomenon of fluorescence can be mentioned [15]. The application of fluorescent dyes involves various differentiated fields. Recently, the application of fluorescent dyes in medical diagnostic and biochemical investigations has developed extremely dynamically. Fluorescent dyes have also been used for the construction of lasers, photoelectric cells, and solar batteries.

The application of fluorescent dyes in medium flow control, as well as for testing material defects and equipment damage, has been well known for many years. But one of the major application fields where fluorescent dyes have long been used is for the dyeing of flat materials, especially textiles. The use of fluorescent dyes causes a significant increase in colour brightness, which makes the dyed materials more easily perceptible, or more accurately, have

increased visibility. This intensified perceptibility of materials dyed with fluorescent dyes is an advantage in preparing coloured advertisements, information descriptions, road and traffic signs, and to a great extent for manufacturing sports clothing and clothing for special services, such as fire brigades and the police. As the use of every fluorescent dye seemingly causes a desired increase in the depth of colour of the dyed textiles, an independent test was accepted for materials with high visibility to avoid a subjective estimation of the fluorescent dyes' usability.

Looking at some basic principles of fluorescence: Fluorescence is a member of the ubiquitous luminescence family of processes in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical mechanism. Generation of luminescence through excitation of a molecule by ultraviolet or visible light photons is a phenomenon termed photoluminescence, which is formally divided into two categories, fluorescence and phosphorescence, depending upon the electronic configuration of the excited state and the emission pathway. Fluorescence is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval, termed the fluorescence lifetime. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime. An energy diagram below shows outline for fluorescence and phosphorescence.

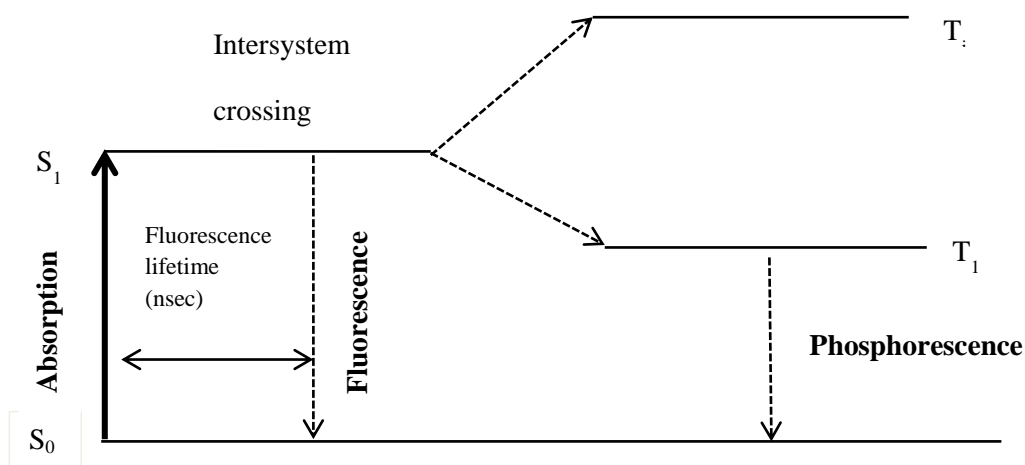
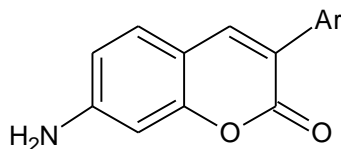


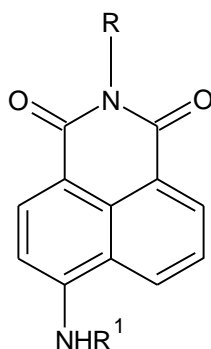
Fig. 2-4 Schematic energy diagram for phosphorescence and fluorescence.

On absorption of light the molecule is excited from its ground level state  $S_0$  to the first excited singlet state  $S_1$ . Energy can be dissipated from this state by collision deactivation causing a reduction in the intensity of the resultant emitted light. If the molecule returns to the ground state rapidly then fluorescence occurs at a longer wavelength than absorption due to a loss of vibrational energy in the excited state; this difference in absorption and emission is called the Stokes shift. Another process involves intersystem crossing from  $S_1$  to the triplet state. Energy emission from this triplet state  $T_1$  back to the ground state  $S_0$  causes phosphorescence. Phosphorescence always occurs at a longer wavelength than fluorescence because the energy difference between  $T_1$  and  $S_0$  is always lower than that between  $S_1$  and  $S_0$ . In organic fluorophores, especially dyes, excitation from the ground level  $S_0$  to the first excited state  $S_1$  is generally a  $\pi-\pi^*$  electronic transition. During the extremely short time ( $1-10 \times 10^{-9}$  s) that the excited molecule spends in the various higher vibrational levels of the excited  $S_1$  state it loses energy by various actions in its molecular environment. If the molecule returns to the ground state emitting the radiation as visible light it exhibits fluorescence, which, due to the loss of vibrational energy, is at a longer wavelength than the initially absorbed light. As already stated this difference in wavelength between absorption and emission is known as the Stokes shift. In general the Stokes shift is in the region of 30–70 nm but can be as high as 150–250 nm, a necessary condition in some applications where it is essential to separate the absorption maximum from the emission maximum in the spectra. The quantum yield of a fluorescent molecule is defined as the ratio between the emitted and the absorbed quanta [2].

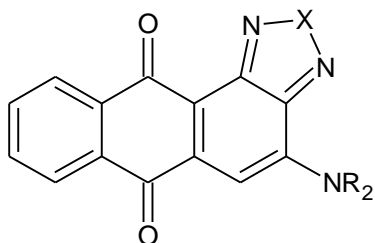
A vast range of organic chromophoric ring systems exhibit fluorescence. There are different fluorescent chromophores which exhibit different fluorescence depending on the chemical structure. These include coumarins, naphthalimides, perylene esters, perylenediimides, benzantrones, benzoxantrones and benzothioxantrones. Bright yellow and orange red fluorescent dyes based on the coumarin ring have been used commercially for many years. Below is a basic chemical structure of coumarins:



Many derivatives of this can be obtained from this basic structure through substitution of in proper positions by certain groups. By so doing, there can be obtained disperse dyes in a variety of colours. Also, with the help of chemistry on the synthetic routes to fluorescent coumarin dyes, cationic dyes suitable for use in dyeing acrylic fibres can be obtained. The same principle goes for the naphthalimides having their basic chemical structure shown below:



Studies in these reported to have led to the commercialisation of yellow disperse dyes for polyester. There are also anthraquinone dyes. More intense fluorescence in these, the conjugation beyond the parent ring system as in the anthraquinone diazole ring shown below.



These are reported to be red to violet with long wavelength luminescence making them useful as daylight fluorescent pigments. Dyes derived from extended benzoxanthene and thioxanthene ring systems give extremely bright, light fast fluorescent disperse dyes for polyester.

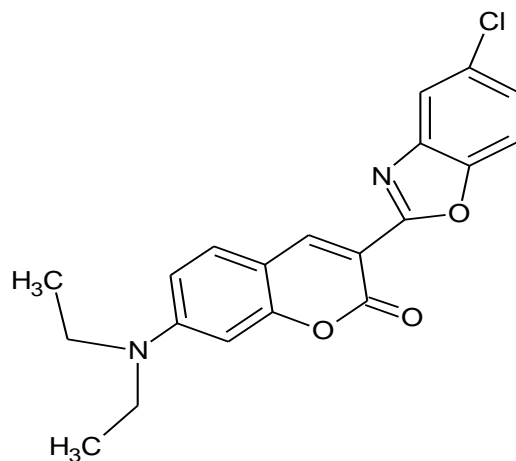
There are many different kinds of the fluorescent dyes which include the ones not applied in textile materials. A lot more of these applied in different industries. Below are some features of the fluorescent dyes:

- Water solubility
- Highly detectable (some even below 1 part per trillion)

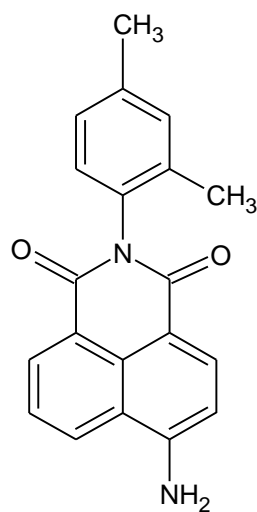


- Fair stability in a normal water environment
- They are easy to see with the visible eye.
- High colour strength
- Excellent fastness properties
- Displays good stability

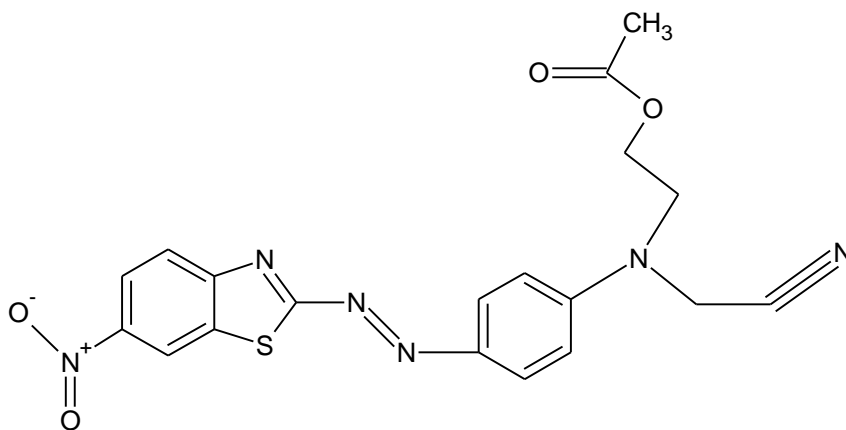
Fluorescent colours, especially daylight fluorescent pigments, have become increasingly important as there has been a sociological move in the developed world towards a society devoted to spending an increasing amount of time on outdoor leisure activities coupled with a greater awareness of the need for safety, especially visibility, and security in all aspects of our everyday lives. The main use of fluorescent dyes is in the coloration of synthetic fibres, especially polyester, polyamide and acrylics in conjunction with elastane fibres, for fashion, leisure and especially sportswear uses. In this particular review, a more precise definition fluorescent dyes can be given is – materials that both absorb and emit strongly in the visible region of the spectrum and that owe their potential for application principally to their intense fluorescence [5]. This definition is said to be somehow more restrictive than that used by many authors since it excludes fluorescent brightening agents, i.e. compounds which emit visible light but absorb in the UV region. Thus it is said that these types of dyes are required to absorb in the visible region and to exhibit intense emission. The fluorescent textiles offer not only high design options but also a large degree of safety in use, for instance increasing the visibility of cyclists and runners in busy urban areas. The largest usage has been said to be in polyester and many dyestuff companies have disperse dye ranges for this purpose, some of which are also applied to polyamide fibres. The main colours are in the yellow, orange, red, pink and violet areas with coumarins, methines and perylene dominating the structural classes [2]. Some examples of commercial products include the dyes with the following chemical structures:



**Coumarin CI Disperse Yellow 232**



**Aminonaphthalimide CI Disperse Yellow 11**



**Disperse Red 277**

Also, there are daylight fluorescent pigments which are described as the ones having a property of fluorescing when activated by visible light at the blue end of the spectrum. They are composed of fluorescent dyes and a range of special polymers. The polymer, the choice of which depends on the end application, is said to play a very important role in the fluorescent properties of the pigments, being responsible for the colour development and also for most of the physical properties such as softening point and solvent resistance of the derived pigments. However, these pigments have been reported to suffer from poor fade resistance as compared with conventional pigments. That is, talking of their light fastness, they tend to fade gradually on outdoor exposure. A reported reason for this is the excited state molecules, which have relatively long lifetimes, transferring their energy to oxygen, creating singlet oxygen which then reacts with other fluorescent dye molecules causing degradation. The pigments have a variety of applications which of course include their usage in textiles. Also, coating application include the coloration of textiles.

In addition, with regard to the fluorescent materials, studies have been conducted where ultraviolet absorbers have been examined as a method amongst many for reducing light-induced fading and degradation. Of course there have been attempts of reducing fading and/or degradation in textiles in a variety of ways including the use of lower levels of lighting in exhibit areas, the use of incandescent lighting instead of fluorescent lighting, and the use of ultraviolet filters on fluorescent lights. "Ultraviolet absorbers are compounds that preferentially absorb ultraviolet radiation and re-emit it as harmless infrared radiation thereby stabilizing fibers and dyes against light-induced changes" [1].

## **2.4 Jablonski Diagram & Stokes shift description**

Fluorescence activity can be schematically illustrated with the classical Jablonski diagram, first proposed by Professor Alexander Jablonski in 1935 to describe absorption and emission of light. Prior to excitation, the electronic configuration of the molecule is described as being in the ground state. Upon absorbing a photon of excitation light, usually of short wavelengths, electrons may be raised to a higher energy and vibrational excited state, a process that may only take a quadrillionth of a second (a time period commonly referred to as a femtosecond,  $10^{-15}$  seconds). Once a molecule has absorbed energy in the form of electromagnetic radiation, there are a number of routes by which it can return to ground state. The Jablonski Diagram, seen

below (fig. 2-5), shows a number of possible routes by which an excited molecule can return to its ground or room temperature state via unstable triplet states. A rapid return results in fluorescence and a delayed return results in phosphorescence.

Emission or luminescence is referred to as fluorescence or phosphorescence, depending on whether it corresponds to a spin-allowed or a spin forbidden transition, respectively. Similarly, radiationless transitions between states of the same multiplicity and of a different multiplicity are known as internal conversion (IC) and intersystem crossing (ISC), respectively. From Figure 2-5 below it can be seen that a molecule can reach an excited vibrational level of the electronically excited state  $S_1$  either by the absorption of a photon of appropriate energy or by internal conversion from one of the vibrational levels of a higher electronic state such as  $S_2$ .

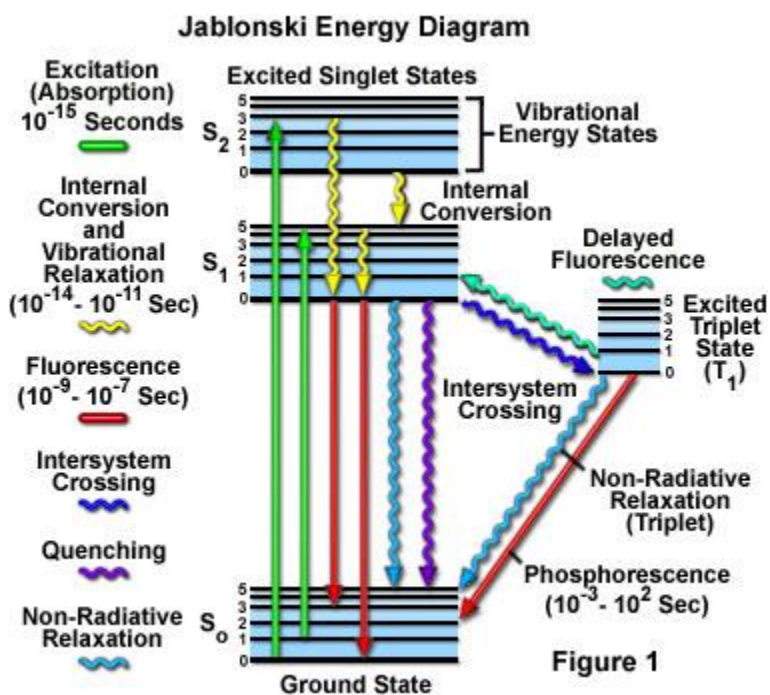


Fig. 2-5 Jablonski diagram.

Absorption and emission processes are indicated by straight arrows (fluorescence, phosphorescence), radiationless processes by wavy arrows (internal conversion, vibrational relaxation, intersystem crossing).<sup>[22]</sup>

From the zero-vibrational level of the  $S_1$  state the molecule can return to the ground state  $S_0$  by fluorescence (F), or it can reach the triplet state  $T_1$  by intersystem crossing (ISC), and after loss of excess vibrational energy it can return to the ground state  $S_0$  by phosphorescence. Radiationless deactivation from  $S_1$  to  $S_0$  can occur via internal conversion (IC) and subsequent vibrational relaxation. Radiationless deactivation from  $T_1$  to  $S_0$  can occur by intersystem crossing (ISC) followed by vibrational relaxation [9]. Vibrational relaxation occurs in liquid/solution phase. In the gas phase, fluorescence, phosphorescence and internal conversion processes are important.

Let us take a look at the Planck's Law - expressed by the equation (for energy in a quantum):

$$E = h\nu = hc/\lambda \quad (1)$$

where  $E$  is the energy,  $h$  is Planck's constant,  $\nu$  and  $\lambda$  are the frequency and wavelength of the incoming photon, and  $c$  is the speed of light. It is clear from the equation that the radiation energy of an absorbed photon is directly proportional to the frequency and inversely proportional to the wavelength, meaning that shorter incident wavelengths possess a greater quantum of energy. If the absorbed photon contains more energy than is necessary for a simple electronic transition, the excess energy is usually converted into vibrational and rotational energy. If, however, a collision occurs between a molecule and a photon having insufficient energy to promote a transition, absorption is reported as not possible to occur in this case.

Furthermore, since the excitation of a molecule by absorption normally occurs without a change in electron spin-pairing, the excited state is also a singlet. As much as there are quite a few different processes which can occur immediately after photon absorption, the most likely will be relaxation to the lowest vibrational energy level of the first excited state  $S_1 = 0$ . This process is known as internal conversion or vibrational relaxation (loss of energy in the absence of light emission) and generally occurs in a picosecond ( $10^{-12}$  s) or less. And since a significant number of vibration cycles transpire during the lifetime of excited states, molecules virtually always undergo complete vibrational relaxation during their excited lifetimes. The excess vibrational energy is converted into heat, which is absorbed by neighboring solvent molecules upon colliding with the excited state fluorophore. An excited molecule exists in the lowest excited singlet state  $S_1$  for periods on the order of nanoseconds ( $10^{-9}$  s) before finally relaxing

to the ground state. If relaxation from this long-lived state is accompanied by emission of a photon, the process is formally known as **fluorescence**. The closely spaced vibrational energy levels of the ground state, when coupled with normal thermal motion, are said to produce a wide range of photon energies during emission. As a result, fluorescence is normally observed as emission intensity over a band of wavelengths rather than a sharp line.

In addition to this, most fluorophores have been said to be able to repeat the excitation and emission cycle many hundreds to thousands of times before the highly reactive excited state molecule is photobleached, resulting in the destruction of fluorescence. For example, the well-studied probe fluorescein isothiocyanate (FITC) can undergo excitation and relaxation for approximately 30,000 cycles before the molecule no longer responds to incident illumination. Moreover, the intersystem crossing is relatively rare, but ultimately results either in emission of a photon through **phosphorescence** or a transition back to the excited singlet state that yields **delayed fluorescence**. Transitions from the triplet excited state to the singlet ground state are **forbidden**, which results in rate constants for triplet emission that are several orders of magnitude lower than those for fluorescence. As mentioned above that ISC is rare, the low probability of intersystem crossing arises from the fact that molecules must first undergo spin conversion to produce unpaired electrons, an unfavorable process. The primary importance of the triplet state is the high degree of chemical reactivity exhibited by molecules in this state, which often results in photobleaching and the production of damaging free radicals.[8]

With ultraviolet or visible light, regions in which radiation wavelength used in general fluorescence investigations range, common fluorophores are usually excited to higher vibrational levels of the first  $S_1$  or second  $S_2$  singlet energy state. In a typical fluorophore, irradiation with a wide spectrum of wavelengths is said to generate an entire range of allowed transitions that populate the various vibrational energy levels of the excited states. Some of these transitions will have a much higher degree of probability than others, and when combined, will constitute the absorption spectrum of the molecule. Note that for most fluorophores, the absorption and excitation spectra are distinct, but often overlap and can sometimes become indistinguishable. In other cases (fluorescein, for example) the absorption and excitation spectra are clearly separated.

When a molecule or atom absorbs light, it enters an excited electronic state. The Stokes shift occurs because the molecule loses a small amount of the absorbed energy before re-releasing the rest of the energy as luminescence or fluorescence (the so-called Stokes fluorescence), depending on the time between the absorption and the reemission. This energy is often lost as thermal energy. Stokes shift is the difference (in wavelength or frequency units) between positions of the band maxima of the absorption and luminescence spectra (or fluorescence) of the same electronic transition. It is named after Irish physicist George G. Stokes. Stokes fluorescence is the reemission of longer wavelength photons (lower frequency or energy) by a molecule that has absorbed photons of shorter wavelengths (higher frequency or energy). Both absorption and radiation (emission) of energy are unique characteristics of a particular molecular structure during the fluorescence process.

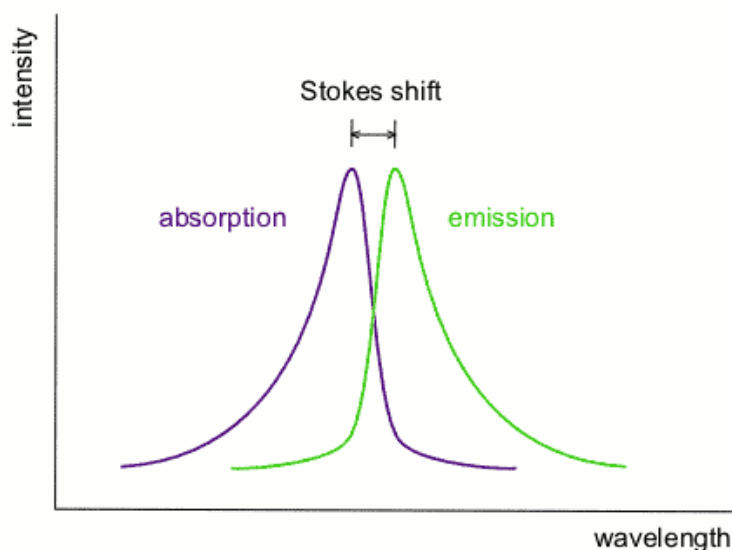


Fig. 2-6: Diagram illustrating Stokes shift.

If a material has a direct bandgap in the range of visible light, the light shining on it is absorbed, causing electrons to become excited to a higher energy state. The electrons remain in the excited state for about  $10^{-8}$  seconds. This number varies over several orders of magnitude depending on the sample, and is known as the fluorescence lifetime of the sample. The electron returns to the ground state and energy is emitted [17]. The fluorescence lifetime refers to the average time the molecule stays in its excited state before emitting a photon.

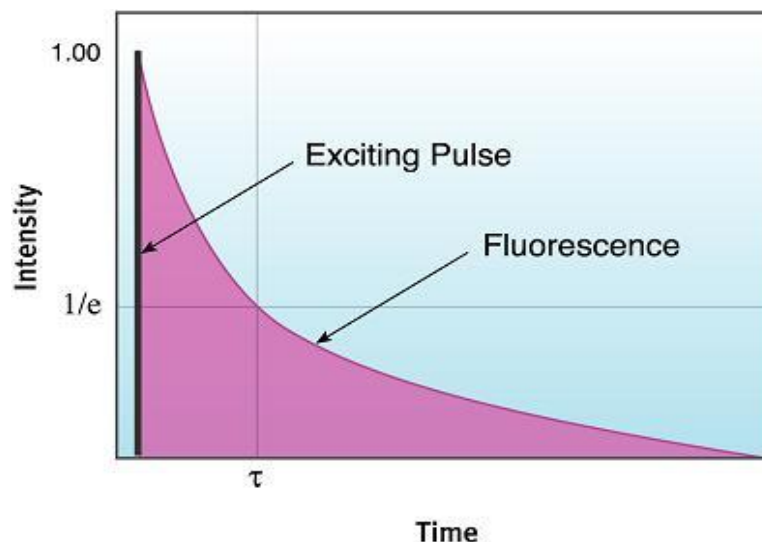


Fig. 2-7: Practical display of fluorescence lifetime. <sup>[18]</sup>

As shown in the intensity decay figure, the fluorescence lifetime,  $t$ , is the time at which the intensity has decayed to  $1/e$  of the original value. The decay of the intensity as a function of time is given by:

$$I_t = \alpha e^{-t/\tau} \quad (2)$$

Where  $I_t$  is the intensity at time  $t$ ,  $\alpha$  is a normalization term (the pre-exponential factor) and  $\tau$  is the lifetime.

## 2.5 Colorimetry: Lab color space and visibility of light

Colorimetry is the science of measuring colors. The primary objective of colorimetry is the numerical description of colours by means of physical measurements. Any two samples with the same numerical colour specification, for a given set of viewing conditions, will always have identical perceived colours under those conditions. The difference in the numerical descriptions of two colours should also correlate with the actual degree of colour difference seen by an observer. Such a system of colour specification is extremely valuable and has been reported to allow rapid and objective communication of colour information, the specification of acceptable colour differences and the resolution of colour matching disagreements between observers. Many industries producing coloured materials now use colorimetry [4].



There is no colour without an observer, just as there is no colour without light. Hence, it can be said that, basically, colour is normally experienced by us as a result of the interaction between light, materials (objects) and our visual apparatus, eye and brain. Light is a form of radiant energy, which acts as a stimulus to the eyes and causes the observer to see. The correlation between physics and physiology when it comes to color perception was recognized very early on. While physicist Isaac Newton had already made a key contribution to spectrophotometry and colorimetry in 1704 with his attempts to split white light into spectral colors, the effect on the human eye was actually defined 100 years later by the physician Thomas Young. Young was reportedly the first to describe how color was perceived with the three receptors in the eye for the primary colors red, green and blue. It is now known that every color impression can be fully described by three values.

In the illuminant mode of observation, light enters the eye directly from the light source. In the object viewing mode, the colorants present in a material selectively absorb part of the light illuminating it and transmit or reflect the remainder into the eye of the observer. It is this light that stimulates the sensation of what we call the 'colour' of the material. This 'colour' is not an extremely important and basic property of the object and its perception may vary depending on three important factors:

- a) the wavelength distribution, or colour, of the light source illuminating the object;
- b) the degree of reflection or transmission of each wavelength of the incident light by the object;
- c) the visual response of the observer's eye to the wavelengths of light entering from the object.

The numerical specification of a colour requires numerical descriptions of each of these factors.[4] At present, color spaces and numerical values are used to create, represent and visualize colors in two and three dimensional space. According to Silja Holopainen (2006), the cone cells (for color vision) contained in a human eye's retina has got three types: one has peak sensitivity to blue light, one to green light and one to red light. All colors can be matched by varying amounts of red, green and blue lights (X, Y and Z). The amounts of X, Y and Z that must be mixed to match a color are called the tristimulus values. The tristimulus values depend on the reflectance or transmittance of the object, the illuminant and the observer. Pairs of

objects are said to match when their tristimulus values are the same. XYZ values, however, are not easily understood in terms of object color, hence other color scales have been developed to:

- ✓ Relate better to how we perceive color
- ✓ Simplify understanding
- ✓ Improve communication of color differences
- ✓ Be more linear throughout color space

The CIELAB colour space was developed from earlier attempts to transform the X, Y and Z tristimulus values into coordinates that would provide better uniformity. The CIE 1976 uniform colour space, as CIELAB is being referred to, is said to be introduced as an improved coordinate system, based on mathematical transformations of the CIE colorimetric system which was defined in 1931 as a standard system enabling the specification of all colours as points within a 3-dimensional colour space. This system is a very popular one for colour and colour difference specification. The hunter L, a, b color space is a 3-dimensional rectangular color space based on the opponent-colors theory. The L (lightness) axis runs from top to bottom. The maximum for L is 100 (white), which will be a perfect reflecting diffuser. The minimum for L is zero, which would be black. The a and b axis have been said to have no specific numerical limits. Positive a is red. Negative a is green. Positive b is yellow. Negative b is blue. Below is a diagram L, a, b space.

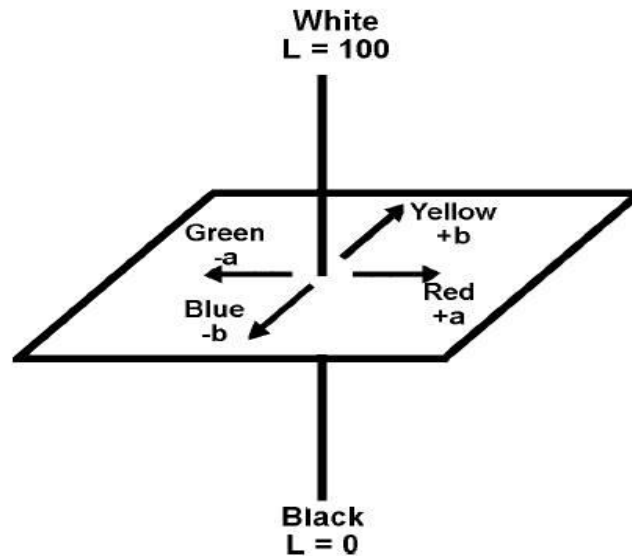


Fig. 2-8. The CIE LAB color space. <sup>[23]</sup>

All colors that can be visually perceived can be plotted in this L, a, b rectangular color space. There are two popular L, a, b scales in use today – Hunter L, a, b and CIE  $L^*$ ,  $a^*$ ,  $b^*$ . Both scales are mathematically derived from the X, Y, Z values. According to Silja Holopainen (2006), the current CIE recommendation is to use CIE  $L^*$ ,  $a^*$ ,  $b^*$ .

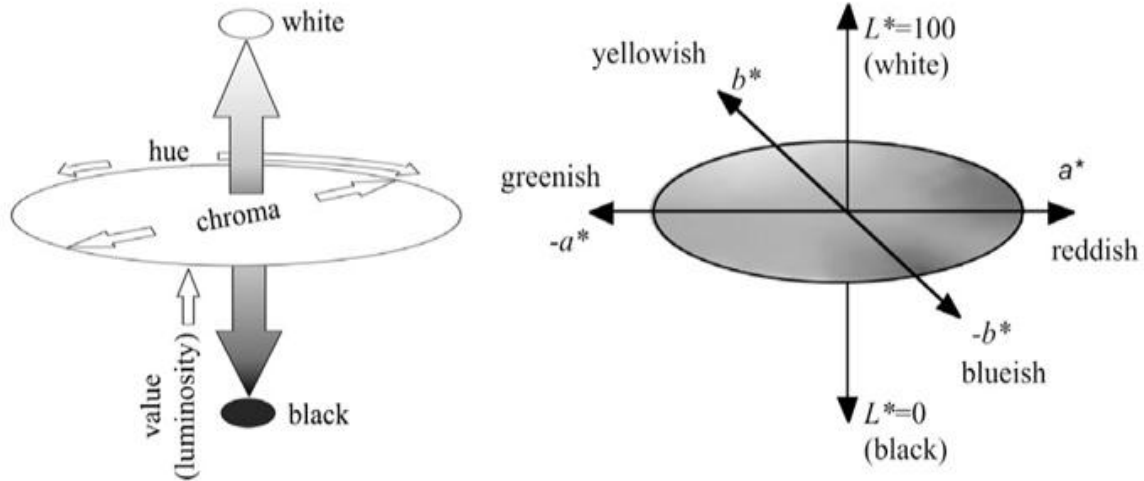


Fig. 2-9: CIE  $L^*a^*b^*$  color system (CIE, 1976).<sup>[23]</sup>

CIE  $L^*$ ,  $C^*$ ,  $h^*$  is a polar representation of the CIE  $L^*$ ,  $a^*$ ,  $b^*$  rectangular coordinate system. Numerically, CIE  $L^*$ ,  $C^*$ ,  $h^*$  describes color in the same way that we verbally communicate color in terms of lightness, chroma (saturation) and hue. Derived mathematically from the CIE  $L^*$ ,  $a^*$ ,  $b^*$ , its uniformity has been said to be no better than CIE  $L^*$ ,  $a^*$ ,  $b^*$ . The values of  $L^*$ ,  $a^*$  and  $b^*$  for a given colour locate its position in the three dimensional CIELAB space. The colour difference between two similar non-matching colours is the distance between the points for their respective coordinates in the CIELAB colour space. Color differences are always calculated as sample – standard values. If  $\Delta L^*$  is positive, then the sample is lighter than the standard. If negative, it would be darker. If  $\Delta a^*$  is positive, then the sample is more red (or less green) than the standard. If negative, it would be more green (less red). Likewise, if  $\Delta b^*$  is positive, then the sample is more yellow (less blue) than the standard. If negative, it would be more blue (less yellow). If  $\Delta C^*$  is positive, then the sample is more saturated than the standard. If negative, it is less saturated.  $\Delta H^*$  indicates the magnitude of a change in hue. So, basically, the delta values indicate how much a standard and sample differ from one another in L, a, and b. Tolerances maybe set for the delta values. Delta values that are out of

tolerance indicate that there is too much difference between the standard and the sample. The type of correction needed may be determined by which delta value is out of tolerance. For example, if delta a is out of tolerance, the redness/greenness needs to be adjusted.

Colorimetric practice often makes use of CIELAB colour spaces for the measurement of colour differences; a colour difference is computed in a simple way as the Euclidean distance between two points representing the colour stimuli in the colour space. Therefore it is expressed by a single number independently of where the two colours are located in the colour space. The difference of two stimuli can be calculated using formula:

$$\begin{aligned}\Delta E^*_{ab} &= [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \\ &= [(\Delta L^*)^2 + (\Delta C^*)^2 + (\Delta H^*)^2]^{1/2}\end{aligned}\tag{3}$$

The objective of CIELAB was a more uniform colour space in which instrumental colour differences such as  $\Delta E^*_{ab}$  would always correlate with visually perceived colour differences. Such a measurement of colour difference is very useful for establishing whether a coloured sample is an acceptable match to the target. We find some color difference attributes more objectionable than others. Hue differences are said to be most objectionable. Chroma differences, on the other hand, are said to be less objectionable than hue differences and lightness differences are the list objectionable. Due to non-uniformity of color space, the lighter the color the larger the  $L^*$  tolerance and frequently the smaller the  $a^*$  and  $b^*$  tolerance. The more chromatic (saturated) the color, the larger the  $a^*$  and  $b^*$  tolerance. Many colour matchers consider that a value of  $\Delta E^*_{ab}$  less than 1.0 unit corresponds to an acceptable colour match. [4] A single value of the CIELAB colour difference is not a completely reliable colour tolerance. In other words it can be said that  $\Delta E^*$  is not always reliable by itself. To clarify this, one of the two samples can be visually a good match to the standard while the other sample is not, but they, however, both have the same  $\Delta E^*$  value.

## 2.6 Measuring methods: Radiometry and Fluorometry

Scientists and engineers have been involved in the measurement of light since the early experiments and instruments described by P. Bouguer in 1729 and by J. H. Lambert in 1760. Exploration into other spectral regions has been reported to have begun with the discovery of

the infrared region by W. Herschel in 1800 and the ultraviolet region by J. W. Ritter the following year. The measurement of light is often critical in transitioning from theory to the development of systems and techniques. Although instrument and system design may be based on theory, performance evaluation and system improvement require that accurate radiometric measurements be applied. Radiometry is said to be an essential part of the optical design of almost every optical instrument. Such instruments are usually used to focus and detect radiation for some particular purpose, and for many applications it is absolutely essential to know how much radiation gets to the detector array [16]. Radiometry is the science of measuring light in any portion of the electromagnetic spectrum. "In practice, the term is usually limited to the measurement of infrared, visible, and ultraviolet light using optical instruments" (Ashdown 2002: A-1). The practical aspect of radiometry involves the scientific instruments and materials used in measuring light, including radiation thermocouples, bolometers, photodiodes, photosensitive dyes and emulsions, etc... To fully understand and appreciate a radiometric measurement, we must understand the processes of generation, transmission, and detection of optical radiation. A target, or object of measurement interest, can be either active, emitting radiation by virtue of its temperature or some form of atomic excitation, or passive, reflecting radiation from a different active or passive illuminator. Examples of active sources include the sun, tungsten or fluorescent lamps, lasers, and any nontransparent object with a temperature greater than 0 K. Passive sources include the entire range of natural and artificial reflective surfaces that make up our environment. After traversing the atmosphere, the rays from the target reach our instrument, whose parameters define the ranges over which the spatial, spectral, temporal, and radiometric characteristics of incoming radiation will be accepted. The optical radiation transmitted through the instrument is finally incident on one or an array of detectors, transducers which convert the incident optical radiation to a more tractable form of energy. Detectors may be thermal (thermoelectric, bolometric, and pyroelectric) or photon (photoemissive, photoconductive, and photovoltaic) in character; other viable detectors include the human eye and photographic film. Most of the detectors in common use generate electrical signals. Radiometric quantities include: the **energy**  $E$  of the emitted radiation measured in Joule (J); the radiometric power  $P = dE/dt = \int f$  emitted from a surface  $dS$  is called the **radiant flux**, and it is measured in  $J/s = \text{Watt (W)}$ ; the power per unit area  $dP/dS = M$  is called the **radiant emittance**. It is measured in  $W/m^2$ ; the power per unit solid angle  $dP/d\Omega = I$  is called the

**radiant intensity.** It is measured in unit of W/sr. It can have an angular dependence; the power per unit solid angle per unit projected area is called the **radiance** L. It is measured in W/sr/m<sup>2</sup>.

Some common applications of radiometry, amongst many, include appearance measurement, colorimetry, materials science, photochemistry, photometry and visual displays.

Fluorometry, on the other side, is another spectrophotometric technique based on the absorption of light by molecules. In this case, however, the molecules lose some of the absorbed energy by irradiating light of a longer wavelength. This property is known as fluorescence as it has been described above (section 2.3). As discussed in section 2.2 above, fluorescence is a member of the ubiquitous luminescence family of processes (photoluminescence, to be specific), phosphors (luminescent materials) contain lanthanides. Individual lanthanides are difficult to determine from their mixtures since they have very similar chemical properties. Take cerium for example, analytically it is usually differentiated from its lanthanide family members on the basis of the strong oxidizing power of cerium(IV) in acidic solution. Several absorption photometric methods are based on the ability of cerium (IV) to oxidize organic reagents to colored products. Since fluorimetric methods are inherently more sensitive and selective than absorption methods, it was considered worthwhile to develop fluorimetric procedures for the determination of trace amounts of this increasingly important element. Fluorimetric determinations of trace amounts of cerium have been accomplished by several workers. Most of these methods are based on the fluorescence of cerium(III) in dilute sulfate and chloride solutions at different pH levels, but several interfering species (e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>) exist in acidic media. A fluorimetric determination of cerium by means of sulfonaphtholazoresorcinol has been reported by Hjeu *et al.* A fluorimetric method for the determination of cerium (IV) has been based on the oxidation of oxine-5-sulfonic acid in sulfuric acid medium. Another fluorimetric determination of cerium has been accomplished by Salinas *et al.* based on the oxidative reaction between cerium (IV) and 1-amino-4-hydroxyanthraquinone. And a recent study on the fluorimetric determination of cerium (IV) based on the oxidative reaction between cerium (IV) and paracetamol has been reported by Jie *et al.* (Rakicioglu and Akseli: 1998).

Fluorometry may achieve limits of detection several orders of magnitude lower than those of most other techniques. Because of the low detection limits, fluorometry is widely used for quantification of trace constituents of biological and environmental samples. Fluorometry is also used as a detection method in separation techniques, especially liquid chromatography and electrophoresis. Fluorometry is said to be more selective than UV/Vis absorption spectrometry with one of the reasons being that many molecules absorb strongly in the UV or visible range but do not exhibit detectable fluorescence.

In addition to all discussed above, the rate of fading and degradation of textiles and other organic materials on display is influenced by the intensity and wavelength distribution of the light source to which they are exposed and by other environmental factors, such as temperature, relative humidity, and atmospheric pollutants. Ultraviolet rays are, to a large extent, responsible for the ageing of textile materials because the majority of fibres are sensitive to this radiation. The condition necessary for the ageing polymer fibre structures exposed to light radiation is the absorption of sun rays, occurring when quantum and photon energy introduced to the fibre structure corresponds to the differentiated energy of its molecules. Egerton, in his theory, proved the existence of two different phenomena of photochemical fibre degradation – photolysis and photo-oxidation. The photolysis phenomenon can take place only in the presence of ultraviolet radiation. Photo-oxidation takes place during fibre exposure to light rays of a length above 340 nm [12]. Talking of these phenomena, to activate molecules, radiant energy must be absorbed. So, it can be confidently said that no photochemical or photolytic reaction can take place without absorption. Feller (1994) mentioned that, on absorption of a photon by a molecule, the excited molecule may then lose the absorbed energy (a) by heat, (b) by the emission of radiant energy in the form of fluorescence or phosphorescence, (c) by undergoing a chemical change within the molecule, (d) by the breaking of chemical bonds (photolysis), or (e) by transfer of the energy to another atom or molecule. The first two are considered photophysical processes (Geuskens 1975); the other three are considered photochemical. Lowering the intensity of illumination lowers the number of photons per minute but does not alter their energy, for this is a function of their wavelength. It is the energy of the photons absorbed that is able to initiate a photochemical change. As a consequence, there is theoretically no threshold of intensity of light below which photochemical reactions will cease to take place.[6]

Photochemical reactions decrease the degree of fibre polymerisation, and in consequence their mechanical and chemical resistance as well as their dullness drop. The UV radiation falling on the textile is partially reflected by its surface, partially going through the fabric structure. Some of this radiation is absorbed by the fibres, as result of which some changes occur in them i.e. physical and physico-chemical properties and colour (fading). The following factors influence the velocity of the degradation process: the length of the radiation wave, the radiation intensity and time of exposure. With a decrease of wavelength, the effectiveness of photolysis as well as the fibre destruction and dyestuff degradation processes increase. A similar result is obtained when the intensity and time of light exposure increase. As the wavelength of radiation gets shorter and shorter, through the blue and violet region of the visible and into the ultraviolet, the photons possess an increasing amount of energy and are capable of inducing significant photochemical changes. Apart from these factors, Color fastness depends on dye durability, the substrate properties, dye bonding and distribution in the material. In relation to these factors a dye may increase the degradation rate of material (photo tendering) and may also inhibit photochemical changes in the material. The morphology of the polymer (crystalline or amorphous) is another factor reported to contribute to the light fastness of textile materials. Therefore it is important to consider this factor in a broader context.

Moreover, Sunlight, heat and moisture combination can cause serious material deterioration which, amongst others, includes fading, color change, oxidation, loss of strength, etc... Damage from weathering or corrosion occurs both outdoors and indoors, and its severity can vary greatly in different climates. Even materials that are resistant to sunlight alone or to moisture alone often fail when exposed to sunlight and moisture in combination.

The current methods used for light fastness measurements were originally developed for non-fluorescent materials. The aim of this study was to confirm if the methods are valid or applicable to fluorescent materials. This was done by exposing fluorescent materials used in warning clothes to a lamp in a light box (daylight simulator) with the purpose of measuring fluorescence/reflectance after prolonged exposure. Also, to do the evaluation of a simple testing in the small laboratory. This information is crucial for somebody wanting to use such simple testing without having to pay huge money in the companies and wait long for the results.



## 2.7 Definitions of terms

**High visibility materials:** a type of personal protective equipment (PPE), is any clothing worn that has highly reflective properties or a colour that is easily discernible from any background.

**Conspicuity:** The characteristics of an object influencing the probability that it will come to the attention of an observer at critical observation distance.

**Retroreflective materials:** Material that reflects and returns a relatively high proportion of light in a direction close to the direction from which it came.

**Absorption:** (of electromagnetic radiation) is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom.

**Excitation:** The addition of a discrete amount of energy (excitation energy) to a system such as an atomic nucleus, an atom or a molecule that results in its alteration, ordinarily from the condition of lowest energy (ground state) to one of higher energy (excited state). In atoms, the excitation energy is absorbed by the orbiting electrons that are raised to higher distinct energy levels. In a molecule, the energy is absorbed not only by the electrons, which are excited to higher energy levels, but also by the whole molecule, which is excited to discrete modes of vibration and rotation.

**Dopant:** a trace impurity element that is inserted into a substance (in very low concentrations) in order to alter the electrical properties or the optical properties of the substance.

**Rare earth ions:** also referred to as Lanthanides, found in the periodic table of elements from La-Lu and Scandium & Yttrium. Sc and Y are considered as rare earths because they occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. Lanthanides represent a unique class of luminescent molecules. They absorb and emit photons due to forbidden transitions between partially filled 4f orbitals.

**Photolysis:** is a chemical reaction in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule.

**Photo-oxidation:** Oxidation reactions induced by light. Common processes are: 1, the loss of one or more electrons from a chemical species as a result of photoexcitation of that species; 2,

the reaction of a substance with oxygen under the influence of light. It can be simply described as the degradation of a polymer surface in the presence of O<sub>2</sub> or O<sub>3</sub>.

***Vibrational relaxation:*** A process in which a polyatomic molecule in an excited vibrational state returns to a lower vibrational state in the same electronic state by colliding with other molecules.

***Internal conversion:*** is a transition of energy from a higher to a lower electronic state in a molecule or atom. It is sometimes called "radiationless de-excitation", because no photons are emitted.

***Intersystem crossing:*** A photophysical process. An isoenergetic radiationless transition between two electronic states having different multiplicities. It often results in a vibrationally excited molecular entity in the lower electronic state, which then usually deactivates to its lowest vibrational level.

***Lightness:*** (sometimes called value or tone) is a property of a color, or a dimension of a color space, that is defined in a way to reflect the subjective brightness perception of a color for humans along a lightness–darkness axis.

***Chroma:*** The aspect of color in the Munsell color system by which a sample appears to differ from a gray of the same lightness or brightness and that corresponds to saturation of the perceived color.

***Hue:*** This is what we usually mean when we ask "what color is that?" The property of color that we are actually asking about is "hue". For example, when we talk about colors that are red, yellow, green, and blue, we are talking about hue. Different hues are caused by different wavelengths of light. Therefore, this aspect of color is usually easy to recognize. Theoretically all hues can be mixed from three basic hues, known as **primaries**.

***Half-life,  $t_{1/2}$ :*** is the period of time it takes for the amount of a substance undergoing decay to decrease by half.

## Chapter 3: Experimental Section

### 3.1 Materials

Twenty three (23) fluorescent fabric pieces (green and orange colours) for fabrics destined for warning clothing dyed with different fluorescent dyestuffs and with different finishing were tested. These are fluorescent woven and knitted fabrics used as a background material in warning clothing. Most samples were made of polyester. There were also polyamide/elastane, cotton/polyester and polyester/viscose blends.

Table 1: shows the measured and calculated basic parameters of fabric pieces that are used in results and discussion section

Sample name	Green 4A	Green 4B	Orange M3	Orange 6
Fabric construction	Knitted	Knitted	Woven	Knitted
Thickness (mm)	0.21	0.86	0.47	0.58
Mass m (g)	0.228	0.734	0.713	0.751
Warp density (woven) OR Wale density $D_w$ (knitted)	13 loops/1cm	31 loops/1cm	19 yarns/1cm	26 loops/1cm
Weft density (woven) OR Course density $D_c$ (knitted)	23 lines/1cm	30 lines/1cm	9 yarns/1cm	25 lines/1cm
Width a (m)	0.030	0.031	0.030	0.035
Length (m)	0.055	0.095	0.040	0.092
Area density $\rho_s$ (woven) Aerial density $D_a$ (knitted)	$2.99 \times 10^6 \text{ m}^{-2}$	$9.3 \times 10^6 \text{ m}^{-2}$	$0.596 \text{ kgm}^{-2}$	$1.352 \times 10^7 \text{ m}^{-2}$
Material composition	Polyester	Polyester	Polyester	Polamide/elastan

#### Sample calculations

$$\text{Orange M3: } \rho_s = m/(a.b) = 0.715/(0.03 \times 0.04 \times 1000) = \mathbf{0.596 \text{ kgm}^{-2}}$$

$$\text{Green 4A: } D_a = D_w \times D_c = 13/0.01 \times 23/0.01 = \mathbf{2.99 \times 10^6 \text{ m}^{-2}}$$

### 3.2 Reflectance measurements (spectrophotometer) and materials analysis

Microscopic identification of materials fibers was first performed so to see if the material is made up of synthetic or natural fiber. This was then followed by determination of melting points of fibers using melting point meter (fig 3-1). Iodine reagent test was then performed on the microscope slides to distinguish between polyester (no reaction) and polyamide (produce reddish brown colour in iodine) since the two are similar in longitudinal and cross-sectional look.



Fig. 3-1 Melting point meter

Reflectance of the specimens was measured using spectrophotometer SF600, Datacolor (see fig. 3-2). The instrument has got wavelength measuring range of 360-700 nm. Illuminant: D65 10 deg, A 10 deg, F11 10 deg. For the measurements, d/8 geometry was applied. i.e. diffuse illumination of the sample from all directions, using an integrating sphere, and detection of reflected light at close to perpendicular to the sample/specimen. Instrument set-up: Specular – excluded; UV filter – UV D65/10; Aperture – large.



Fig. 3-2: ELREPHO 3000 spectrophotometer, Datacolor.

Firstly, before light exposure, the specimens were tested at 100% UV. A 400 nm cut-off filter was then used and the reflectance for all specimens was measured. Same procedure was performed for 420 nm and 460 nm cut-off filters. Four different devices were also used for reflectance measurements of samples. Two portable devices or miniscans and two normal ones as in fig. 3.2. Data obtained was used to draw graphs of wavelength vs reflectance for the results of each device used and were compared.

### 3.3 Exposure to light

The specimens were mounted into exposure masks and exposed to Ultramed 400 130V R7s UV lamp in a light box. The Ultramed 400 lamp (fig. 3-3 below) was used in the accelerated light exposure as it simulated spectral characteristics of daylight. It provides high radiation intensity in the ultraviolet range. It provides fairly well daylight spectrum.

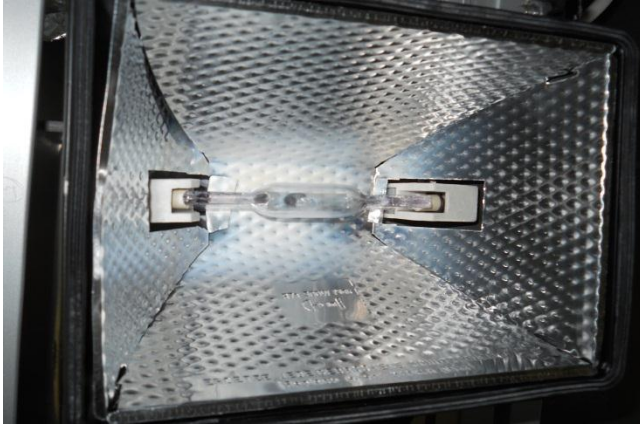


Fig. 3-3: left is a picture of the whole lamp taken in the laboratory. [28]

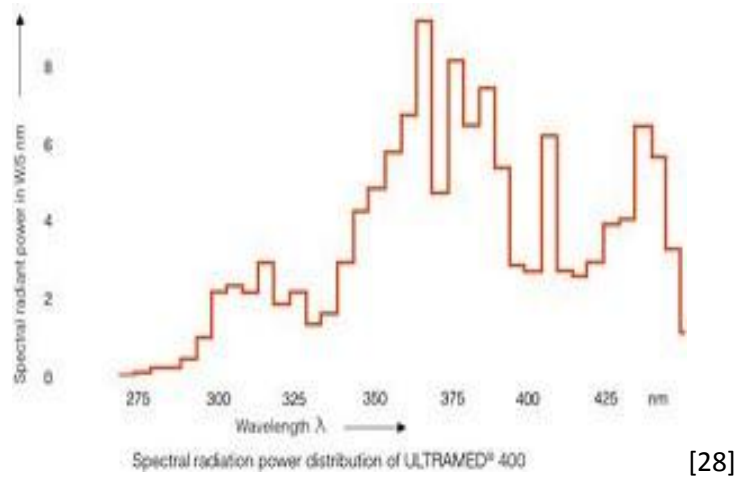


Fig. 3-4: Spectral Power Distribution of Ultramed 400 Lamp

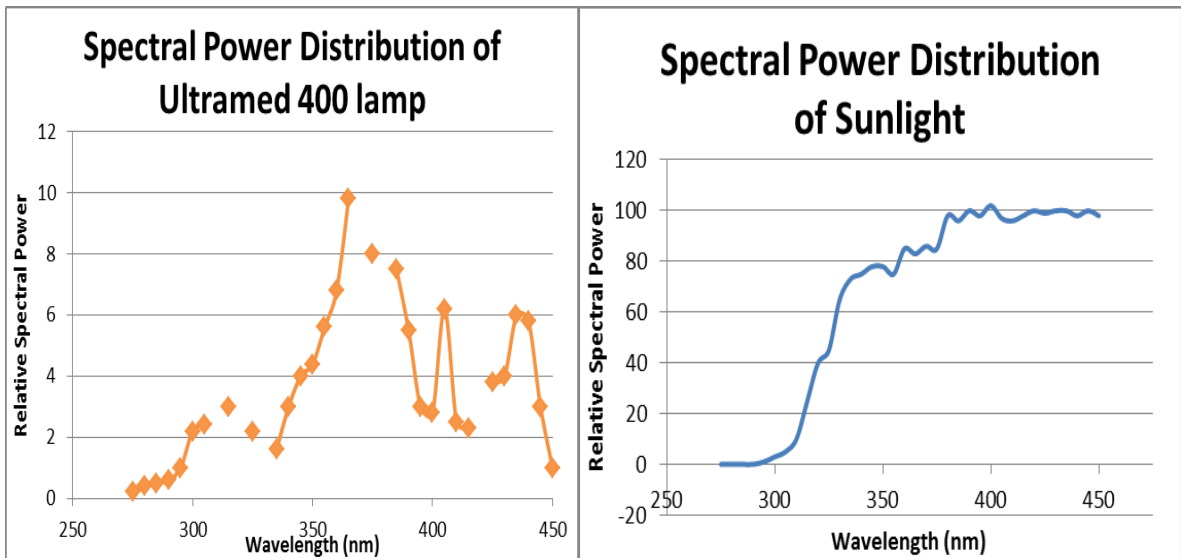




Fig. 3-5: Laboratory pictures of the whole light exposure equipment/set up.

The exposure periods were reported in terms of clock hours. Specimens were exposed for 1 hour, taken out for reflectance measurements using spectrophotometer described in 3.3 above, and then exposed for another measured hour. Light exposure-reflectance measurement procedure was continued until the test specimens were exposed for a total of 33 hours. The colorfastness to light of the specimen was then evaluated by comparison of the color change of the exposed samples to the unexposed original material by instrumental colour measurement. Colour differences were calculated using the CIELAB 1976 equation (equation 3 in section 2.5) and the graphs showing color difference with time of exposure were plotted (see results and discussion section).



Fig. 3-6 Reflectance measurements performed on the spectrophotometer



### CHAPTER 4: Results and Discussion

The fading of dye on a material is caused by radiation of certain wavelengths. The damaging wavelengths vary from one dye to another. For this reason, dyes do not generally fade at the same rate in artificial light as in daylight of equal illuminating power. The results of the light exposure summarized from the data obtained from the spectrophotometer are presented on the tables below (Table 1, 2, 3, and 4). The first two tables are examples of the samples that display strong resistance to light and the last two are for the samples that showed weakness in terms of colour change (or fading).

Table 2. The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester).

Sample name	time of exposure (hrs)	max. reflectance (at 520 nm)	$\Delta E$
Green 4B	0	1.3668716	
	1	1.37518859	2.315811
	2	1.32474554	1.691646
	3	1.33491302	1.128811
	4	1.29258525	2.278486
	5	1.3231082	1.432024
	6	1.30988765	1.793218
	7	1.34549189	1.546225
	8	1.31727982	2.471459
	9	1.30251241	3.25815
	10	1.31336737	3.30241
	11	1.28856075	4.455385
	12	1.29708683	4.757501
	13	1.32698154	3.724672
	14	1.29631436	5.16067
	15	1.31027937	5.397226
	16	1.28747416	6.117608
	17	1.2697376	6.899373
	18	1.2847116	7.190219
	19	1.26942897	7.765848
	20	1.26992476	8.164069
	21	1.27370727	8.48838
	22	1.25935817	9.139385
	23	1.2531724	9.947986
	24	1.26470637	9.916112
	25	1.24576044	10.99942
29	1.24158967	13.72434	
33	1.23089278	15.29394	

Obviously, the reflectance at 0 hour time of exposure shows the reflectance measurements of the textile material before exposure to light (i.e. original samples).

Table 3. The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester).

Sample name	time of exposure (hrs)	max. reflectance (at 610 nm)	$\Delta E$
Orange M3	0	1.56800985	
	1	1.53913534	1.76934
	2	1.52197301	3.031669
	3	1.52184021	3.130549
	4	1.5065248	4.166943
	5	1.51987517	3.436396
	6	1.51002324	4.263126
	7	1.52875185	4.790531
	8	1.50752461	5.792935
	9	1.50204861	5.733464
	10	1.51176834	6.021944
	11	1.49123836	6.737095
	12	1.50426745	6.876545
	13	1.51224732	6.916503
	14	1.49338293	7.730157
	15	1.50987589	8.14138
	16	1.48723888	8.479925
	17	1.47720766	9.315697
	18	1.48709655	9.785584
	19	1.47629821	10.36763
	20	1.47805452	10.72201
	21	1.4809438	11.00245
	22	1.46986163	11.67733
	23	1.46249616	12.16625
24	1.47956324	11.93066	
25	1.46746981	12.53983	
29	1.46730745	14.48474	
33	1.46244013	16.27407	

Analyzing investigation results obtained and presented on the tables 1 to 4, it can be observed that, basically, as the time of sample exposure to light increases, the reflectance (at the peak) decreases. However, this differs for each sample tested (this will be clearly shown graphically later in this section). The opposite trend is observed for  $\Delta E$  (color difference) values which are increasing with time of exposure. As can be expected, the light fastness of a dye depends

greatly on the dye structure and the fiber to which it is applied. This is evident from the results obtained in the performed experiments since the tested samples gave different values for colour difference and thus fade differently (remember, as mentioned in section 3.1, the tested pieces of fabrics were dyed with different dyestuff and were of different finishing technologies). Higher values of colour difference represent greater change in colour. Such values are observed in samples 'Green 4A' and 'Orange 6'. Again, this will be further elaborated graphically later on this section. As far as the colour measurement on samples are concerned, it should be noted that calculated  $\Delta E$  values provide information about the whole spectrum while maximum reflectance just give information on the peak (i.e. at a specific wavelength)

**Table 4.** The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyester).

Sample name	time of exposure (hrs)	max. reflectance (520nm)	$\Delta E$
Green 4A	0	1.36600316	
	1	1.31956136	4.381066
	2	1.28544164	6.504959
	3	1.30319905	5.808177
	4	1.26981115	7.528589
	5	1.28981709	7.264817
	6	1.28073883	8.158527
	7	1.29792547	8.39953
	8	1.28103459	10.07142
	9	1.2632736	11.53561
	10	1.26981723	12.54804
	11	1.2589767	14.08001
	12	1.25715601	14.57723
	13	1.26677001	14.95357
	14	1.24728298	16.11885
	15	1.2516396	16.44733
	16	1.23082793	17.64486
	17	1.22908664	19.01693
	18	1.22876763	18.98483
	19	1.23040462	19.91329
	20	1.20977759	19.85193
	21	1.21872902	20.30645
	22	1.20377636	21.27376
	23	1.19901443	22.16603
24	1.2044493	22.09661	
25	1.19896269	23.11297	
29	1.18609321	27.23363	
33	1.20804489	29.00234	

**Table 5.** The values of measured maximum reflectance at specific wavelength, calculated colour difference and light exposure time of the textile material (dyed polyamide/elastane).

Sample name	time of exposure (hrs)	max. reflectance (at 610nm)	$\Delta E$
Orange 6	0	1.48499012	
	1	1.47380972	0.622792
	2	1.37938035	3.590146
	3	1.3521874	4.664692
	4	1.32086515	5.781746
	5	1.32710361	5.233374
	6	1.28727448	7.023708
	7	1.37714434	3.61073
	8	1.27275372	8.698979
	9	1.25203061	9.741061
	10	1.26480556	9.436307
	11	1.24193776	10.53563
	12	1.24955428	10.87881
	13	1.26055396	10.78599
	14	1.22335589	12.71395
	15	1.24074554	12.79729
	16	1.20705187	14.39866
	17	1.19225931	15.22898
	18	1.19503999	15.84472
	19	1.18127322	16.634
	20	1.18704367	16.61557
	21	1.19658041	16.32976
	22	1.16626167	18.00337
	23	1.15811205	18.85665
	24	1.17067122	18.96934
25	1.14808691	20.15982	
29	1.12843478	25.95839	
33	1.10998416	29.44641	

Moreover, other than light source/wavelength, factors such as time of exposure and actual material composition are amongst the factors that contribute to colour change (or fading). All samples were exposed for the same number of hours (33 hours), but the behavior, in terms of colour changing, was completely different. As a basic requirement for colour difference, for instrumental measurements, numbers should predict what the observer sees. i.e. calculated  $\Delta E$  values should predict visual color differences. The figure on the next page (fig. 4-1) shows the comparison of four selected samples (corresponding with the tables above) with the original (non-exposed) samples.



Fig. 4-1 A photograph showing visual inspection of samples. Comparison of UV exposed samples (left) and unexposed samples (right).

From this, it can be confidently said that calculated  $\Delta E$  truly reflects visual colour differences. The first two samples (green 4B and orange M3, respectively) are amongst the samples that had lower  $\Delta E$  values for the duration of the experiment. On the figure above, the visual differences in colour is much smaller in comparison to their counterparts (Green 4A and Orange 6) which are amongst the samples that had higher  $\Delta E$ . The later visually display highly noticeable colour differences in comparison to the original samples.

By means of CIE colour difference calculations (using equation 3), curves were developed to show how does the time of sample exposure to light relates (in a linear/non-linear fashion) to the perceived color of the material. The curves represent the behavior of each of the selected samples to light exposure in terms of colour change. Before looking straight on the graphs from the experiments' results, a general graph (Fig. 4-2) showing colour difference with relation to

time was prepared to bring clarity on how the materials behave when exposed to light over a period of time. This particular graph was constructed strictly looking on a complete behavior of a material should the enough time has been provided to expose the sample to a point where all dyestuff is completely removed from the material.

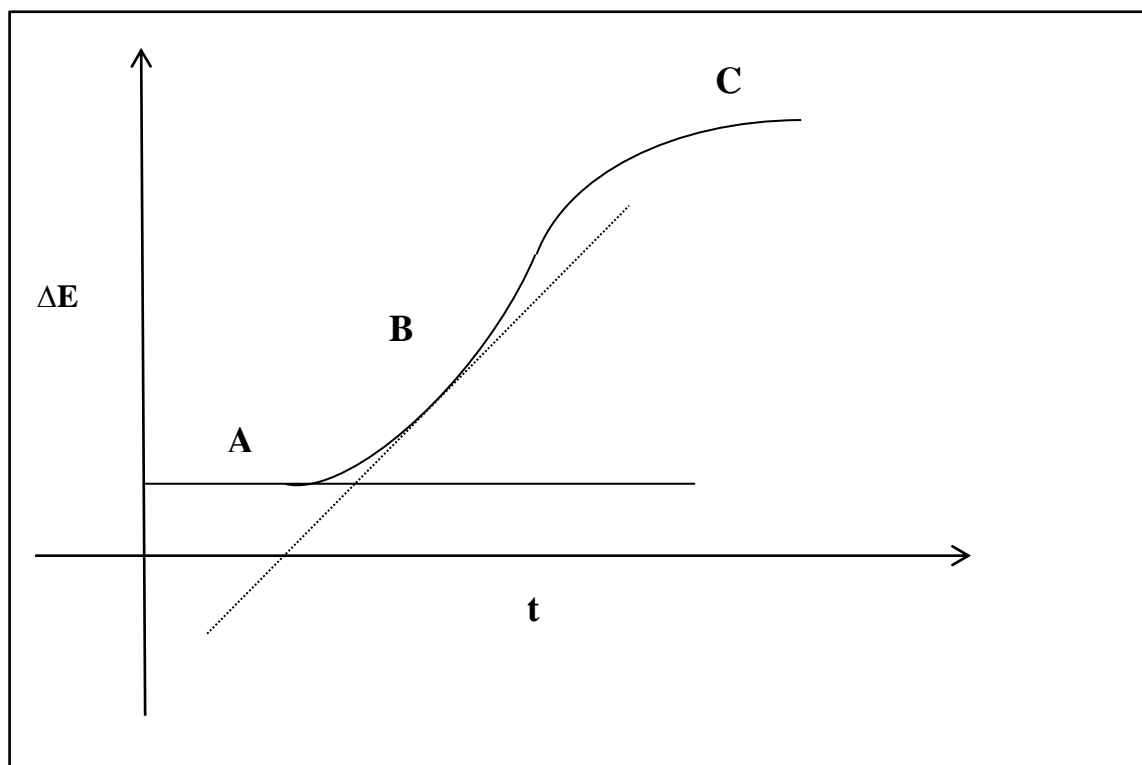


Fig. 4-2 Colour change of a dyed textile material on exposure to light over a period of time. Typical for fading resistant materials.

From the graph above, region A (at the start of light exposure) represents part where a particular material is displaying resistance to fading. Region B represents part where the material is changing colour (fading). C represents a region where the dyestuff on a material is completely removed or, more precisely, the dyestuff molecule containing chromophoric part has completely degraded. However, such kind of graph is observed only for resistant materials. Materials which are weak in terms of resisting colour change due to light show a bit different graphical behavior. From fig. 4-3 on the next page, it can be seen that for such weak materials the A region of the previous graph do not exist. These have been reported to normally start fading (B region) as soon as the light is radiated onto them (i.e. enough light to cause degradation of a particular dyestuff. Enough to be absorbed and cause photochemical aging

which results in radical processes and photooxidative reactions and therefore destruction of chromophores), hence getting to reach C region much faster. Depending on some factors associated with fading, samples showing such behavior also fade differently.

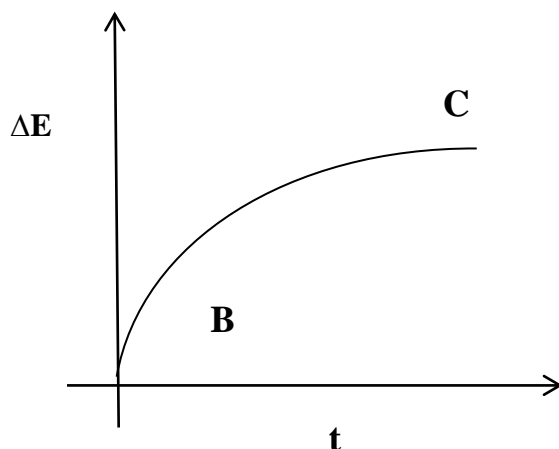


Fig. 4-3 Colour change of a dyed textile material on exposure to light over a period of time. Typical curve for colour change weak materials.

The kinetic model was applied to treat fading data obtained from the spectrophotometer measurements. Such treatment of light fastness data from materials has resulted in fading curves that show good correlation. This was performed by taking and contrasting  $\Delta E$  with respect to time of exposure for each tested sample. Same was also done for maximum reflectance with respect to time. Fig.4-4 is showing the graph of a material with a good resistance to fading. At an early stage of the sample exposure to light, the material displays resistance to light fading (constant blue line which is almost parallel to the x-axis). This corresponds to region A of fig 4-2. After approximately 7 hours of exposure, the material starts to fade as shown by linear increase of  $\Delta E$  with increase in light exposure time (corresponds to region B). For fig. 4-5, the best fit of the data the model constructed was the straight line. This is implying the quick fading of the material on the light irradiation. We are right on region B. However, Orange M3 as seen on table 2 above that it gave lower value of  $\Delta E$  compared to many samples tested. This was further witnessed as well on visual comparison. Therefore, even though it graphically not displaying same resistance as Green 4B, it is good.

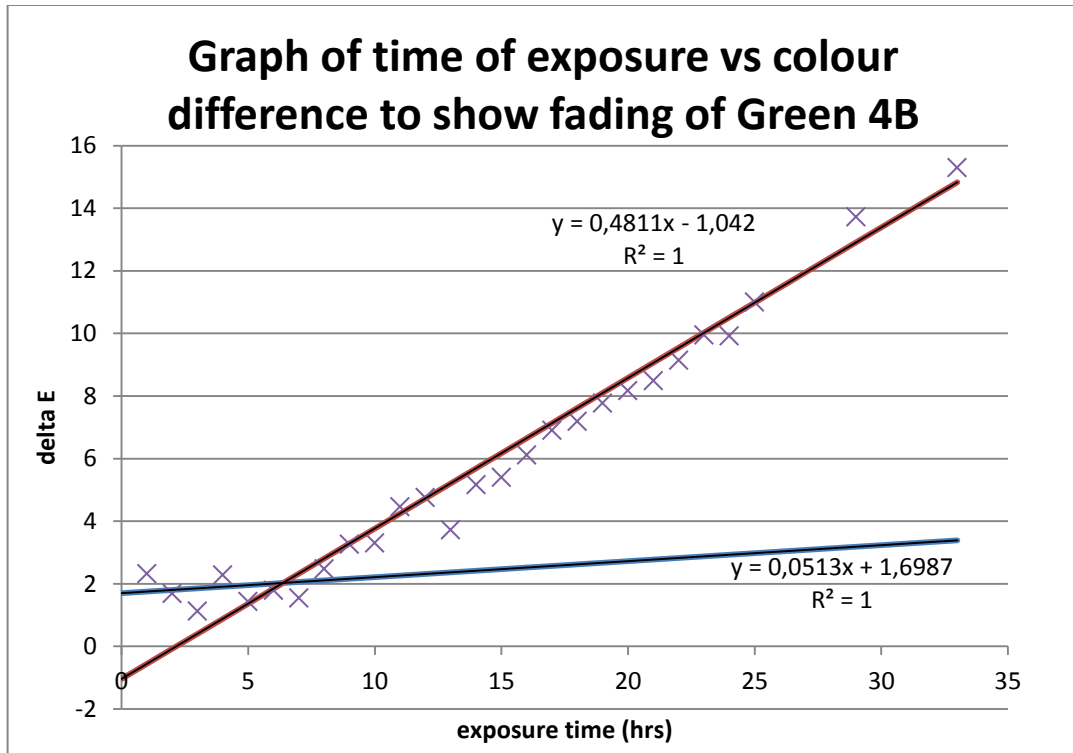


Fig. 4-4 Color difference graph showing fading of a resistant textile material Green 4B

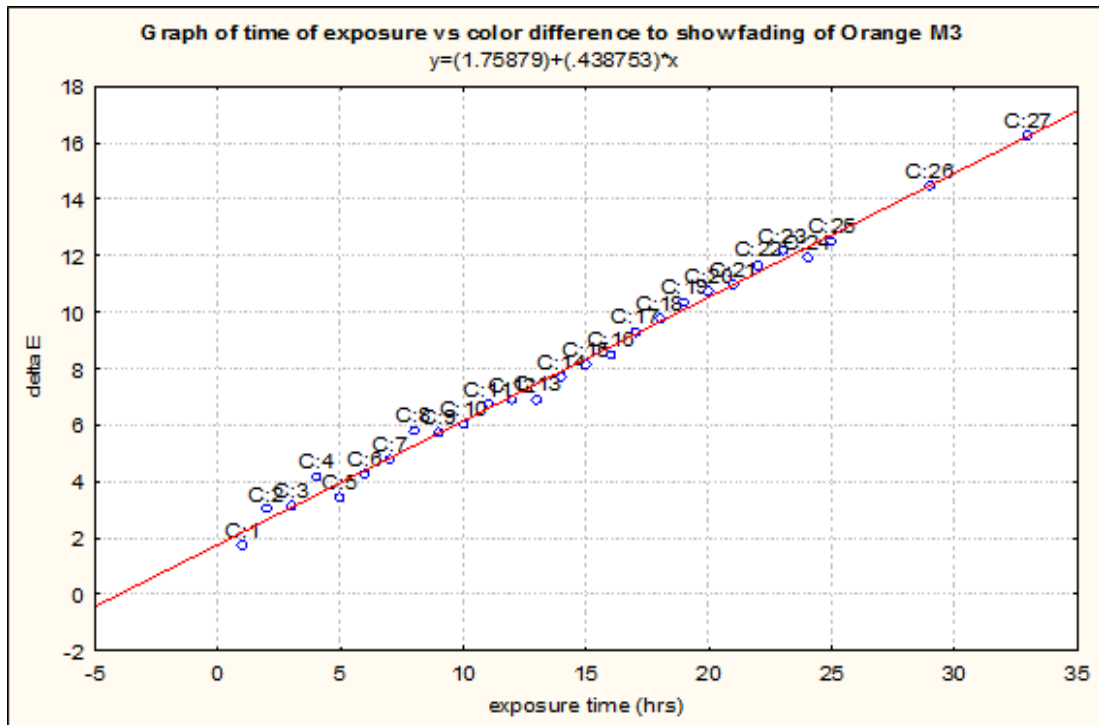


Fig. 4-5 Color difference graph showing fading of a resistant textile material Orange M3.

Correlation, R = 0.99686



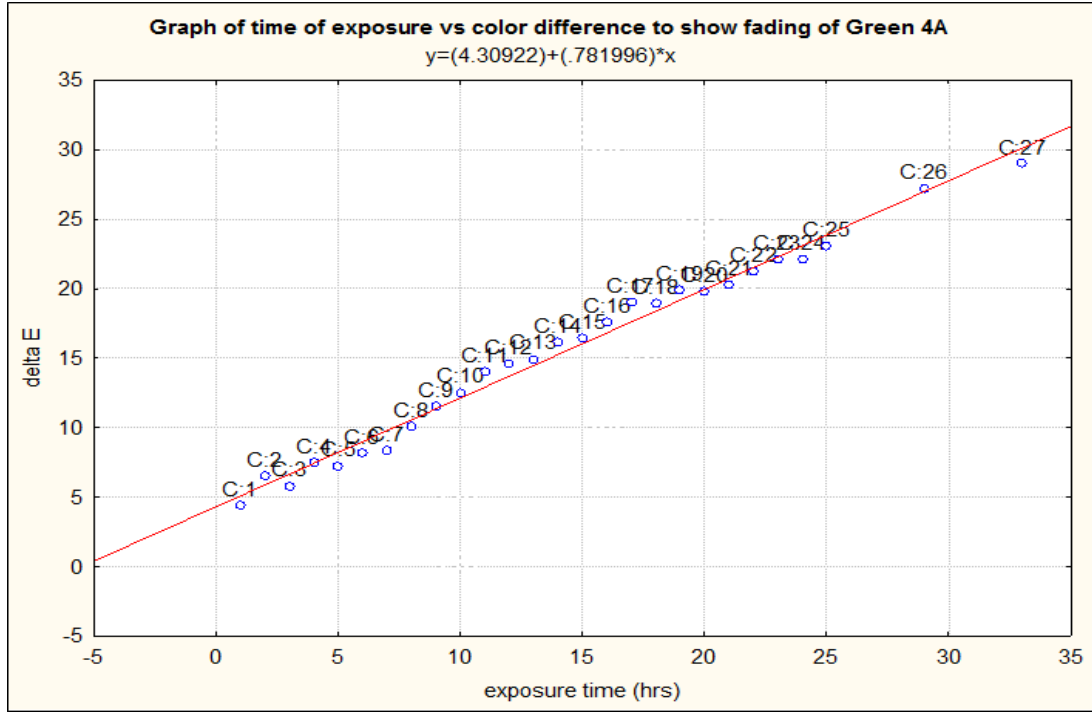


Fig. 4-6 Color difference graph showing fading of weakly colour changing textile material Green 4A.

Correlation, R = 0.99339

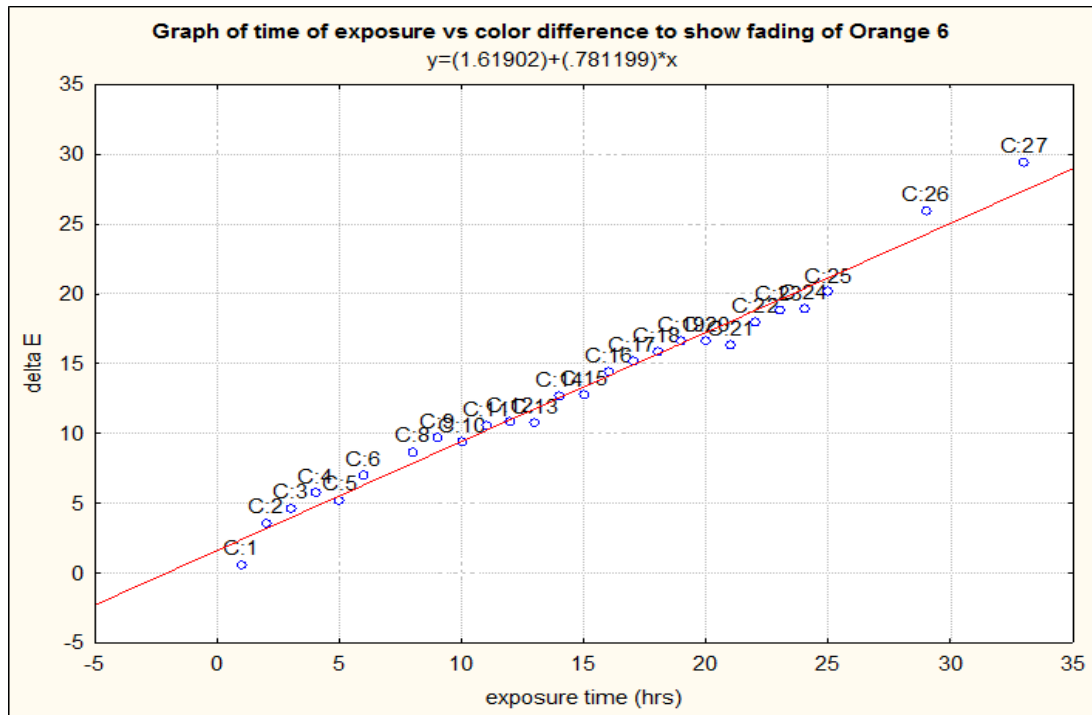


Fig. 4-7 Color difference graph showing fading of weakly colour changing textile material Orange 6.

Correlation, R = 0.98979

For the figures 4-6 and 4-7 (weakly color changing materials), we are on the fading region, B. Even though the model could not construct a typical curve for so behaving materials as in fig. 4-3, we are confident to regard them as such based on the evidence from tables 3 and 4 (high  $\Delta E$  values obtained) as well as in visual comparison. Further evidence for this is seen on the reflectance curves. It should be noted that for a given time of the experiment, none of the selected samples is yet showing signs of reaching region C.

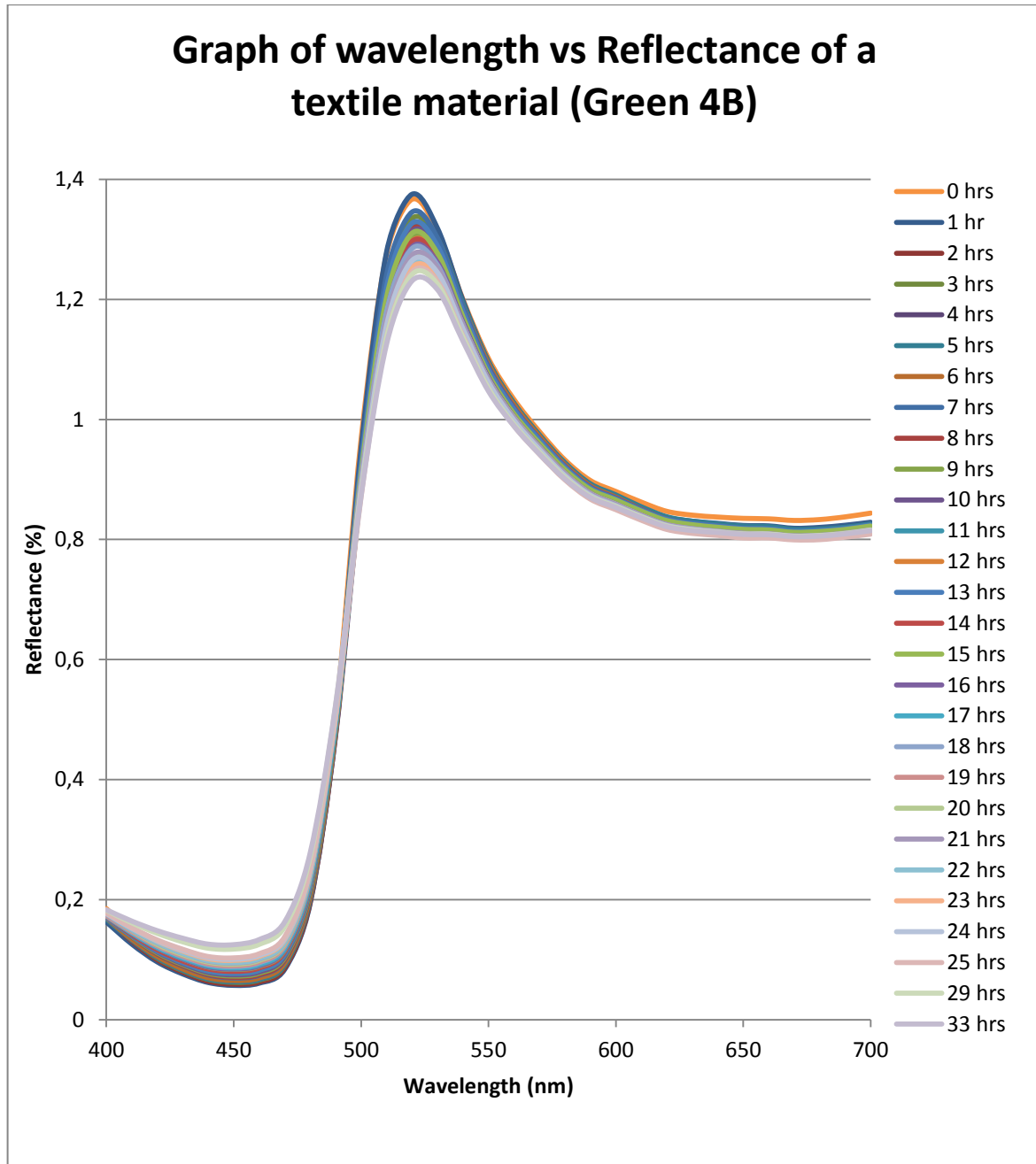


Fig. 4-8 Reflectance as a function of wavelength plotted from the spectrophotometer data (1).

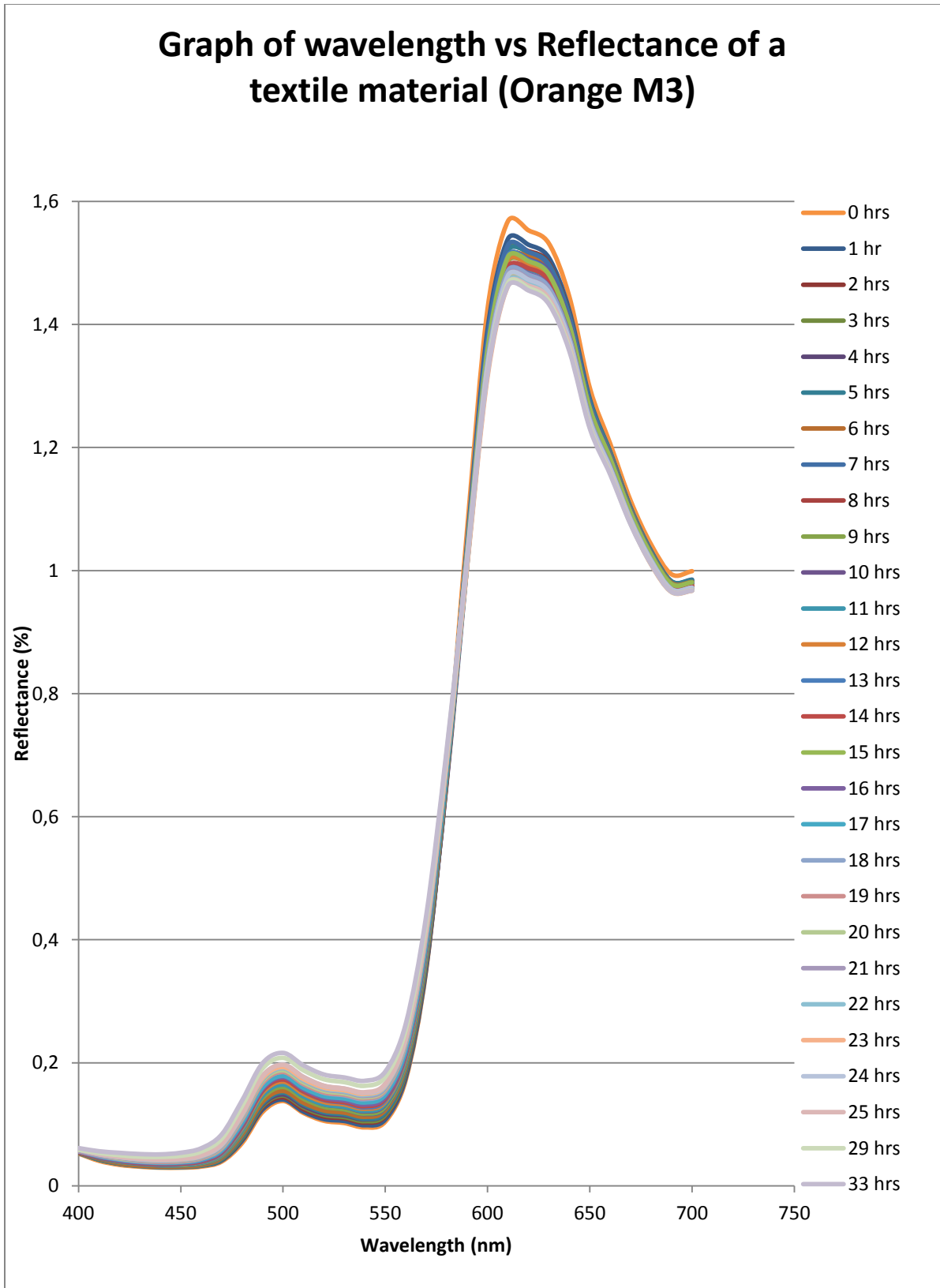


Fig. 4-9 Reflectance as a function of wavelength plotted from the spectrophotometer data (2).

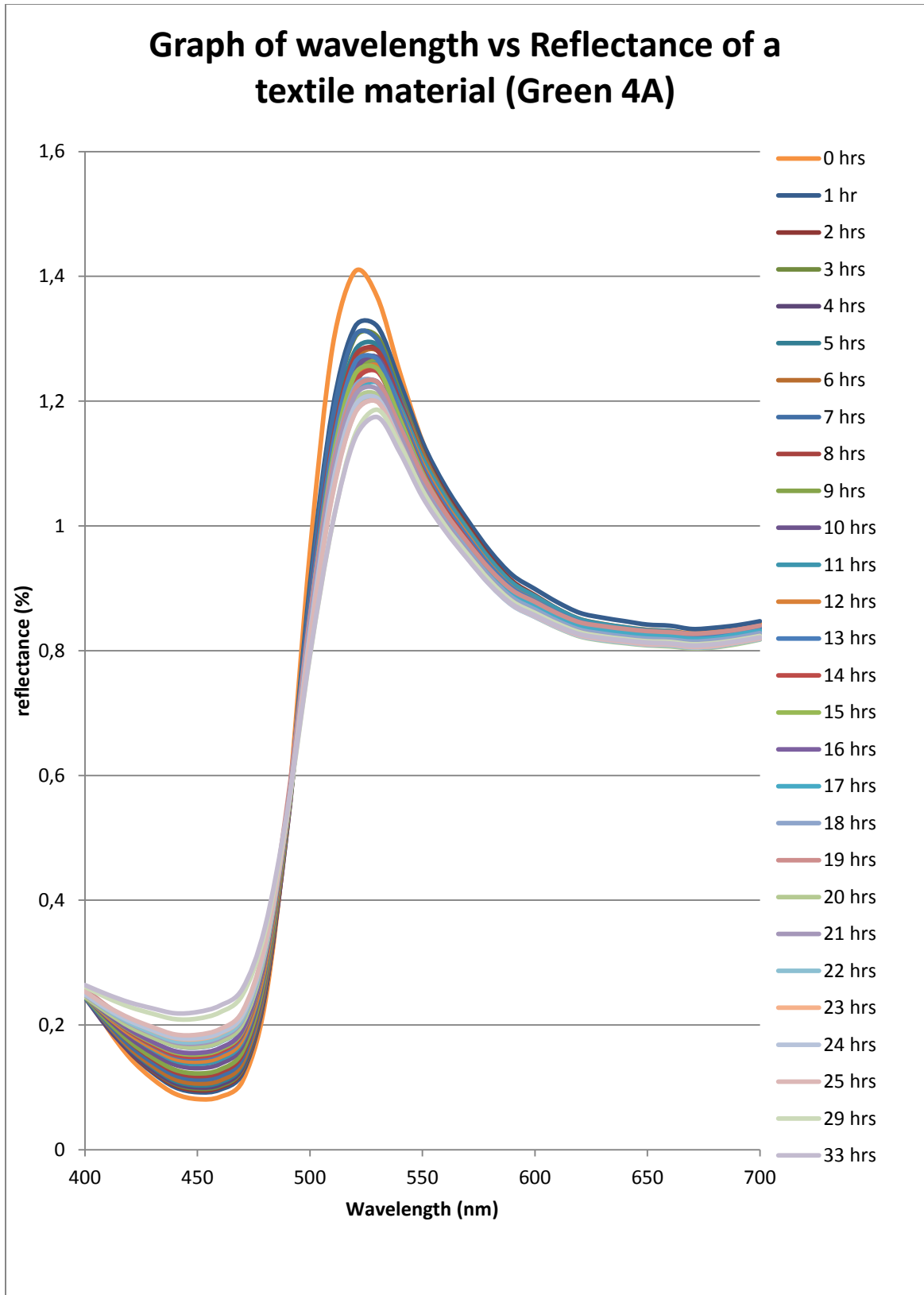


Fig. 4-10 Reflectance as a function of wavelength plotted from the spectrophotometer data (3).

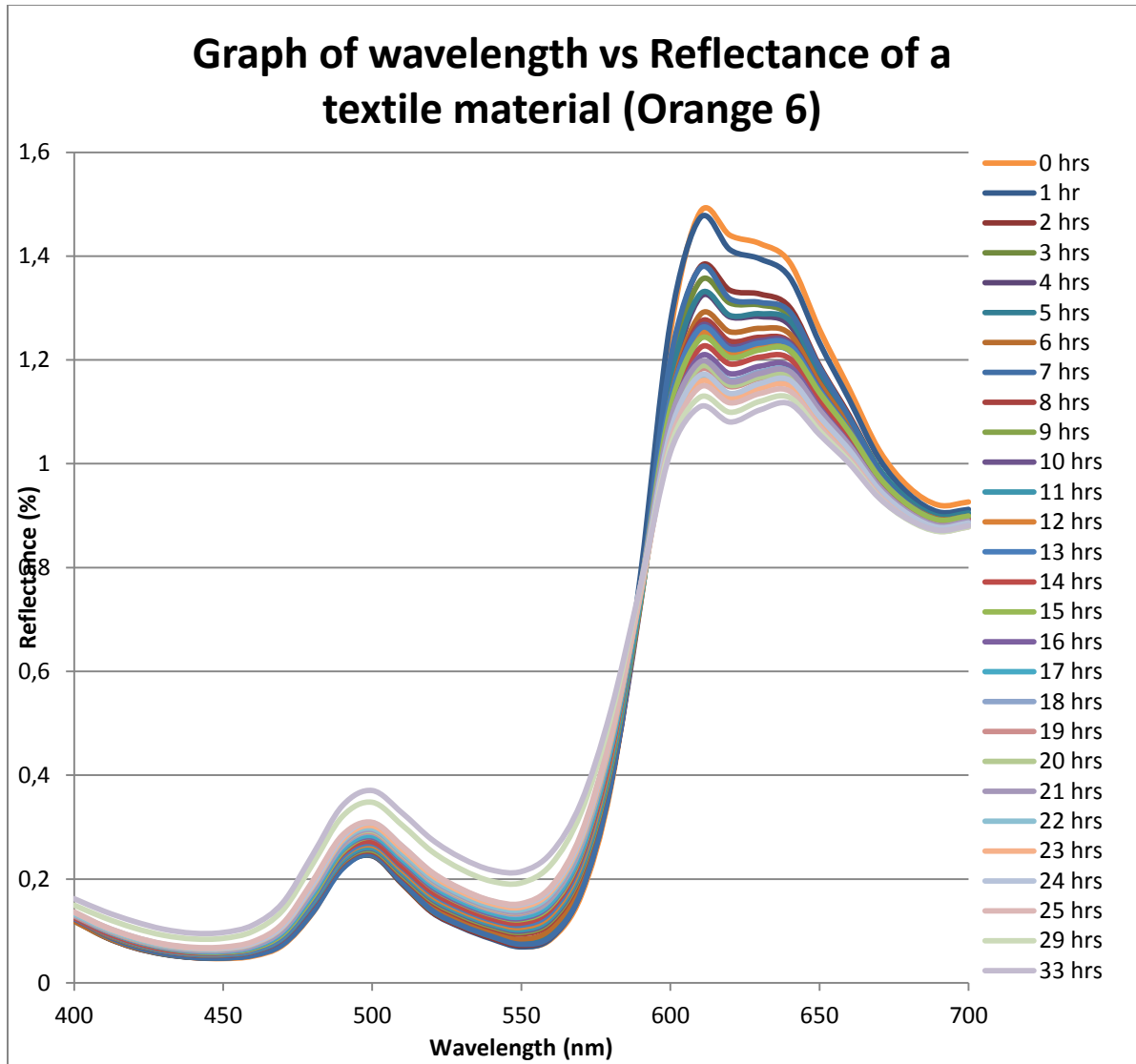


Fig. 4-11 Reflectance as a function of wavelength plotted from the spectrophotometer data (4).

The fading of most dyes is said to become slower as fading proceeds. The same effect was observed on the tested samples (reflectance/wavelength graphs above). When looking on the graphs, the gaps at the beginning (from the top curve at 0 hour to 1 and 2 hours). However, the gaps on the weak samples are observed for almost every hour of light exposure while the resistant samples only display such gap/s at a very early stage of the experiment (first hour). Moreover, the rate of fading of the specimen was shown by the construction of the graphs (figures 4-12 to 4-15) of all the reflectance peaks plotted as a function of time and the graphs displayed good correlation. From these graphs, fading rate constant was obtained as coefficient of the independent variable (time, t) in the exponent.

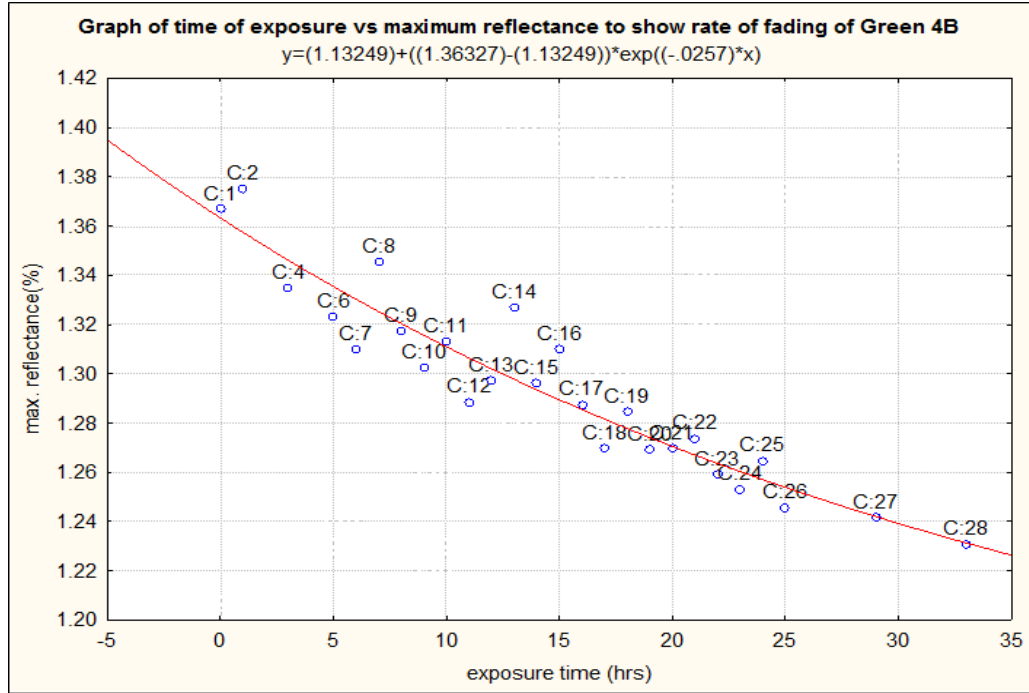


Fig. 4-12 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (1).

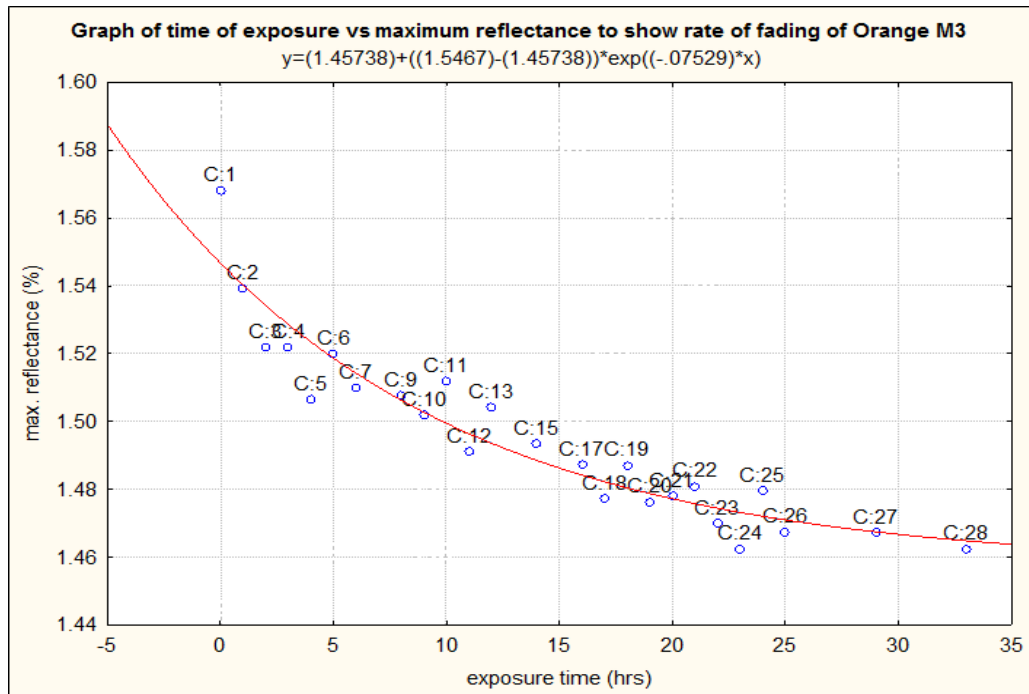


Fig. 4-13 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (2).

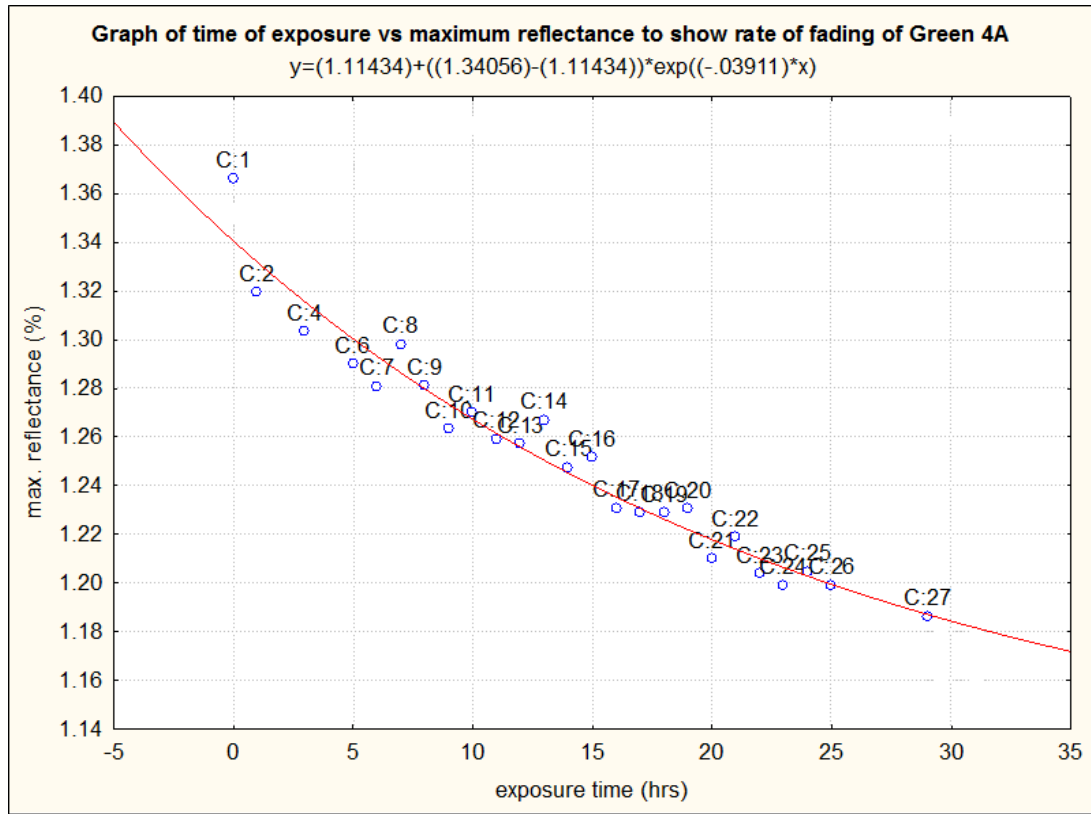


Fig. 4-14 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (3).

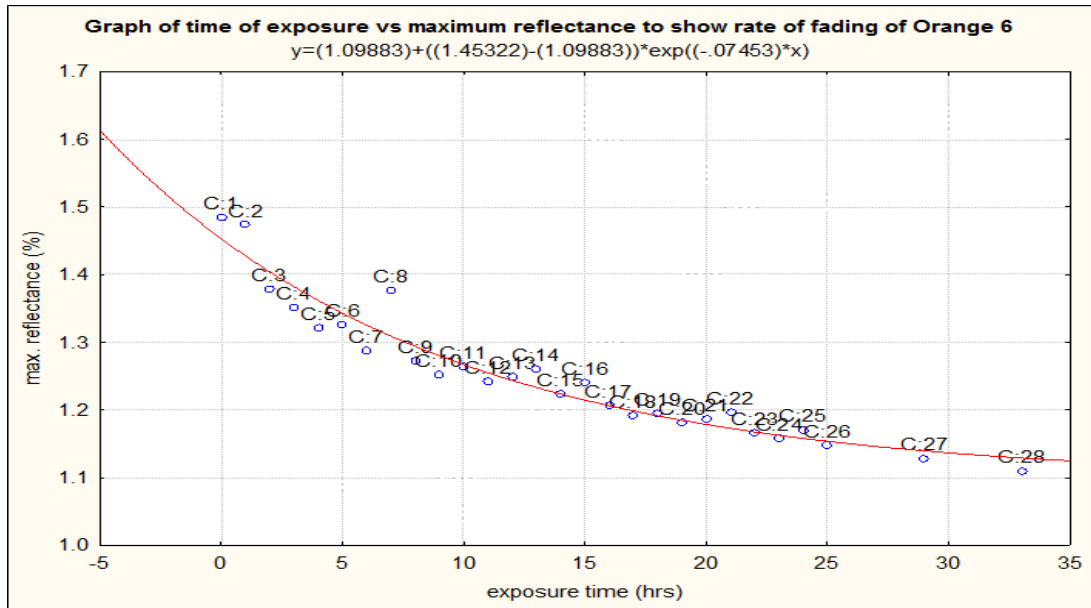


Fig. 4-15 Rate of fluorescence fading during UV irradiation. Rate shown by maximum reflectance (peak) as a function of time (4).

The fading rate constant, according to Daniels [32], is related to  $\Delta E$  which measures changes in visual appearance. Photodegradation, as a chemical process, can as well be explained using rate constant. The negative sign implies decreasing of a measured quantity (fluorescence/reflectance maxima in this case). From the graphs above, doing a colour based comparison seems to provide good results interpretation.

**Green:** 4B - rate constant = 0.0257/hr

4A – rate constant = 0.03911/hr

**Orange:** M3 – rate constant = 0.07529/hr

6 – rate constant = 0.07453/hr

It can be then confidently said that sample green 4A fades faster than green 4B. Orange samples appear to have approximately the same number of rate constant, but looking at the formulae (exponential) provided by the model used, we observe higher and lower values. For a given experiment duration (same for both samples), orange M3 faded from a maximum reflectance of approximately 1.55 to 1.46 while orange 6 faded from 1.45 to 1.1. For all tested samples, lower rate constant values were observed for most green samples as compared to the orange coloured samples.

In addition, half-life which measures the rate of the first order reaction was calculated and tabulated on the table below:

**Table 6.** Calculated half-lives of the tested materials.

Sample name	$t_{1/2}$ (hrs)
Green 4B	26.97
Green 4A	17.7
Orange M3	9.21
Orange 6	9.30

Sample calculation: Green 4B

$$\begin{aligned}
 t_{1/2} &= \ln 2/k \\
 &= \ln 2/0.0257 \\
 &= \mathbf{26.97 \text{ hrs}}
 \end{aligned}$$



The shorter half-life represents faster fading of the material while the longer one is showing a greater stability.

**Graph of time vs temperature**

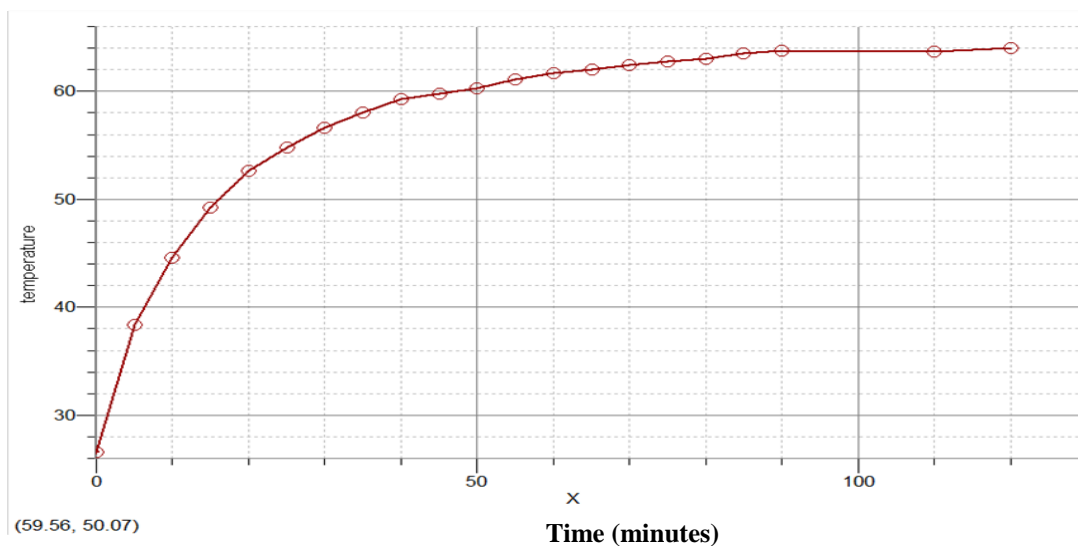


Fig. 4-16 Temperature increase inside the chamber as a function of time

As described in section 2.4 that excess energy is normally converted into vibrational energy which is then converted into heat. A temperature increase (unwanted effect) is produced on the surface of a material. This increase causes chemical changes including loss of color. Heat also reduces moisture content on the fabric.

One of the problems associated with fluorescent materials is the difficulty of comparing different samples even with the same device. Such challenge is observed with orange samples selected and with others of similar composition (Orange M1, M2, 7, and 8. See appendices A and B). The samples that showed resistance (showing both smaller color difference and visual comparison) has displayed the rate constant almost equal or greater than the weak samples. This is the case where a very rapid slight change is observed on the specimen on exposure but do not change further as the time progress. However, the case is with polyamide/elastane samples compared to polyester samples. i.e. totally different substrates with different dyestuffs. This brings a question of a polymer morphology and chemical structure of dye which might be a good approach angle for further research on this particular topic. The other factor involved is

the texture effect on colour difference measurement. Smooth specimens are reported to give accurate measurements for sphere geometry specular exclusion than textured ones.

In addition, just as we need light to observe the beauty of fluorescence in high-visibility clothing, the absorption of radiant energy is also necessary for ageing polymer fiber structure. The energy necessary for the purpose of bond breaking depends on crosslinking nature and reacting atoms. Different fibers require different energies for their crosslinks to be broken. This implies that even with the same dyestuff applied on different substrate, fading will not occur at the same rate. This is explained by the UV-material interaction principle that, some light partially absorbed (that is, not reflected part of light) go through fabric structure, absorbed by fibers, and hence resulting to fading. Again, this serves another factor to look close on further research for this topic.

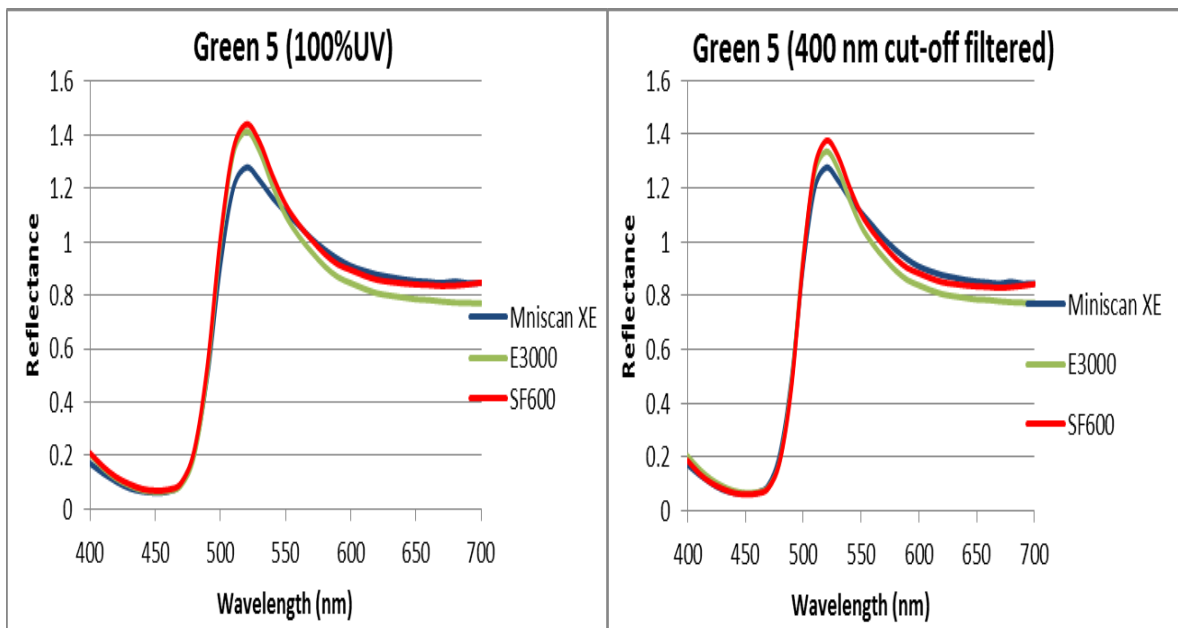


Fig. 4-17 Comparison of results for three different devices used to measure same sample.

*Left:* E3000 and SF600 had setup with no cut-off filter (100% UV).

*Right:* 400 nm cut-off filters used for E3000 and SF600 devices.

The results of different reflectance/fluorescent measuring devices gave different results for the same sample tested (see graphs in appendix C). This is another problem associated with fluorescence. Fluorescence/reflectance measured by datalcolor instruments, SF600 and E3000,

gave higher reflectance (%) than obtained for miniscan. This, however, is because of high power Xenon lamps used in datacolor devices.

The four additional samples of the materials used in parachutes were put as part of the investigation, but these were only measured for 24 hours (Green: 286, 67, and 759. Orange: 66). However, in comparison to the warning cloth materials, these samples were of smaller thickness and translucent. This means that they will behave in a totally different way in terms of interaction with light. From the results, orange sample displayed very high colour difference value as compared to green samples (refer to appendix A).

## **CHAPTER 5: Conclusion and recommendations for future research**

The main purpose of light fastness testing is the prediction of a material's fading (colour loss). The observations of the investigation on the specimens tested for light fastness clearly demonstrate different fading rate for different materials. The kinetic model graphs of colour difference for the specimens along with maximum reflectance graphs displayed different shapes and different fading rate constants. For the selected samples, this was further emphasized by half-lives calculated. Also, on the four selected samples, the green coloured samples gave lower fading rate constants and therefore longer half-lives in comparison to the orange coloured samples.

Apart from many factors to be considered when performing such tests and difficulties associated with fluorescent materials, we are, however, able to compare the results for different materials tested under same conditions. For this reason, the main goal for this particular work of confirming the validity of standard methods for fluorescent materials testing has been accomplished. This also serves as the confirmation of the usability of such simple testing for people planning to perform such in the small laboratories without any need to pay money for big companies and yet wait long for the results to come back. However, most importantly, the international ISO standards should be met if one is to perform this. This includes laboratory exposure device, proper test specimen preparation, exposure conditions, exposure methods, etc... In addition to that, such lightfastness testing instruments as Xenotest alpha of Atlas company, cost about \$120 000. The simple chamber used in the laboratory for this project allows relative comparison between products tested. Such chamber costs about \$2-5000, a simple low price system for small and medium enterprises (SMEs).

For further research on the topic, the recommendation is the consideration of effects such as material construction, finishing technology applied on a material, texture effect on colour difference measurements, and energy required to break the bonds of an involved fiber. It might be as well wise to have same number of each colour measured so as to draw conclusions onto which of the high visible colours is least stable and also most degradable on a material as observed in parachute materials' results. The difference was so huge in terms of colours. Due to a limited amount of time provided for the practical work, it was not possible to see a complete behavior of the tested specimen upon exposure to light. A much longer time of exposure will

allow us to see an exact behavior of the samples without speculating. This will again allow the graphical confirmation of the half-lives apart from calculating from the computer calculated rate constants. Basically, more options of analyzing the investigation results can be possible and thus more solid conclusions can be drawn. As far as the instrument set-up is concerned, the recommendation is that 400 nm cut-off filters should be used to avoid an increased fluorescence/reflectance obtained when 100% UV set-up is used.

The proposals on the future research can be:

- ✓ Thermal fading of fluorescent materials
- ✓ Effect of fluorescent dye – substrate bond on photodegradation
- ✓ Cyclic fading test. That is, the use of time periods instead of continuous exposure. For example, a 5 minutes time period can be used. The results can then be compared with long hour exposure.

## REFERENCES

1. Barbara M. R. and Crew P, *Ultraviolet Absorbers: A Treatment to Reduce Fading and Degradation of Textiles*, university of Nebraska-Lincoln, 1987, [http://digitalcommons.unl.edu/textiles\\_facpub/16](http://digitalcommons.unl.edu/textiles_facpub/16)
2. Bamfield P. 2001. *Chromic Phenomena: The Technological Applications of colour chemistry*, Cambridge: The Royal Society of Chemistry, UK, pp. 157-182
3. Blasse G. (1989), "New Luminescent Materials", American Chemical Society, page 294, <http://pubs.acs.org/doi/pdf/10.1021/cm00003a005>
4. Broadbent A. 2001. *Basic Principles of Textile coloration*, England: Society of Dyers and Colourists, pp. 427-466
5. Christie R.M. 2008. *Fluorescent dyes*, Scottish College of Textiles, Netherdale, UK, Rev. Prog. Coloration Volume 23, 1993
6. Feller R. 1994. *Accelerated Aging: Photochemical and Thermal Aspects*, The J. Paul Getty Trust, pp. 45-
7. Harold R.W. and Hunter R.S. 1987. *The measurement of appearance. 2<sup>nd</sup> edition*. New York: John Wiley & Sons, pp 29, 23
8. Johnson I. and Davidson M., National High Magnetic Field Laboratory, 1800 East Paul Dirac Dr., The Florida State University, Tallahassee, Florida, 32310, <http://www.olympusmicro.com/primer/java/jablonski/jabintro/>. [Accessed 20 November 2011]
9. Klessinger M. and Michl J. 1995. *Excited states and Photochemistry of Organic molecules*, New York: VCH Publishers, Inc. pp 245
10. Kuehni R.G. 1997. *Color – An introduction to Practice and Principles*, Canada: John Wiley & Sons, Inc. page 11
11. Laamanen T., *Defects in persistent luminescence materials*, Turun Yliopisto University of Turku, (2011), pg 8
12. Lezak k. and Frydrych I., *Ageing Simulation of Fabrics Destined for Protective Clothing*, Central Institute for Labour Protection-National Research Institute. *Fibres & Textiles in Eastern Europe* 2011, vol. 19, No. 2(85) pp. 54-60

13. Pagani A. *Organic and Biomolecular Chemistry*, – Vol. II Organic Photochemistry, Encyclopedia of Life Support Systems (EOSS)
14. Rakicioglu Y. and Akseli A. 1998 *New Fluorimetric Reagent, Sodium Pyrophosphate, Sodium Trimetaphosphate, and Sodium Tetrametaphosphate, for the determination of Cerium (III)*, Journal of Fluorescence, Vol. 8, No. 1
15. Szuster L., Kazmierska M. and Krol I., *Fluorescent Dyes Destined for Dyeing High-Visibility Polyester Textile Products*, 2003
16. Wolfe W (1998), *Introduction to RADIOMETRY*, Washington: The society of Photo-Optical Instrumentation Engineers, pp 1
17. Prof. Michal Vik, MSc., PhD.: Pretreatment – PTE1
18. [http://www.iss.com/resources/research/technical\\_notes/K2CH\\_FLT.html](http://www.iss.com/resources/research/technical_notes/K2CH_FLT.html)
19. [http://en.wikipedia.org/wiki/Electromagnetic\\_radiation](http://en.wikipedia.org/wiki/Electromagnetic_radiation)
20. <http://guweb2.gonzaga.edu/faculty/cronk/CHEM240pub/L03-index.cfm>
21. <http://www.wilsonhurst.com>
22. <http://www.olympusmicro.com/primer/java/jablonski/jabintro/>
23. <http://www.tmj.ro/article.php?art=860258468412442>
24. <http://www.brittanica.com/EBChecked/topic/197770/excitation> article from Encyclopedia Britannica. [Accessed 02 February 2012]
25. <http://www.spaceandmotion.com/Physics-Quantum-Theory-Mechanics.htm> Geoff Haschurst. [ Accessed 08 October 2011]
26. Chen R. and Lockwood D. 2002. *Developments in Luminescence and Display Materials Over the last 100 Years as Reflected in Electrochemical society Publications*, The Electrochemical Society, Inc., Journal of The Electrochemical Society, 149 (9) S69-S78
27. Justel T., Nikol H. and Ronda C, *New Development in the field of Luminescent Materials for Lighting and Displays*, Wiley:VCH Verlag GmbH, D-6951 Weinheim, 199, pg 3085-3087
28. <http://www.firstlight.nl/lampen/speciale-uv-lampen/osram-ultramed-400-130v-r7s-uv-lamp-let-op-voor-de-huid-en-ogen/>
29. [http://www.satrap.co.uk/spotlight/download.php?file=spot\\_high\\_visibility\\_clothing](http://www.satrap.co.uk/spotlight/download.php?file=spot_high_visibility_clothing)
30. <http://www.ihvca.org/downloads/IHVCA%20Standard.pdf>

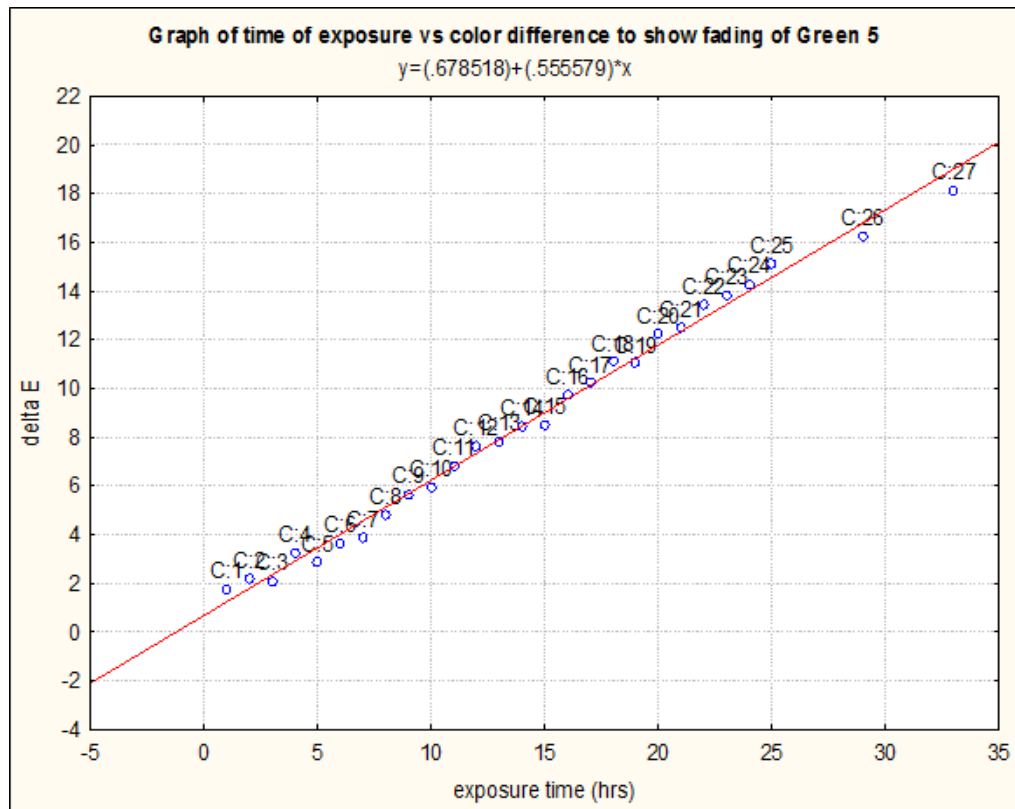
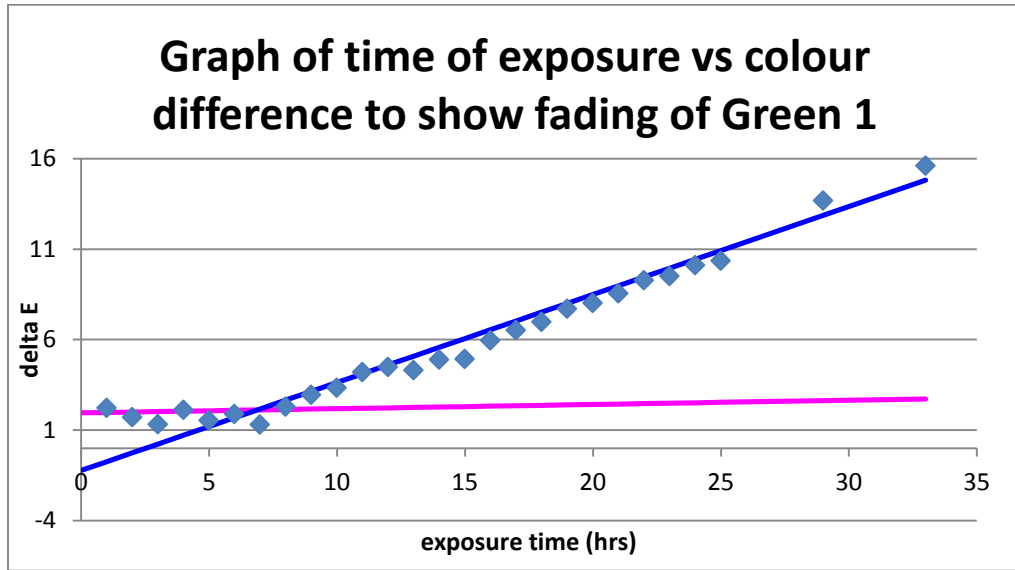
31. [http://203.158.253.140/media/e-Book/Engineer/Material/Handbook%20of%20Material%20Weathering/98127\\_12.pdf](http://203.158.253.140/media/e-Book/Engineer/Material/Handbook%20of%20Material%20Weathering/98127_12.pdf)  
Colour fading in Textile Materials.
32. <http://onlinelibrary.wiley.com/doi/10.1111/j.1478-4408.2012.00359.x/pdf> Mecklenburg M. and del Hoyo-Melendez J. 2011. *Development and application of a mathematical model to explain fading rate inconsistencies observed in light-sensitive materials*, cited in Daniels V, *J. Photochem. Photobiol. A Chem*, 184 (2006) 73.
33. <http://www.bsigroup.com/en/Standards-and-Publications/Current-work/DPCs> Draft BS ISO 105-B02 Textiles - Tests for colour fastness. Part B02: Colour fastness to artificial light: Xenon arc fading lamp test: London, 2009

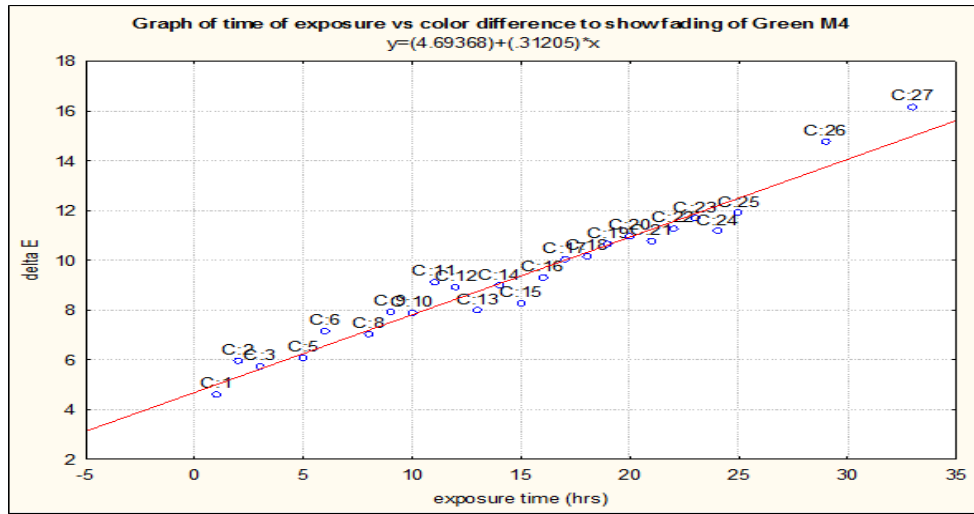
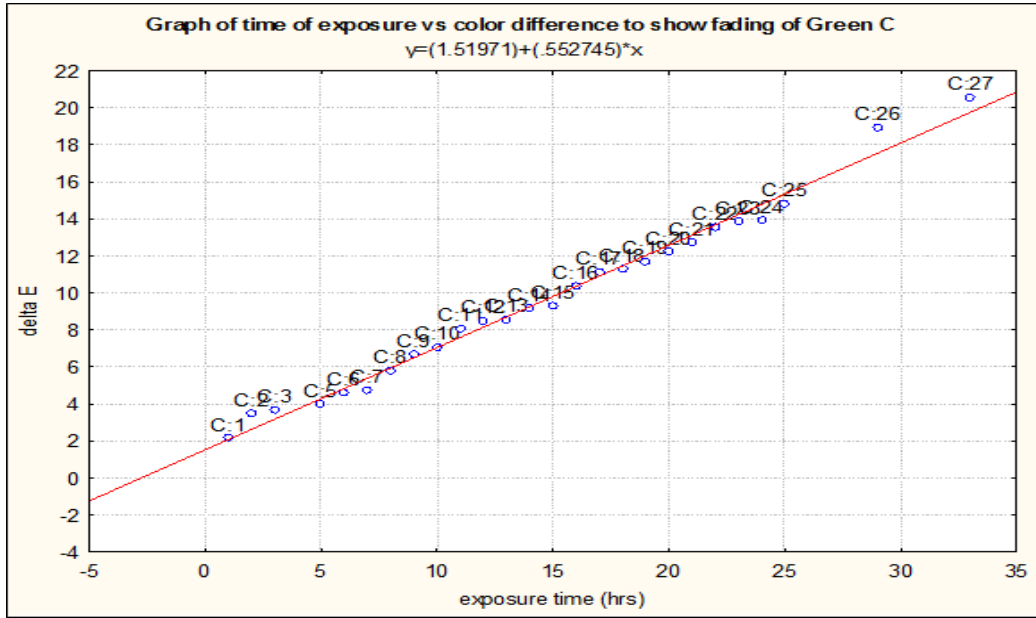


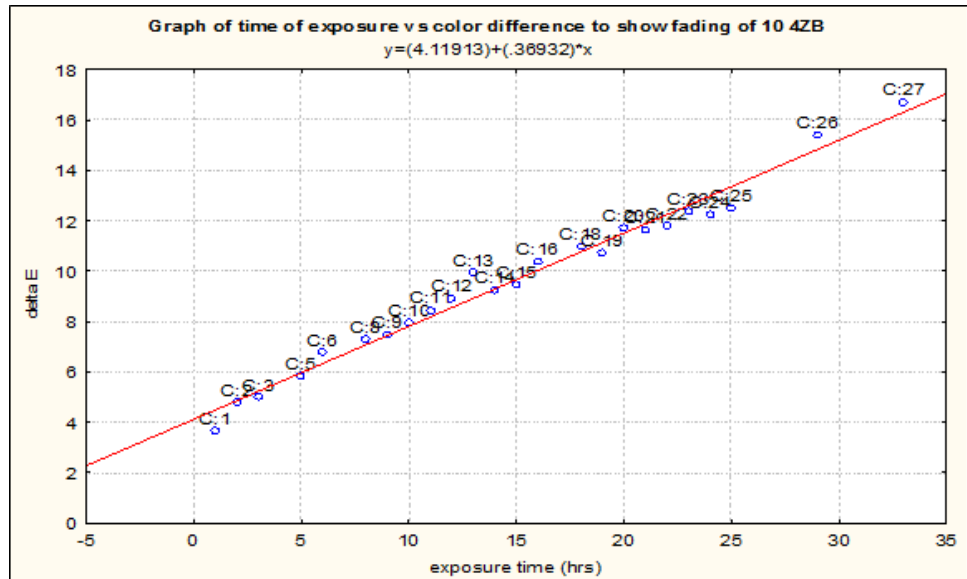
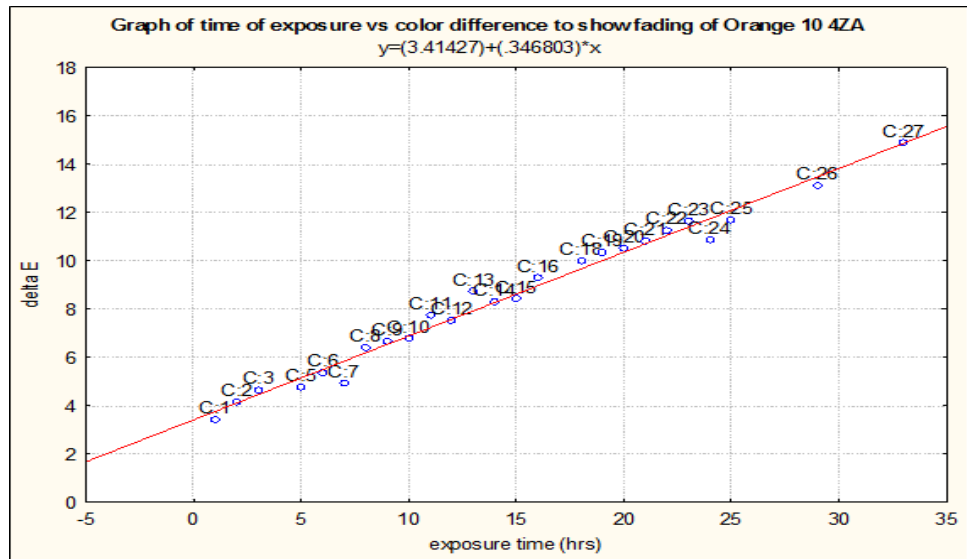
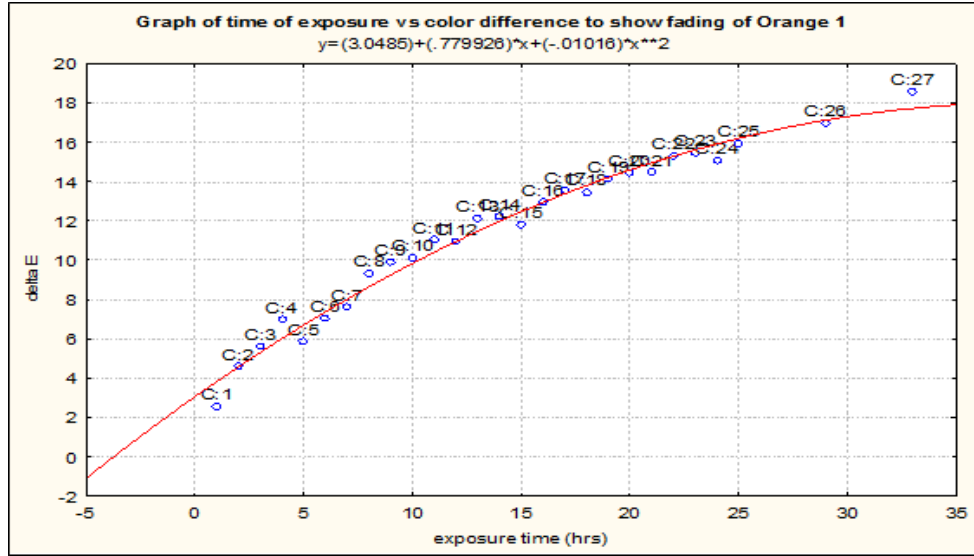
## APPENDICES

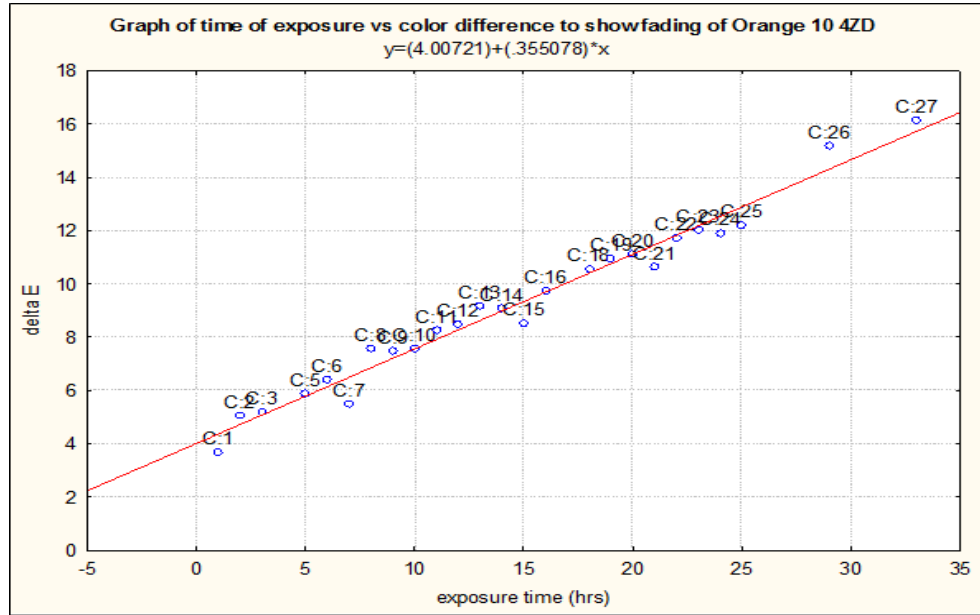
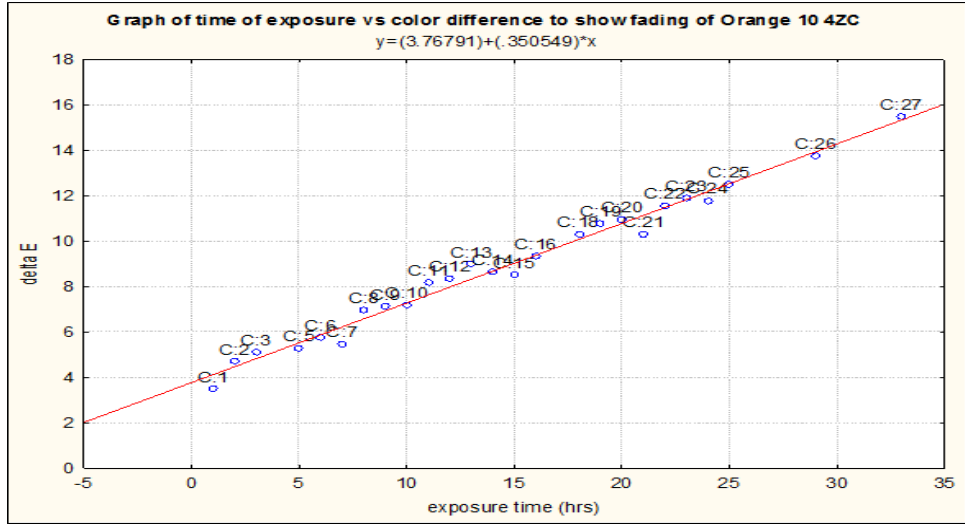
### Appendix A

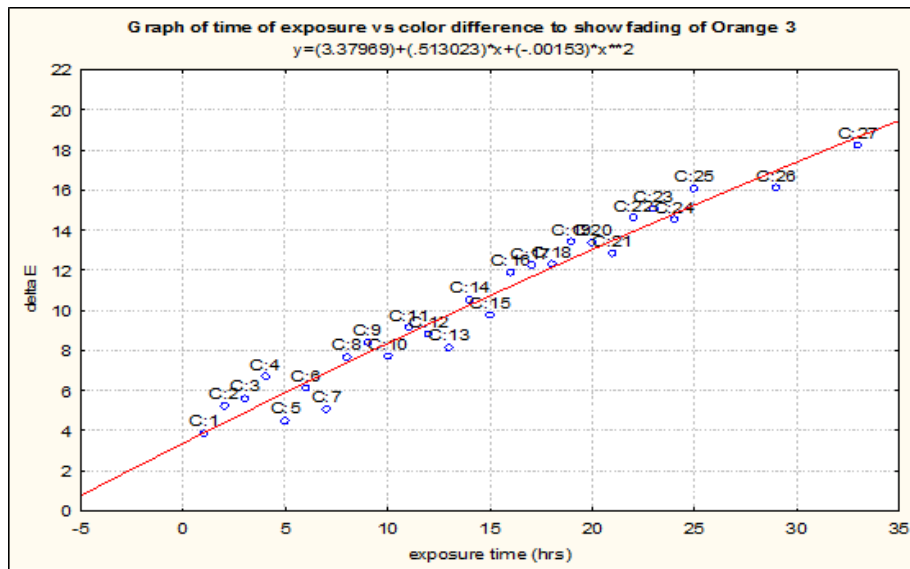
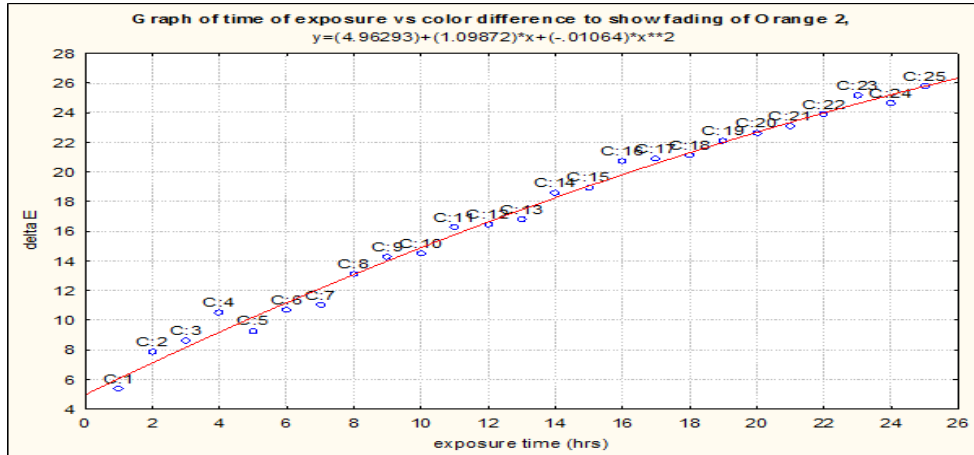
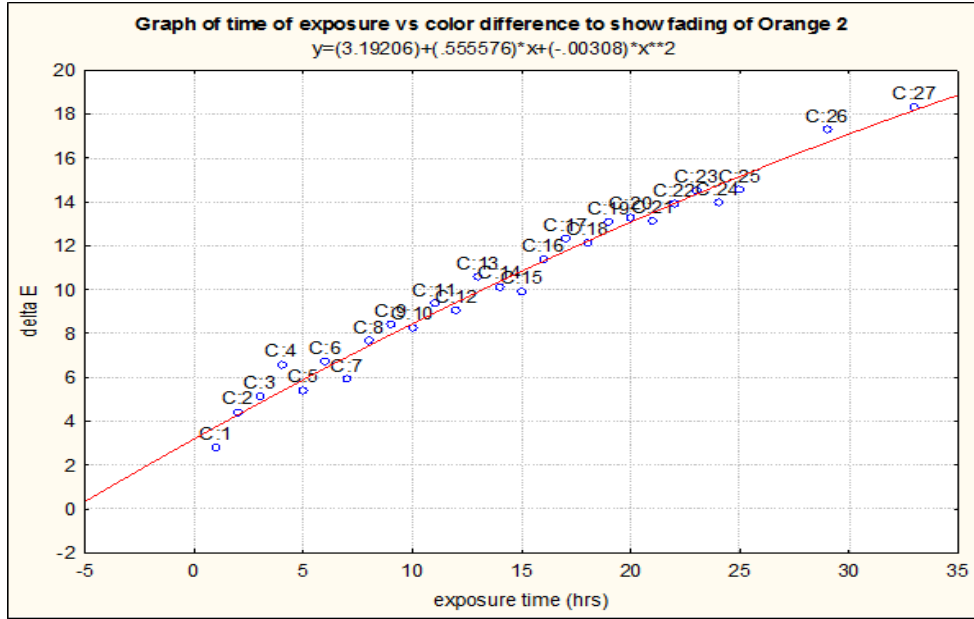
This appendix shows the rest of the obtained colour difference ( $\Delta E$ ) graphs vs time of light exposure.

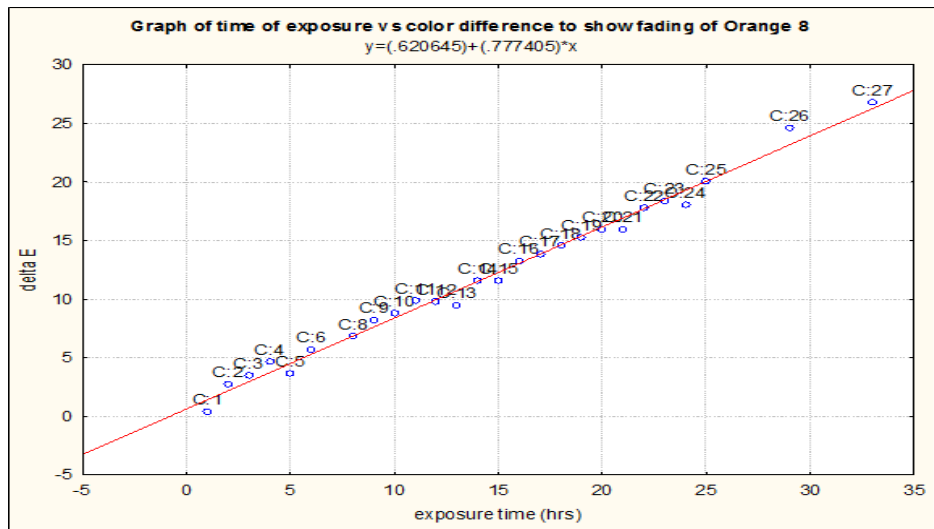
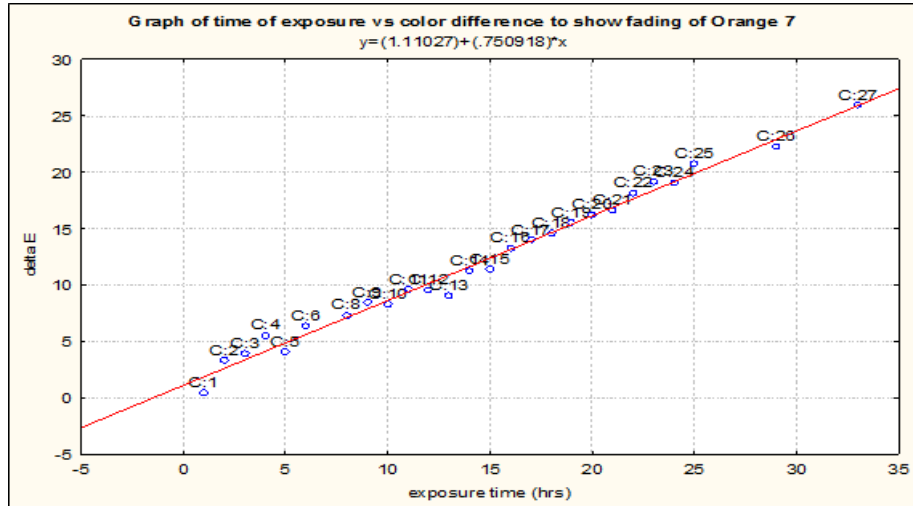
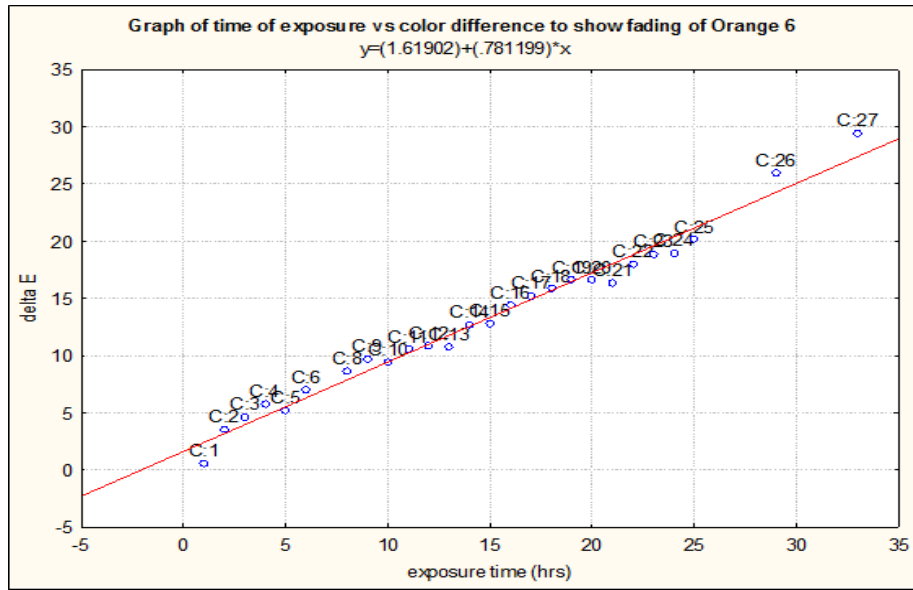


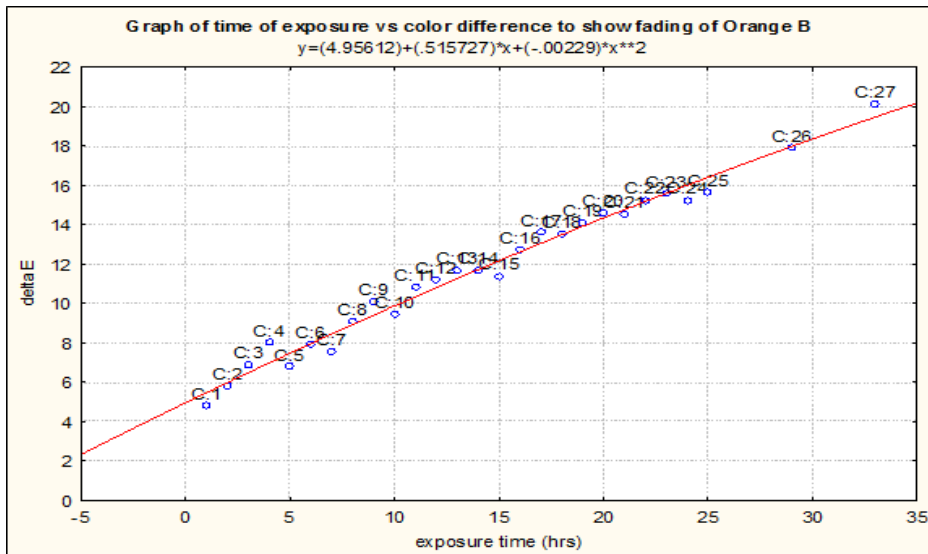
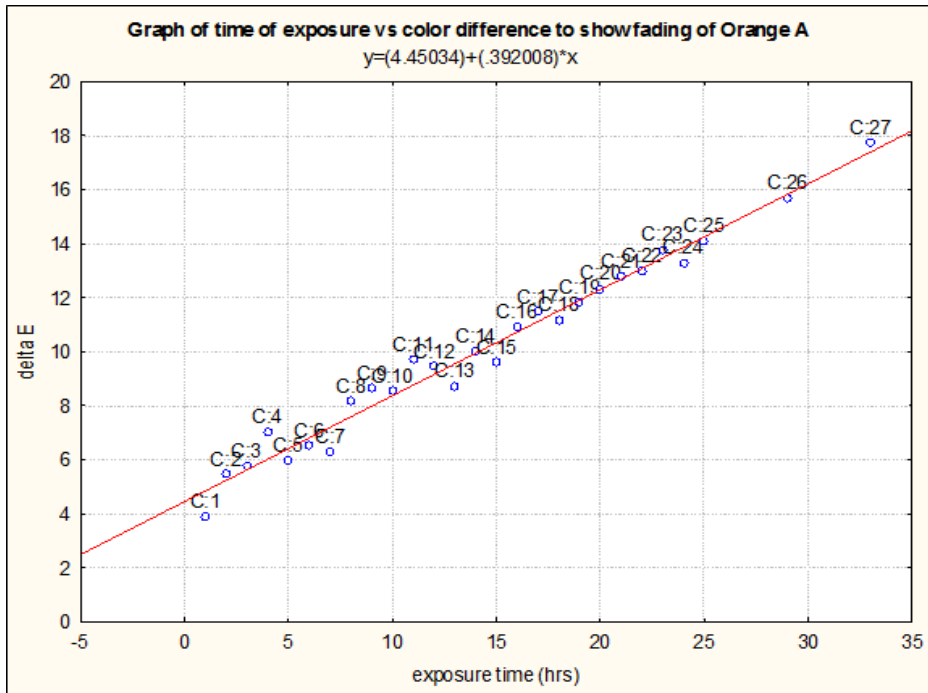
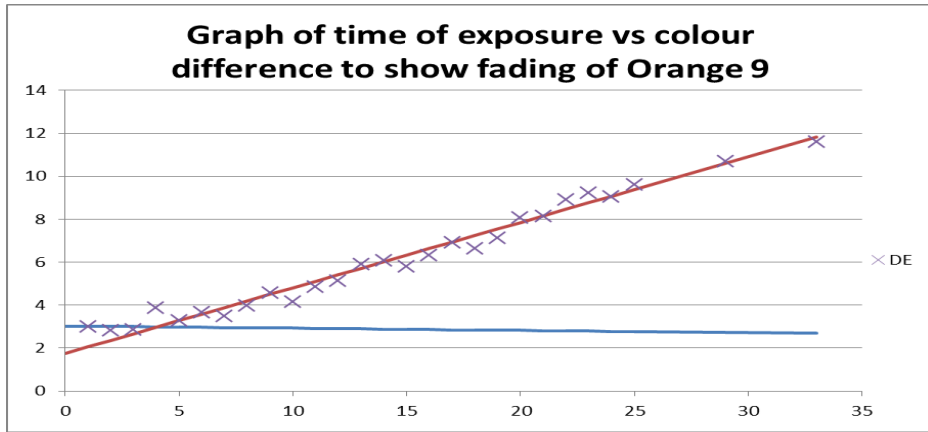


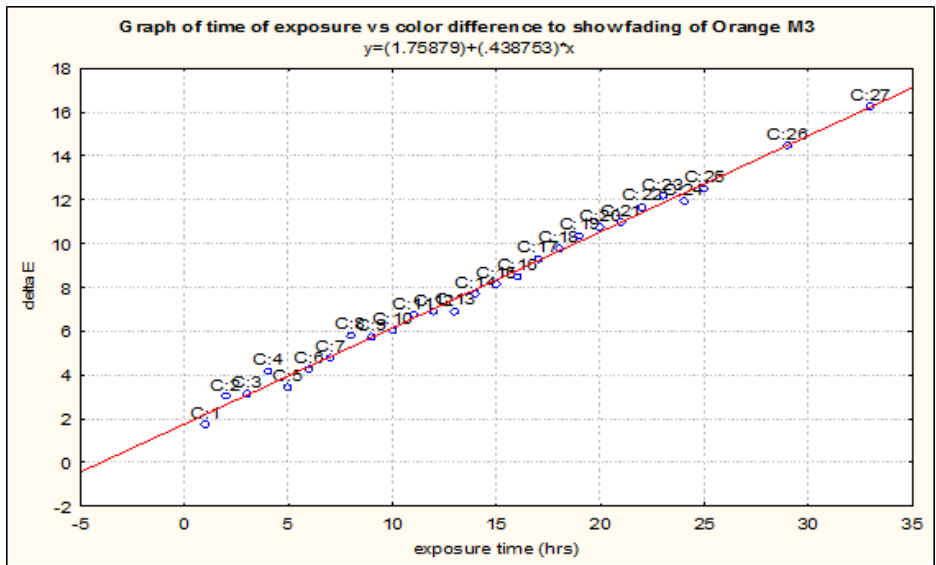
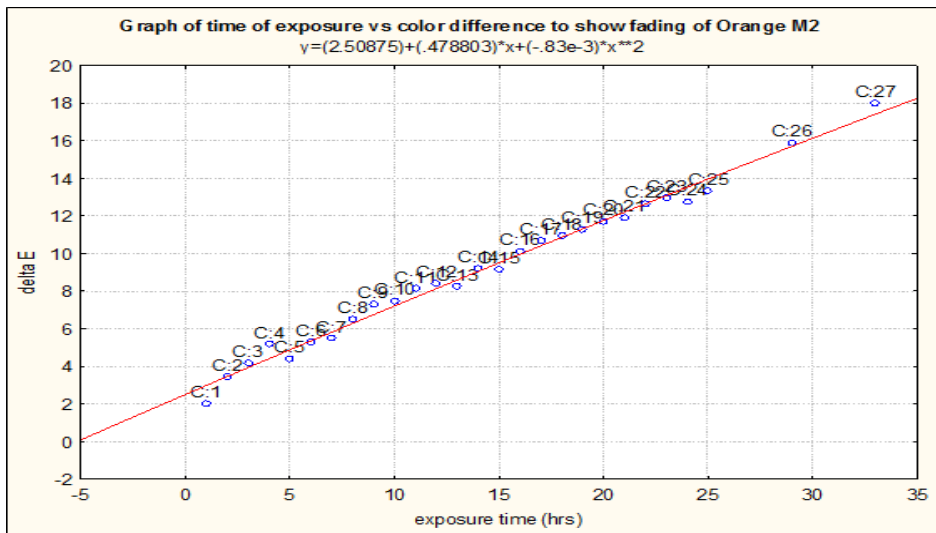
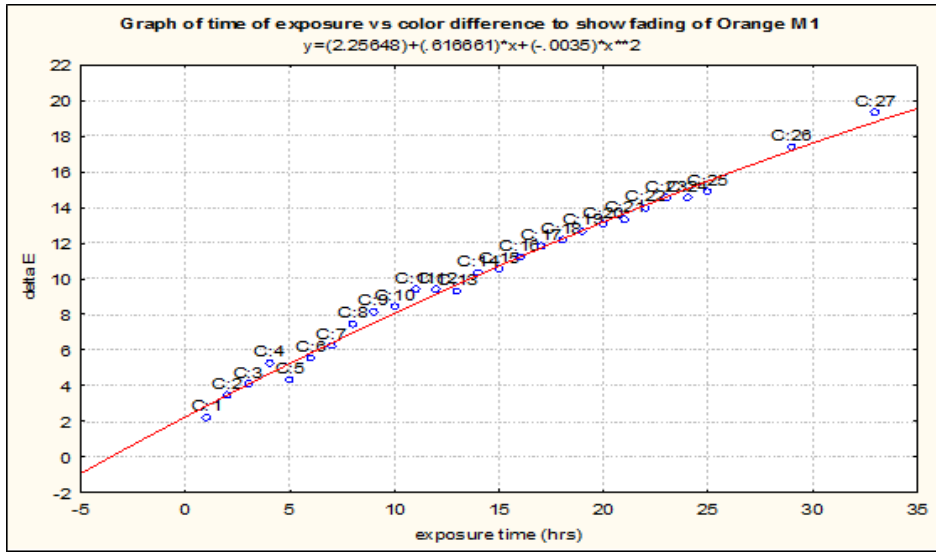




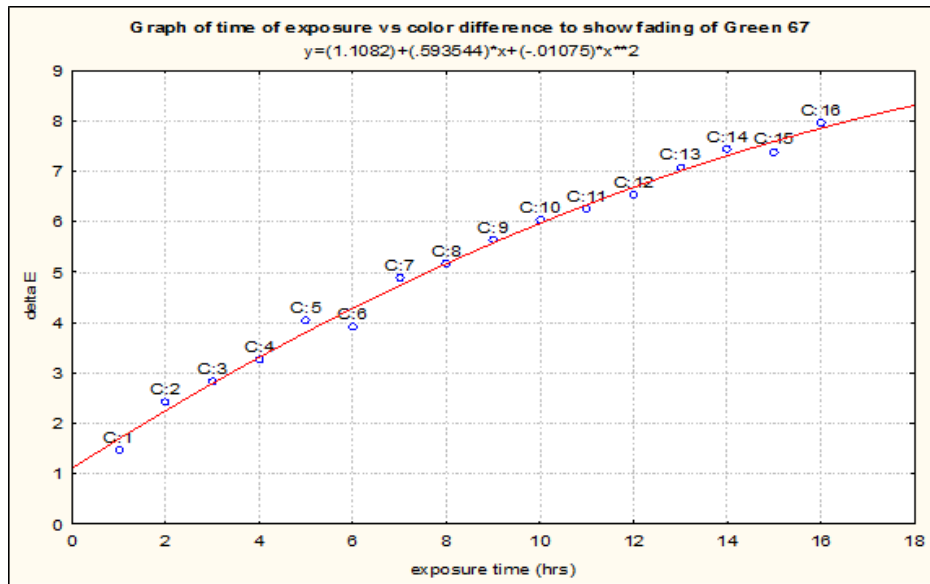
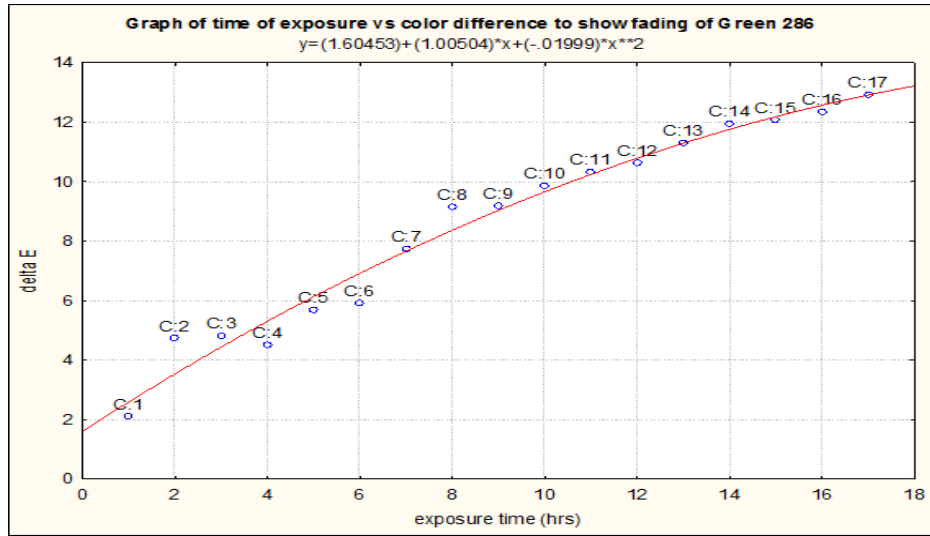


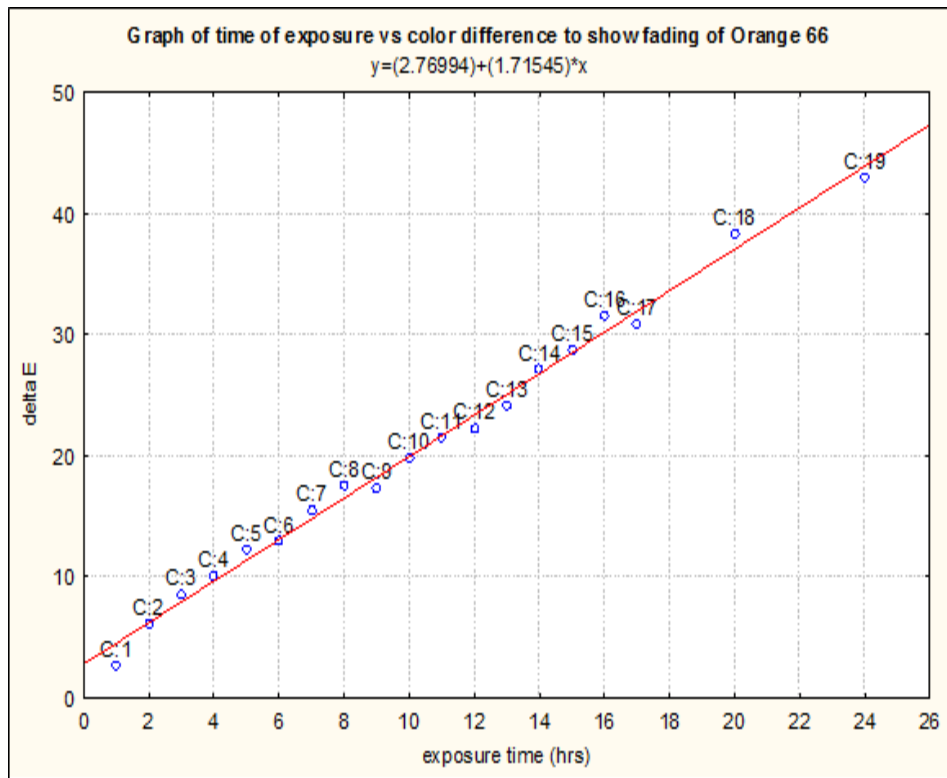
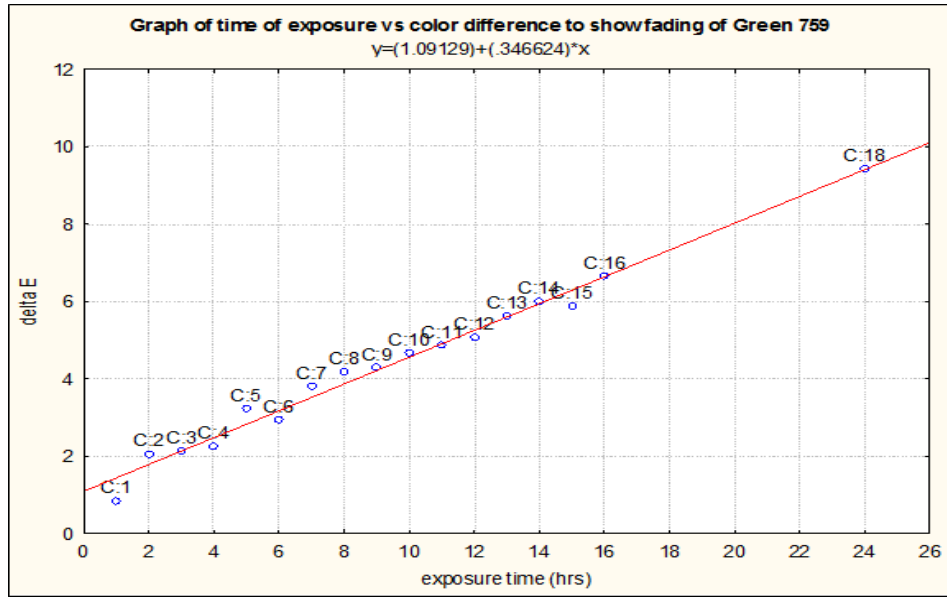






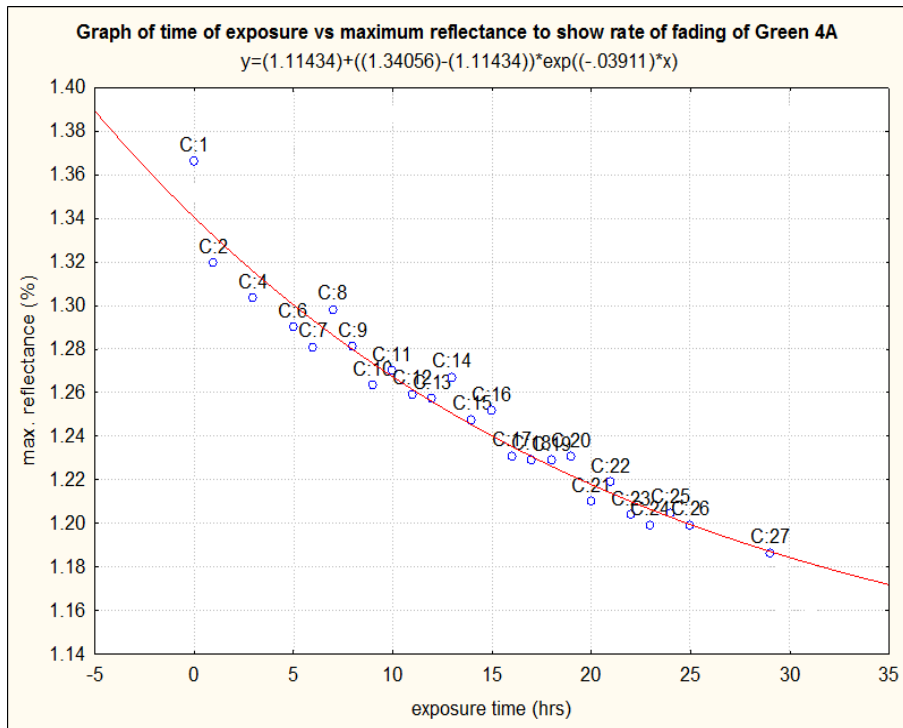
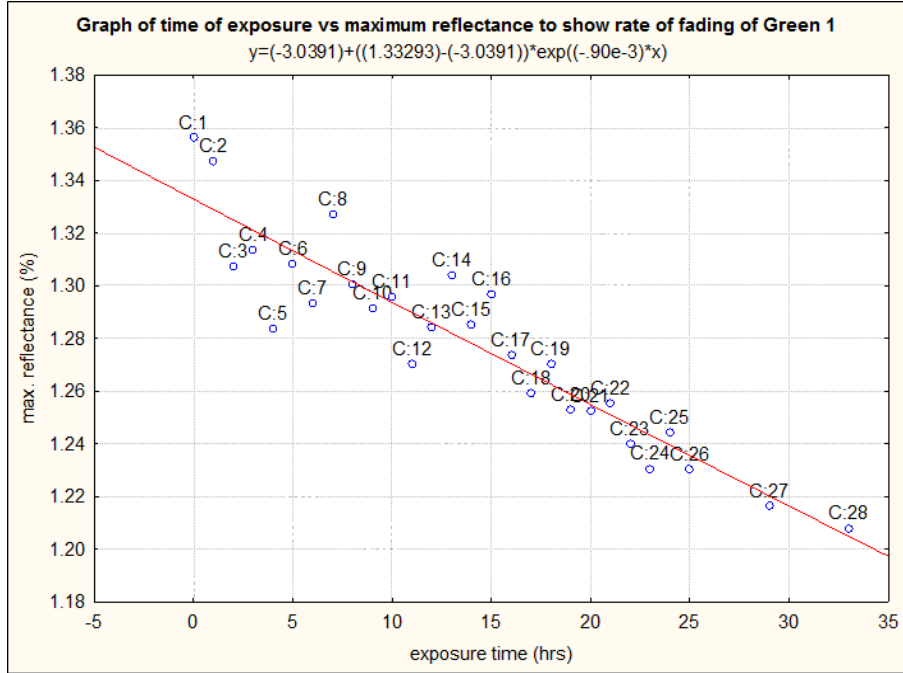


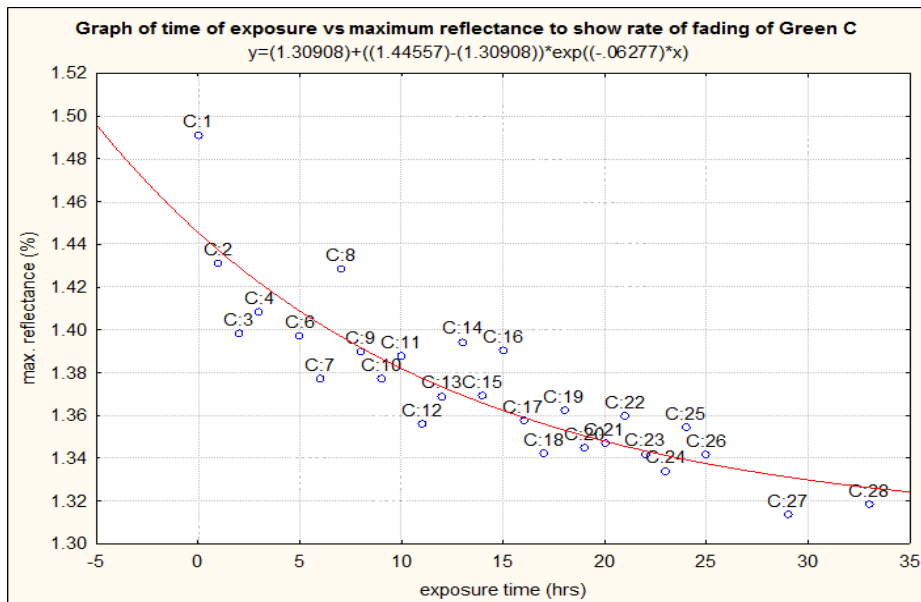
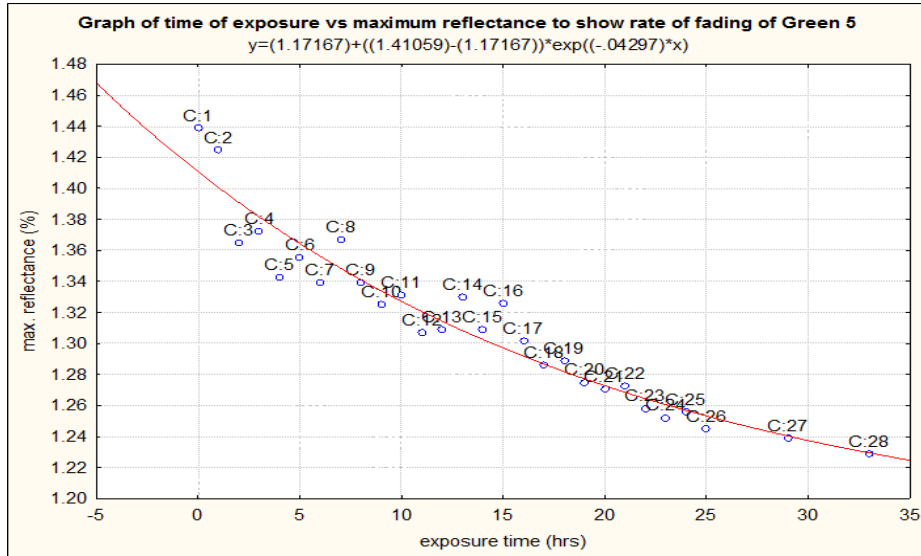
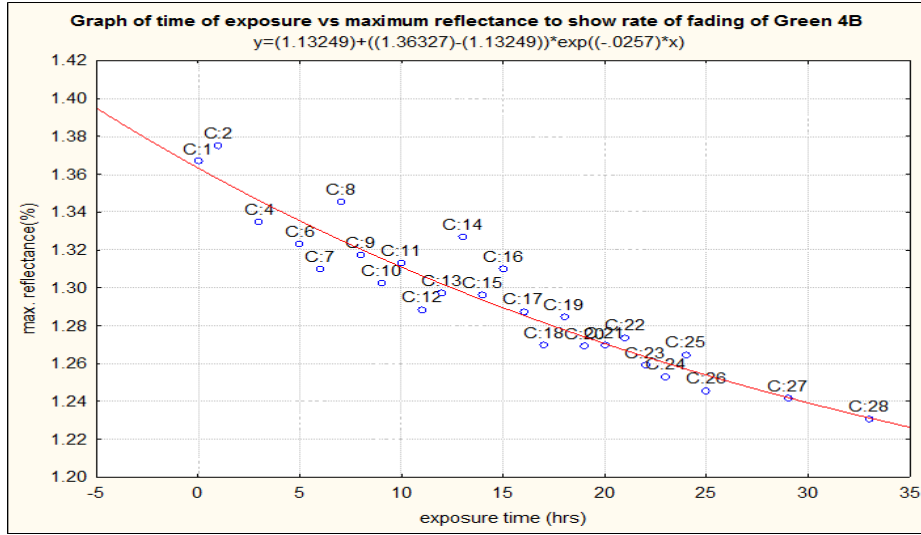


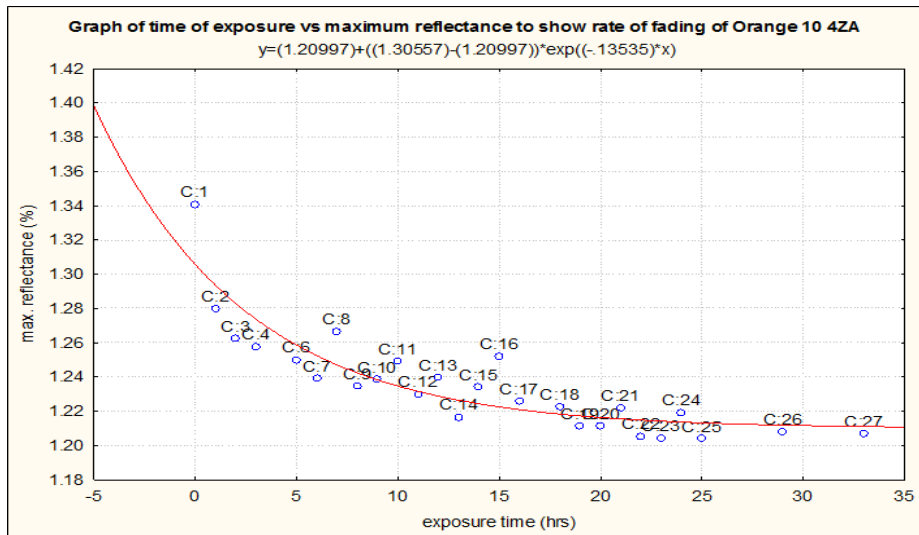
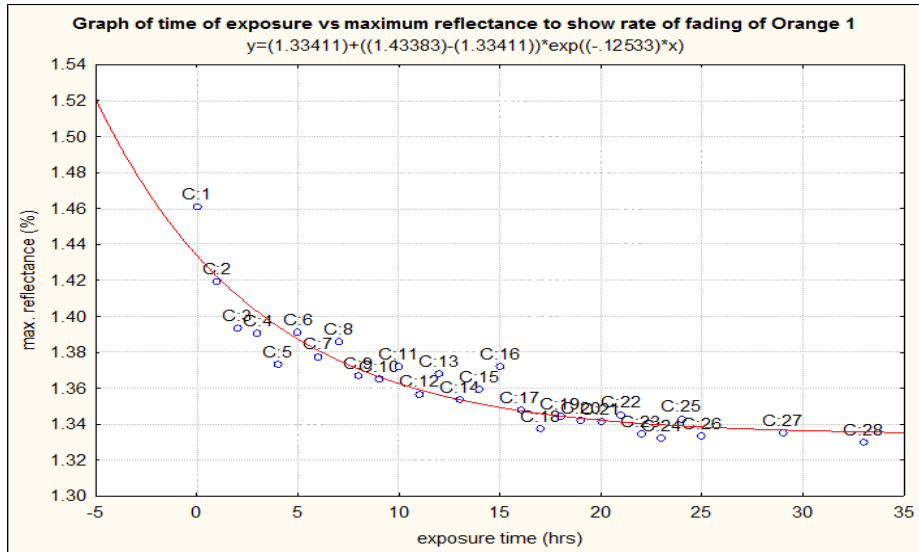
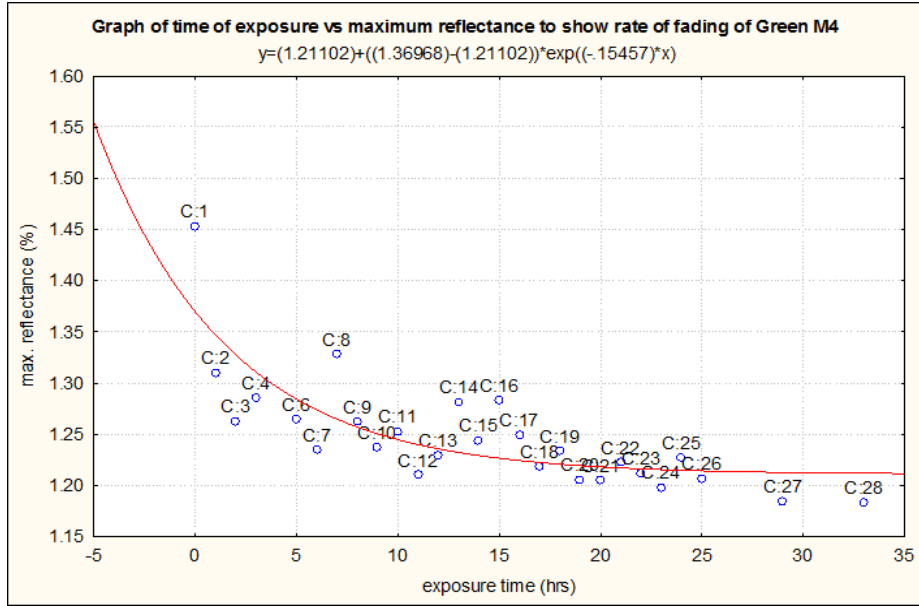


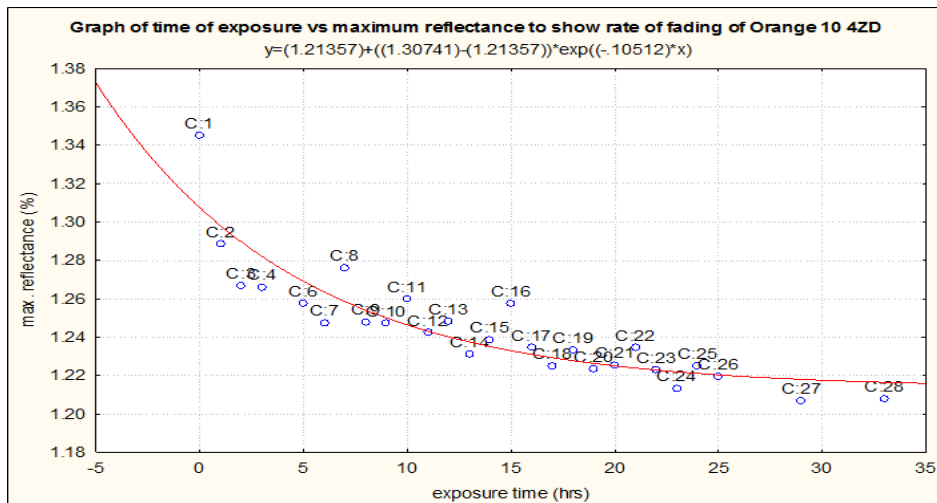
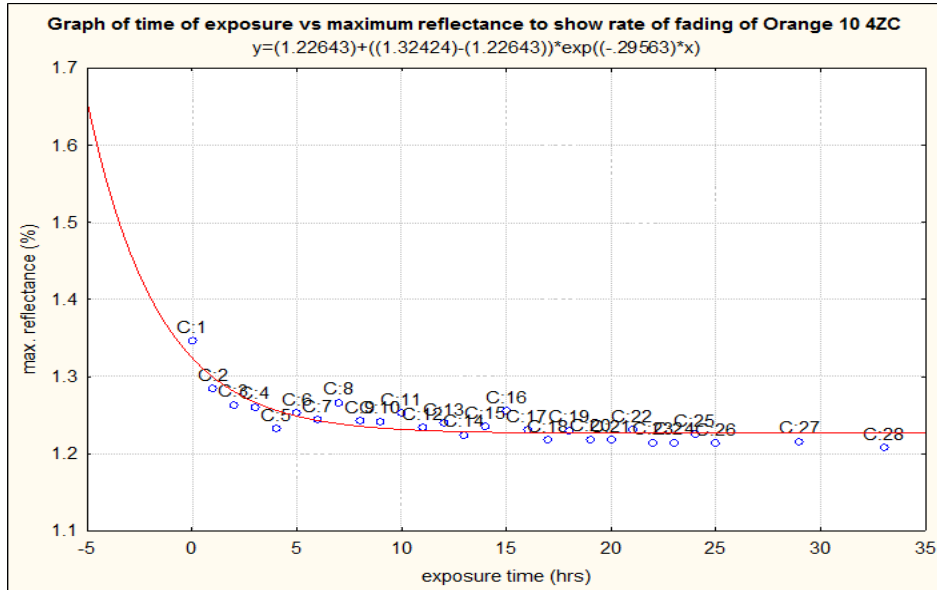
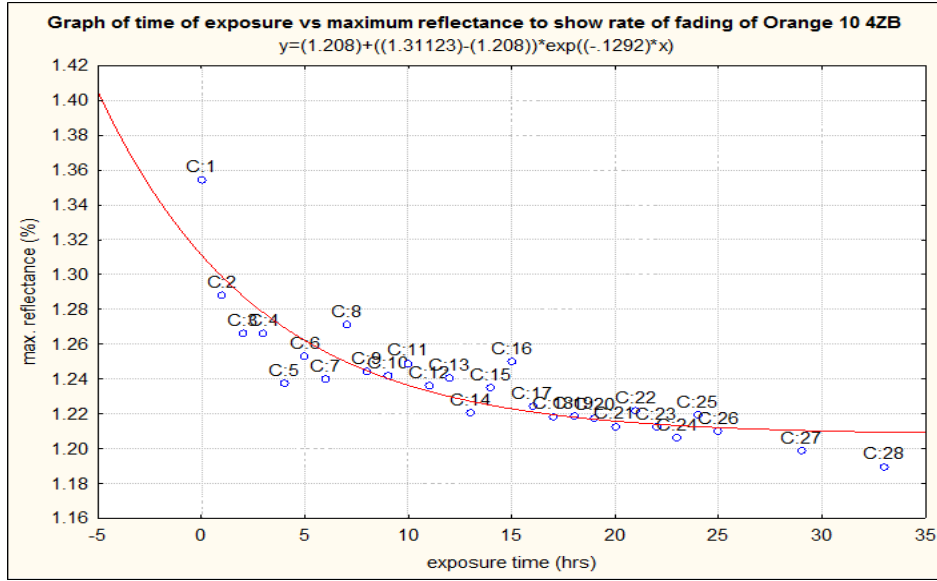
### Appendix B

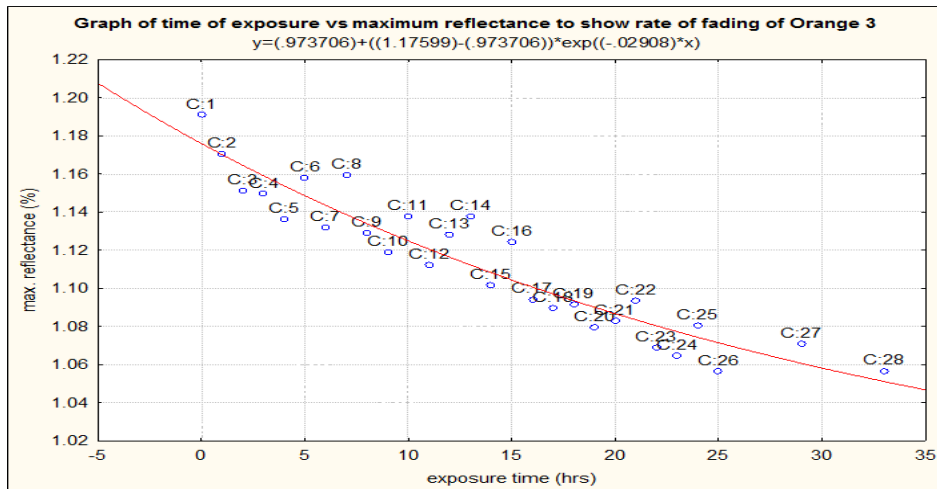
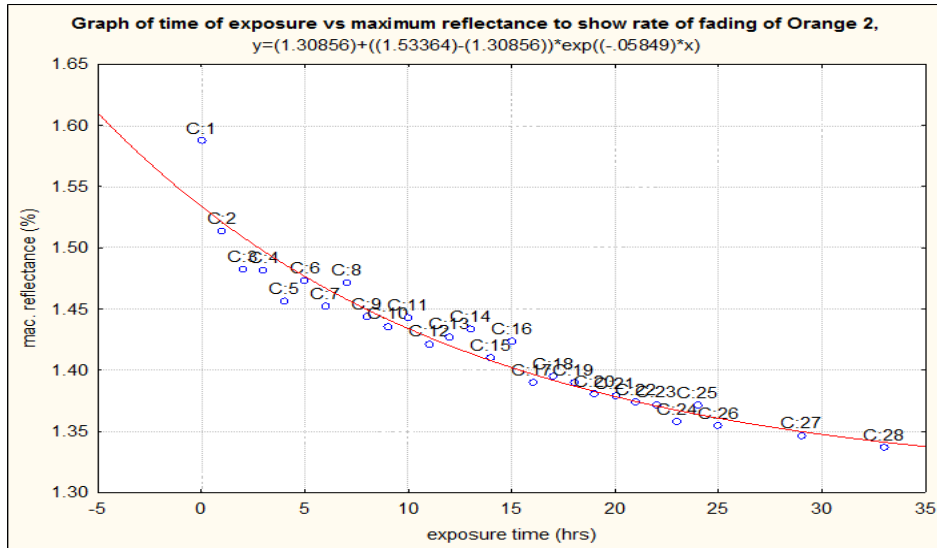
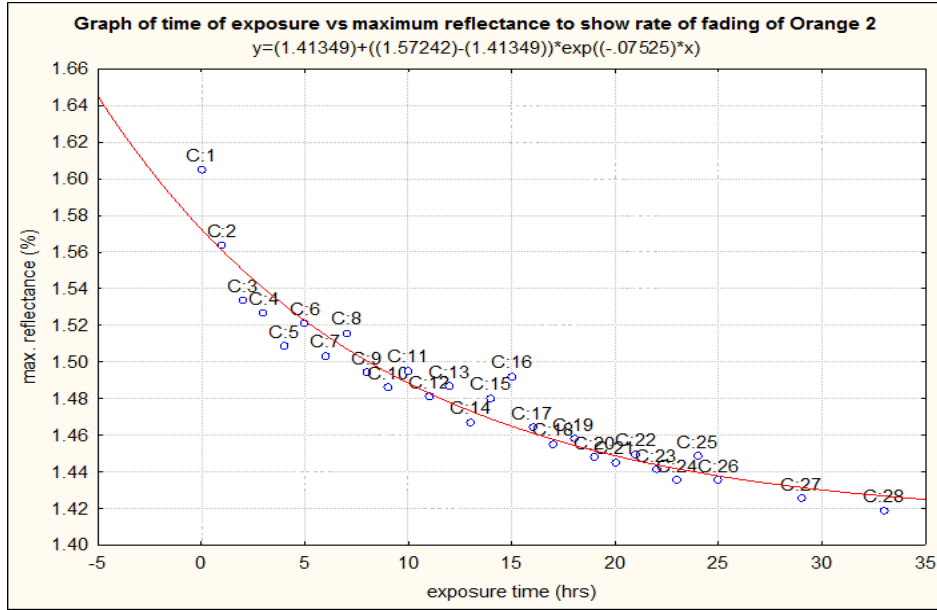
This appendix shows the rest of the obtained maximum reflectance graphs vs time of light exposure for the rate of fading of tested specimen.

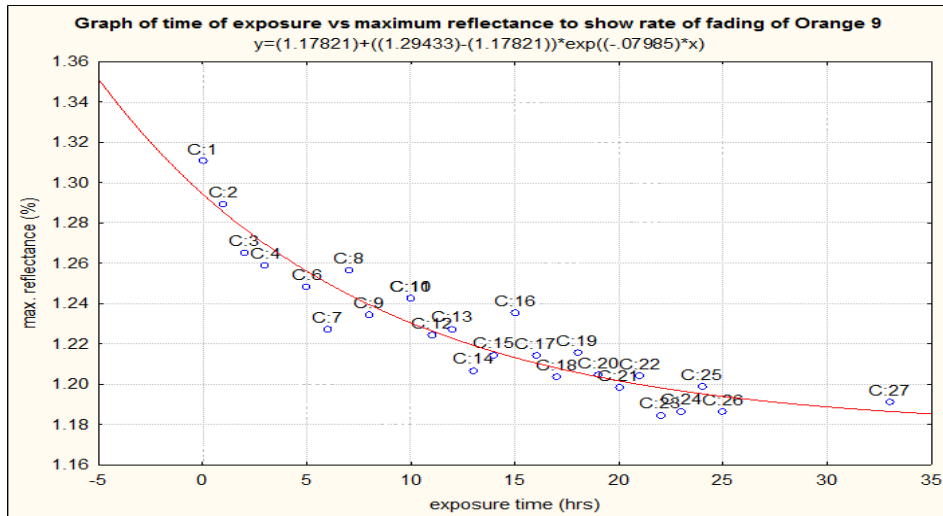
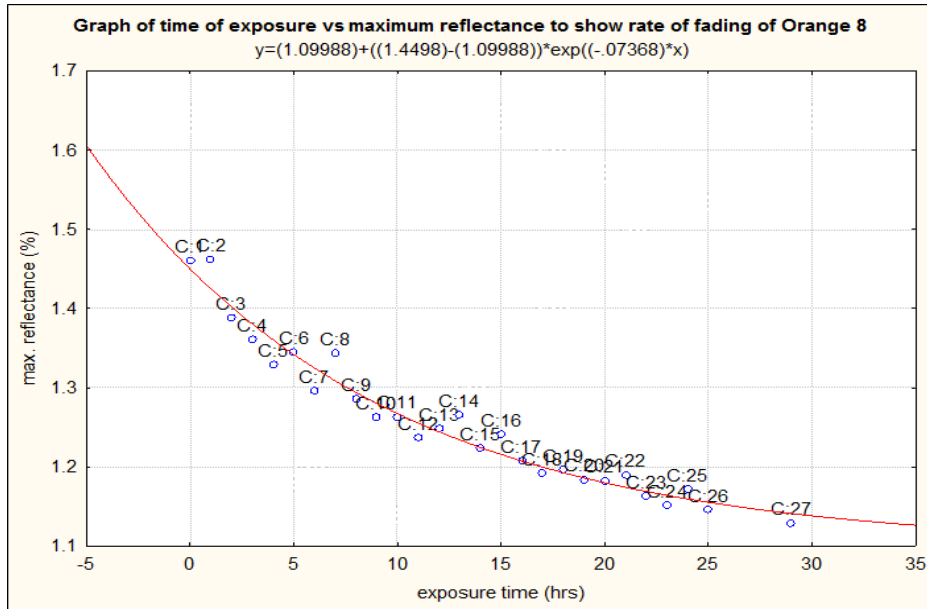
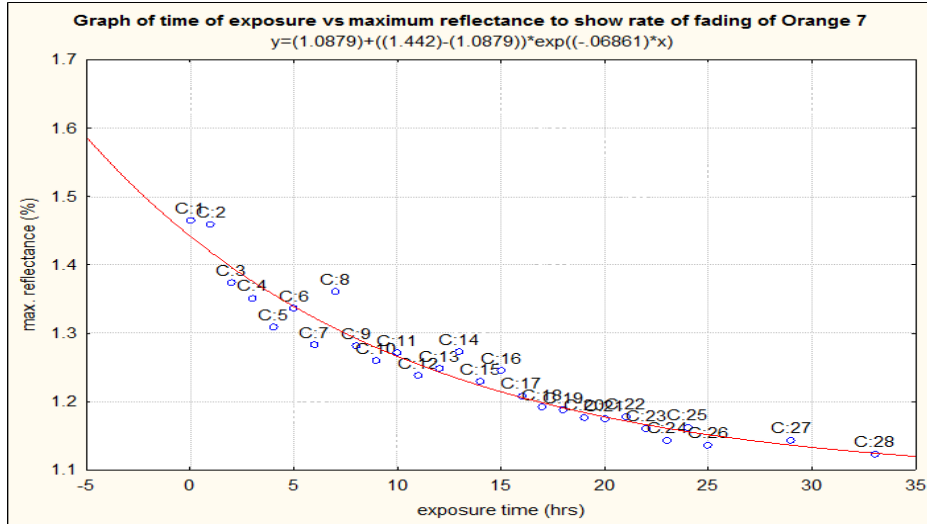




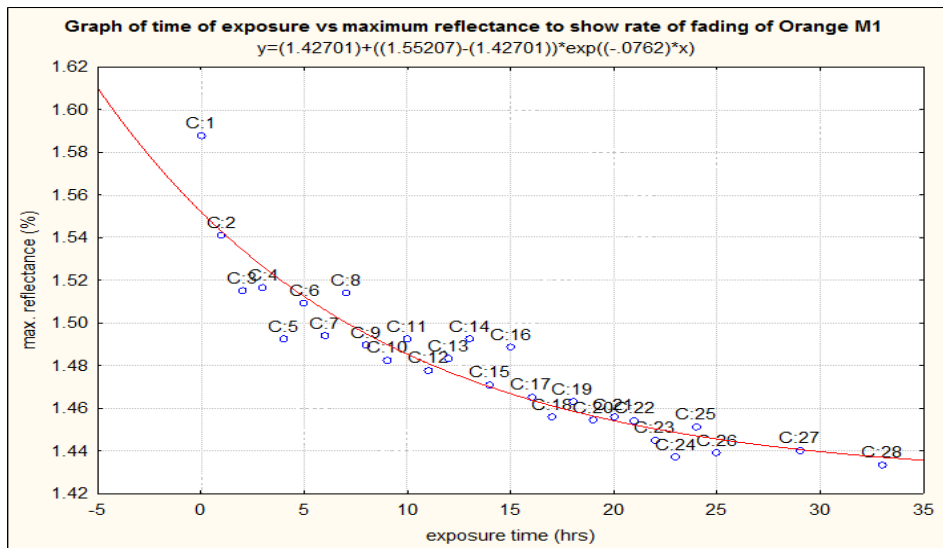
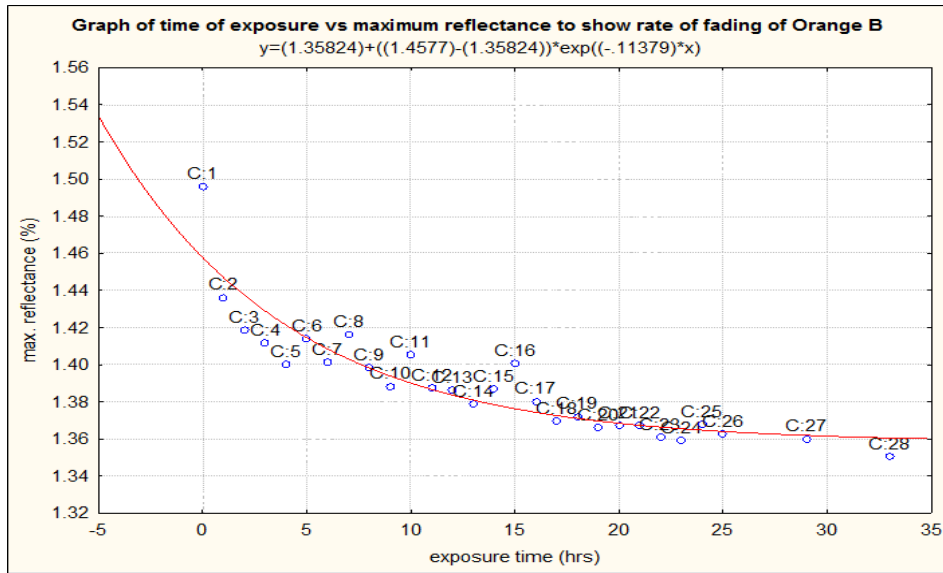
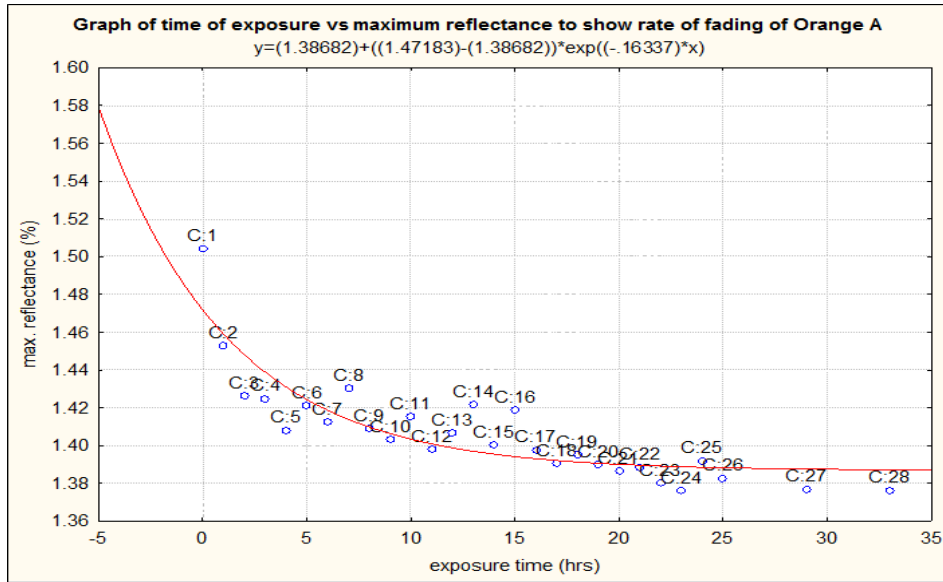


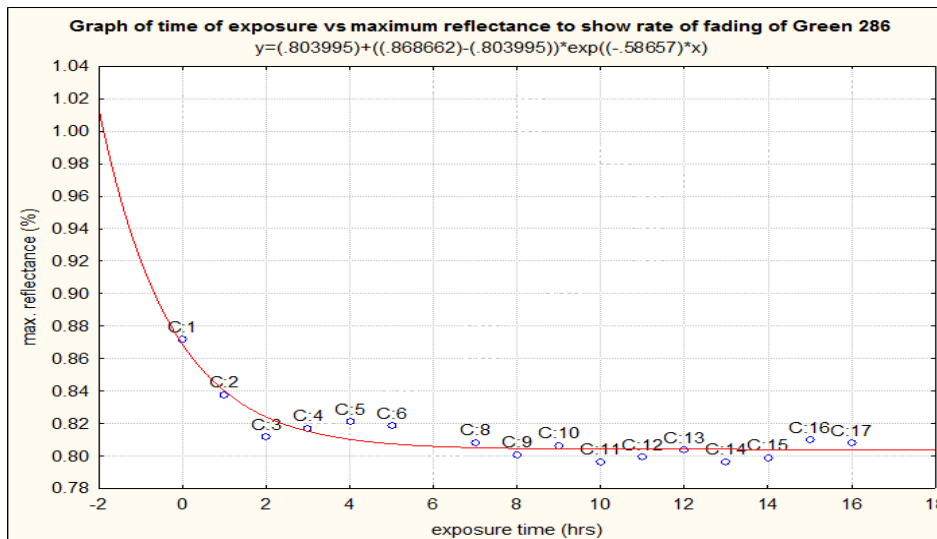
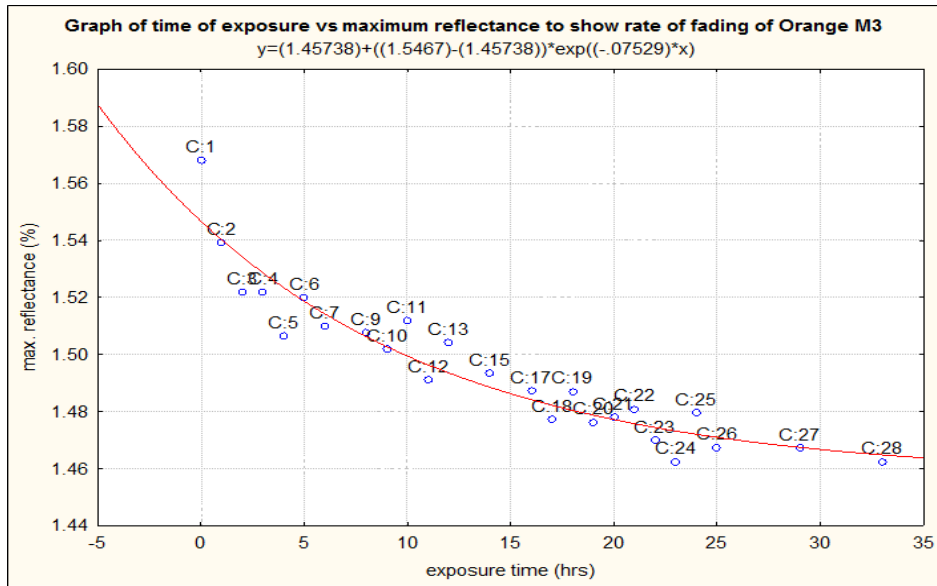
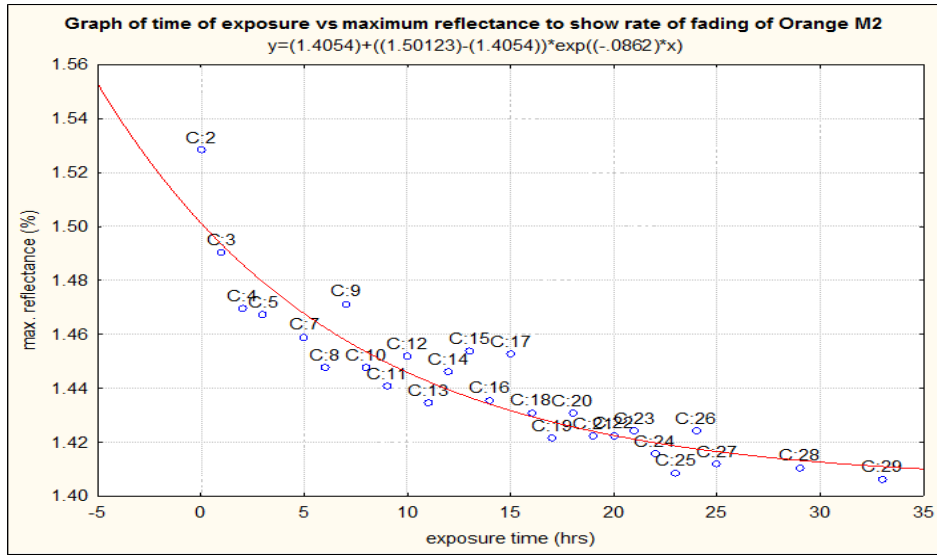


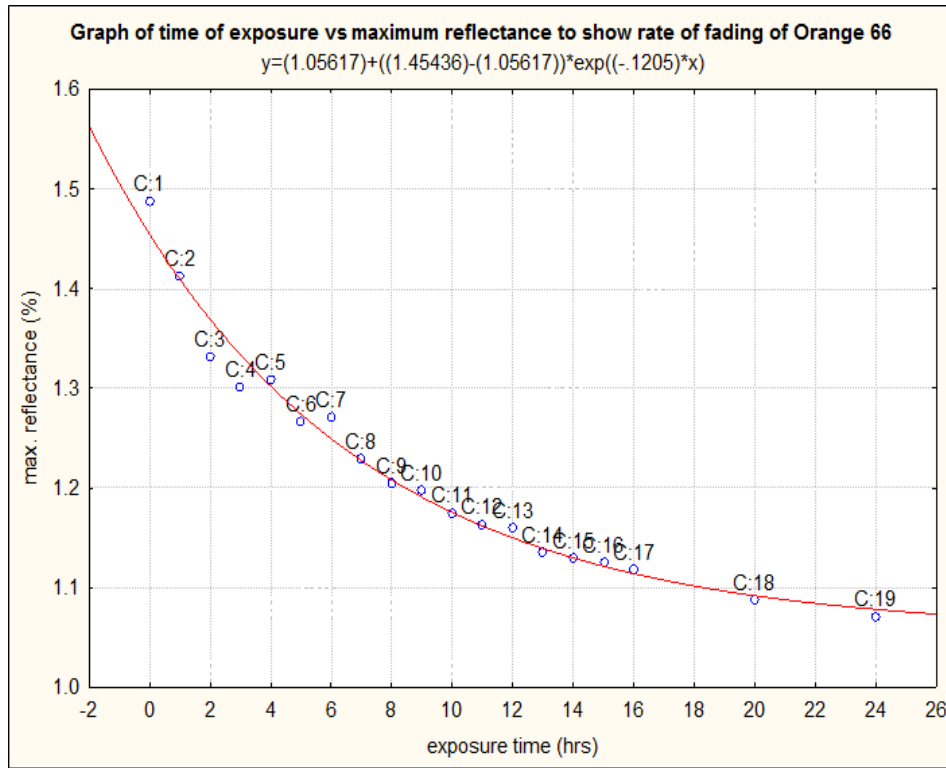












### Appendix C

This appendix shows reflectance as a function of wavelength for the comparison of three different reflectance measuring devices.

