THE PHOTODEGRADATION OF COTTON DYEINGS IN THE PRESENCE OF BINARY MIXTURES OF DIRECT DYES

by

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ABSTRACT

When dyed textiles are exposed to sunlight they absorb some
of the radiation which may consequently lead to
deterioration of mechanical and chemical properties, such as
losses in tensile strength and degree of polymerization and
to changes in colour. Most researchers have concentrated on
studying the photodegradation of textiles dyed with a single
dye. This laboratory research was aimed at evaluating the
photodegradation of cotton dyeings containing binary
mixtures of four direct dyes. Following exposure in the
WeatherOmeter for 120 standard fading hours, the extent of
degradation of 34 dyeings and an undyed control was measured
in terms of losses in tensile breaking strength, degree of
polymerization and total colour change. While the strength
and degree of polymerization results showed no clear or
consistent trends, the extent of colour change of the binary
mixtures was found to be dependent on the type of dyes
present but could not be predicted from the behaviour of the
two dyes. With reference to colour change of the mixtures,
Ultrasol Yellow BG was found to be a photosensitizer,
whereas Direct Brown 1 was found to behave as a
photoinhibitor in mixtures of red and blue.

ACKNOWLEDGEMENTS

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CHAPTER ONE

INTRODUCTION

1.1 STATEMENT OF PROBLEM

At some time during the life of most textile materials they are exposed to sunlight. Textiles used for furnishings receive more exposure than cloth used for other purposes (Egerton 1956). It should be noted that in some countries sunlight is relied upon as the main energy source for drying clothing; clothing can spend as much as eight hours in the sun each time it is washed. For items such as uniforms that are worn and laundered regularly this amount of exposure cannot be ignored.

Appleby (1949), noted that of the numerous factors which comprise the weather, it is generally conceded that sunlight is the most active in causing the deterioration of textiles.

When dyed or printed fabrics are exposed to light, some part of the light energy is absorbed and the remainder is reflected, thus giving rise to the phenomenon of colour (Egerton 1956). It is the reflected light that gives the aesthetic effects seen by the human eye, whereas it is the absorbed light that can cause subsequent damage to the fabric. According to Little (1964), the extent of fading of a dyed fabric or dyeing depends on the stability of the dye on the material. Robinson and Reeves (1961) also noted that the useful life of cotton fabrics and clothing is often

limited by the quality of dyestuff used. Very often fabrics are considered worn out when the aesthetic value imparted by the dye is lost.

The degradation of a fabric by light can involve both fading and loss of strength or tendering. Some authors describe them both as fading effects and use the terms "fading of colour" and "fading of strength" respectively. With respect to colour, Little (1964) pointed to the fact that while lightfastness requirements have risen considerably since the introduction of vat dyes, the general public is still ignorant about this subject. Even less is known about tendering, and complaints usually arise only in extreme cases or where damaged and sound areas occur within the same cloth.

Since cotton consists of about 80-85% cellulose (Hearle and Peters 1963), it is one of the fibres most susceptible to degradation in the presence of light. Over the years researchers studying this phenomenon have found that the rate and extent of cellulose degradation is influenced by the presence of dyes in the cotton fibres. Most of the work in this area has been done on the interaction of single dyes with cotton, whereas in practice mixtures of dyes are more often used in order to obtain the desired colour or shade.

A limited number of studies have addressed the effects of dye mixtures and lightfastness properties. Scholefield and his associates (1933) in their description of the behaviour of vat dyes on cotton observed for example that

in mixtures of yellow and blue dyes, the lightfastness of the blue component is generally reduced by the presence of the yellow. Consequently they designated the yellow as a photosensitiser and the blue as a non-active dye. They pointed out that the non-active dyestuff may be a vat dye or any other type of cotton dye with any degree of lightfastness. However, in almost every case a yellow or orange vat dye causes a marked decrease in the lightfastness of the other dye while at the same time increasing that of the yellow or orange dyestuff.

All these observations have been made with respect to vat dyes, which, while generally having a superior lightfastness, tend to be relatively expensive and difficult to apply. Direct dyes on the other hand, are one of the cheaper dyes for cellulose. They are easy to use and continue to be one of the leading dyes used in the commercial dyeing of cotton.

At this time little work has been undertaken to study the photodegradation of cotton associated with mixtures of direct dyes. It might seem logical to assume that the photosensitising effect of mixtures is the combination of that of the individual dyes but random observations by some researchers in the dyeing industry suggest the degradation behaviour of dye mixtures on cotton cannot always be predicted. Smith (1950) described the effect of a combination of certain direct dyes when exposed to light under moist conditions. He showed that dyes such as Durazol

Yellow and Yellow GRS are fast by themselves, but fade when used in combination with other fast dyes such as Durazol Blue or Durazol Violet 2BS. However, when the yellows are combined with Dural Flavine RS the combination is unexpectedly fast.

Such observations point to the need for more systematic research on this topic. The purpose of this study therefore is to investigate the photodegradation of cotton dyeings in the presence of binary mixtures of direct dyes.

1.2 OBJECTIVES:

1. To determine the extent of photodegradation of cotton by single direct dyes.

2. To determine the extent of photodegradation of cotton by binary mixtures of direct dyes.

3. To determine if there is a relationship between the photosensitizing properties of single direct dyes and that of their binary mixtures.

4. To determine if the photodegradation of cotton dyed with mixtures of direct dyes can be predicted from the proportion of the individual dyes in the mixture.

1.3 HYPOTHESES:

The first two hypotheses are related to the first objective, while the remaining three address each of the other hypotheses respectively.

1. There is no significant difference in the extent of photodegradation of cotton due to the presence of direct dyes.

2. There is no significant difference in the extent of photodegradation of cotton in changing from one dyestuff to another.

3. There is no significant difference in the extent of photodegradation of cotton by using different proportions of the same binary dye mixture.

4. If Hypothesis 3 is rejected, then there is no relationship between the extent of photodegradation of cotton and the proportion of dyes in a binary dye mixture.

5. The extent of photodegradation of a cotton dyeing containing a mixture of direct dyes cannot be predicted from the behaviour of the same proportion of the individual dyes.

1.4 TERMS AND DEFINITIONS :

1. Photodegradation: Degradation caused by the absorption of light or other radiation and by consequent chemical reaction. Ultraviolet radiation is an especially potent cause.[1] (In this text the extent of degradation will be

measured in terms of colour change, losses of strength and degree of polymerization).

2. Direct dye: An anionic dye having substantivity for cellulosic fibres, normally applied from an aqueous dyebath containing an electrolyte.[1]

3. Cotton dyeing: A piece of dyed cotton fabric.

4. Fugitive dye: A dye that is readily faded by light.

5. Protective dye: A dye that reduces the normal extent photodegradation of cotton.

6. Photosensitization: The rapid oxidation of a polymer system (cellulose) by a dye in the presence of light, such a system not being readily oxidised in the absence of the dye under identical conditions.[2]

7. Photosensitiser: A dye that increases the normal extent of photodegradation of cotton.

8. Photoinhibitor: A dye that retards the normal extent of photodegradation of cotton.

(In this text an increase or retardation is in relation to the control sample in terms of single dye samples and in relation to the component single dye samples in terms of the mixtures.)

[1] Textile Terms and Definitions: The Textile Institute, Seventh edition, Manchester. 1975.

[2] Egerton, G.S.,"The Role of Hydrogen Peroxide in the Photochemical Degradation of Cotton Sensitized by Vat Dyes and Some Metallic Oxides" Journal of The Textile Institute. Vol. 39 , 1948, pp. T305.

1.5 ASSUMPTIONS:

The component dyestuffs in the various mixtures used in the experiment did not react with each other during the dyeing procedure.

1.6 LIMITATIONS:

1. Only four direct dyes were used in this experiment so the results cannot be generalised for other direct dyes or any other dye mixture.

2. The affinity of the four dyes for cellulose was not the same. Consequently the ratios of the mixtures during dyeing were not necessarily the same as the ratios of dyestuffs absorbed by the cotton.

3. All dyed cotton samples did not contain the same concentration of dyestuff or dyesfuffs.

4. The dyeing procedure was carried out without the addition of commercial auxillary chemicals that might have changed the performance of the dye.

5. The degree of polymerization measurements were carried out about four months after exposing the fabrics to the WeatherOmeter. The cellulose may have continued to degrade during this four month period since the samples were stored in a conditioning room at about 64% relative humidity and a temperature of $20^{\circ}C$ under fluorescent light.

CHAPTER TWO

LITERATURE REVIEW

This chapter reviews previous work and research related to the area of photodegradation of cotton. The energy distribution of light is explained, followed by descriptions of the two types of photodegradation reactions, the concept of colour, the different methods by which cotton is degraded and then the oxidative process of cellulose itself. It also addresses the degradative properties of various dyestuffs used on cotton, the factors affecting photochemical oxidation and the methods employed for its prevention. The chapter concludes with a description of methods used to measure the photodegradation of cotton.

2.1 LIGHT AND ENERGY DISTRIBUTION

Light is part of the spectrum of electromagnetic radiation which travels in the form of waves. Wavelength( ), the distance between two successive peaks, is measured in nanometres(nm). As the wavelength increases, the energy associated with the light and the ability of the absorbed light to produce chemical changes decreases. This is because the energy (E) is the product of the frequency of the radiation(v) and Planck's constant(h). The frequency is equal to the speed of light divided by the wavelength. (Robinson and Reeves 1961).

2.2 LIGHT AND PHOTODEGRATION REACTIONS

The starting point of any photochemical reaction is the established principle that only light absorbed by a molecule is effective in producing a chemical change (Phillips et al 1960). Giles and McKay (1963) noted that when radiation falls upon an absorbing molecule some of the energy increases the vibrational and rotational energy of the molecule or excites the electron system to higher energy levels. Scholefield and his associates also observed that in terms of the quantum theory, when a quantum of light is observed, the energy may be utilised in the following ways:

a. To excite the molecule which will try to dispose of some or all of its extra energy either by passing it to another molecule with which it comes into contact, through chemical reactions or by sending it out again as a quantum of light of the same or smaller size.

b. To decompose the molecule.

c. To increase the kinetic energy of the molecule so that when it collides with a slower moving molecule, it will transfer some of its kinetic energy (Scholefield et al 1933).

Not all the radiation emitted by the sun reaches the surface of the earth. Robinson and Reeves (1961) stated that ultraviolet solar radiation below 270nm never reaches the surface of the earth and that most of the ultraviolet rays reaching the surface of the earth have a wavelength between 350-390nm. Also, radiation received at the earth's

surface varies in terms of its total intensity and its distribution of energy within the spectrum. Such factors as the season, the time of day, the altitude, the amount of water vapour and atmospheric contaminants all influence the amount and type of radiation that penetrates the earth's atmosphere.

2.3 COLOUR AND LIGHT ENERGY ABSORPTION

The sensation of colour that is observed when dyed or printed surfaces are illuminated involves the reflection of visible light from their surfaces. Wavelengths of the visible light range from 400-750nm. White light is a combination of these wavelengths. When light strikes an object, some of the wavelengths are absorbed while others are reflected, thus giving rise to the general phenomena of colour (Egerton 1956). The reflected light corresponds to the colour seen whereas the absorbed light may initiate photochemical reactions and consequently, is of concern in photosensitization processes. The observed or reflected colour of a dyestuff is complementary to the light absorbed as shown in the following table below.

	LIGHT ABSORBED		COLOUR SEEN
Wavelength(nm)	Colours	or	REFLECTED LIGHT
400 - 435	Violet		Green - Yellow
435 - 480	Blue		Yellow
480 - 490	Green - Blue		Orange
490 - 500	Blue - Green		Red
500 - 560	Green		Purple
560 - 580	Yellow - Green		Violet
580 - 595	Yellow		Blue
595 - 605	Orange		Green- Blue
605 - 750	Red		Blue- Green

The region of maximum absorption of any given dyestuff however depends on the chemical structure of the particular dyestuff.

2.4 THE STRUCTURE OF DYESTUFFS

The colour of a dye is due to the fact that their molecules are able to reflect light selectively.

Dyes are organic molecules which containstypes of groups: chromophores, which give a dye its particular colour, and auxochromes, which intensify the hue of the colour. Chromophores are unsaturated groups whose loosely held electrons in the unsaturated bonds cause the selective absorption of light. Apart from intensifying a hue, auxochromes also make a dye molecule more soluble in water

and improve the colourfastness properties of a dye due to their polarity.(Gohl and Vilensky 1985; Trotman 1984).

2.5 MECHANISMS OF PHOTODEGRADATION

It is generally accepted that there are two ways in which cotton is degraded by sunlight, namely, photolysis and photosensitization.

2.5.1 Photolysis

Photolysis is the breakdown of textile fibres under the direct action of short wave ultraviolet radiation (Egerton 1956). Undyed cellulose absorbs little or no light from the visible region but undergoes photochemical degradation when it is exposed to ultraviolet radiation of 253nm in the presence of air. This energy is sufficiently high to rupture carbon-carbon and carbon-oxygen bonds and to remove hydrogen atoms. (Lanigan 1948; Phillips and Arthur 1964 b.; Robinson and Reeves 1961). Impurities such as dyestuffs do not take part in photolysis.

2.5.2 Photosensitization

The dominant mechanism that initiates the degradation of cellulose is the reaction between light and foreign matter present in the fibre. (Robinson and Reeves 1961). Egerton (1948), also noted that photochemical oxidation may occur rapidly when the dyed fibres are exposed to light in the presence of air. This does not seem to be the case for

undyed fibres. The action of the dye is known as photochemical sensitization. The dye is called the sensitiser and the fibre whose oxidation is accelerated, the acceptor .

The first step in any photochemical reaction is the absorption of light leading to a reaction between the light wave and the sensitizer (Robinson and Reeves 1961; Egerton 1948). Sensitizers have the ability to absorb light in the near ultraviolet or visible part of the spectrum. They carry the absorbed energy to the reacting molecule in the fibre and initiate degradation. Sensitizers absorb the energy and in their excited state cause a reaction in which the water or the oxygen present is converted to either hydrogen peroxide or ozone respectively. These oxidising agents in turn react with cellulose in a chemical reaction causing it to degrade (Phillips and Arthur 1964 b; Robinson and Reeves 1961).

2.6 CELLULOSE AND CELLULOSE OXIDATION

Cotton constitutes about 80-85% of raw cellulose. It is made of several thousand units of glucose joined by glucosidic linkages. The repeat unit of cellulose is cellobiose and it has a degree of polymerisation of about 5000.

The photodegradation of cellulose has been accepted as an oxidative process. Although many theories have been proposed, no research has yet been able to pinpoint the

exact mechanism by which oxidative photodegradation takes place. However a look a the chemical oxidation of cellulose may shed some light on the photodegradation of cellulose since they are both oxidative processes.

2.7 THE EFFECT OF LIGHT ON COTTON DYEINGS

The degradation of a fabric by light is a matter of both tendering and fading. It should however be noted that some authors describe all degradation as a fading effect and use the terms "fading of strength" and "fading of colour" to distinguish the two distinct facets.

Some dyes can act as catalysts in promoting photochemical degradation of irradiated acceptors while they themselves remain unchanged. The acceptor may be another dye molecule or a polymer molecule in the fibre. A typical reaction scheme is noted by Giles and McKay (1963) to be as follows:

$$D \xrightarrow{\text{light}} D^* + AH$$
$$\xrightarrow{O_2} DH + A$$
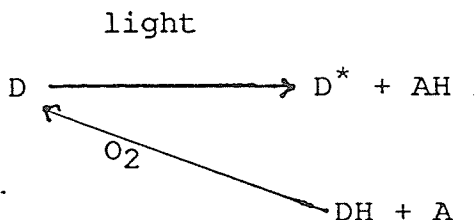
Where:

D = The dye.

AH = The acceptor molecule.

DH = The reduced dye.

A = The oxidised acceptor.

Egerton (1956), stated that absorption of light by textile materials may involve sufficient energy to cause chemical changes in the fibre. The length of the molecular chain and degree of cross linking between adjacent molecules may be reduced and in practical terms may result in a deterioration of the fibre's physical and chemical properties.

Although the general notion is that degradation takes place via the formation of radicals, there is really no agreement as to how these radicals are formed and how they take part in photodegradation. However, current thought is that there is an initial reaction between the cellulose(R-H) and the excited dye radical (D^*). This is then followed by other degradative reactions as illustrated below.

$$D \ \text{-----------}\!\!\!\rightarrow\ D^*$$

$$D^* + R\text{-}H \ \text{-----}\!\!\!\rightarrow\ R + DH$$

$$R + O_2 \ \text{-------}\!\!\!\rightarrow\ RO_2$$

$$RO_2 + D\text{-}H \ \text{----}\!\!\!\rightarrow\ RO_2H + D$$
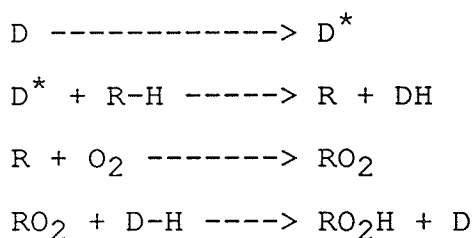
In this particular case the cellulose is oxidised while the sensitiser remains unchanged (Phillips and Arthur 1964 b).

Since the colour of a fabric imparted by a dye is often an important factor if not the most important property of a textile product, Robinson and Reeves (1961), pointed to the fact that the useful life of dyed cotton is often limited by the quality of the dye and very often the fabric is discarded when the aesthetic value imparted by the dye is lost by fading.

Organic colouring matter is faded by absorbed ultraviolet and visible radiation up to a critical wavelength above which radiation is non-active, even if strongly absorbed (McLaren 1956). Egerton (1971), noted that the extent of fading depends on the type of dye-polymer complex because a dye fugitive on one polymer may be fast on another. The process of light absorption by a dye involves the initial formation of an electronically excited dye molecule, which may either react with the polymer or atmospheric oxygen in some other way to produce a change in the chemical state of the dye.

This change in the state of a dye molecule may be accompanied by an observed change in colour of the dyed material. When dyes absorb light, those fugitive to light experience an observed change in colour while those that are fast tend to dissipate the absorbed energy harmlessly as thermal energy (Egerton 1971).

2.8 DEGRADATIVE PROPERTIES OF DYESTUFFS USED ON COTTON

There are various groups of dyes commonly used on cotton. Research into the degradative properties of these various dyes on cotton has continued over a number of years.

2.8.1 Vat Dyes

Robinson and Reeves (1961), observed that, of the common groups of dyes used in the cotton industry, vat dyes have received the most attention. They have always been

considered desirable because of their superior colourfastness to light. However research has identified deficiencies in this class of dyestuff, particularly the red, brown, orange and yellow colours which have sensitizing effects on cotton (Egerton 1948; Robinson and Reeves 1961; Scholefield et al 1933). It has been noted that anthraquinoid vat dyes have excellent photochemical stability. However the yellow and orange sensitize the photochemical oxidation of textile materials, making them more susceptible to tendering. In such cases the stability of the colour to light is achieved at the expense of a decrease in the stability of the fibre. These colours absorb in the region of 300-400nm. These wavelengths absorbed involve high energies capable of causing chemical changes and an increase in the yield of free radicals in dyed cotton. The degree to which each particular dye promotes oxidation depends on the extent to which they actively absorb in the visible and ultraviolet spectrum. (Egerton 1948; Lanigan 1948; Phillips et al. 1960; Scholefield et al 1933).

Scholefield and his associates (1933) have explained the accelerated photosensitisation of vat dyes in terms of absorption of large quanta of light energy in the ultraviolet region which supply energy for exciting celluose and making it more susceptible to atmospheric oxidation. They noted that the vat blue and green dyes have their maximum absorption in the 580-605nm region (i.e.

yellow and orange), where the quantum size is smaller and therefore of a lower energy level. Blue and green vat dyes therefore do not lead to much chemical tendering of cellulose (Scholefield et al. 1933).

2.8.2 Reactive Dyes.

Reactive dyes are one of the more recently developed types of dyestuff and are the only dyestuffs that form covalent bonds with cellulose. It has been observed that on irradiation reactive dyes generally yield low levels of free radicals in dyed cotton (Phillips et al. 1960). In fact research has indicated that reactive dyes generally exert a protective effect on cotton. Ladisch and her associates (1983), in their study of five Procion reactive dyes found four of them the-- green, red, orange and yellow to be protective. They also found that these four protective dyes had good lightfastness. The fifth dye, which was blue was found to accelerate tendering of cotton and also to exhibit poor fastness to light. They also noted that as the concentration of the protective dye on the cotton increased, there was an increase in their protective behaviour whereas for the fugitive dyes, as their concentration increased, so too was there an increase in their tendering activity (Ladisch et al 1983).

2.8.3 Sulphur Dyes

A similar behaviour has been observed with sulphur dyes. Some are protective while others are fugitive and their respective activities increase with an increase in their concentration. Of the dyes studied by Shenai and Rao (1973), blue and green exhibited a protective effect while yellow, brown and khaki were found to sensitize the photodegradation of cotton.

2.8.4 Direct Dyes

Similarly, some direct dyes are known to initiate photodegradation while others exibit protective behaviour. In their study of the oxidation of cellulose in the presence of direct dyes, Datye et al (1961), found that dyes themselves in their undecomposed state appear to protect cotton on exposure in a fadeometer while their products of decomposition either enhance or retard the tendering of cotton. Smith (1950) in his observation of a combination of certain direct dyes exposed to light under moist conditions, noted that certain yellows although fast tend to fade when combined with Durazol Blue or Durazol Violet 2BS. These same yellows however were unexpectedly fast in combination with Dural Flavine RS.

2.8.5 Dye Mixtures

Scholefield and his associates noted that the combined photodegradative activity of a mixture of dyes depends on

which individual dyes are present. They cited an example in
which there was a mixture of yellow (or orange) and blue vat
dyes on cotton. The lightfastness of the blue component was
generally found to be reduced by the presence of the yellow
or orange dye, while at the same time the lightfastness of
the yellow component was increased. This occurs when the
non-active dyestuff is any type of dyestuff used for cotton
such as a direct, sulphur or reactive dye with any degree of
lightfastness.

2.9 FACTORS AFFECTING PHOTOCHEMICAL DEGRADATION

Phillips and his colleagues observe that in order to
achieve a clear understanding of the processes which operate
during the deterioration of cotton cellulose under the
influence of light, it is necessary to consider a number of
factors including: a) the wavelength of the irradiation, b)
the proportion of water associated with the textile, c) the
absorption characterisitics of any reacting chemicals or
dyes and d) the composition of the atmosphere surrounding
the textile during exposure (Phillips and Arthur a. 1964).

Most researchers point to the fact that oxygen and
water vapour are the most important atmospheric substances
which play a leading role in photochemical degradation.In
fact oxygen in the atmosphere has been found to be the most
important factor controlling the effect of light on cotton
(Daruwalla et al 1967). For example it has been noted that

mechanical as well as chemical damage is limited in an oxygen free atmosphere (Daruwalla et al 1967; Little 1964).

In addition it has also been observed that the rate of photochemical attack is slower in dry air than in humid air. With an increase in relative humidity the rate of fading of most dyes increases (Egerton 1971; Little 1964). Egerton noted that among the inorganic acceptors of radiation, water or water vapour is of particular importance since when photochemically oxidised, it is converted to hydrogen peroxide which is a particularly potent oxidising agent for dyestuffs and organic polymers. Water therefore occupies a special position in the general study of photosensitized reactions; the critical factor in the rate of fading being the relative humidity of the air in immediate contact with the exposed textile surface (Egerton 1948, 1971). But hydrogen peroxide has also been found to be closely related to the extent of oxidative degradation of cotton. Besides oxidising the cellulose in immediate contact with the photosensitizer, hydrogren peroxide can also oxidise other dyes that may be in the system either on the same yarn as the sensitizer or separately on an adjacent yarn (Egerton 1948).

The effect of temperature on the photosensitized degradation of cotton has received different points of view from different researchers. Some contend that an increase in temperature tends to lower the relative humidity and therefore leads to a decrease in degradation, while others

observe that according to the laws of thermodynamics, an increase in temperature leads to an increase in photochemical degradation. Egerton (1971), however noted that when the relative humidity of the air is maintained constant an increase in temperature leads to a significant increase in the amount of fading. There is approximately a 10% increase in the rate of fading with a temperature rise of 100°C.

The effect of the physical state of dyes on photodegradation has been the main focus of some researchers. Most of them agree that the lightfastness of dyes is determined by both chemical and physical factors especially their physical state in the fibre. It has been observed that many of the phenomena associated with fading are best interpreted by the fact that dyes are usually present in fibres as a homogenous collection of particles ranging in size from molecular dispersions through microcrystals to aggregates (Giles 1957; Baxter et al 1957).

Dyes fade initially on their surface. Since the surface area of a given amount of dye is reduced as the particle size increases, the more aggregated a dye, the higher the lightfastness of the fabric. Heat generated during fading may also cause large aggregates to break up and so promote further fading. By partially filling some of the spaces within fibres during manufacture and finishing, the amount of space available for dyes to form aggregates is

decreased. This will have the tendency to reduce lightfastness. Conversely, aftertreatments which permit microscopically visible growth of dye particles will improve their lightfastness. It has also been noted that the lightfastness of water soluble dyes is improved by increasing the porosity of the substrate (Giles 1957).

Some treatments which are regarded as normal parts of particular dyeing processes or aftertreatments and are designed to improve the wetfastness properties of the dyed material, have been noted to influence the photochemical degradation of cotton dyeings. For example, in the application of vat dyes it has been pointed out that the final treatment of boiling the dyed fabric with soap or a detergent results in the aggregation or crystallization of the dye (Egerton 1971; Robinson and Reeves 1961). On the other hand, Gill (1955) observed that compared to vat and azoic dyes, direct dyes are usually applied to cellulosic fibres by simpler and cheaper means but are accompanied by inferior fastness properties to wet processing. Unfortunately some of the products and processes on the market used to overcome this disadvantage tend to reduce the lightfastness of direct dyes. For example cationic surface active agents assist in the spread of anionic dyes in a monolayer on the fibre surface leading to a decrease in lightfastness.

Egerton (1971) has noted that colourless inorganic substances like zinc oxide and titanium dioxide, which are

added to man-made fibres as delusterants to increase their opacity, sensitize many photochemical oxidation reactions involving gaseous oxygen and water vapour.

Little (1964) observed that the residual alkali in an undyed or vat dyed fabric usually tends to increase the amount of tendering when exposed to light. On the other hand, fabrics treated with urea formaldehyde crease-resistant finishes always retain a small amount of free formaldehyde which, being a reducing agent, tends to retard the oxidative process and as such reduces tendering (Giles 1957).

A study by Daruwalla (1961), showed that when cellulose containing fluorescent compounds were exposed to a carbon-arc ultraviolet source, photodegradation of the cellulose did occur due to the activity of the fluorescent brightening agent and its decomposition products. He noted that the extent of tendering depended on the chemical composition of the brightener, and the nature and duration of the radiation.

2.10 PREVENTION OF PHOTODEGRADATION

Just like other problems in the textile industry, prevention of photodegradation has received considerable attention. There are some routine processes for dyes that have a protective effect on cellulose. However for substances that still sensitize photodegradation there continues to be concern over finding a means of prevention

without affecting the other desirable properties of cotton and its applied finishes.

It has been found that in order to protect fabrics, a means must be provided either to remove the photosensitizers from the fabric or to add other materials that will deactivate them. This can be accomplished by the use of materals which act as screeners, light scatterers or utilisers of the radiant energy (Robinson and Reeves 1961).

Little (1964), has observed that the acetylation of cotton has been the most successful method of protecting it from light. He noted however that this caused an initial loss in tensile strength which cannot always be tolerated.

2.11 METHODS OF MEASURING THE EXTENT OF PHOTODEGRADATION OF CELLULOSE

The common methods used to determine the extent of degradation of irradiated cotton involve measuring the changes in certain mechanical and chemical properties. Measurement of breaking strength of the fabric under tensile loading give a direct indication of any deterioration in mechanical properties. Techniques to monitor the chemical structure of cellulose include measurements of i) the fluidity and viscosity of cellulose which yield information about the average molecular weight, ii) copper number, which indicates the concentration of aldehyde reducing groups present, and iii) methylene blue absorption which determines the concentration of carboxylic

acid groups present in hydrocellulose or oxycellulose structures (Garner 1967).

Appleby (1949), noted that loss in strength is due primarily to the cellulose chains breaking of into smaller fragments. She pointed to the fact that the measurements of loss in strength are not strictly comparable with the values for changes in chemical structure. She went on to say that fluidities or viscosities seem to give the most accurate indication of degradation since they are able to detect incipient chemical damage. She added that although increases in copper number and methylene blue absorption also measure changes in the chemical structure of cotton, researchers disagree on their accuracy and their significance in the study of photodegradation.

While considerable attention has been given to the degradation of fibres by individual dyes, there is however little research in the area of dye mixtures. This is surprising when one realizes the frequency with which dye mixtures are used to impart colour to a fabric.

It is believed that a systematic study in the area of dye mixtures will shed light on the photosensitizing behaviour of dye mixtures, in relation to their component dyes and help explain some of the anomolous behaviour previously found to have been exhibited by dye mixtures.

CHAPTER THREE

EXPERIMENTAL PROCEDURES.

This chapter describes the experimental methods that were used in the research. It includes the selection of experimental materials and their preparation, dyeing and exposure of dyed samples in the WeatherOmeter and the measurements of colour, tensile strength and the degree of polymerization before and after exposure in the WeatherOmeter; it also describes the statistical methods used in analysing the results.

3.1 SELECTION OF EXPERIMENTAL MATERIAL

The following commercial direct dyes were used for the study.

Ultrasol Yellow BG.

Direct Red 1

Direct Blue 1

Direct Brown 1

These were selected on the basis that the red and brown were protective on cotton, while the yellow and blue were degradative to cotton (Datye et al 1961). The Ultrasol Yellow BG was obtained from Sandoz Canada Inc., Dorval, Quebec, while the blue, red and brown were purchased from Pylam Products Company Inc., Garden City, New York, USA. 80 by 80 bleached and mercerised cotton print cloth obtained from Testfabrics Inc.,USA was used throughout the study.

3.2   PREPARATION OF COTTON PRINT CLOTH SAMPLES

Samples of cotton print cloth were cut to weigh approximately 40g and about 50cm by 100cm in size with the longer dimension parallel to the warp direction. These samples were conditioned according to CAN2-4.2-M77 method 2 at 65±2% relative humidity and a temperature of 20±1°C. Since there were 4 single dyes, 30 binary mixtures and 1 control, a total of 35 print cloth samples were prepared, one for each dyeing condition.

3.3   PREPARATION OF DYE SOLUTIONS

Using 1g dyestuff per 20g of fabric and a liquor:fabric ratio of 20:1, approximately 8 litres of bulk solution were prepared for each dyestuff. From these bulk solutions, binary mixtures of yellow and blue, yellow and red, yellow and brown, blue and red, blue and brown and red and and brown were prepared. For each mixture, five combinations in proportions of 2:8, 4:6, 5:5, 6:4, and 8:2 were prepared, resulting in 30 mixtures and four individual dyes giving 34 dye solutions in total.

3.4   DYEING OF COTTON PRINTCLOTH SAMPLES

The cloth was initially wetted out with distilled water and an anionic wetting agent. It was then placed in a LaunderOmeter canister with a capacity of 1000ml, together with 40 steel balls, 800ml dye solution and 2g of common

salt. The salt is an electrolyte and increases the repulsion forces between the dye molecules and water so that the dye is attracted to the fibre. The canisters were then closed and rotated for 60 minutes at about 90°C . A control sample was also given the same treatment but distilled water was used instead of the dye solution. After the dyeing process was completed, the samples were rinsed separately in 8 litres of distilled water twice. The samples were then air dried at room temperature and pressed to remove creases.

3.5 EXPOSURE TO WEATHEROMETER.

The dyed samples were exposed in a xenon arc WeatherOmeter Model RB.65WRC. for 120 standard fading hours in accordance with AATCC Test Method 169-1987 under the following conditions:

Light only

Black temperature of 77 ± 3°C

Inner and outer Borosilicate filters

Xenon burner 64911.

The Xenon burner emits radiation between 300 and 700nm (Giles 1971).

3.6 ASSESSMENT OF BREAKING STRENGTH.

The ultimate tensile strength of each sample was determined before and after exposure in the weatherometer using an Instron Model 4206 and testing according to the standard method ASTM D 1682-64. For each sample, five conditioned specimens were tested in the warp direction, the

average breaking strengths calculated and the differences between the before and after exposure conditions were determined.

3.7 ASSESSMENT OF DEGREE OF POLYMERIZATION

The viscosity of each sample was determined before and after exposure to the WeatherOmeter using a cadoxen solution as the solvent prepared using a method described in Donetzhuber (1960).

Segal and Timpa's (1972) method was used to prepare the cellulose solutions. For each sample, about 0.02g of ground dried cotton fibre was placed in a 25ml conical flask. Ten ml of cadoxen solution was added, and the solution stirred for about an hour using a magnetic stirrer. Ten ml of distilled water were added and the solution was filtered through a coarse fritted glass filter under suction to remove any undissolved impurities.

To determine the intrinsic viscosity of each sample, 10ml of the filtered solution were pipetted into the reservoir . of a size one Cannon-Ubbelohde dilution viscometer. The viscometer was placed in a water bath at 25.0±0.2°C for 20 minutes prior to measuring the flow time of the solution. The flow times of two other dilutions were determined by adding two successive 5ml aliquots of 1:1 cadoxen:water directly into the viscometer. The flow time for the 1:1 cadoxen:water alone was also measured.

The viscosity data was used to calculate the degree of polymerization (DP) of the cellulose as follows. First the relative viscosities $[n_{rel}]$ were calculated from the flow times at each concentration.

Relative Viscosity $[n_{rel}] = t_x/t_o$

where t_x = Flow time of solution.

and t_o = Flow time of solvent.

From these data the specific viscosities $[n_{sp}]$ were determined as follows:

Specific viscosity $[n_{sp}] = n_{rel} - 1$

The specific viscosity divided by concentration (in g/100ml) was then plotted against concentration, and the line extrapolated to zero concentration, to determine the intrinsic viscosity.

Intrinsic viscosity $[n] = \lim_{c \to 0} n_{sp}/c$

From the intrinsic viscosity, the degree of polymerization (DP) was calculated using the following relationship

$$[n] = KDP^a$$

Where K and a are constants for these particular solvent-solute and temperature conditions. Their values are as follows:

K= 0.0184

a= 0.76   (Segal and Timpa 1972)

3.8 ASSESSMENT OF COLOUR CHANGE

The colour of each sample was measured before and after exposure in the WeatherOmeter. Four layers of each sample were measured at five different locations using a Hunterlab Tristimulus colourimeter Model D25-9. The values of the Hunter L,a,b opponent-colours scale were recorded and the colour difference (ΔE) for each sample was calculated as follows:

$$\Delta E = \{ (\Delta L)2 + (\Delta a)2 + (\Delta b)2 \}1/2$$

Where: $\Delta L = L_{(before)} - L_{(after)}$. (If ΔL is positive, then the sample was lighter before than after).

$\Delta a = a_{(before)} - a_{(after)}$. (If Δa is positive, it implies that the sample was redder·before than after).

$\Delta b = b_{(before)} - b_{(after)}$. (If Δb is positive, it implies that the sample was more yellow before than after).

The precision of each mean L,a,b value was approximately $\pm$ 0.1

3.9 MEASURING THE AMOUNT OF ABSORBED DYES

A spectrophotometric method outlined by Giles and Shaw (1969), was adopted in determining the amount of dye absorbed by each cotton fabric sample. 0.01g of ground dried sample was dissolved in 20ml of 80% sulphuric acid. This was left in the refrigerator for 24 hours and the absorption measured by a spectrophotometer using a dissolved but undyed cotton sample as a blank.

3.9.1 DETERMINATION OF CONCENTRATION(S) OF DYE(S) ON SAMPLES

A series of dye solutions was prepared for each individual dye and their absorptions at the maximum wavelength of absorption for the dyes measured. The results for absorption were used to plot calibration curves. The concentrations of the single dye samples were read from these calibration curves. For the mixtures, their concentrations were determined by a procedure outlined in Giles (1971), using the following formulae:

$$C_A = \frac{K_{B2}d_1 - K_{B1}d_2}{K_{A1}K_{B2} - K_{A2}K_{B1}}$$

$$C_B = \frac{K_{A1}d_2 - K_{A2}d_1}{K_{A1}K_{B2} - K_{A2}K_{B1}}$$

where;

A and B $\quad$ = The two dyes on the sample.

$C_A \quad$ = Concentration of dye A.

$C_B \quad$ = Concentration of dye B.

d $\quad$ = Optical densities

1 $\quad$ = Maximum wavelength of absorption of A.

2 $\quad$ = Maximum wavelength of absorption of B.

K $\quad$ = Constant.

3.9.2. DETERMINATION OF THE K CONSTANTS

To be able to use the formulae outlined by Giles (1971), for calculating the concentrations of each dye on the binary samples, it was necessary to determine the various constants in the formulae. For each binary mixture

the different values of the constant K were determined by measuring known concentrations of the two dyes A and B in solution at their the maximum wavelength of absorption of λ_1 and λ_2 respectively. The optical densities of A and B at concentrations C_A and C_B are as follows:

At λ_1 .... $K_{A1}C_A$ and $K_{B1}C_B$ respectively,

At λ_2 .... $K_{A2}C_A$ and $K_{B2}C_B$ respectively,

3.10. TABULATION OF DATA

The average results for tensile strength, degree of polymerization and colour measurements were manipulated to show the changes in colour strength and molecular weight for each sample during exposure.

To assist in evaluating the objectives of the research, the data were regrouped into two types of tables: Firstly, the control and the single dyes, and then the single dyes and their binary mixtures. This approach will help to provide the mean changes necessary to answer the specific objectives. Some of the grouped data are presented graphically to complement the statistical analysis.

3.10.1 STATISTICAL ANALYSIS

Data analysis was perfomed using a SAS statistical package.

For the first and second objectives which were aimed at finding out the extent of the photosensitizing effects of

single direct dyes on cotton, descriptive statistics were used for comparisons.

For the third and fourth objectives, each series of a binary mixture was compared within the series first without the single dye samples and then including them. Regression analysis and correlation coefficients were calculated to determine the existence of any relationships between the type of dye mixture and their degradative behaviour. Graphs were also plotted to give a pictorial presentation and to determine whether any observed relationship could be used to predict the behaviour of the dye mixtures from that of the individual dyes.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the results of the study in tables and graphs as well as listing the means and standard deviations where appropriate for the different variables. This chapter also includes results of statistical evaluations and attempts to explain the observed behaviour.

4.1 DESCRIPTION OF DATA

The mean results of the independent variable, namely the proportions of dyes, and the dependent variables of changes in tensile strength, colour and degree of polymerization are presented in the tables together with supplementary graphs and statistical data.

Table 1a lists the spectrophotometric readings used to draw calibration curves for the various dyes. These data are plotted in Figures 1a to 1d, and were used to determine the total amount of dye absorbed by the single dyed samples. Table 1b presents the values of the constant K for the various dyes at the maximum wavelengths of absorption for each dye. These K values were used in calculating the total amounts of the various dyestuffs absorbed by the samples dyed with binary dye mixtures.

Since the nominal ratio in which the dyes were mixed during the dyeing procedure was not necessarily the same ratio as that in which the dyes were absorbed into the cotton fibres, it was necessary to determine the actual proportions in which the dyes were absorbed. These proportions are summarized in Table 2.

Tables 3a,4a,6a,8a,10a,12a and 14a summarize the results of the losses in breaking strength of the different combinations of the dye mixtures. For clarity of comparison and analysis the results are grouped in a table for each of the six binary mixtures. Each table includes both single dyes and the five different proportions of dyes absorbed. Tables 3b,4b,6b,8b,10b,12b and 14b present a summary of the results of changes in colour while Tables 3c,4c,6c,8c,10c,12c and 14c summarize the results for losses in degree of polymerization.

Regression and correlation analyses were used to determine any relationships that might exist between the dye mixtures and changes in the dependent variables and also to determine the strength of such relationships. Tables 6a-7g show the results of these statistical analyses. For ease of comprehension, the results of the analysis of variance, regression and correlation analyses are all presented together.

Graphs to supplement the tables have also been plotted for each mixture with the three dependent variables plotted

against the actual proportions of absorbed dyes. These are seen in Figures 2-7 with each figure showing all the three dependent variables.

4.2 DISCUSSION OF RESULTS

Descriptive methods were mainly used in discussion of the results and although statistical analyses were carried out on the data, they were used in the discussion only to complement the graphs and the tables.

4.2.1 DISCUSSION OF RESULTS ASSOCIATED WITH EACH OBJECTIVE

The main aim of this research was to examine the photodegradation of cotton in the presence of binary mixtures of direct dyes. In order to achieve this it was important to determine the photodegradation of single dyed cotton samples to see if there is any relationship with respective binary dye samples.

The first part of this discussion will therefore focus on the results of the undyed control and the individual dyes, and the second part will combine the last three objectives of a) determining the photodegradation of cotton by binary mixtures of direct dyes, b) determining any relationships between single direct dyes and their mixtures, and c) determining if the photodegradation of binary dye mixtures can

Table 1a

Spectrophotometric Readings at Different Dye concentrations.

Dye Concentration in g/litre	Spectrophotometric Readings.			
	Yellow 500nm*	Brown 580nm*	Red 610nm*	Blue 670nm*
0.002	0.08	0.17	0.165	0.025
0.005	0.18	0.33	0.275	0.075
0.01	0.375	0.63	0.535	0.15
0.015	0.585	0.94	0.785	0.275
0.02	0.72	1.24	1.04	0.365
0.03	1.07	1.78	1.50	0.530
0.04	1.41		1.94	0.800
0.06				1.11

Table 1b

The Constant K Values used to Determine the Concentration of Each Dye in the Dye Mixtures.

Dyestuff	K Value Measured at Maximum Wavelength of Absorption			
	Yellow 500nm*	Brown 580nm*	Red 610nm*	Blue 670nm*
Yellow	37.2	5.2	1.31	–
Brown	38.65	61.58	51.96	6.58
Red	30.69	31.17	34.08	6.85
Blue	6.94	13.54	15.51	17.31

* Maximum Wavelength of Absorption.

Table 2

Total Amounts and Proportions of Absorbed Dyes.

Nominal ratio	Actual Proportion	Total amount (g/g of fabric 10^{-3})
Red		24.00
Brown		43.00
Blue		26.00
Yellow		34.00
Red:Yellow		
2:8	2.3:7.7	41.3
4:6	3.1:6.9	43.8
5:5	4.1:5.9	41.2
6:4	5.0:5.0	39.2
8:2	7.1:2.9	39.5
Red:Blue		
2:8	3.9:6.1	41.5
4:6	4.7:5.3	50.1
5:5	4.9:5.1	43.5
6:4	5.1:4.9	46.7
8:2	6.4:3.6	32.9
Red:Brown		
2:8	2.1:7.9	41.5
4:6	6.3:3.7	50.5
5:5_	0.9:9.1	43.3
6:4	3.6:6.4	35.2
8:2	3.6:6.4	67.1
Yellow:Brown		
2:8	0.4:9.6	42.9
4:6	2.1:7.9	45.9
5:5	2.4:7.6	41.0
6:4	4.6:5.4	41.6
8:2	7.0:3.0	38.0
Brown:Blue		
2:8	3.7:6.3	42.7
4:6	6.6:3.4	39.4
5:5	8.0:2.0	37.8
6:4	8.7:1.3	42.6
8:2	9.8:0.2	42.8
Yellow:Blue		
2:8	2.6:7.4	44.5
4:6	6.0:4.0	42.0
5:5	6.5:3.5	28.4
6:4	7.6:2.4	36.1
8:2	8.6:1.4	37.8

Figure 1a

Calibration Curve for Blue Dye

Concentration of Blue Dye (in g/litre)
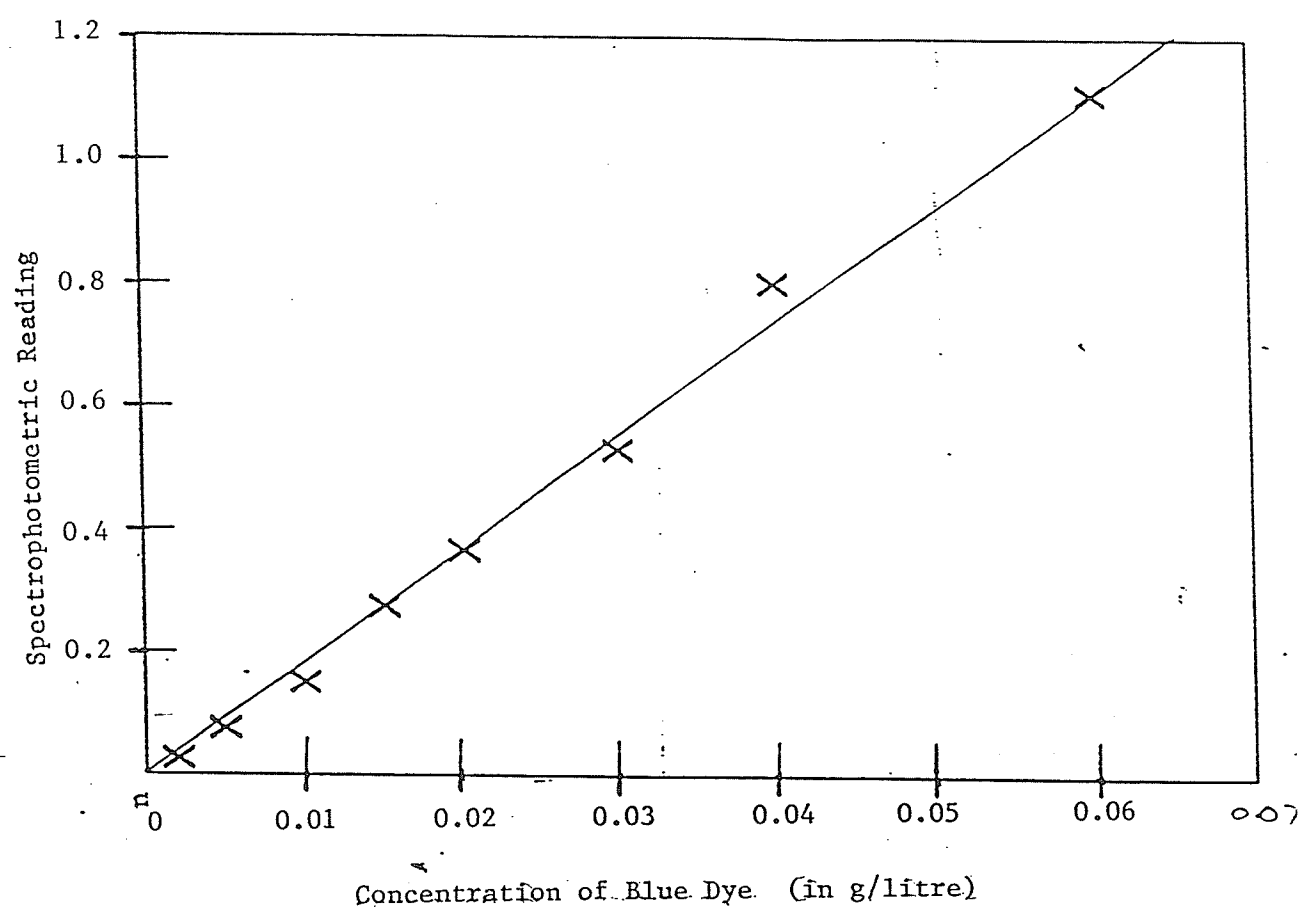
Figure 1b

Calibration Curve for Brown Dye
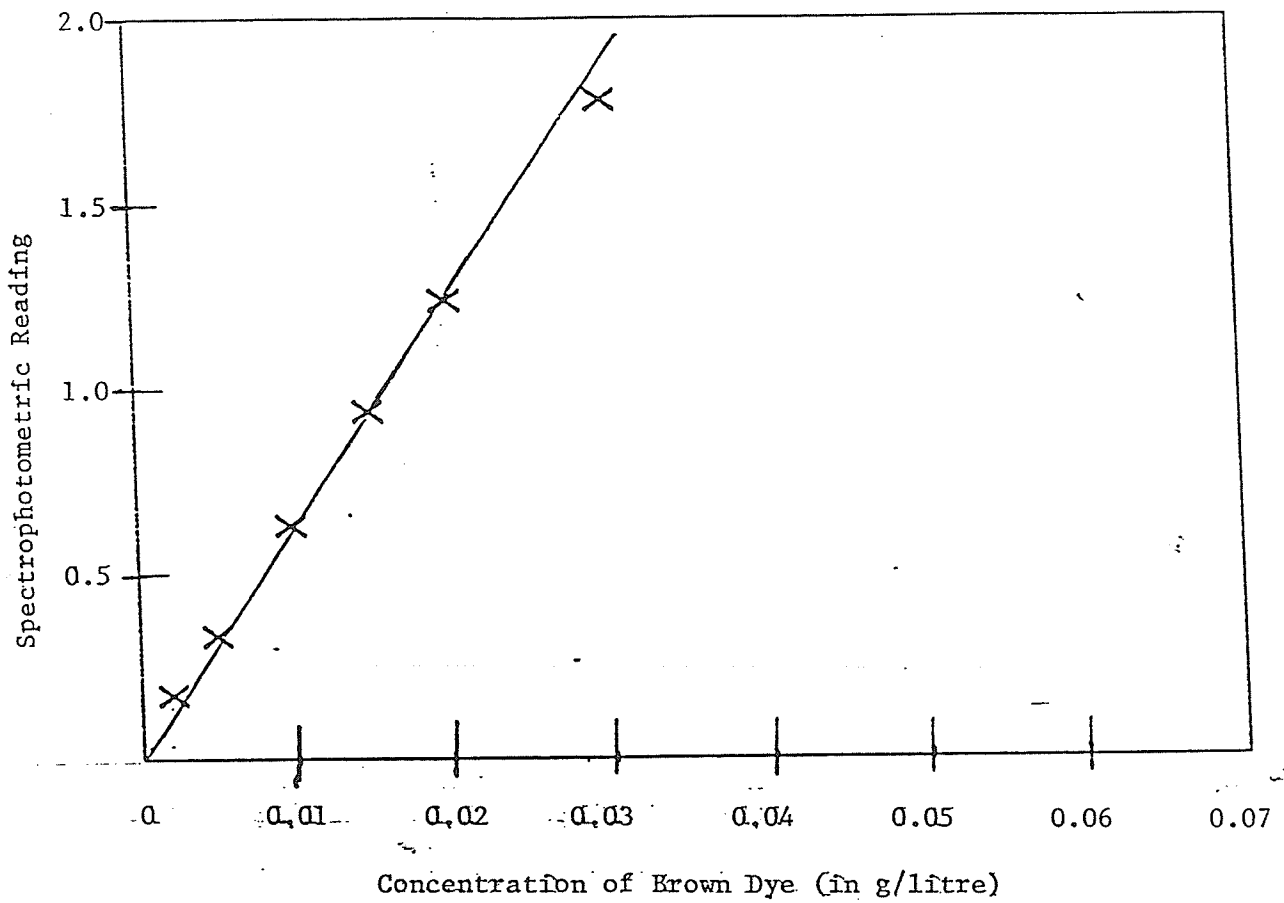
Figure 1c

Calibration Curve for Yellow Dye

Concentration of Yellow Dye (in g/litre)
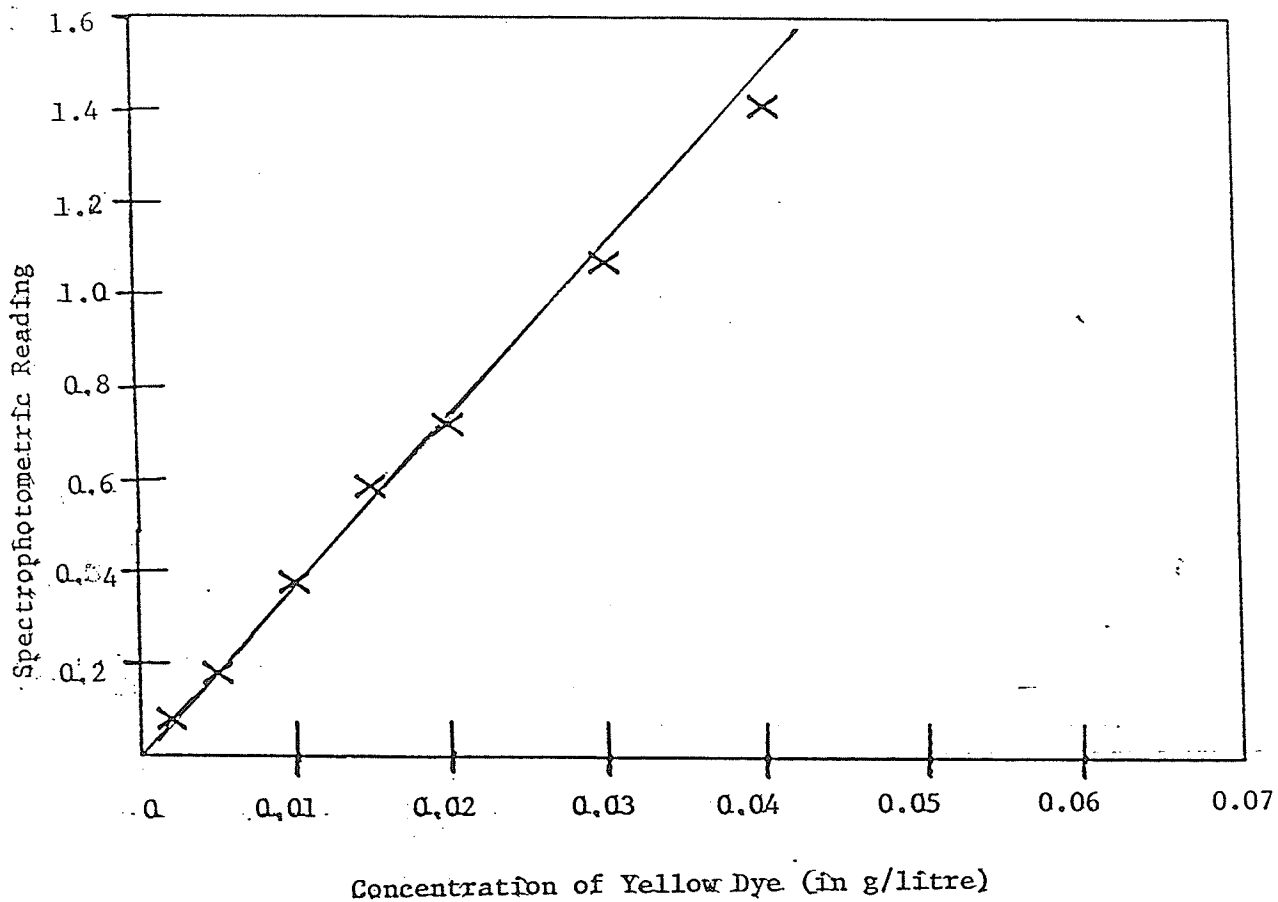
Figure 1d

Calibration Curve for Red Dye

Concentration of Red Dye (in g/litre)
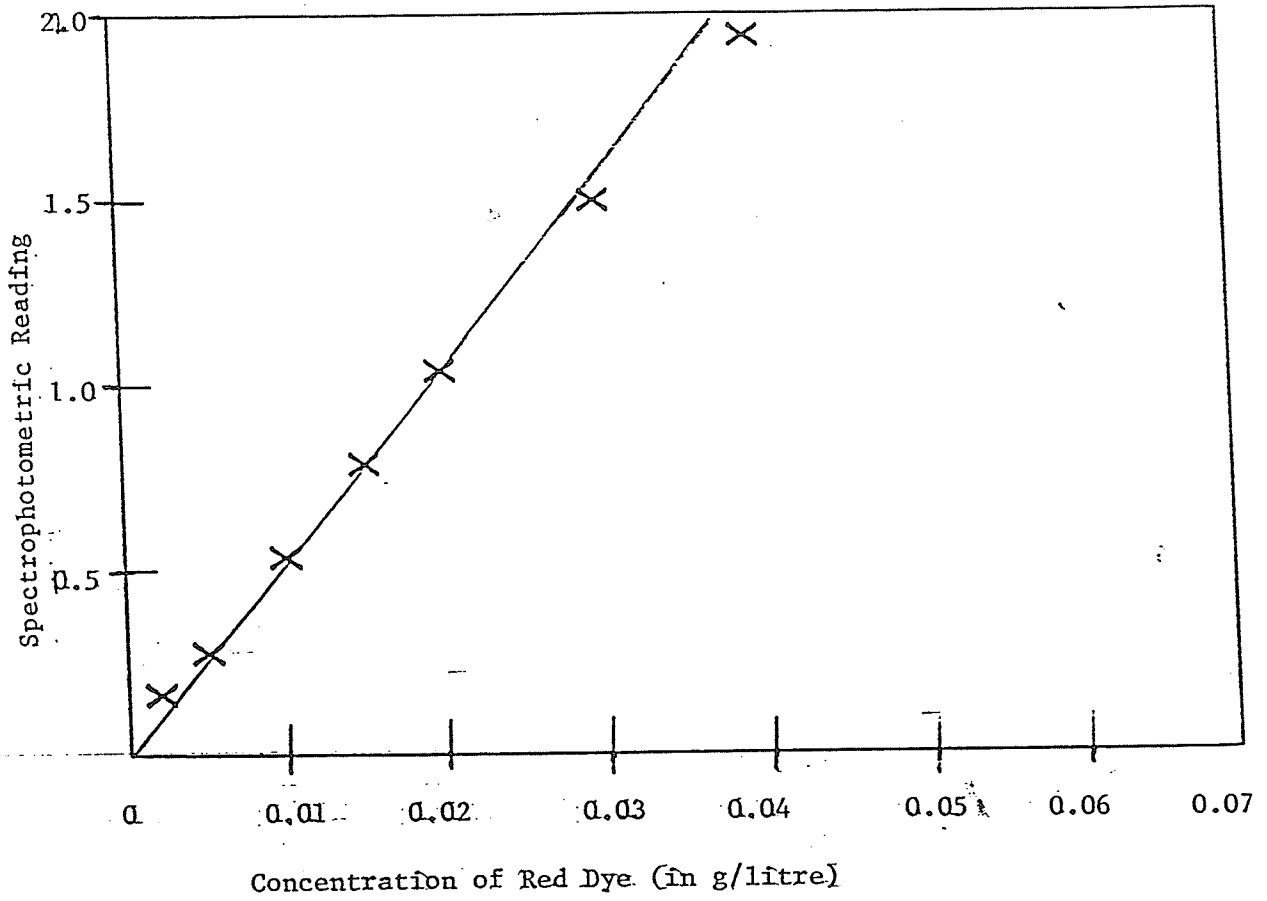
be predicted from that of the individual dyestuffs they contain.

4.2.1.1 PHOTODEGRADATION OF COTTON BY SINGLE DIRECT DYES

Tables 3a-3c summarize the results of the control and single dyed samples. The change in strength results show a definite difference among the five samples. With three of the dyed samples having a significantly smaller loss in breaking strength than the control it can be said that red, brown and yellow have a protective effect on cotton with red being the most protective, followed brown and then yellow. There was however no significant difference between the strength loss of the control and the blue sample.

The changes in colour for all the dyed samples were greater than that of the control. Blue showed the greatest amount of colour change followed by red, then brown and finally yellow. The changes in L,a,b values indicate that apart from yellow all the samples became lighter. They all turned greener and the red, brown and blue turned yellower while the control and yellow turned bluer.

With respect to losses in degree of polymerization, all the samples except brown exhibited losses greater than the undyed control, and so indicated a photosensitizing effect. Blue showed the highest degradation, followed by red, then

Table 3a

Losses in Breaking Strength of Single Dyeings and the
Controls after Exposure in the Weatherometer.
(kqf)

sample	before exposure		after exposure		Loss	
	mean	S.D.	mean	S.D.	mean	Percent
Control	20.90	1.09	16.17	0.44	4.73	22.6
Red	20.72	0.45	19.75	0.96	0.97	4.7
Brown	20.69	0.42	19.42	0.54	1.27	6.1
Blue	21.77	0.61	17.07	0.91	4.71	21.6
Yellow	21.62	0.39	18.43	1.22	3.19	14.8

Table 3b

Changes in L, a, b Values and Total Colour Difference
of Single Dyeings and the Control after Exposure
in the WeatherOmeter

sample	ΔL	Δa	Δb	ΔE
Control	-0.6	0.4	1.4	1.6
Red	-11.3	18.3	-0.1	21.5
Brown	-12.1	9.4	-0.3	15.3
Blue	-16.2	10.6	-15.7	24.9
Yellow	1.4	6.9	6.9	9.9

Table 3c

Losses in Degree of Polymerisation of the Single Dyeings
and the Control after Exposure in the WeatherOmeter

sample	Before exposure	After exposure	Loss
control	3198	2281	917
Red	3462	1811	1651
Brown	3324	2224	1100
Blue	3602	1165	2437
Yellow	2877	1306	1571

yellow and finally brown, which did different significantly from the control.

4.2.1.2 PHOTODEGRADATION OF COTTON BY BINARY MIXTURES OF DIRECT DYES

Tables 4a-c, 5a and b and Figure 2 present a summary of the results for the binary mixtures of blue and yellow.

The strength results showed no strong linear relationship amongst the mixtures and this was confirmed by Figure 2 and an R-square value of 0.5682 (Table 5a). In addition, no relationship was noted for the individual dyes and their mixtures as seen in Figure 2 and a very low R-Square of 0.0014 in Table 5b.

With the changes in colour the mixtures showed that as the amount of yellow in the mixture decreased and that of blue increased, the change in colour decreased steadily. This was confirmed by the graph in Figure 2 and an R-Square value of 0.7574 in Table 5a which although not very strong can be attributed to the fact that the difference between the highest change and the lowest change was only 5.2.

The individual dyes and their mixtures however showed no relationship. The yellow had the lowest colour change of 9.9 but with the smallest amount of blue added to the mixture the colour change for that sample was the highest for all the samples in this group. Small amounts of yellow added to blue

Table 4a

Losses in Breaking Strength of Mixtures of Blue and
Yellow Dyeings after Exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Blue:Yellow						
10:0	21.77	0.61	17.07	0.91	4.71	21.6
7.3:2.	21.11	0.77	18.39	0.91	2.72	12.9
4.0:6.0	22.56	1.36	17.66	1.05	4.90	21.7
3.5:6.5	22.19	1.10	18.34	0.60	3.85	17.4
2.4:7.6	22.89	0.72	17.22	0.65	5.67	24.8
1.4:8.6	22.28	0.23	17.84	1.74	4.44	19.9
0:10	21.62	0.39	18.43	1.22	3.19	14.8

Table 4b

Changes in L, a, b Values and Total Colour Difference
of Mixtures of Blue and Yellow Dyeings after
Exposure in the WeatherOmeter

Sample	ΔL	Δa	Δb	ΔE
Blue:Yellow				
10:0	-16.2	10.6	- 15.7	24.9
7.4:2.6	-16.7	1.6	-9.3	19.1
4:6	-17.3	-2.7	-9.0	19.7
3.5:6.5	-18.6	-4.4	-9.8	21.5
2.4:7.6	-18.2	-7.4	-9.7	21.9
1.4:8.6	-19.3	-11.1	-9.5	24.3
0:10	1.4	6.9	6.9	9.9

Table 4c

Losses in Degree of Polymerization of Mixtures of Blue
and Yellow Dyeings after Exposure in the WeatherOmeter

Sample Blue:Yellow	Before Exposure	After Exposure	Loss
10:0	3602	1165	2437
7.4:2.6	3210	1308	1902
4.0:6.0	3178	1614	1564
3.5:6.5	3468	1383	2086
2.4:7.6	2974	1029	1945
1.4:8.6	2793	978	1815
0:10	2877	1306	1571

Table 5a

Regression analysis for Mixtures of Blue and Yellow Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	3.948	0.1441	0.5682
Colour Change	9.364	0.0550	0.7574
DP Loss	0.000	0.9911	0.0000

Table 5b

Regression Analysis for Blue and Yellow and their Mixtures

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	0.007	0.9376	0.0014
Colour Change	1.632	0.2576	0.2460
DP Loss	5.472	0.0664	0.5226

Figure 2

Changes in Colour, Breaking Strength and D.P. with
Changes in Proportions of Blue and Yellow Mixture
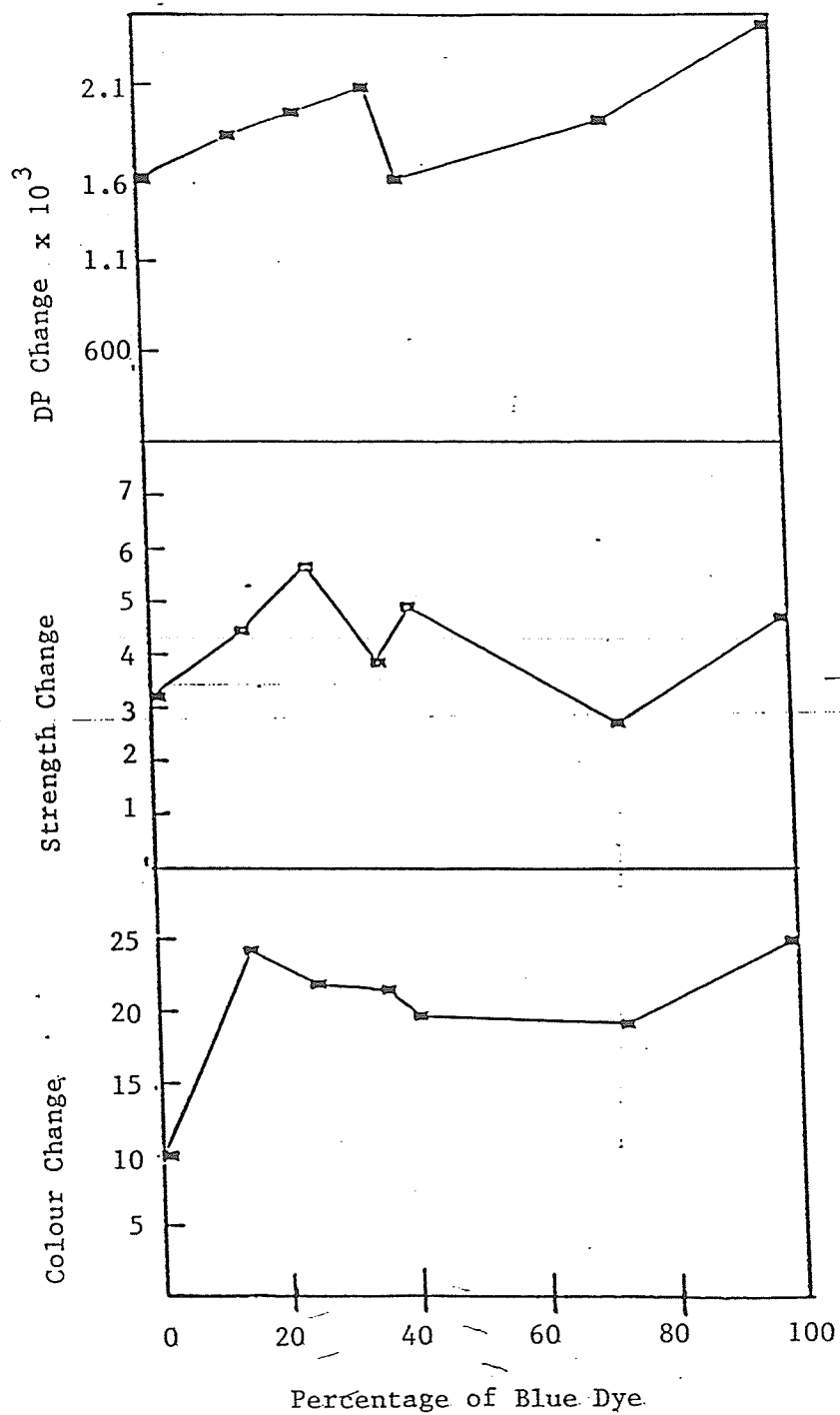
resulted in the smallest colour change for that mixture. A possible explanation is that the yellow transfers most of the energy it absorbs to the blue (Scholefield et al 1933), causing its colour change to increase while that of the yellow is reduced. The changes in L,a,b values showed all the samples, except the one with the highest proportion of yellow, for the mixtures becoming lighter, redder and yellower. It is however interesting to note that the sample with the highest proportion of yellow, was the lightest, the reddest and the yellowest of all the mixtures. The addition of yellow therefore causes the changes in blue to be increased while its own changes are greatly reduced.

For both the mixtures alone and the mixtures together with the single dyes the loss in degree of polymerization showed no relationship and this was confirmed in Table 5a and b by very low R-Square values of 0.5226 and 0.1954 respectively.

The results for mixtures of the brown and yellow dyes are summarised in Tables 6a-c,7a and b and Figure 3.

The loss in strength results did not indicate any relationships. This was confirmed by regression analyses in Tables 7a and b with R-Square values of 0.2723 for the mixture and 0.4225 for the mixture together with the single dyes.

The change in colour results showed a direct relationship between the proportion of yellow and the colour change of

Table 6a

Losses in Breaking Strength of Mixtures of Brown and Yellow Dyeings after Exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Brown:Yellow						
10:0	20.69	0.42	19.42	0.54	1.22	5.9
9.6:0.4	21.23	0.79	18.63	0.78	2.60	12.5
7.9:2.1	22.60	0.73	19.45	1.66	3.15	13.9
7.6:2.4	22.31	0.60	20.40	0.50	1.91	8.6
5.4:4.5	23.01	0.86	19.69	0.67	3.32	14.4
3.0:7.0	20.83	0.79	17.62	0.35	3.21	15.4
0:10	21.62	0.39	18.43	1.22	3.19	14.8

Table 6b

Changes in L, a, b Values and Total Colour Difference of Mixtures of Brown and Yellow Dyeings after Exposure in the WeatherOmeter

Sample	$\triangle$ L	$\triangle$ a	$\triangle$ b	$\triangle$ E
Brown:Yellow				
10:0	-12.1	9.4	-0.3	15.3
9.6:0.4	-12.7	9.5	-1.3	15.9
7.9:2.1	-13.8	8.6	-3.2	16.6
7.6:2.4	-14.2	9.9	-3.1	17.6
5.4:4.6	-15.8	9.4	-5.1	19.1
3.0:7.0	-16.8	10.0	-6.4	20.5
0:10	1.4	6.9	6.9	9.9

Table 6c

Losses in Degree of Polymerization of Mixtures of Brown and Yellow Dyeings after Exposure in the WeatherOmeter

Sample	Before Exposure	After Exposure	Loss
Brown:Yellow			
10:0	3324	2224	1100
9.6:0.4	3002	1887	1116
7.9:2.1	3574	1944	1630
7.6:2.4	3311	2233	1078
5.4:4.6	3489	1956	1533
3.0:7.0	2837	1705	1132
0:10	2877	1306	1571

Table 7a

Regression Analysis for Mixtures of Brown and Yellow Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	1.122	0.3672	0.2723
Colour Change	110.849	0.0018	0.9736
DP Loss	0.000	0.9932	0.0000

Table 7b

Regression Analysis for Brown and Yellow and their Mixtures

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	3.658	0.1140	0.4225
Colour change	0.434	0.5392	0.0799
DP Loss	1.214	0.3207	0.1954

Figure 3

Changes in Colour, Breaking Strength and D.P. with
Changes in Proportions of Brown and Yellow Mixture
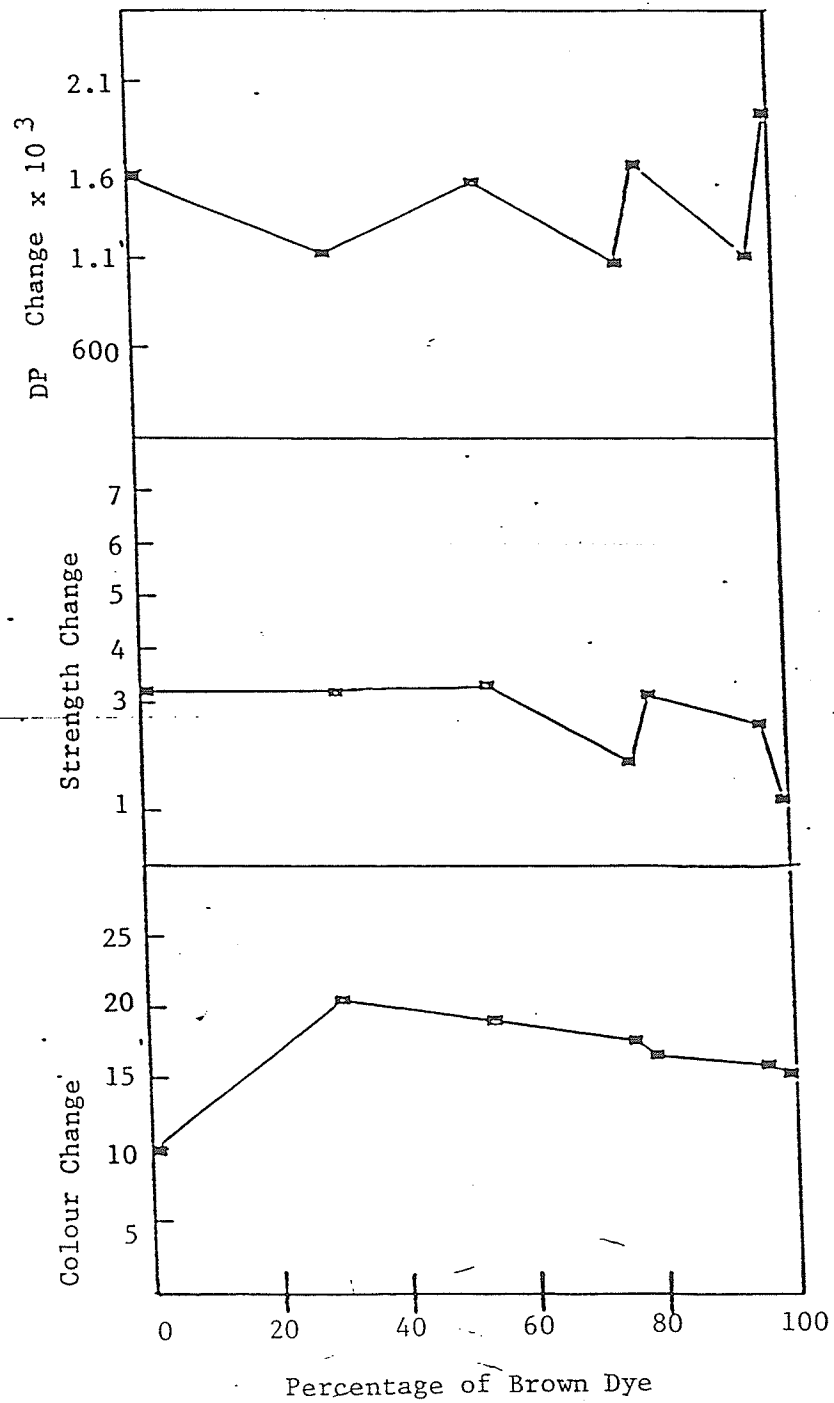
binary the mixture samples. This relationship was confirmed
by an R-Square value of 0.9786 as seen in Table 6c. There is
however no relationship when the values for the single dye
samples are included. Although yellow has a much lower colour
change than brown, the mixture with the highest proportion of
yellow had the highest change of colour while that with the
highest brown had the lowest colour change. It was also
observed that all the mixtures had colour changes higher than
that of the single dyes. The changes in L,a,b values followed
similar trends to the pure brown sample. The sample with the
highest proportion of yellow was lighter, greener and
yellower. Once again it seems yellow's colourfastness is
greatly enhanced by the presence of another dye. Although the
overall colour change of the yellow is increased, the
addition of a little brown greatly increases the yellowness
of the sample which shows that yellow reduces the values of
the brown while it increases its own.

The results indicate no linear relationships between
losses in degree of polymerization and the proportion of dyes
in the mixture.

Tables 8a-c, 9a and b and Figure 4 summarise the results
and regression analyses for the red and yellow mixtures.

The losses in strength did not indicate any strong linear
relationships with the proportions of dyes present. As seen
in Tables 9a and b, the data from the mixtures gave an R-

Table 8a

Losses in Breaking Strength of Mixtures of the Red and
Yellow Dyeings after exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Red:Yellow						
10:0	20.72	0.45	19.75	0.96	0.97	4.7
7.1:2.9	21.69	1.09	18.51	1.27	3.18	14.7
5.0:5.0	20.63	0.74	18.22	1.10	2.41	11.7
4.1:5.9	21.94	0.86	19.63	0.52	2.31	10.5
3.1:6.9	22.59	0.64	19.02	1.00	3.57	15.8
2.3:7.7	22.15	0.54	18.65	1.00	3.50	15.8
0:10	21.62	0.39	18.43	1.22	3.19	14.8

Table 8b

Changes in L, a, b Values and Total Colour Difference
of Mixtures of Red and Yellow Dyeings after
Exposure in the WeatherOmeter

Sample	ΔL	Δa	Δb	ΔE
Red:Yellow				
10:0	-11.3	18.3	-0.1	21.5
7.1:2.9	-12.7	19.9	-2.2	23.7
5:5	-14.5	21.5	-4.3	26.3
4.1:5.9	-14.4	21.3	-4.5	26.1
3.1:6.9	-15.5	21.8	-5.9	27.4
2.3:7.7	-15.7	23.1	-6.1	28.6
0:10	1.4	6.9	6.9	9.9

Table 8c

Losses in Degree of Polymerization of Mixtures of Red
and Yellow Dyeings after Exposure in the WeatherOmeter

Sample	Before Exposure	After Exposure	Loss
Red:Yellow			
10:0	3462	1811	1651
7.1:2.9	2977	1844	1133
5.0:5.0	3136	1618	1518
4.1:5.9	3663	1675	1988
3.1:6.9	3181	1538	1643
2.3:7.7	2810	1456	1354
0:10	2877	1306	1571

Table 9a

Regression Analysis for Mixtures of Red and Yellow Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	0.355	0.5934	0.1057
Colour Change	51.324	0.0056	0.9448
DP Loss	0.630	0.4854	0.1735

Table 9b

Regression Analysis for Red and Yellow and their Mixtures

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	6.051	0.0572	0.5476
Colour Change	0.415	0.5477	0.0767
DP Loss	0.050	0.8319	0.0099

Figure 4

Changes colour, Breaking Strength and D.P. with
Changes in Proportions of Red and Yellow Mixtures
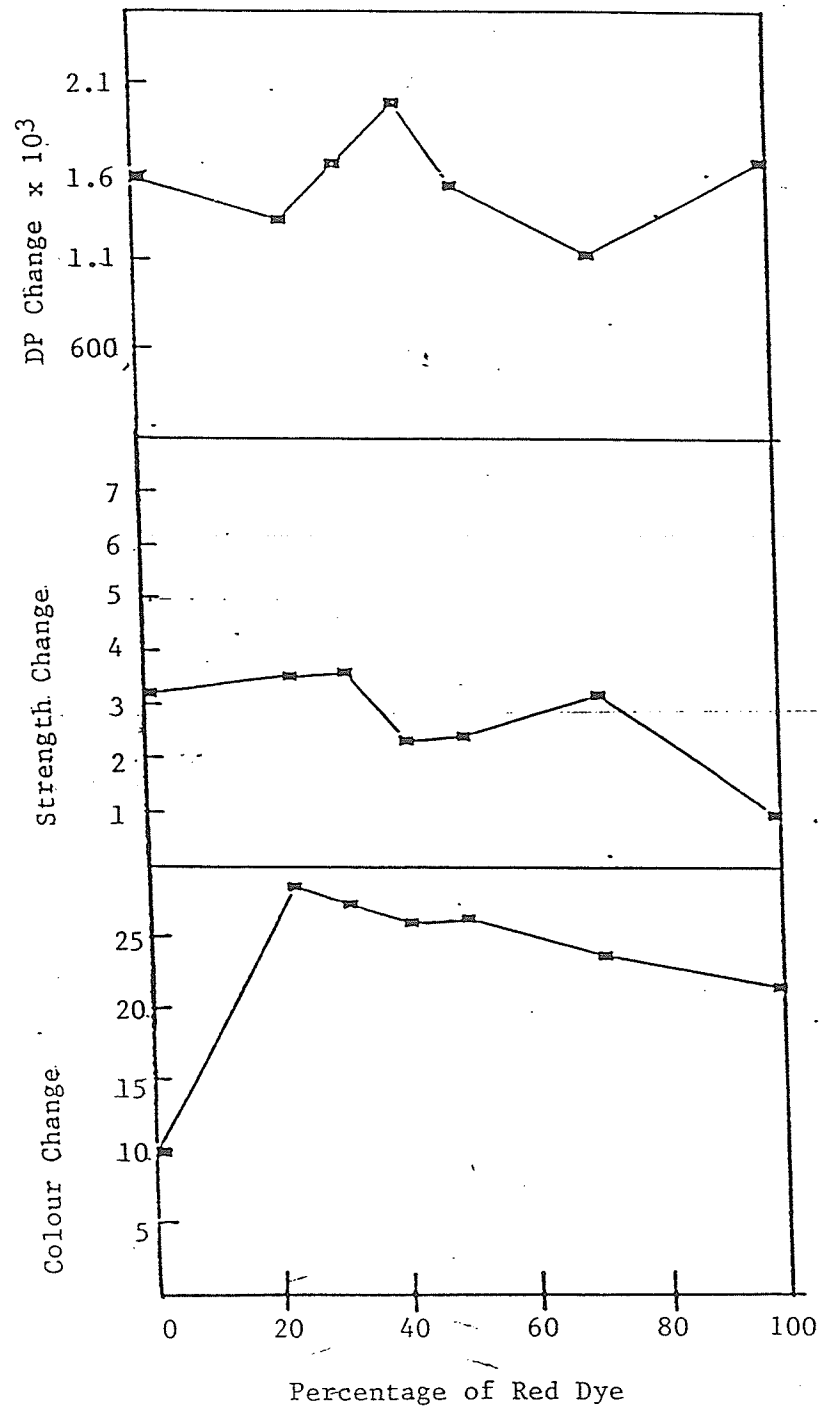
Square of 0.1057, whereas, when the single dyes were included, it was 0.5476 which indicates only a weak relationship at best.

The changes in colour did show a positive linear relationship with the proportion of yellow. Regression analysis in Table 9a gave an R-Square of 0.9448. When the single dyes were added, however, the results did not indicate a linear relationship. All the mixtures had a higher colour change than both single dye samples. Yellow had the lower colour change of the two dyes, but it is the mixture with the highest amount of yellow that had the highest change of colour. Once again yellow had its colourfastness enhanced by the presence of another dyestuff. The change in L,a,b values showed the mixtures had become lighter, greener and yellower as the proportion of yellow in the mixture increased.

The losses in degree of polymerization did not show any linear relationship with the proportion of red or yellow dye either when the mixtures were analyzed alone or with the inclusion of the single dye samples.

The results for the brown and red mixture dyeings are summarised in Tables 10a-c, 11a and b and Figure 5.

The changes in strength varied between samples and did not indicate any linear relationship with the proportion of brown and red either when the mixtures were analyzed alone or with the single dye samples included.

Table 10a

Losses in Breaking Strength of Mixtures of Brown and
Red Dyeings after exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Brown:Red						
10:0	20.69	0.42	19.42	0.54	1.27	6.1
9.0:0.9	21.78	0.58	20.14	0.94	1.64	7.5
7.9:2.1	21.65	0.51	19.89	1.22	1.76	8.1
3.7:6.3	22.76	0.52	20.21	1.03	2.55	11.2
6.4:3.6	22.82	0.78	20.68	1.10	2.14	9.4
6.4:3.6	20.56	0.68	19.86	0.48	0.70	3.4
0:10	20.72	0.45	19.75	0.96	0.97	4.7

Table 10b

Changes in L, a, b Values and Total Colour Difference
of Mixtures of Brown and Red Dyeings after
Exposure in the WeatherOmeter

Sample	ΔL	Δa	Δb	ΔE
Brown:Red				
10:0	-12.1	9.4	-0.3	15.3
9.1:0.9	-10.7	10.8	-0.3	15.2
7.9:2.1	-11.1	9.8	-0.1	14.8
3.7:6.3	-10.4	9.9	-0.1	14.4
6.4:3.6	-10.4	10.9	-0.2	15.0
6.4:3.6	-10.7	12.7	0.1	16.6
0:10	-11.3	18.3	-0.1	21.5

Table 10c

Losses in Degree of Polymerization of Mixture of Brown and Red Dyeings after Exposure in the WeatherOmeter

Sample	Before Exposure	After Exposure	Loss
Brown:Red			
10:0	3324	2224	1100
9.1:0.9	3132	2215	917
7.9:2.1	2824	2375	449
3.7:6.3	3295	1169	2126
6.4:3.6	3163	2464	698
6.4:3.6	3755	1714	2041
0:10	3462	1811	1651

Table 11a

Regression Analysis for Mixtures of Brown and Red Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	0.743	0.4522	0.1984
Colour Change	0.185	0.6964	0.0580
DP Loss	----	------	-----

Table 11b

Regression Analysis for Brown and Red and their Mixtures

Dependent variable	F Value	Prob>F	R-Square
Strength Loss	0.008	0.9315	0.0016
Colour Change	5.653	0.0634	0.5306
DP Loss	-----	-----	-----

Figure 5

Changes in Colour, Breaking Strength and D.P. with
Changes in Proportions of Brown and Red Mixtures
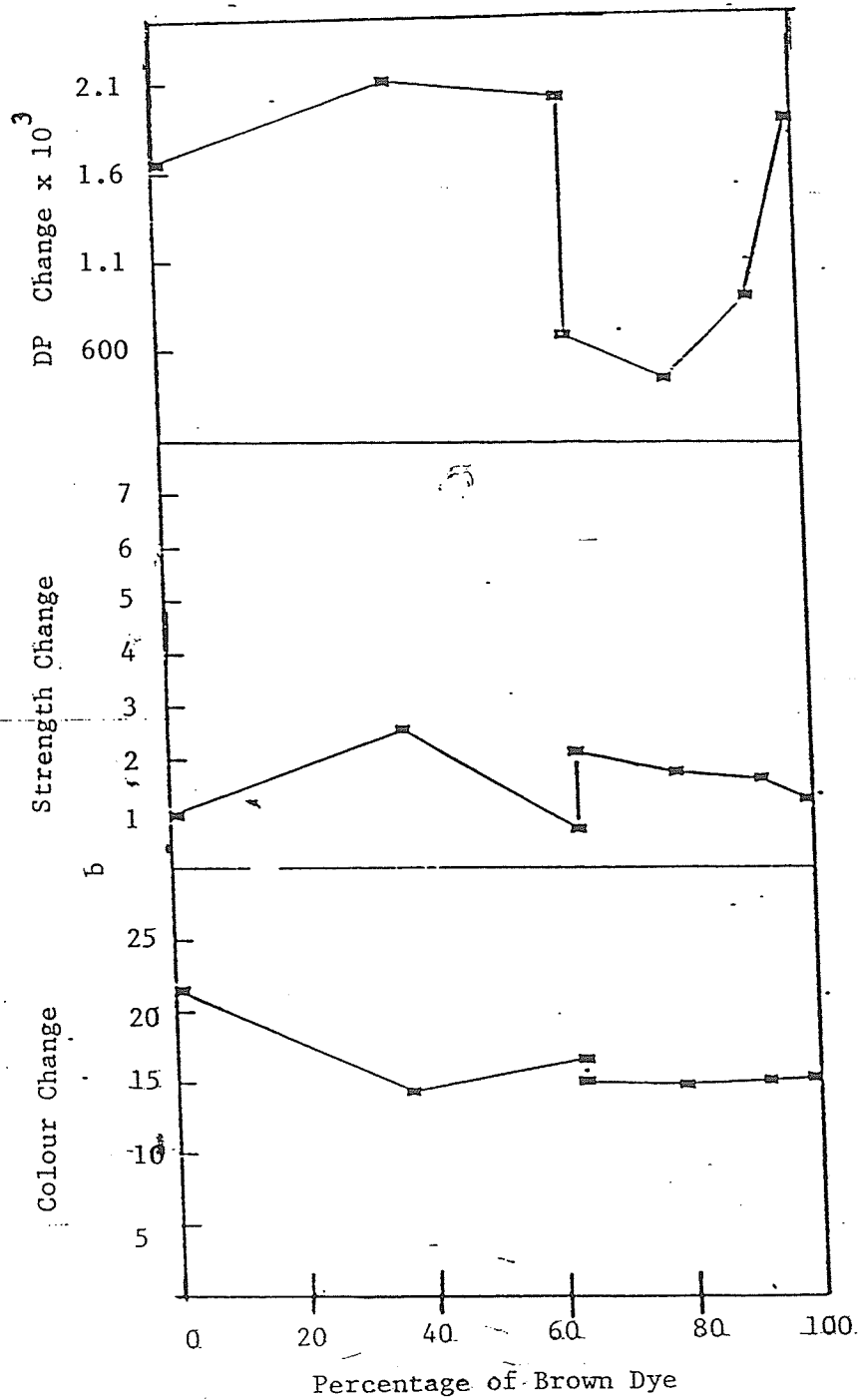
With colour change the variation amongst the mixed dyeings was minimal. As seen in Figure 5 the increase in colour change from 14.8 to a maximum of 15.2 is negligible and the regression analysis confirms this in Table 11a with an R-Square of 0.058. There was no relationship when the single dye samples were included. However red, which had the higher degree of colour change, when added to brown, gave a lower change of colour than the brown.

The degree of polymerization losses varied greatly but did not show any pattern either with the mixtures alone or with the single dye samples as part of the analysis.

Tables 12a-c, 13a and b and Figure 6 show the results of the of mixtures blue and red dyeings.

Change in strength results pointed to the fact that as the proportion of red increased the change in strength decreased. This inverse relationship was confirmed in Table 13a by an R-Square value of 0.8818. A similar relationship was found with the single dyes included and has an R-Square of 0.8783 as indicated in Table 13b. Figure 6 shows the degradation of the mixture was that of a combination of the individual dyes it contained.

The results for colour change did not show any linear relationship with the proportion of blue and red dye with the mixtures alone or with the single dyes included. All the mixtures had lower colour changes than both individual

Table 12a

Losses in Breaking Strength of Mixtures of Blue and
Red Dyeings after Exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Blue:Red						
10:0	21.77	0.61	17.07	0.91	4.71	21.6
6.1:3.9	22.25	0.53	18.82	1.09	3.43	15.4
5.3:4.7	21.57	1.27	18.24	1.14	3.33	15.4
5.1:4.9	21.94	0.44	19.51	1.16	2.43	11.1
4.9:5.1	21.75	0.96	19.31	0.83	2.44	11.2
3.6:6.4	20.51	0.51	19.18	0.78	1.33	6.5
0:10	20.72	0.45	19.75	0.96	0.97	4.7

Table 12b

Changes in L ,a, b Values and Total Colour Difference
of Mixtures of Blue and Red Dyeings after
Exposure to the WeatherOmeter

Sample	ΔL	Δa	Δb	ΔE
Blue:Red				
10:0	-16.2	10.6	-15.7	24.9
6.1:3.9	-17.3	8.2	-8.0	20.7
5.3:4.7	-14.4	5.0	-5.6	16.3
5.1:4.9	-15.5	3.3	-6.0	17.0
4.9:5.1	-15.1	3.1	-5.3	16.3
3.6:6.4	-15.8	3.3	-5.5	17.0
0:10	-11.3	18.3	-0.1	21.6

Table 12c

Losses in Degree of Polymerization of Mixtures of Blue
and Red Dyeings after Exposure in the WeatherOmeter

Sample	Before Exposure	After Exposure	Loss
Blue:Red			
10:0	3602	1165	2437
6.1:3.9	3840	1564	2276
5.3:4.7	3112	1627	1485
5.1:4.9	2979	1462	1517
4.9:5.1	3382	1879	1503
3.6:6.4	3075	2069	1006
0:10	3462	1811	1651

Table 13a

Regression Analysis for Mixtures of Blue and Red Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	22.372	0.0179	0.8818
Colour Change	1.591	0.2964	0.3465
DP Loss	22.689	0.0176	0.8832

Table 13b

Regression Analysis for Blue and Red and their Mixtures

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	36.097	0.0018	0.8783
Colour Change	0.718	0.4355	0.1255
Mol. Wt. Loss	3.106	0.1383	0.3832

Figure 6

Changes in Colour, Breaking Strength and D.P. with
Changes in Proportions of Blue and Red Mixtures

Percentage of Blue Dye
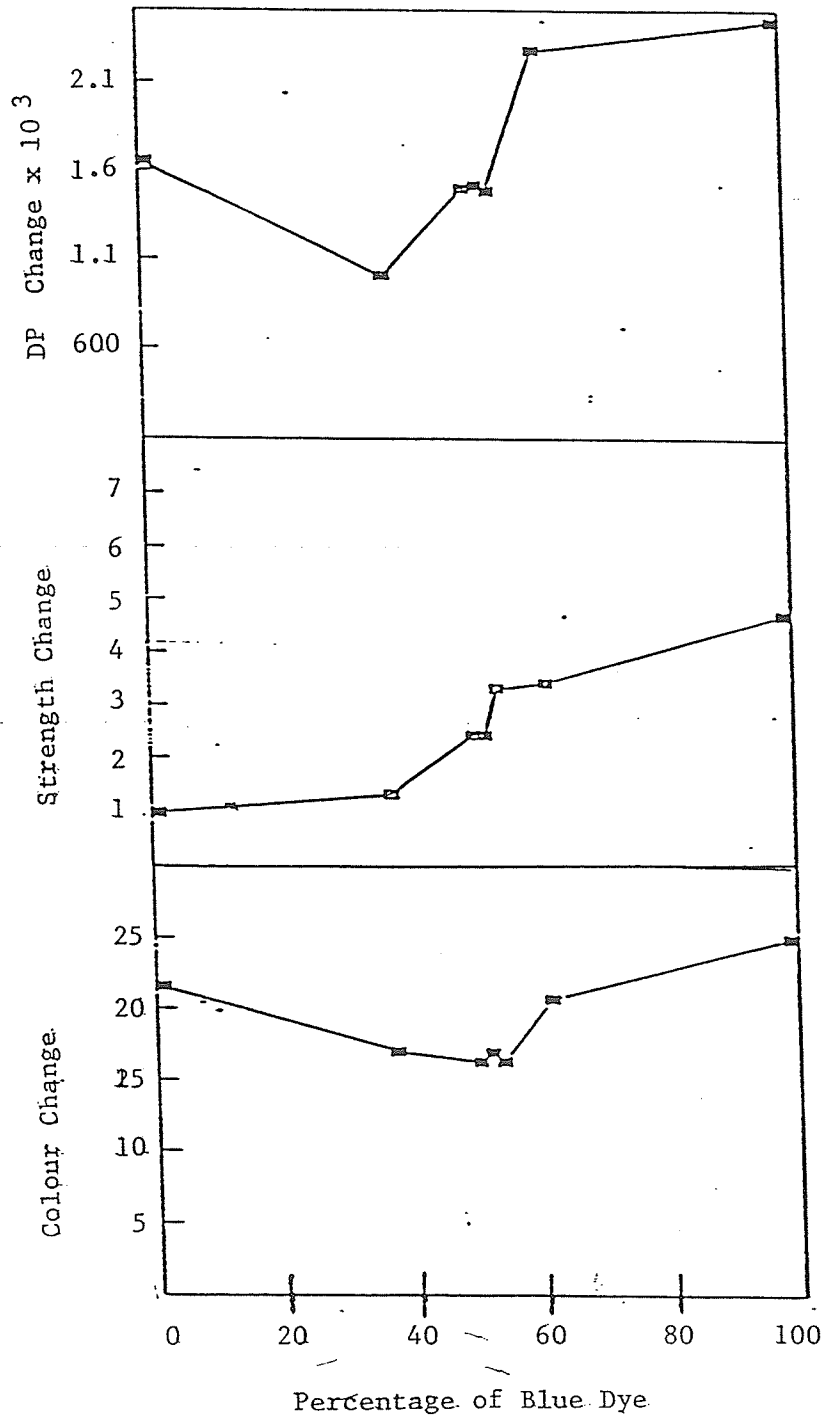
dyeings. The changes in L,a,b values indicated that all the samples for the mixture became lighter, greener and yellower. They also showed that a little addition of blue to red reduces the redness of the mixture while the b values showed an additive effect.

With respect to the degree of polymerization values, as the amount of blue in the mixture increased, the degradation of the sample also increased which was the same as that for strength. The regression analysis gave an R-Square of 0.8832 as shown in Table 13a while that with the single dye samples included in Table 13b was 0.3832 indicating no linear relationship. It was observed that with a little addition of blue to red the change in degree of polymerization dropped significantly and then started rising to a maximum which was below that of the pure blue sample but higher than that of the red only sample.

The results for mixtures of blue and brown dyeings are shown in Tables 14a-c, 15a and b and Figure 7.

The changes in strength showed great variation between samples, but there was no linear relationship with the proportion of blue and brown in the mixtures, which was confirmed in Table 15a by a very low R-Square of 0.0076. A similar behaviour was observed with the single dye samples included and that gave an R-Square value of 0.4675 as shown in Table 15b.

Table 14a

Losses in the Breaking Strength of Mixtures of Blue and Brown Dyeings after Exposure in the Weatherometer.
(kgf)

Sample	Before Exposure		After Exposure		Loss	
	Mean	S.D.	Mean	S.D.	Mean	Percent
Blue:Brown						
10:0	21.77	0.61	17.07	0.91	4.71	21.6
6.3:3.7	20.44	0.57	17.70	0.46	2.74	13.4
3.4:6.6	22.12	1.04	21.20	1.21	0.92	4.2
2.0:8.0	21.68	1.12	20.13	1.02	1.57	7.2
1.3:8.7	20.82	0.83	18.90	1.01	0.67	3.2
0.2:9.8	22.28	0.66	19.07	1.17	3.25	14.6
0:10	20.69	0.42	19.42	0.54	1.27	6.1

Table 14b

Changes in L, a, b Values and Total Colour Difference of Mixtures of Blue and Brown Dyeings after Exposure in the WeatherOmeter

Sample	Δ L	Δ a	Δ b	Δ E
Blue:Brown				
10:0	−16.2	8.7	−15.7	24.9
6.3:3.7	−15.6	4.1	−4.0	16.6
3.4:6.6	−14.4	3.1	−2.3	14.9
2.0:8.0	−13.9	2.9	−2.1	14.3
1.3:8.7	−13.5	3.2	−1.7	14.0
0.2:9.8	−12.3	6.2	−0.8	13.8
0:10	−12.1	9.4	−0.3	15.3

Table 14c

Losses in the Degree of Polymerization of Mixtures of Blue
 and Brown Dyeings after Exposure in the WeatherOmeter

Sample	Before Exposure	After Exposure	Loss
Blue:Brown			
10:0	3602	1165	2437
6.3:3.7	3262	1236	2027
3.3:6.7	3149	1193	1956
2.0:8.0	3419	1695	1725
1.3:8.7	3731	1239	2492
0.2:9.8	3042	1631	1411
0:10	3324	2224	1100

Table 15a

Regression Analysis for Mixtures of Blue and Brown Dyeings

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	0.023	0.8888	0.0076
Colour Change	100.082	0.0021	0.9709
DP Loss	0.240	0.6580	0.0740

Table 15b

Regression Analysis for Blue and Brown and their Mixtures

Dependent Variable	F Value	Prob>F	R-Square
Strength Loss	4.390	0.0903	0.4675
Colour Change	19.130	0.0072	0.7928
Mol. Wt. Loss	3.492	0.1206	0.4112

Figure 7

Changes in Colour, Breaking Strength and D.P. with
Changes in Percentages of Blue and Yellow Mixtures.
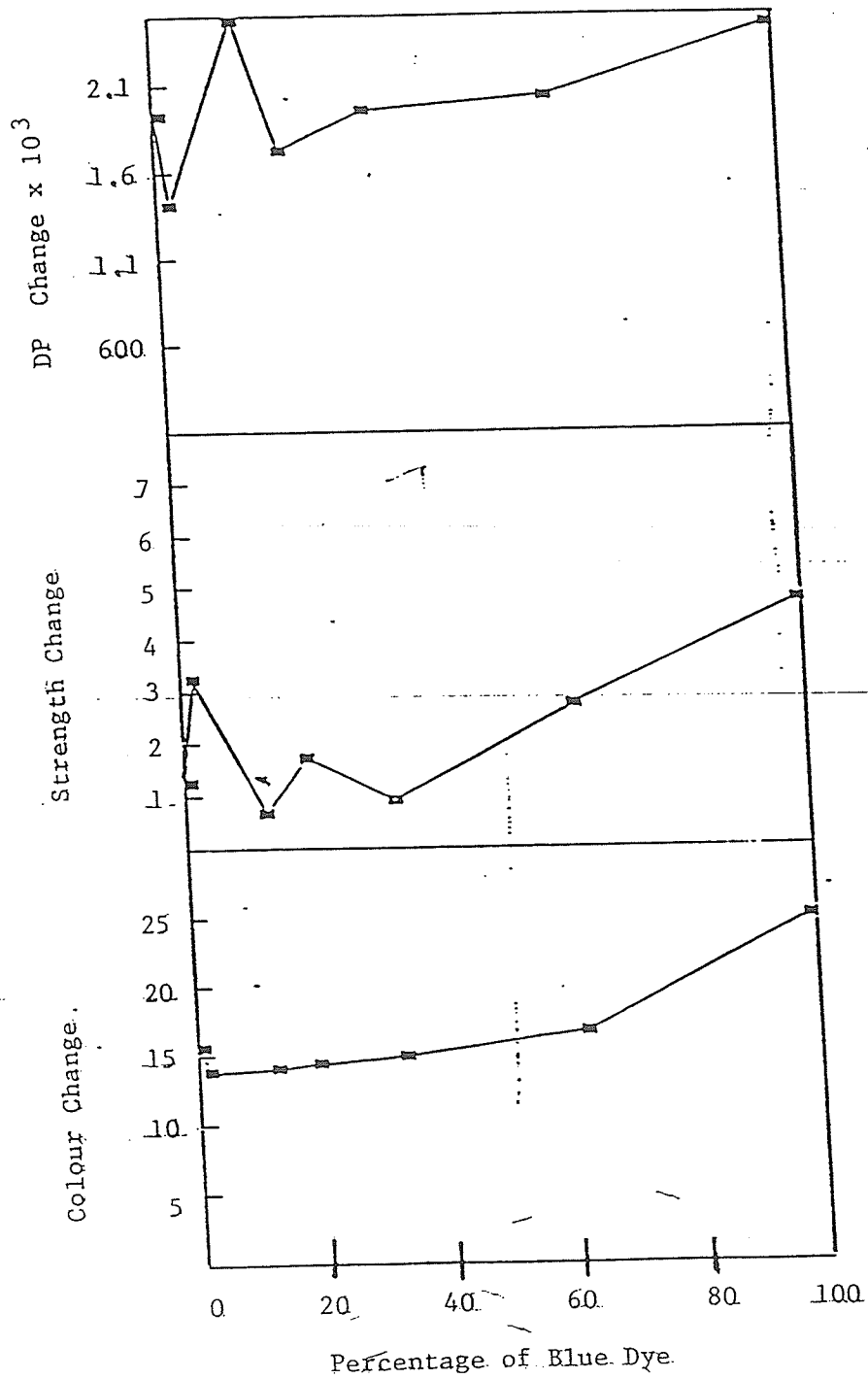
It was observed that there was not much variation in the change in colour values for the mixtures. The proportion of blue in the mixture was found to be directly proportional to the extent of colour change giving an R-Square value of 0.9709 as shown by Table 15a. A similar relationship was found with the inclusion of the pure dye samples. As shown in Table 15b this gave an R-Square value of 0.7928. When a small amount of brown was added to the blue the colour change decreased greatly. The L,a,b values showed that all the binary mixture samples became lighter, greener and yellower after exposure.

The results of the degree of polymerisation did not show any linear relationship with the proportion of blue and brown either in the mixtures alone or with the single dye samples included.

Since the change in colour results showed a number of relationships with the proportion of dyes in the mixture, the next section will discuss how each dye behaves in combination with the others.

Of all the single dye samples, the yellow sample showed the least change in colour. As illustrated in Figure 8 all the yellow mixtures however showed large changes in colour with a little addition of either brown, blue or red. These changes, apart from the blue mixtures, were all higher than that of both single dyes in thé mixture. This degree of colour change then decreased slowly to a minimum, as the proportion

Figure 8

Colour Changes of Mixtures with Yellow
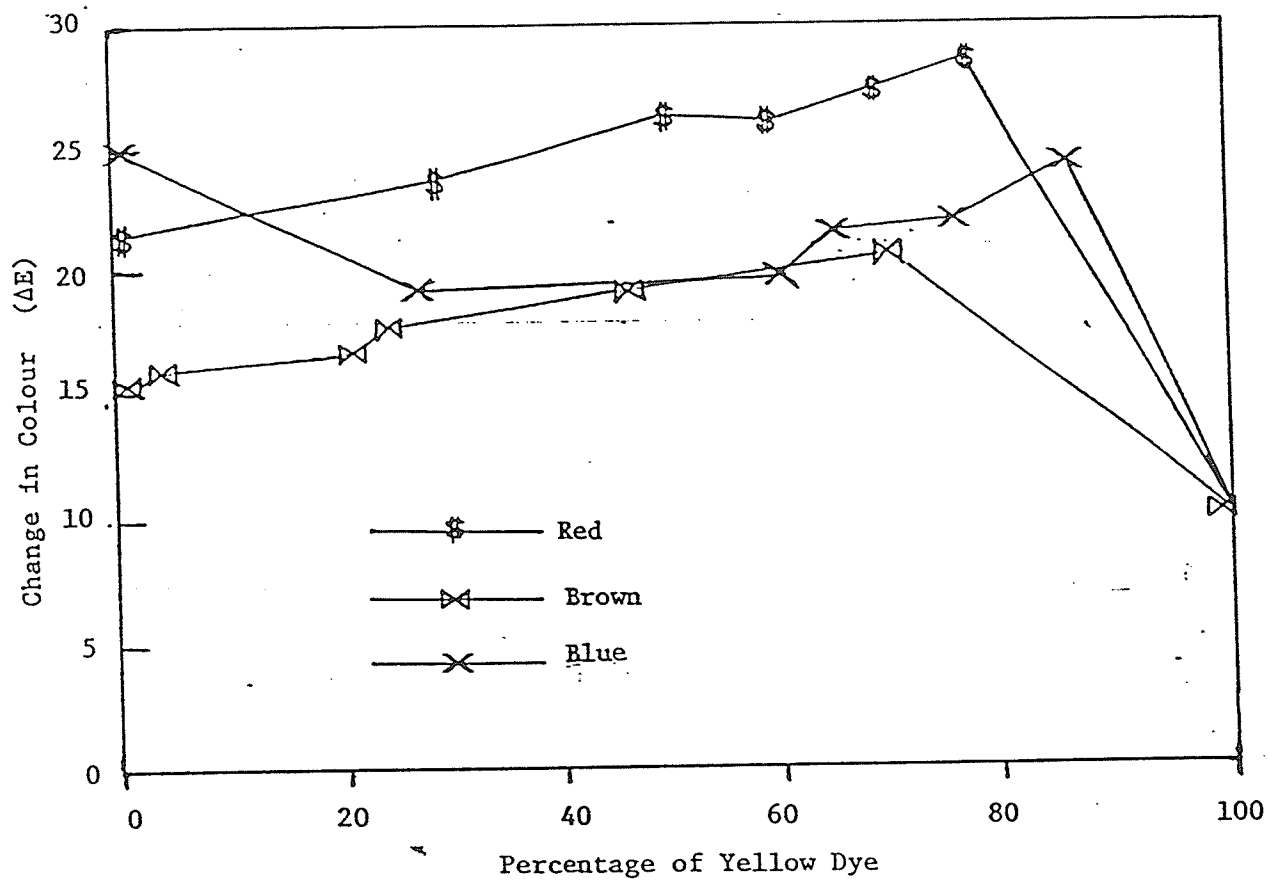
of the other dye was increased, but this minimum, except for the blue, was still higher than that of both the red and brown single dye samples. Although the yellow sample became darker, redder and bluer, the L,a,b changes show that the addition of any of the other colours to yellow reduces the bluing of the sample. In fact they became more yellow after exposure than before. They also became lighter and redder.

Blue had the highest extent of colour change among the single dye samples. The results showed that a little addition of brown or red caused a large reduction in the degree of colour change of the sample as shown in Figure 9. This amount of colour change was higher than that of the single dye samples of the other colours and then fell to a minimum below that of the single dye samples. With the yellow, the change initially decreased to a value below that of blue when the lowest proportion of yellow was added. Then as the proportion of yellow in the mixture increased the colour change gradually increased to a maximum which was about the same as that the single blue dyeing. A little addition of blue to red decreases the greening of the red while a little addition of blue to yellow enhances the yellowness of the sample. The addition of small proportions of these dyes to blue however does not seem to affect on the blueness of the sample.

Red had the second highest degree of colour change. As indicated in Figure 10 the results indicated that apart from
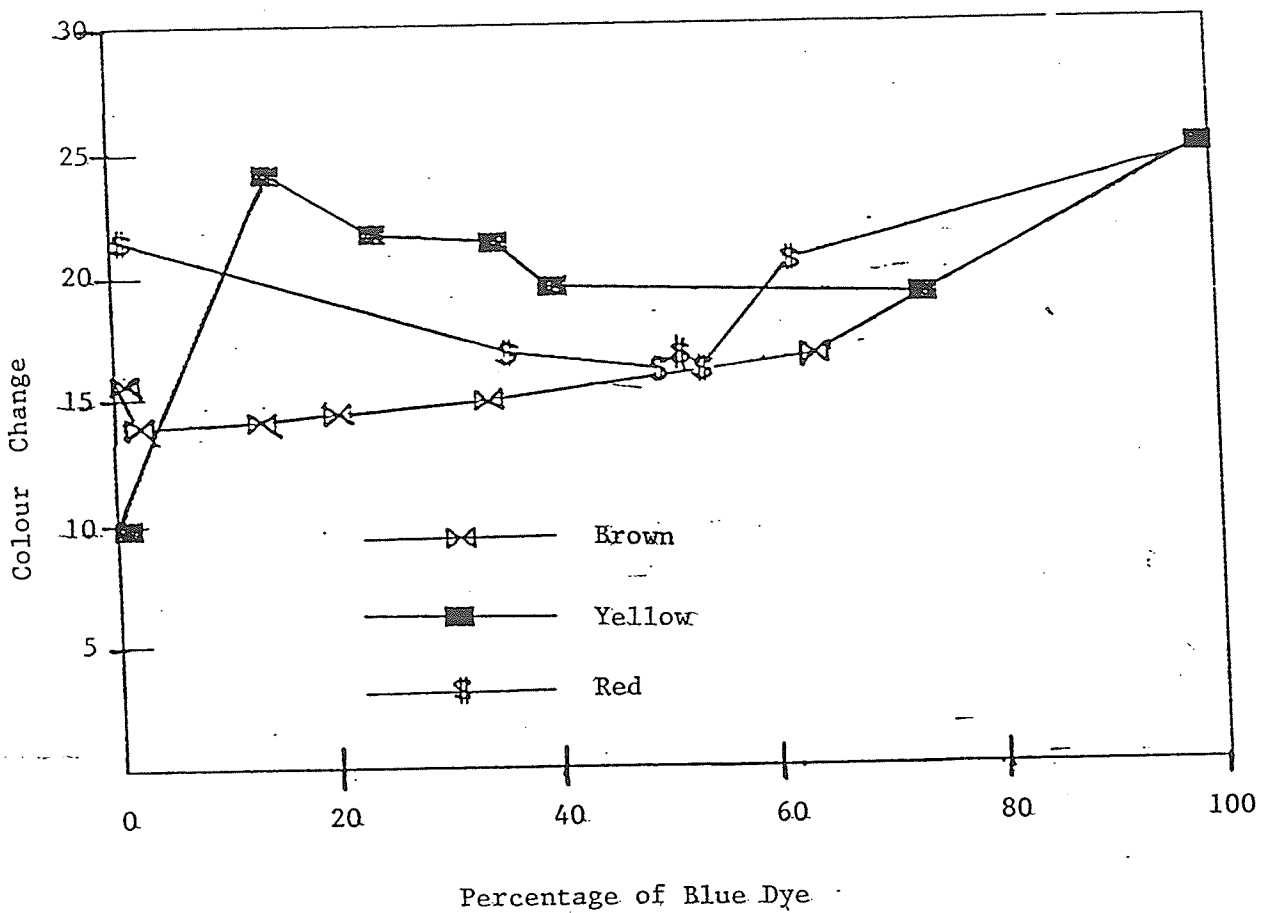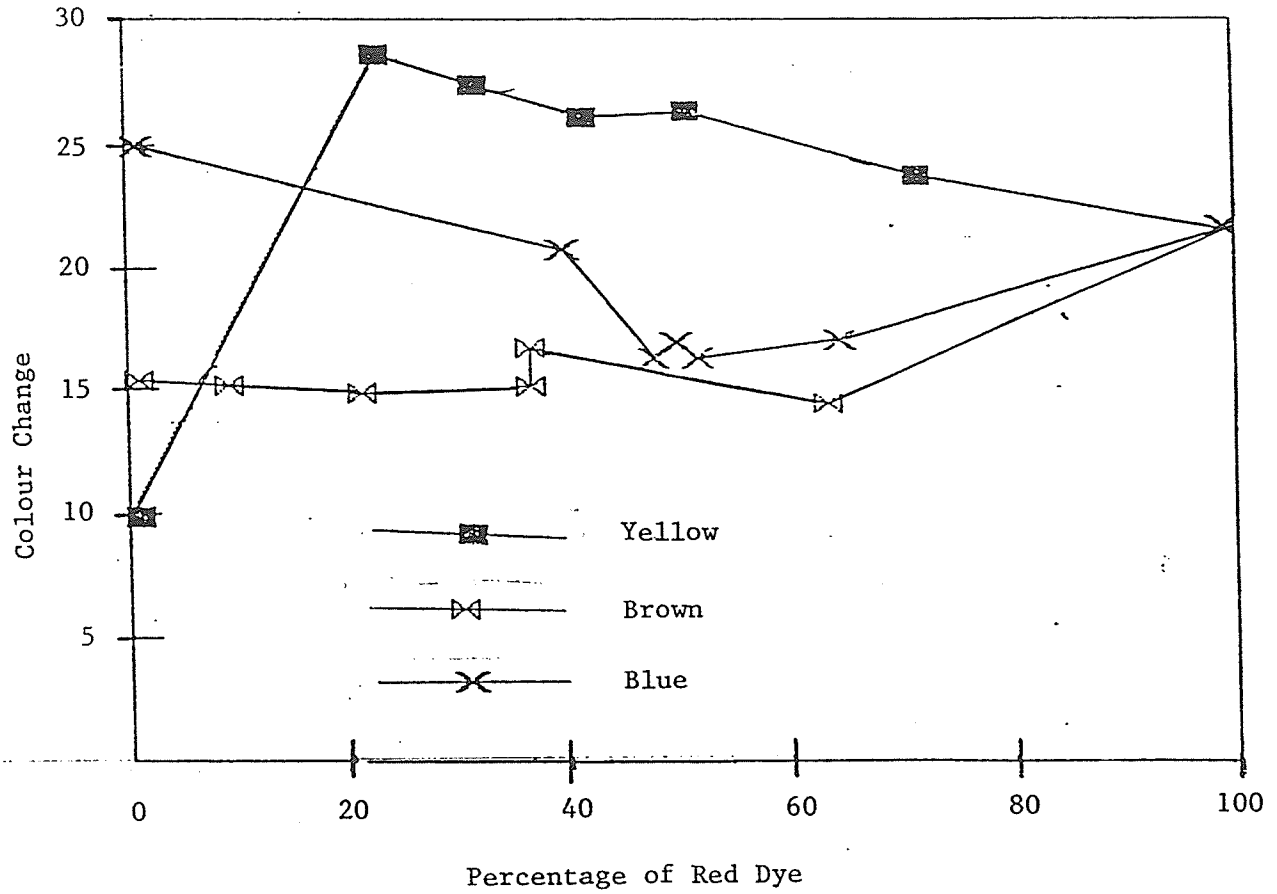
Figure 9

Colour Changes of Mixtures with Blue

Figure 10

Colour Changes of Mixtures with Red

Percentage of Red Dye

the yellow the addition of either blue or brown caused a significant decrease in the colour change of the sample. The changes in L,a,b indicate that the addition of these colours to red decreases the reddening of the red, except for blue which did not have the same effect.

The brown was the dye that gave the second lowest amount of colour change among the single dye samples. As illustrated in Figure 11, with the addition of a small proportion of blue or red the colour change of the sample is reduced slightly. These changes then increased but very minimally and the mixture with the highest proportion of blue was just slightly higher than that of the brown only sample while, for the red, it was about the same as that of the brown only sample. The addition of the lowest proportion of yellow however caused an increase in the degree of colour change of the sample. The brown therefore seemed to have a photoinhibiting effect in its mixtures with red and blue.

Apart from the mixtures of yellow all other binary mixture samples had lower degrees of colour change than one would expect from an additive effect.

Overall one cannot predict the behaviour of dye mixtures from that of the individual dyeings. A possible explanation could be that the dyes interact in solution or in the fibre when mixed with each other. In relation to colour change which

Figure 11

Colour Changes of Mixtures with Brown

Percentage of Brown Dye
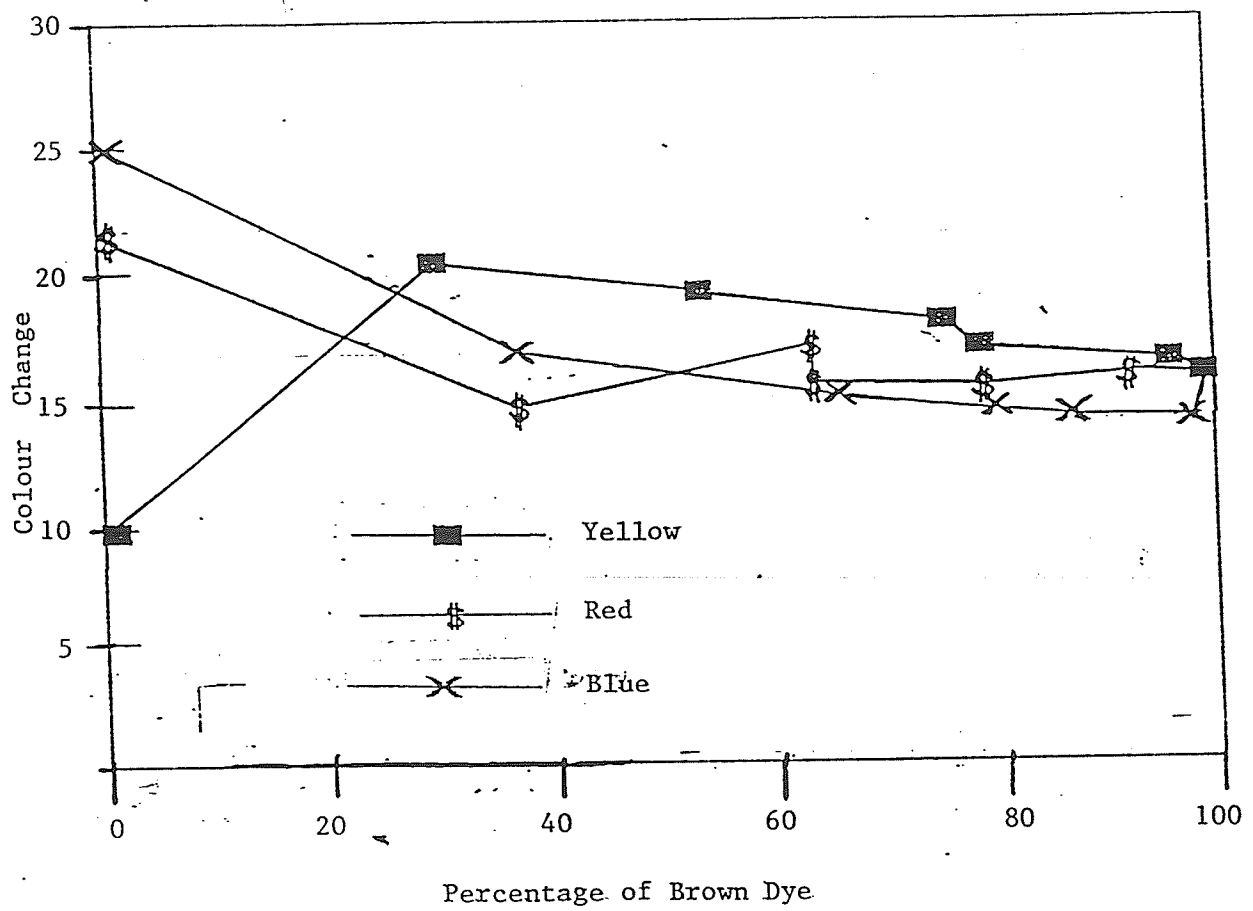
gave the only consistent results, it could be that when mixed with the other colours, yellow tends to reduce the tendency for dyes to aggregate, thereby exposing a greater surface area to the light and leading to a relatively higher degree of colour change. It is however interesting to note that for all these samples the colourfastness of yellow in the mixture is enhanced. A possible explanation is that although the dyes aggregate less in the mixture, most of the energy absorbed by the yellow component is transmitted to the other dye so that there is virtually no colour change of the yellow while the colour change of the other dye is increased. With the other mixtures that do not contain yellow, there was less colour change on the whole than what one would obtain if the proportion of the individual colour changes of the individual dyeings were added together. This could be explained as follows. In the mixtures they tend to aggregate more than as individual dyes resulting in less colour change. In fact the literature shows that dyes that aggregate in a fibre tend to fade to a lesser extent than those that do not (Baxter et al 1957; Baxter et al 1971).

CHAPTER FIVE

SUMMARY AND CONCLUSIONS

5.1 SUMMARY

The major aim of this research was to discover how binary mixtures of direct dyes degrade cotton dyeings. Four commercial dyes namely, Ultrasol Yellow BG, Direct Red 1, Direct Blue 1 and Direct Brown 1 were used in dyeing cotton from an aqueous dye bath containing an electrolyte. These four single dyes were combined to form six binary mixtures each of which was used at five different proportions. The four individual dyeings, thirty mixtures and one undyed control sample were exposed in a xenon-arc WeatherOmeter for 120 standard fading hours. Tristimulus colour values, tensile breaking strength and the degree of polymerization were measured before and after exposure. Degradation was then assessed by changes in these three variables. The amount of each individual dye absorbed, the total amount and the actual proportion of each dye absorbed by each sample were also determined.

The results for the single dyeings do not provide clear evidence of photosensitizing and protective behaviour. The strength results revealed that three of the single dye were protective; the most protective dye being red, followed by brown then yellow. On the other hand the colour change and loss in degree of polymerization data showed that at least three dyes were photosensitizers. The colour change data ranked blue, red, brown and yellow with yellow

degrading the least, while the degree of polymerization data indicated that blue had the most photosensitizing effect followed by red and then yellow.

The results for breaking strength and degree of polymerization of the cotton dyed with binary mixtures were very inconsistent and revealed no definite patterns. Also there was no linear relationships found between these properties and the proportion of dyes except for the red and blue binary mixture. For this mixture the loss in breaking strength was found to be a combination of that of the individual dyes. The same combination also showed that for the change in degree of polymerization as the proportion of blue increased, the degradation of the sample also increased, but failed to show any direct linear relationship between the extent of change and the proportion of dyes in the mixture.

The results of change in colour generally revealed definite patterns of behaviour within each binary mixture. They do not however show direct linear relationships between the individual dyes and their mixtures. For example, with the blue and brown combination a small amount of brown in the mixture decreased the amount of colour change much below that expected for an additive process. This signifies that the brown dye was acting as a photoinhibitor. This was also evident with the brown and red combination.

Mixtures of yellow with blue, red and brown reveal similar patterns of behaviour. The extent of colour change

was found to be directly proportional to the amount of yellow in the mixture and the presence of the lowest proportion of yellow increased the colour change of the red and brown mixtures above their performance as pure shades. The red and blue mixture did not show any linear relationship. The results of the red and brown mixture revealed the combined colour change was not additive. In fact the brown component appeared to be the dominant influence, maintaining approximately the same low level of colour change regardless of the proportion of red in the mixture.

The results also revealed that when yellow is mixed with other dyes the colourfastness of the yellow component is enhanced while that of the other dye is diminished. Apart from the combination with yellow, the colourfastness of blue is not affected by mixing with the other dyes.

On the whole the results for fibre degradation as indicated by changes in strength and degree of polymerization were not consistent. The results for colour change were however more consistent and reliable. This could be due to the fact that colour is a surface measurement and therefore is not affected much by variations in total amount of dye. The other two factors however measure changes in the bulk properties such as molecular structure which are manifested physically or chemically. These changes can therefore be influenced by the amount of dye in the fibre. The fact that the samples were left for about four months

and viscosity measurements carried out over a period of about two months could have contributed to the high variation and inconsistencies in the degree of polymerization measurements and also to the disparity in the changes in strength and degree of polymerization results.

5.2 CONCLUSIONS

From the results obtained it is difficult to draw consistent conclusions about which dyes should be classified as photosensitizers and which as protectors when the method of classification depends on how the degadation is measured. The breaking strength results reveal that three of the four dyes protected cotton while the degree of polymerization results show that two of the same dyes could behave as photosensitizers. From the colour change results yellow was the most colourfast with the least amount of change followed by brown, then red and blue.

The only pattern emerging from the breaking strength results involved the blue and red mixture in which the degradation of the fibre was directly proportional to the proportion of blue in the mixture. However there was no relationship between the extent of mechanical degradation of cotton and the combination of dyes present nor can the extent of mechanical degradation be predicted from that of the ratio of the individual dyes.

The degradation of colour in a binary mixture depends on the types of single dyes in the mixture. Although there appear to be some type of relationships between the extent of degradation and the proportion of dye in the mixtures, these are not necessarily direct relationships. The extent of degradation of a mixture cannot be predicted directly from that of the proportion of the component dyes. Mixtures of yellow, where the extent of colour change was higher than that of the individual dyeings, supports observations that generally yellow dyestuffs act as photosensitizers (Smith 1950; Scholefield et al 1933). This behaviour was not observed with any of the other three dyes. In fact the colour change results of the brown point to the fact that with certain other direct dyes like Direct Blue 1 and Direct Red 1, Direct Brown 1 can behave as a protector.

By measuring degradation in terms of degree of polymerization and colour it was hoped that relationships between these three variables could be identified. However since the results describing the degradation of the fibre were inconsistent it is difficult to draw conclusions about the ability of the dye to change colour as compared to its ability to degrade the fibre.

5.3 IMPLICATIONS OF STUDY

It is believed that this research has added to the understanding of the behaviour of direct dyes on cotton and more specifically of direct dye mixtures. It has been

confirmed that when a dye with good lightfastness like Ultrasol Yellow BG is combined with another dye having any lightfastness, the new shade is not as fast as either of the component dyes. On the other hand certain dyes when mixed together tend to produce shades that have a better lightfastness than the component dyes.

5.4 RECOMMENDATIONS

1. Since the strength and degree of polymerization results did not provide conclusive evidence in terms of fibre degradation, it would be of interest to repeat the experiment but this time maintaining closer control over the total amount of dyestuff absorbed by the samples. In future when undertaking similar experiments, the amount of time between exposure and measuring the dependent variables should be kept to a minimum, since it has been observed that degradation reactions can continue after exposure to sunlight is completed. Keeping specimens in dark, frozen conditions can help overcome this problem.

2. In this experiment the dyeing procedures were simplified by omitting the auxillary chemicals that are normally present in commercial dyeing operations to enhance dye performance. It would be of interest to know how the same single dyestuffs behave if dyed with the addition of these industrial chemicals.

3. Other types of direct yellow and brown dyes could be studied to find out how they behave.

4. The chemical and physical nature of the dye mixtures used in this research could be studied both in terms of interactions in the dye solution and on the fibre. This might lead to a clearer understanding of how they affect photodegradation.

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