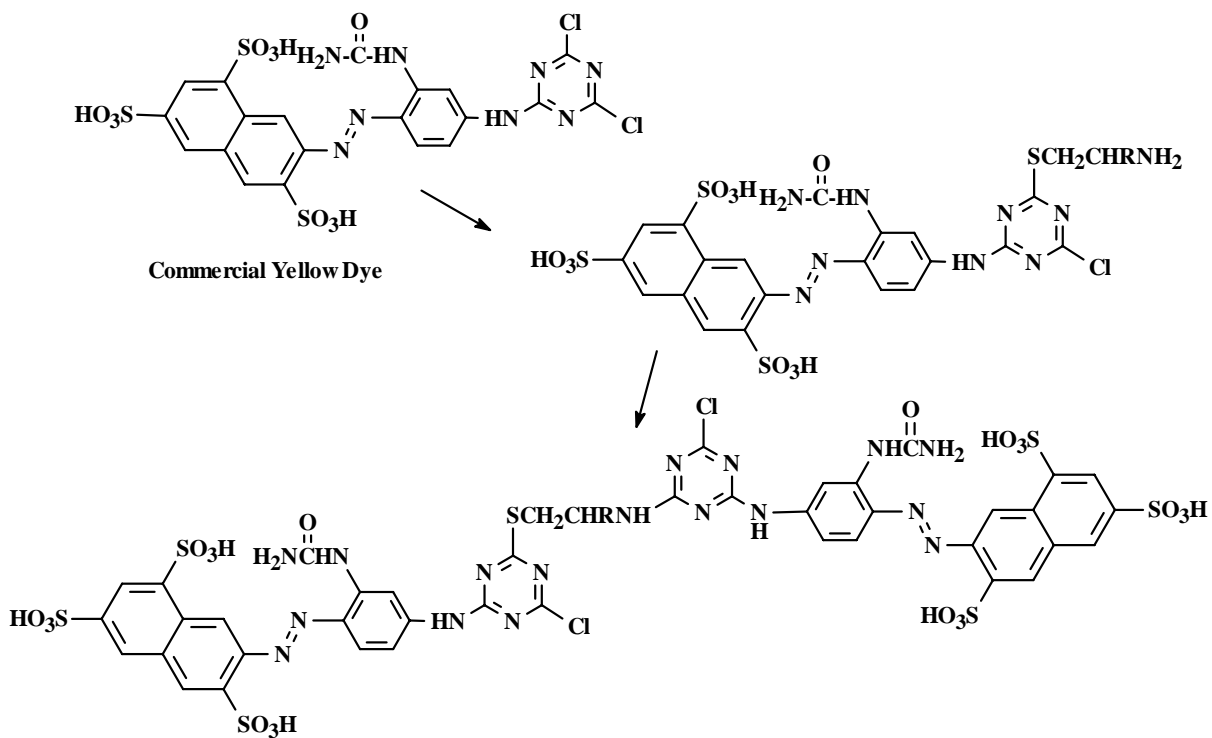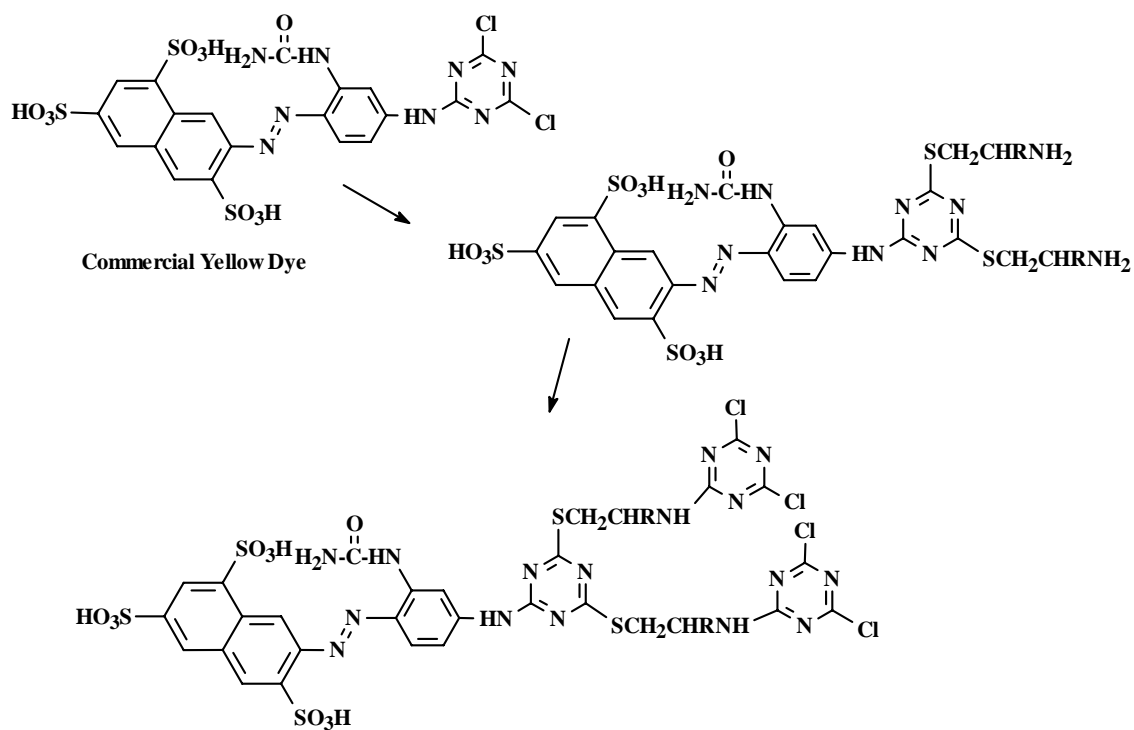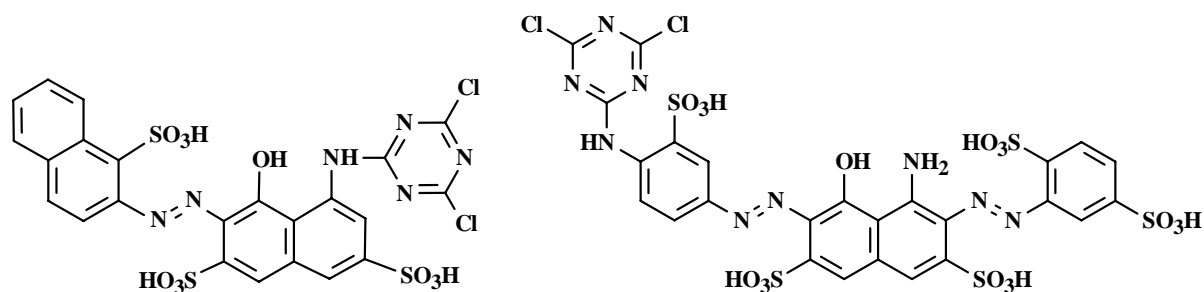# Abstract

Berger, Rebecca Riley.  Fiber Reactive Dyes with Improved Affinity and Fixation Efficiency. (Under the direction of Dr. C. Brent Smith and Dr. Harold S. Freeman)


Although fiber reactive dyes are widely used in the dyeing of cellulosic materials, several economical and environmental problems are associated with their application.   Problems include residual color in wastewater, cost of wastewater treatment, raw material cost (salt, dye, and water), and quality of goods produced are examples of areas where improvements are needed.  The afforementioned costs could be reduced by increasing the fixation efficiency and exhaustion of reactive dyes.  In turn, fixation efficiency and exhaustion could be increased by increasing dye-fiber affinity.

This thesis pertains to an evaluation of four types of dye structures arising from novel but straightforward modifications of commercially available fiber reactive dyes to produce colorants designated by Proctor and Gamble as Teegafix Reactive dyes.  Teegafix dyes are produced in 2 steps from dichlorotriazine (DCT) type reactive dyes, using either cysteamine or cysteine and then reacting the intermediate structures with either cyanuric chloride (cf. Type 1 and 2 yellow dyes) or a second molecule of the starting dye (cf. Types 3 and 4 yellow dyes).  In the same way, red and blue DCT dyes were converted to the corresponding Teegafix structures.  The resultant homobifunctional dyes vary in molecular size and reactivity and are designed to enhance dye-fiber fixation efficiency and affinity.

Synthesis of types 1 (R = CO$_2$H) and 2 (R = H) Teegafix yellow dyes.



Synthesis of types 3 (R = CO$_2$H) and 4 (R = H) Teegafix yellow dyes.

Commercial red (left) and blue (right) dyes used in this study.

In this study, the affinity of the new structures has been assessed using equilibrium exhaustion and dyeing experiments.  Equilibrium exhaustion experiments were conducted on the four dye types at two temperatures and four salt concentrations.  Types 2 and 4 dyes had a greater affinity on cotton than the corresponding commercial dyes.  These two dye types were examined further in dyeing experiments.

Laboratory dyeing experiments were conducted on the commercial dyes and the type 2 and 4 dyes.  These experiments included an assessment of the effects of temperature, salt, dye concentration, and alkali.  Increased affinity was observed as increased fixation levels for the Teegafix dye structures.  Physical testing was also conducted on the dyed fabric samples, including crockfastness, wetfastness, and lightfastness.  There were no significant decreases in the performance properties of the Teegafix dyes when compared to the commercially available dyes.

# Fiber Reactive Dyes with Improved Affinity and Fixation Efficiency

## by

## Rebecca R. Berger

A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Masters of Science

## Textile Chemistry

## Raleigh

## 2005

Approved By:

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| _____ | _____ |
| **Dr. C. Brent Smith** | **Dr. Harold S. Freeman** |
| **Co-chair of Advisory Committee** | **Co-chair of Advisory Committee** |
| | |
| _____ | _____ |
| **Dr. Gary Smith** | **Dr. Henry Boyter Jr.** |

# Dedication

I would like to dedicate this work to my husband, Michael Berger, with his support and love it is possible for me to achieve anything. I would also like to dedicate this thesis to my parents, Ted and Suzanne Riley, who taught me that all dreams could be reached with hard work and determination.

# Biography

Rebecca Riley Berger was born on August 14, 1978 to Ted and Suzanne Riley of West End, North Carolina.  She has one brother, Clay.  She graduated in 1996 from Pinecrest High School in Southern Pines, North Carolina.  Rebecca graduated Magna Cum Laude with a Bachelor of Science degree in Biochemistry in May 2000 from North Carolina State University.  She then worked for several years before returning to North Carolina State to pursue a Master of Science degree in Textile Chemistry as an Institute of Textile Technology Fellow.  On June 9, 2001, she married Michael D. Berger of Pinehurst, North Carolina.  After completing her master's degree, Rebecca will start working for Guilford Mills in Kenansville, North Carolina.

# Acknowledgments

I would like to thank Dr. Smith and Dr. Freeman for their guidance and support throughout this work. A special thank you to Aaron Horton for his hard work and time with the collection of data and other laboratory tasks. Also thanks to Dr. Malgorzata Szymczyk for the synthesis of the dyes that were used in the experiments and to Dr. Ahmed El-Shafei for his work on structures and modeling.

I would like to thank the Institute of Textile Technology for their financial support and expertise. Thanks to Dr. Henry Boyter, Jr., Mr. Chris Moses, Dr. Lei Qian, Mr. Shiqi Li, and Mrs. Patrice Hill for their time, support and knowledge. I greatly appreciate the honor of being an ITT Fellow it was a wonderful opportunity and experience. Also I would like to thank Mrs. Jaime Pisczek and Mr. Kevin Hyde for listening, helping and time during this work.

Special thank you goes to my parents who have always supported and believed in me. Also thanks to Clay for teaching me how to color in the lines and ride my bike, and for being the best big brother. Lastly and most important, I would like to thank my husband, Mike, for pushing me to try something new and for supporting me in all ways during this experience. Without his support this would not have been possible.

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# 1. Introduction

Numerous reactive dyes are commercially available for coloration of cellulosic substrates. Although reactive dyes are one of the most common dyes utilized in the dyeing of cotton and other fibers, they still cause significant environmental concerns for the textile industry in the USA and Europe. Wastewater treatment of pollutants (color and salt) from dyeing is difficult to conduct economically. One method to reduce residual color in wastewater is to increase exhaustion (E) and fixation (F) values of reactive dyes. Increasing the exhaustion and fixation not only decreases the level of color in the effluent, but the application will require lower levels of electrolytes, with an associated reduction of aquatic toxicity of effluent.

This purpose of this research was to evaluate the performance of four homobifunctional reactive dyes that were synthesized by a straightforward modification of commercially available fiber reactive dyes. Based on the performance of the dye structures in initial exhaustion equilibrium experimentation an optimal dye application process was developed for the most promising dye structure by conducting a series of laboratory dyeings.

# 2. Literature Review

## *2.1    Cellulosic Fibers*

Cellulose is the most abundant naturally occurring polymer.  Land plants produce cellulose as one of the main structural units, the cell wall.  Cellulose has proven useful as a raw material for many industrial products.  The textile industry uses many types of cellulosic materials: cotton, flax, hemp, jute, and regenerated cellulosic fibers such as Rayon, Tencel and Lyocell (Preston, 1986).

The *Gossypium* plants produce seed hair, which is commonly known as cotton.  Throughout the world there are many species of cotton produced for their own unique properties.  Species variations can include staple length, strength, elongation at break, uniformity ratio, fineness (micronaire), color and trash content. For the calendar year 2000, it was determined that ~42% of all textile raw materials were derived from cotton (Taylor, 2000). The vast majority of these products were dyed.

## 2.1.2  Cellulose Chemical Structure

The molecular structure of cellulose has always been of great interest to scientists. During the past there have been several proposed structures for cellulose (Ed at al, 1954).  The linear polymer, $\beta(1\rightarrow4)$ linked D-glucosyl residues, is the widely accepted molecular structure for cellulose (Figure 2.1).

$CH_2OH$ with label 6
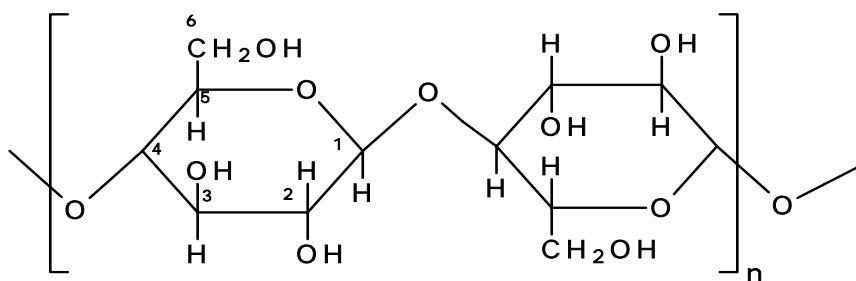
Figure 2.1    Structure of Cellulose (200-10,000 dp).

Cellulose forms a ribbon-like structure, which is capable of bending and twisting due to the oxygen bridges that connect the glucose rings.  Six hydroxyl groups protrude from each cellobiose repeat unit in the chain.  These aid in the stability of the molecule by forming intermolecular and intramolecular hydrogen bonding (Salmon, S. 1995 and Sangwatanaroi, U, 1995).  The hydrogen bonds in the chains help connect the neighboring chains together in the structure.  Intermolecular hydrogen bonds formed between the O-6-H and the O-3 are to stabilize the structure of Cellulose I (Klemm et al, 1998).  The degree of polymerization (DP) for cellulose depends on the source.  The DP can be as low as 200 for regenerated celluloses and as high as 10,000 for natural cellulose fibers such as cotton (Morton et al, 1993).

Naturally occurring cellulosic materials have been evaluated with respect to their fine structure and morphology.  The degree of crystallinity of the cellulose substrate depends on the origin and the pretreatment of the sample (Klemm et al, 1998).  It has been determined that the degree of order for cotton fibers is 2:1 crystalline regions to amorphous regions (Morton et al, 1993).  In the cellulose structure the highly oriented molecules spiral around one another in the fiber.  The

spiral angle for cellulose depends on the source. Cotton has a spiral angle of 20°-30°. Flax, jute and hemp have a smaller spiral angle of 6°, which provide these fibers with higher strength (Morton et al, 1993).

### 2.1.2 Cellulose in the Presence of Alkali

When cellulose (CellOH) is treated with alkali ($OH^-$), a cellulosate anion ($CellO^-$) is formed. The ionization equation for this reaction is:

$$CellOH + OH^- \longleftrightarrow CellO^- + H_2O$$
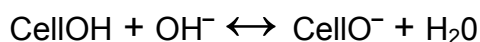
This anion is capable of reacting with suitable dyes by nucleophilic substitution or additions to form covalent bonds (Rattee, 1969). Vickerstaff provided the evidence for reactive dyes forming covalent bond with the cellulosate anion (Vickerstaff, 1957).

Esterification of cellulose is possible with most inorganic and organic acids by methods similarly used with simple alcohols. Through the esterification reaction of the cellulose molecules acetates can be formed. Acetates are important textile fibers and are used in the formation of industrial products (sheeting and moulded plastics). Acetylation is usually achieved through the addition of acetic anhydride and an added acid catalyst (Preston, 1986). The reaction can be written as:

$$CellOH + (CH_3CO)_2O + Acetic\ Acid \longrightarrow CellOCOCH_3 + CH_3COOH$$

### *2.2    Reactive Dyes*

Reactive dyes typically form covalent ether linkages between the dye and the substrate when subjected to the proper conditions. These covalent bonds produce

dyeings with very high wet fastness properties. Reactive dyes are most often used on cellulose, but can be used on fibers such as nylon and wool (Rattee, 1962). Reactive dyes are popular in textile manufacturing due to their fastness properties. These dyes have gained popularity over time and in the year 2000 represented 20-30% of the total dye market, with usage estimated to reach 50% at the end of 2004 (Vandevivere, P, 2000). Since the development of reactive dyes, there have been several useful review papers pertaining to their development, application and usage (Alsberg, 1982, Rattee, 1969, Ratte, 1984).

## 2.2.1 History of Reactive Dyes

During the 20th century, wool and cotton were two obvious choices as a substrates for the development of reactive dyes, due to the presence of nucleophilic groups. Wool contains many sites that could possibly react with a dye molecule such as, amino, carboxyl, mercapto, and hydroxyl groups. The primary and secondary hydroxyl groups are the reactive sites for cellulosic fibers. Although there was some interest in wool the main interest lied with the cellulose fibers. Starting as early as 1890, there were years of research conducted in search of a fiber reactive dye (Beech, 1970).

When the first research was conducted on fiber reactive dyes it was believed that the cellulose materials needed to be treated harshly and under nearly anhydrous conditions to react with acylating agents. It was assumed that the fibers would have to go through a great degree of substitution to obtain the coloration that was desired on the fabric. However, treatments of this nature caused shrinkage and

degradation of the fiber (Ratte, 1984). Work completed in 1895 involved treating

cellulose fibers with strong caustic soda solution and was characterized by the

reaction sequence shown in Figure 2.2. Following formation of the cellulosate

anions benzoylation, nitration, reduction, diazotisation, coupling reactions were

conducted (Preston, 1986).
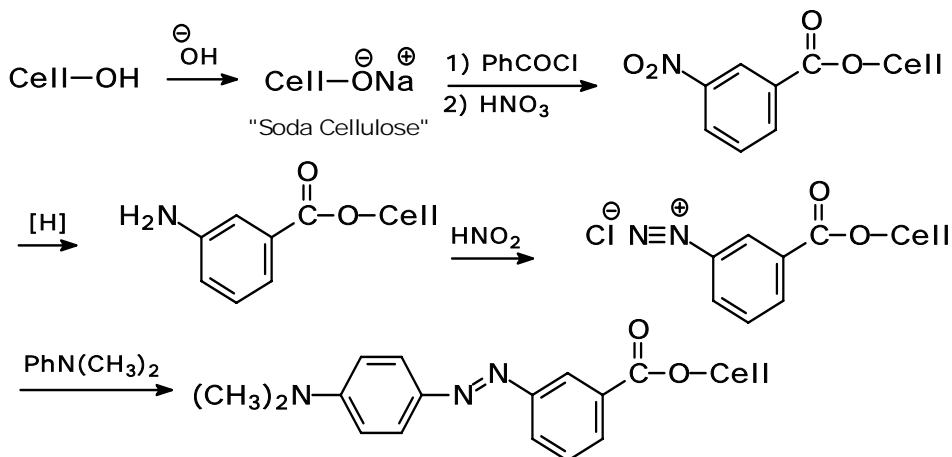


Figure 2.2    Formation of "red cellulose".

These reaction conditions were much too harsh for the cellulose fibers and caused

severe degradation.

ICI patented the first fiber reactive dyes, under the brand name "Procion®" in

1953. These dyes contained dichlorotriazine reactive groups, which were capable of

reacting with CellOH at low temperatures (20-40°C) (Beech, 1970). In 1956,

reactive dyes were made commercially available. In 1957, it was reported by that a

covalent bond was formed between reactive dye molecule and the substrate

(Vickerstaff, 1957). There have been many advances in reactive dyes since the first

commercialization of the Procion® dyes. When the Procion® dyes were patented

and marketed , it was discovered that Ciba was already producing a monochloro-

6

triazine "reactive dye" without knowing that the dye was forming a covalent bond with cellulose.  Ciba began marketing the MCT dyes as Cibacron® dyes in 1957 (Preston, 1986).

In the early 1950's Hoechst developed reactive dyes for wool called Ramalan®.  In 1957, Hoechst brought their vinyl sulphone reactive dyes for cellulose to the market.  These dyes formed covalent bonds with cellulose in a different manner than the mono and dichlorotriazine reactive dyes.  Like the triazines, Remazol® dyes react with cellulose and form a cellulose ether (von der Eltz, 1971).

The molecular structure of reactive dyes (Figure 2.3) consists of a chromogen (C) with solubilizing groups (S), a bridging group (B), a reactive group (R) and a leaving group (X).  The reactive groups are capable of reacting with nucleophilic groups ($NH_2$, -SH, and –OH) in textile fibers by addition or substitution reactions. The chromogen, a conjugated system containing one or more chromophores, provides the color. The bridge separates the reactive group from the chromogen. The bridge prevents the color generated by the chromogen from changing once the chromogen is attached to the reactive group (Rivlin, 1992).
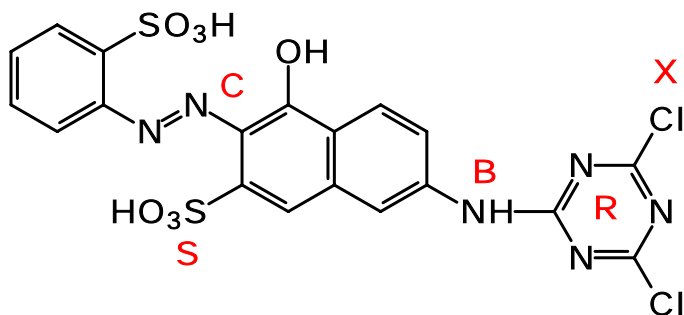


Figure 2.3     Generic structure of a fiber reactive dye.

## 2.2.2 Reactive Groups

There are many different classifications of reactive groups utilized in the different types of reactive dyes. Monoreactive dyes can be based on, but not limited to, triazine, vinylsulfone, quinoxaline, and pyrimidine (Zollinger, 1991).

Cyanuric chloride is a very important synthetic compound because of the three chloride atoms on the triazine ring allow for convenient addition of various moieties (including cellulose) to the ring. By selecting the reaction conditions carefully and accurately there is a wide array of dyes can be developed and applied. The reaction of cyanuric chloride with a chromophore containing an amino group produces a dichlorotriazinyl dye. Dichlorotriazinyl (DCT) dyes are highly reactive and are very sensitive to hydrolysis as shown in Figure 2.4 (Hunger et al, 2003).
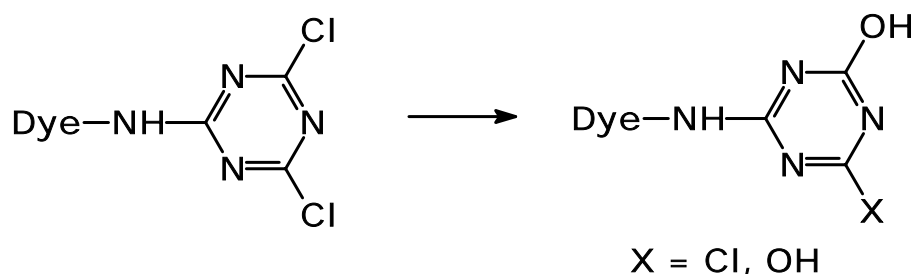


Figure 2.4    Hyrdolysis products of dichlorotriazine dyes.

If two chlorine atoms on the cyanuric chloride molecule undergo reaction, a monochlorotriazinyl (MCT) dye can be formed. The resultant dyes are less reactive than the DCT dyes and require higher temperatures and more alkali for reaction with cellulose. Reactivity of the monochlorotriazinyl dye structures can be increased by

replacing the chlorine atom with a fluorine atom or through reaction with tertiary

amines (Figure 2.5)(Preston, 1986).
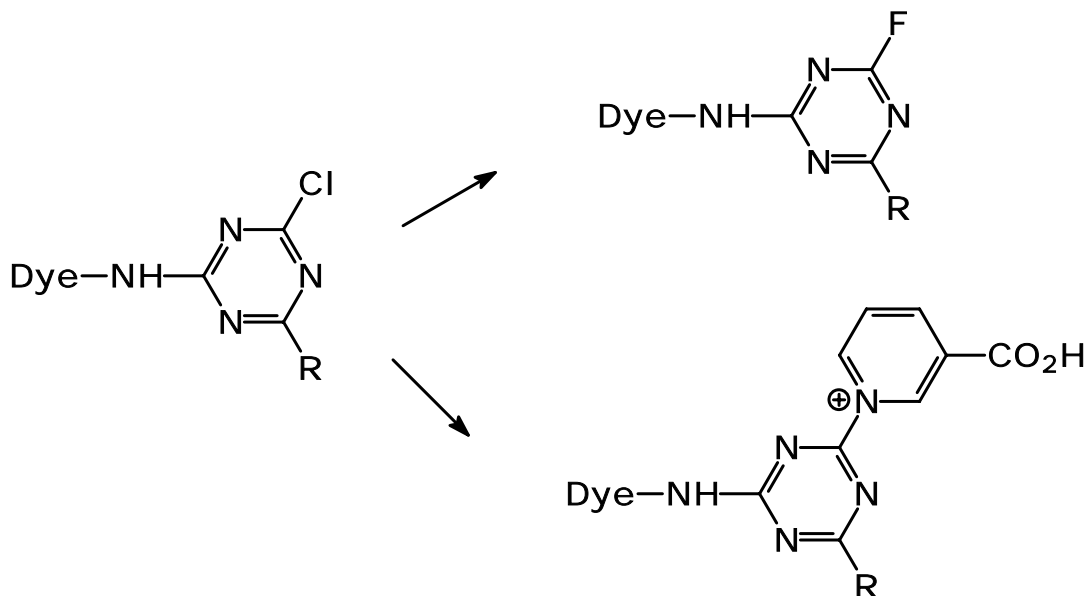


Figure 2.5    Conversion of monochlorotriazines to the with fluoro and ammonium
counterparts.

The Hoechst Remazol reactive dyes which have the 2-sulfoxyethyl-sulfonyl

reactive group is another effective reactive group, which in the presence of alkali

forms a vinylsulfone group that will react with cellulose to form an ether linkage

(Figure 2.6) (von der Eltz, 1971).
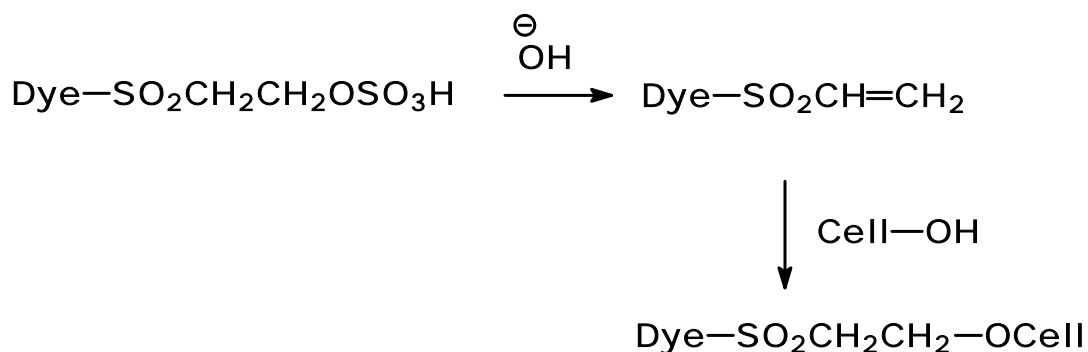


Figure 2.6    Reaction of Remazol dyes with cellulose.

Halopyrimidine and dichloro-quinoxalines (Figure 2.7 and 2.8) are other types of dyes that include reactive groups.  These react with cellulose in a manner comparable to MCT and DCT dyes.
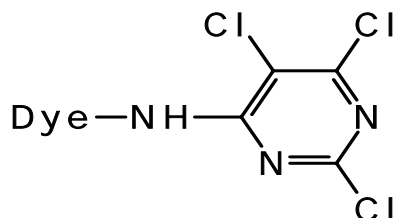


Figure 2.7    The halopyrimidine reactive dye system.
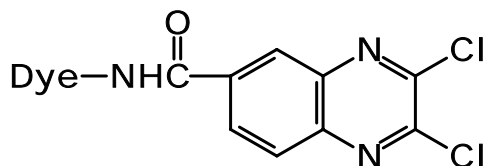


Figure 2.8    The dichloroquinoxaline reactive dye system.

Double-anchor (bireactive) dyes are used as a mechanism for increasing the fixation values for reactive dyes.  These dyes can contain two of the same reactive groups (homoreactive systems) or two different reactive groups (heteroreactive systems) on the reactive dye structure.  One of the most common bireactive structures contains the combination of the monochlorotriazine and vinyl sulphone reactive systems (Freeman, 1999).  The reactive groups are connected through a bridge, which allows structures with either the same or different chromogens to be attached.  C.I. Reactive Red 120 is an example of a double-anchor homobireactive dye (Figure 2.9).  With this system it is possible to obtain shades that were not

previously thought possible, in addition to increasing the fixation efficiencies

(Renfrew et al, 1990).
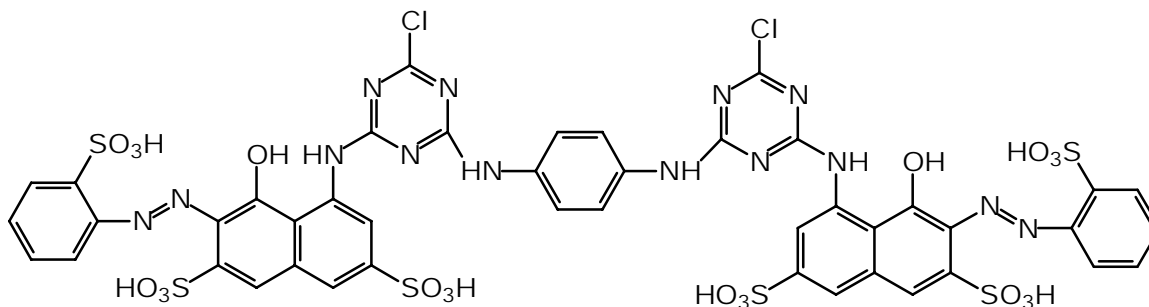


Figure 2.9    C.I. Reactive Red 120.

The reactive dyes that contain two different reactive groups are known as

hetero-bireactive dyes.  In the 1980s the hetero-bireactive dyes became more

widespread on the reactive dye market (Renfrew et al, 1990).  The most common

combination is the monochlorotriazinyl group with the more reactive 2- sulfato

ethylsulfone group (Figure 2.10) (Hunger et al, 2003).  With this system it is possible

to obtain a wide variety of shades.
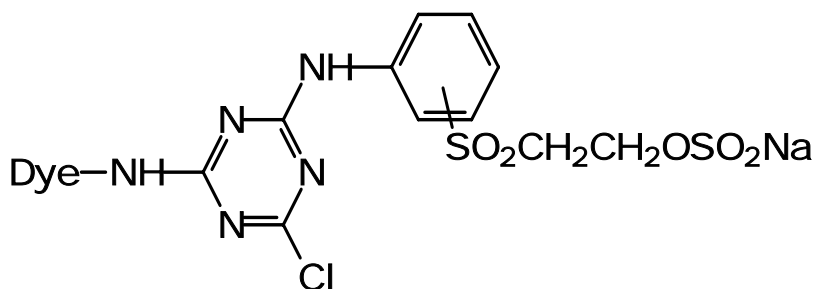


Figure 2.10   Bireactive system with monochlorotriazinyl
and 2-sulfato ethylsulfone reactive groups.

The hetero-reactive dyes offer several advantages over traditional reactive dyes. They are less sensitive to temperature and provide better reproducibility of shade. The combination of these reactive groups also provides good fastness over a wide pH range.

There are also polyreactive dyes, which afford enhanced fixation and are less sensitive to alkali concentrations and salts (Renfrew, 1990). These dyes most commonly are synthesized from cyanuric chloride and are reacted with an amine with two aliphatic 2-chloroethylsulfonyl chains (Hunger , 2003).

## 2.2.3 Dye Classes (Chromogens)

The synthesis of fiber reactive dyes utilizes many different types of chromogens in the development of the dyes. Producers of reactive dyes often use comparable chromogens, but their dyes vary in respect to the reactive groups used and the substitution pattern. Reactive dyes are generated from monoazo or disazo, anthraquinone, triphenodioxazine, and phthalocyanine systems. The structure of the chromogens used in the synthesis of reactive dyes has a direct influence on fiber affinity or substantivity and the diffusion coefficient (Beech, 1970).

Almost 80% of reactive dyes are based on azo chromogens. Almost all hues in the color spectra can be produced with either the monoazo or disazo groups and various combinations of aromatic rings (Zollinger, 1991). C.I. Reactive Yellow 3 is an example of a reactive dye with a monoazo chromogen (Figure 2.11). Metal-complex azo structures produce dyes with increased light fastness in a wide array of

shades (Hunger et al, 2003). C.I. Reactive Blue 40 is an example of a metal-complex disazo reactive dye structure (Figure 2.12).
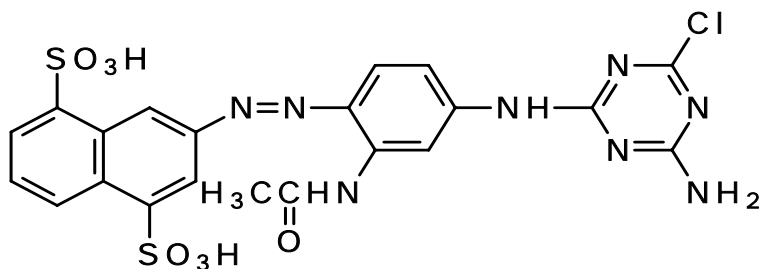
Figure 2.11   C.I. Reactive Yellow 3.
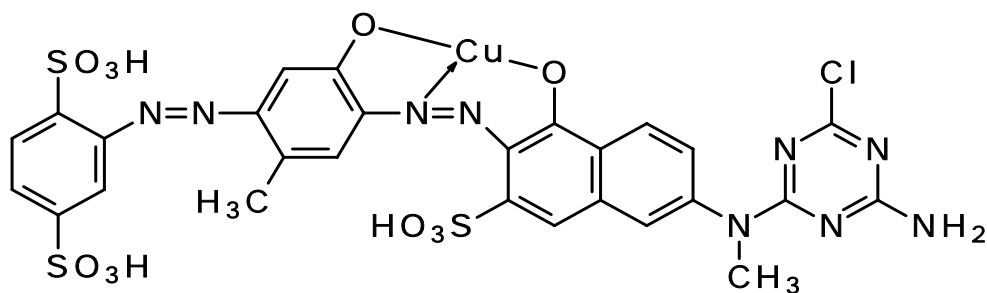
Figure 2.12   C.I. Reactive Blue 40.

Anthraquinone dyes provide good light fastness, brilliance, and stability over a wide pH range.  These dyes are sometimes more costly than other dyes, but they provide important blue and violet shades.  C.I. Reactive Blue 5 is one example of an anthraquinone reactive dye (Figure 2.13).
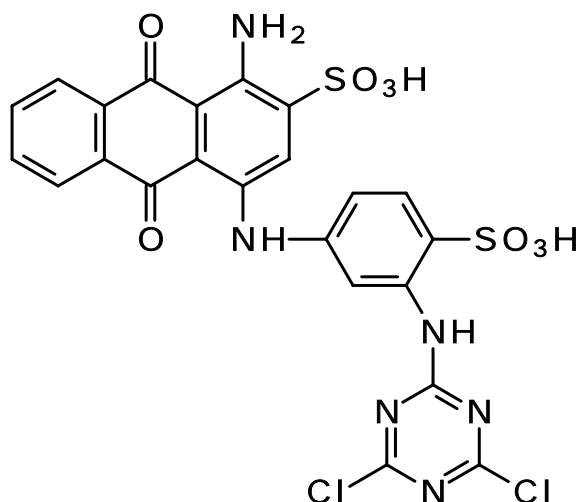
Figure 2.13   C.I. Reactive Blue 5.

Triphenodioxazine dyes have been commercially available since 1928.  By replacing the substituents on the triphenodioxazine structure, different shades of red, orange, and blue can be generated. An example of a triphenodioxazine dye is C.I. Reactive Blue 204 (Figure 2.14).  This dye class has several challenges when using them in the manufacturing setting such as tailing or the removal of unfixed dye (Hunger , 2003).
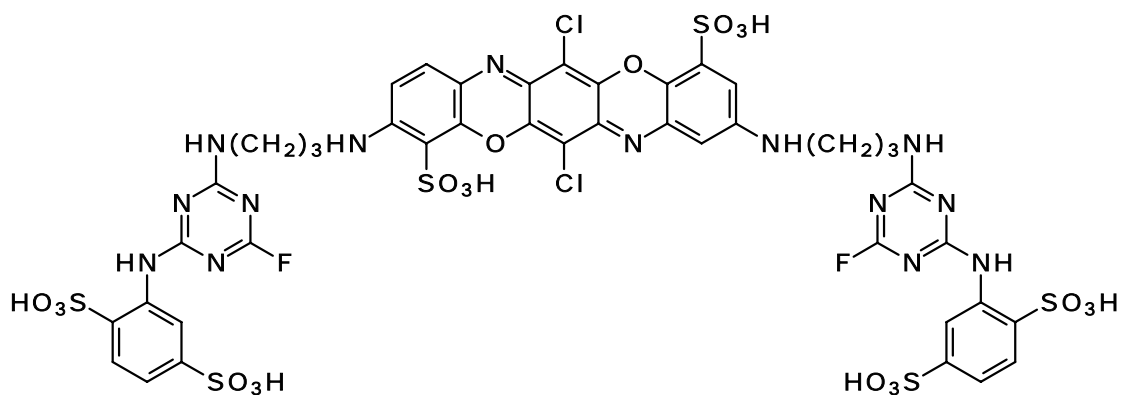


Figure 2.14   CI Reactive Blue 204.

Formazan dyes, which are copper complexes, constitute another type of chromogen utilized in reactive dyes. These dyes provide an alternative to the anthraquinone blues, and have good solubility and reactivity (Figure 2.15).
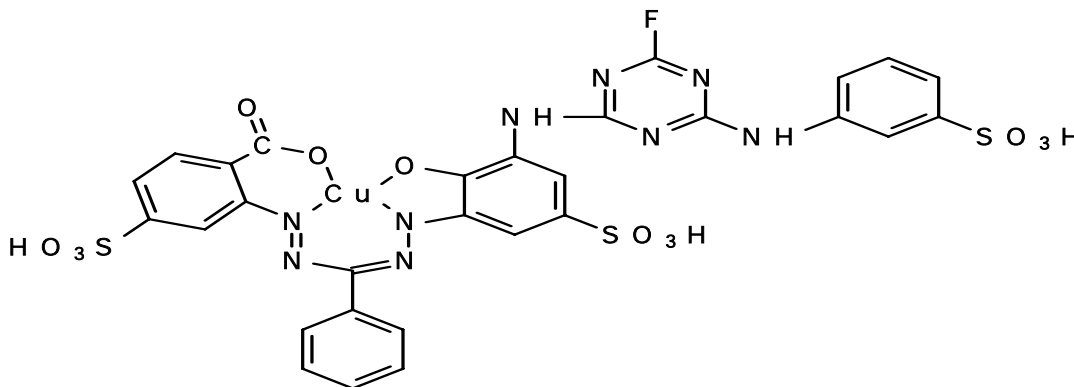


Figure 2.15   Formazan dye structure.

Another reactive dye system is the phthalocyanine group. These dyes are water-soluble and are capable of producing turquoise and other shades of green. No other chromogen effectively produces the shades obtained from this chromogen. The phthalocyanine structure usually contains copper or nickel as the central metal ion (Hunger, 2003). An example of a phthalocyanine reactive dye structure is C.I. Reactive Blue 7 (Figure 2.16).
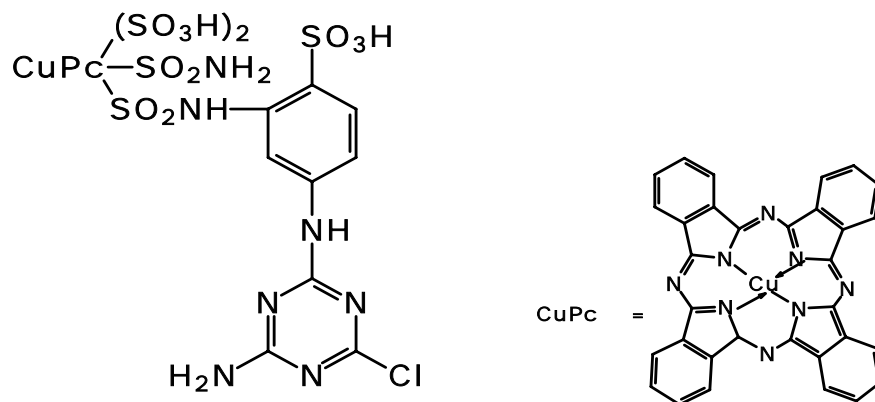
Figure 2.16    C.I. Reactive Blue 7.

## 2.2.4 Kinetics

Reactive dyes can react with either the –OH groups found in the cellulosic fibers or the –OH groups in the dyebath.  For satisfactory dye application, the main objective is to obtain maximum fixation to the fiber and minimal hydrolysis by water.

Kinetic information involving homogenous (water and alcohol) and heterogenous (water and cotton) systems is discussed in several publications (Preston, 1986, Beech 1970, ICI Limited, 1962, Sumner et al, 1963, Sumner, 1965, Peters, A. 1996 and Rattee,1969, Ingemells, 1962), and is synthesized below.


**Homogenous System (Water and Alcohol)**

Homogenous solutions provide a simple way of looking at the competing reactions in reactive dye application.  In this system the reactive dye is present in an alkaline solution of aqueous alcohol.  The two competing reactions in this system are:

1.  Alcoholysis of the Dye      D-X + AO-  →  DOA + X-

2.  Hydrolysis of the Dye      D-X + OH-  →  DOH + X-

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When the reactions occur simultaneously in a homogenous system, the concentration of products formed at any given time, including at completion, is the ratio of the two reaction rates. The efficiency ratio of the alcoholysis reaction is the rate of alcoholysis over the rate of hydrolysis at time, t.

$$\frac{k_{OA} * [DOA]}{k_{OH} * [DOH]} = \frac{dA/dt}{dH/dt} = \text{Efficiency Ratio}$$

Since both reactions are bimolecular, the efficiency ratio can be written as

$$\text{Efficiency Ratio} = R_A \frac{[AO^-]}{[OH\text{-}]}$$

where $R_A = k_A/k_H$, the bimolecular reaction constants for alcoholysis and hydrolysis. In this system, the rate of disappearance of reactive or active dye ([DCl]) molecules over time is the sum of the rates of the two competing reactions. The simplified equation for the disappearance of active dye is:

$$\frac{d[D]}{dt} = k'_H[D]_t$$

where $k'_H = k_H(RA[AO\text{-}]_t + [OH\text{-}]_t)$. The parameters located within the equation are determined to be constant at any pH.


**Heterogeneous System (Water and Cellulose)**

When examining the two-phase system of water and cellulose, the reactions proceed at different rates within the phases. This leads to a much more complex analysis which, in fact, cannot be solved directly, but must be estimated by approximation or by empirical measurements. Within the aqueous phase the rate of hydrolysis occurs as if it were in the homogenous system. The equation used to

consider the concentration of dye in the solution after a certain period of time.  The equation is as follows:

$$dh/dt = k_H[OH^-][D]_s$$

The rate of reaction in the substrate (cellulose) is a more complicated situation, which has to take into consideration the diffusion of the dye within the fiber.  For the reaction to proceed, the active dye must be in the same phase as the substrate.  Previous studies pertaining to the rate of diffusion of solution into a solid medium considered that the reaction would occur according to simultaneous first-order kinetics and diffusion (Danckwert, 1949).  The rate of fixation for a dyeing of an infinitely thick slab of material in a bath with an infinite volume can determined from as this simplified equation:

$$dQ/dt = [D]_f \, \sqrt{(Dk'_f)}$$

where D is the diffusion coefficient, $[D]_f$ is the concentration of dye at the surface of the substrate and $k'_f$ is the pseudo first-order rate constant for the reaction for fixation of the dye in the substrate.  The efficiency of fixation for the heterogeneous solution can be given by the ratio of the rate of fixation of the substrate and the rate of hydrolysis in the aqueous phase.

$$\text{Efficiency of Fixation} = \frac{df}{dh} = \frac{[D]_f \, \sqrt{(Dk'_f)}}{[D]_s k_H [OH^-]_s}$$

When considering the efficiency of fixation, it is to be assumed that there is no hydrolysis of dye occurring in the fiber and that only the reaction with cellulose is occurring.  Without this assumption the equation will be much more complex.  With these assumptions in mind the above equation can be simplified to the following:

$$\text{Efficiency of Fixation} = \frac{df}{dh} = \frac{[D]_f}{[D]_s} \frac{S \sqrt{D} R_F [Cell-]}{L \sqrt{k'_H} [OH-]}$$

When evaluating these expressions it is easy to determine that the fixation efficiency is dependant on the substantivity ratio ($[D]_f / [D]_s$) and the diffusion coefficient of the dye and the cellulose (D). The reactivity ratio plays an integral role as well as the pH of the reaction (Beech, 1970). The variable S represents the structure of the fiber and L is the liquor ratio.

## 2.2.5  Application of Reactive Dyes

Batch and continuous methods of applying reactive dyes to cellulose have been established, according to the analysis provided in the sections above. When applying reactive dyes, it has been noted that individual dyes may behave differently from other dyes in the same class due to differences in reactivity, affinity, and diffusion coefficient (Rattee, 1969).

Batch dyeing is a common method for applying reactive dyes to cellulose fibers. Batch machines used for reactive dyes application include beck, jet, jig, skein, package dyeing and paddle machines. There are three stages that make up the traditional fiber reactive dyeing process (Rivlin, 1992). The stages are:

1.     Exhaustion of dye into the fiber under neutral conditions and in the presence of salt.

2.     Addition of alkali to the bath for chemical reaction of dye with fiber.

3.     Salt, alkali and unfixed dye are removed through washing.

## 2.2.5.1  Substantivity

The affinity of a dye for a substrate can be defined as the combined strength of molecular interactions. Some of the molecular interactions involved in the dyeing process include van der Waals forces, hydrogen bonding, hydrophobic interactions, and electrostatic attraction.  The substantivity of the dye is "less specific", but leads to the estimation of exhaustion.  The term substantivity is the attraction between the dye and the substrate under specific and precise conditions.  Substantivity involves the preferential exhaustion of the dye from the bath into the substrate (Welham, 2000).  Mathematically the substantivity is defined as $[D]_F/[D]_S$ in the kinetic literature (Preston, 1986).

It should be noted that the substantivity value is not independent of the diffusion coefficient of the dye in the substrate.  The magnitude of the substantivity value is mostly determined by the chemical nature of the chromophore and the fiber. The direct measurements for substantivity values under fixation conditions can be difficult to determine, but theoretical values have been reached through previous research on methods and applications (Sumner and Taylor, 1967).  The theoretical values are useful in practical situations and are reasonably accurate in the prediction of trends (Sumner et al, 1967 and Liddell et al, 1974). The factors that influence the substantivity value are the bath ratio, salt concentration, temperature and pH of the system (Sumner, 1963).

Fiber reactive dyes of low substantivity are sometimes desirable in the sense that low-substantivity unfixed dyes can be removed from the substrate easily, and they also do not exhaust during padding operations (which would lead to tailing in

continuous dyeing).  If the substantivity is very high, the hydrolyzed form of the fiber reactive dye will remain on the fiber and will behave as a direct dye.  Dyes of low substantivity are generally more soluble in water, which promotes better migration and leveling properties, as well as higher diffusion rates.  The increase in the rate of diffusion will allow the dye to penetrate deeper further into the fiber (Beech, 1970).

### 2.2.5.2   Electrolyte

Reactive dyes behave like low-affinity direct dyes in a neutral solution.  Consequently, increasing the amount of electrolyte added to the dyebath can increase exhaustion during dye application.  The most common electrolytes used in the batchwise processing are common salt (sodium chloride) and Glauber's salt (sodium sulfate decahydrate).  The salt requirements for the reactive dye application process are often four times the amount required for direct dyes (Beech, 1970).  The need for the large electrolyte concentration is due to the low substantivity value.  The role of electrolyte is to disrupt the structure of water and therefore to reduce hydration of dyes in the dyebath and dye sites in the fiber.

### 2.2.5.3   Bath ratio

The bath ratio, the ratio of the weight of the dyebath used to the weight of the goods, is one of the main variables that can be controlled by dyers during the application process.  When there is a reduction of the bath ratio there is an increase in the efficiency and the rate of dyeing.  If dye concentration is increased, the concentration of electrolyte must be decreased to prevent precipitation of the dye (Preston, 1986).  Even with these factors affecting the efficiency, the decrease in the

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bath ratio will have an overall effect of increasing the efficiency of the process (Sumner et al, 1963, Preston, 1986).  The use of lower bath ratios helps in the conservation of dye in the process.  Additional losses of dye through the hydrolysis of the dye can be avoided when using smaller amounts of water in the application process.

### 2.2.5.4  Alkali

Alkali is added to the dyebath to achieve the fixation of dye on the fiber. When alkali is added to the dyebath it is possible for further exhaustion to occur. The chemical bonding of the fiber and the dye can push the dynamic equilibrium of the dye molecules' movement towards higher exhaustion.

When adjusting the pH of the dyebath there is a compromise between the speed and efficiency of reaction between the dye and the fiber.  When the pH levels are between 7 and 11 there are only slight changes in the substantivity ratios.  Once the level exceeds pH 11 there is a larger decrease in the substantivity ratio.  The magnitude of the decrease in substantivity depends on the basicity of the dyes being evaluated.  If the pH is increased above 11 without altering other dyebath factors, there will be a decrease in the fixation efficiency and the rate of fixation will never be as high as expected.  If there is a desire to increase the pH to levels above 11 then there should be an adjustment in the electrolyte concentration, to avoid a decrease in the substantivity ratio (Sumner, 1963, Beech, 1970 and Preston, 1986).

## 2.2.5.5   Temperature

The temperature of the dye application process has optimal levels, which are dependant on the type of dyes used.  It has been suggested that with every 20°C increase there is 1.5-2.5 fold decrease in the substantivity ratio (Preston, 1986).  When the temperature is increased the substantivity ratio decreases and the reactivity increases.  Both of these changes can cause a decrease in the efficiency (Preston, 1986).  Dichlorotriazinyl dyes can be applied at room temperature due to their higher reactivities (Rattee, 1969).  The cold dyeing temperatures of dichlorotriazines are sensitive to variations in reaction temperatures. Therefore, temperature control of dyeing is crucial.  (Smith, 1987).  The less reactive monochlorotriazinyl dyes are applied at higher temperatures to accelerate the reaction.  The monochlorotriazines are hot dyeing and are more stable to hydrolysis and precise temperature control is not as critical.  Monochlorotriazinyl dyes have a higher affinity, which will help overcome the loss of efficiency due to increased temperatures (Vickerstaff and Sumner, 1961).

## 2.2.5.6  Typical Procedure

A typical procedure for exhaust dyeing at high temperature is: (Rivlin, 1992)

1.  Fill machine with water
2.  Load substrate (yarn or fabric)
3.  Heat to 50 °C
4.  Add pre-dissolved reactive dyes to the bath
5.  Raise the temperature 1 °C/ min until the bath reaches a temperature of 80 °C
6.  During this time add salt to the bath in parts
7.  Run for an additional 15 min
8.  Add alkali over 15 min in parts
9.  Run for an additional 45-75 min
10.  Empty dyebath
11.  Rinse substrate with warm water and then soapy warm water
12.  Rinse final time with cold water

## 2.2.5.7  Continuous Dyeing

When reactive dyes were first developed, it was believed that they offered a great advantage in application through a continuous process.  This advantage was based on the rapid rate of reaction between the fiber and dye.  Reactive dye application could be conducted without the purchase of new and expensive equipment (Rattee, 1965).  In continuous dyeing, the dwell-time is reduced to mere seconds because the substrates are heated, causing the rate of reaction to increase (Rattee, 1969).  There are certain issues that need to be considered when using the continuous dyeing method.  Tailing effects can be seen when using the padding process, due to high the dye-fiber affinity.  The color repeatability in an individual process, with

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respect to the length of substrate is dependent on several factors.  The factors are: the absorbency of the goods, temperature and time of absorption, volume of the pad, and rate of uptake liquor by the substrate (Marshall, 1966 and Procion® Dyestuffs, 1962).  In the continuous dye application, two steps and one step methods are used.

**Two-Step Process**

In the two-step process dye and alkali are added in separate steps.  The substrate is padded with the dye solution containing other necessary chemicals.  The fabric is then dried and padded with aqueous alkali solution containing a large amount of salt.  The fabric is steamed for 30- 60 seconds, and is washed several times to remove hydrolyzed dye (Rivlin, 1992).

**One-Step Process**

In the one-step method, the fabric is padded only once.  There are two methods used in this type of continuous processing.  In the first method, the fabric is padded with a solution of dye and alkali.  Solutions of dye and alkali are prepared separately and then mixed using pumps and transported to the pad.  Once the fabric is padded, it is steamed for 30-60 seconds and then washed and rinsed.  In the second method, a solution of dye, alkali, and urea is applied to the fabric. The substrate is then dried and heated in an oven at 300°F for ~1 minute (Rattee, 1965 and 1969).

## 2.3    *Environmental Considerations*

Reactive dye application introduces certain environmental concerns.  The dyeing process is extremely water-intensive and often requires large amounts of salt. A few dyes contain metals such as copper, nickel, chromium, or cobalt.  These metals can be functional or can be impurities found in the dyes.  The spent dyebaths and rinse water contain various amounts of salt, alkali, color, and auxiliary chemicals, which require treatment to minimize their levels before being released into the environment.  In the average textile dyeing facility, 1-2 million gallons of wastewater are generated daily (Taylor, 2004).  The treatment of this large amount of wastewater requires a large initial and annual capital investment.

### 2.3.1  Color

The dyes and pigments used in textile processes are the main source of color in wastewater.  These colorants are added during printing and dyeing operations in small quantities.  After the process, 50-100% of the dye or pigment is fixed to the fiber or fabric.  The remaining color is discarded as spent dyebaths or wastewater. Under typical reactive dyeing conditions 0-50% of the dye remains in the effluent. The color that remains is mainly hydrolyzed dye that is no longer capable of reacting with the fiber (Lee et al, 2004).  The treatment methods for removal of colorants from wastewater are costly and not always effective.  The color found in wastewater is an aesthetic pollutant that is readily detected through visual inspection.  Color in wastewater can be reduced by primary control methods, waste stream reuse, treatment, or maximizing dye exhaustion (Smith, 1991).  Therefore, optimizing and

controlling the process can reduce waste generation in the form of color, alkali, and salt, in dyeing.  Color can be reduced in the wastewater by using a dye with high or increased affinity and controlling the bath ratio.  Maximizing the fixation of the reactive dyes also helps minimize dye washoff and this will decrease the amount of color in the wastewater.

Fiber reactive dyes are used often and require special attention because of the lower fixation levels.  There are several important factors that are monitored to obtain maximum fixation and minimize color in the wastewater.  These include bath ratio, salt usage, and adequate time for exhaust.  Understanding its relationship with the affinity (K) and bath ratio (L) can maximize exhaustion (E).  An important relationship can be seen in the following equation:

$$E = K/(K+L)$$

When the affinity of the dye decreases, exhaustion will decrease and the amount of color in the wastewater will increase (EPA, 1996).

With increased levels of exhaustion the fixation levels increase.  The increase in fixation decreases the amount of color in the wastewater.  High fixation can be achieved through the use of high affinity dyes, low bath ratio, sufficient time for fixation, optimal temperature, optimal alkali levels, and optimal salt levels.  Fiber reactive dye fixation is effected by several factors.  The reaction rate constant, process design, affinity (K), and the shape of the fiber all have an effect on the fixation of the dye to the fiber (EPA, 1996).  Treating color in wastewater is costly for many textile firms.  The cost for installation and the upkeep of wastewater treatment facilities are large.

## 2.3.2  Salt

Salt is becoming a growing concern environmentally in the textile industry. Electrolytes or salt are common additives in the dye process and in some processes are produced as by-products.  The addition of salt to the dye process has been shown to increase the dyebath exhaustion (Peters, 1975).  The added salt increases exhaustion by decreasing dye solubility in water (Smith, 1994).

Fiber reactive dyes often require a large amount of salt to achieve the necessary exhaustion.  Salt requirements for fiber reactive dyes are much greater than amounts used with other dye classes to achieve the same exhaustion levels. The salt requirement for reactive dyes is 50% to 100% on the weight of the goods. The amount of salt discharged from a textile dyeing facility is approximately 400 million pounds per year (Smith, 1994).   For example, raw wastewater from a reactive dye process can contain as much as 9800 mg/L of chloride, while direct dye raw wastewater contain 61 mg/L of chloride (Smith, 1991).  The average concentration of salt found in the wastewater ranges from 2000 ppm to 3000 ppm. These concentrations are much higher than the levels of textile wastewater allowed to enter a publicly owned treatment facility (250 ppm and up).  It is extremely costly to reduce the high amount of salt (3000 ppm) in mixed textile wastewater to the lower or acceptable chloride concentration (250 ppm).  The treatment of the wastewater is a difficult and extremely costly process by any known method. Decreasing the amount of salt required for a process will be a more economically and environmentally effective method for reducing chloride levels in the wastewater (Smith, 1996).

## 2.4    *Project Proposal*

Teegafix reactive dyes were generated from the reaction of chlorotriazine dyes with cysteamine or cysteine to generate homobireactive dyes with one or two chromogens.  Results from preliminary investigations suggest that Teegafix dyes fixed at levels above those normally reported for reactive dyes.  With this in mind an assessment of the affinity and fixation efficiency of chlorotriazine dyes developed and patented in 2002 by Procter and Gamble as Teegafix dyes is proposed.

### 2.4.1 Types of Dyes

There are four types of  Teegafix homobireactive dyes that have been reported.  The synthesis and potential utility of these dyes are discussed in several US Patents.  The structures for the yellow versions of the new reactive dyes are shown in Figures 2.17-2.20.  These four dyes will be used in the present study, along with the corresponding Teegafix forms of commercial red, blue, and yellow dichlorotriazine dyes (Figures 2.21-2.24).
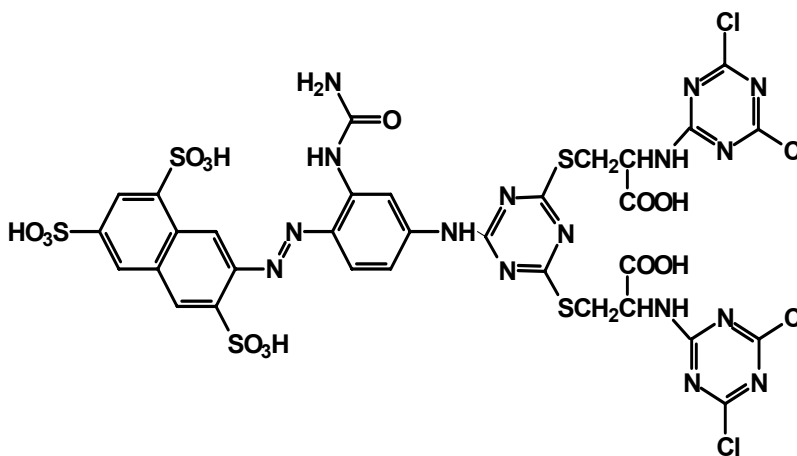


Figure 2.17   Type 1 yellow dye.
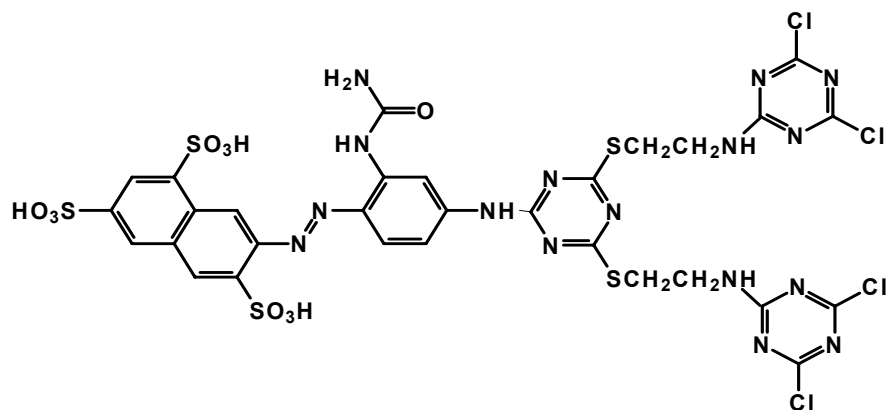
Figure 2.18   Type 2 yellow dye.
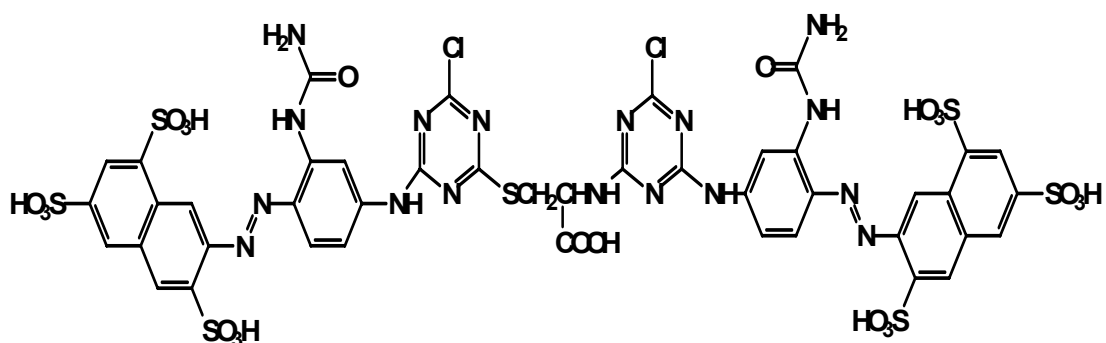


Figure 2.19   Type 3 yellow dye.
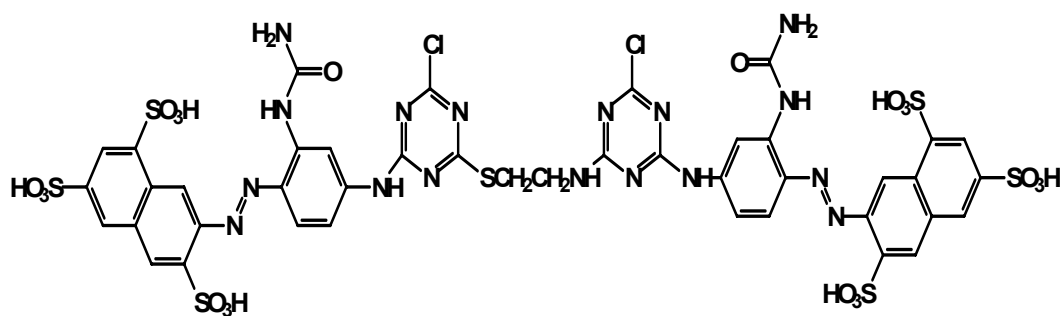


Figure 2.20   Type 4 yellow dye.

## 2.4.2 Dye Characteristics

Results from initial studies have suggested that Teegafix dyes provide higher

levels of exhaustion and fixation compared to the corresponding Procion® reactive

dyes.  During laboratory applications, the dyes required lower electrolyte

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concentrations and temperatures.  Test results also suggest that the dyed substrates possess good lightfastness, wet and dry crock resistance, wash- fastness and dye-transfer staining.

## 2.4.3 Dye Synthesis

The Teegafix dyes used in this study were synthesized according to the sequences outlined in Figures 2.21 and 2.22 for the yellow dyes employed.  Types 1 and 2 dyes were obtained by reacting one mole of the corresponding commercial dichlorotriazine reactive dyes per two moles of either cysteamine or cysteine followed by reacting the intermediate diaminotriazine with two moles of cyanuric chloride per mole of diaminotriazine.  Types 3 and 4 dyes were obtained by reacting one mole of the corresponding commercial dichlorotriazine reactive dyes per mole of either cysteamine or cysteine followed by reacting the intermediate chloroamino-triazine with one mole of the corresponding commercial dichlorotriazine reactive dye.  Following their synthesis, the dyes were desalted by dissolving them in DMF, filtration to remove salt, and evaporation of DMF at the aspirator.

The same methods were used to make the four Teegafix red and blue dyes and the purity of all dyes was confirmed using HPLC analysis on a reverse phase column.
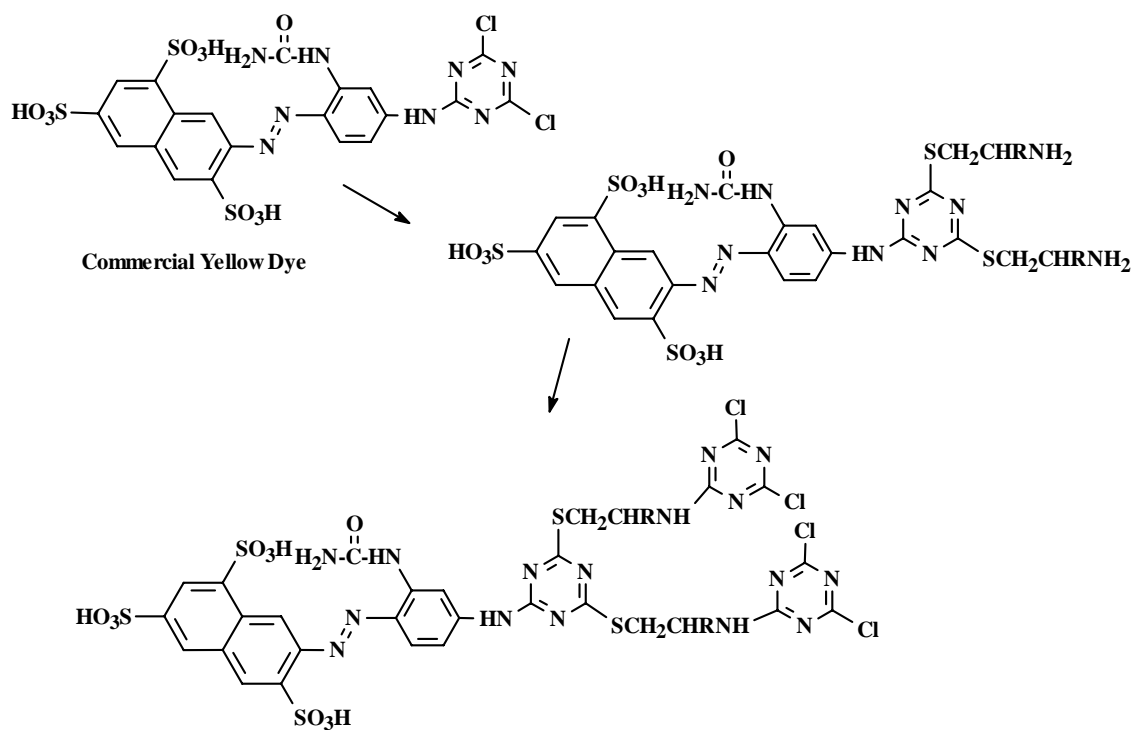
Figure 2.21    Synthesis of types 1 (R = CO₂H) and 2 (R = H) Teegafix yellow dyes.
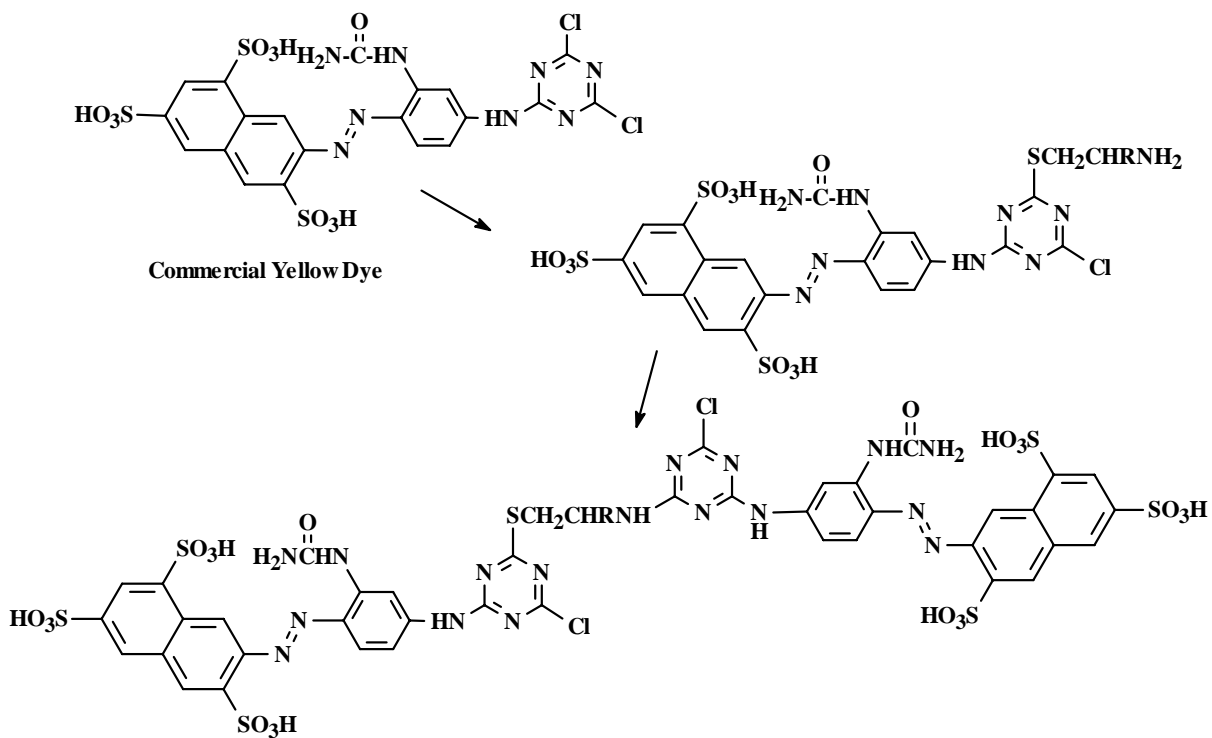


Figure 2.22    Synthesis of types 3 (R = CO₂H) and 4 (R = H) Teegafix yellow dyes.

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## 2.4.4 Chromophore Moiety

The reactive dyes synthesized contained one to six chromogens, with most having one to three such groups. The chromogen can be defined as any "photoactive compound and includes any colored or non-colored light absorbing species." Chromogens are based on: monoazo, disazo, or polyazo, anthraquinone, phthalcyanine, formazan, azomethine, triphendioxazine, stilebene, triphenyl-methane, and xanthene systems. In the present work, polysulfonated azo chromophores, which are present in Procion® dyes, were used in the synthesis of new reactive dyes (Figure 2.23-26).
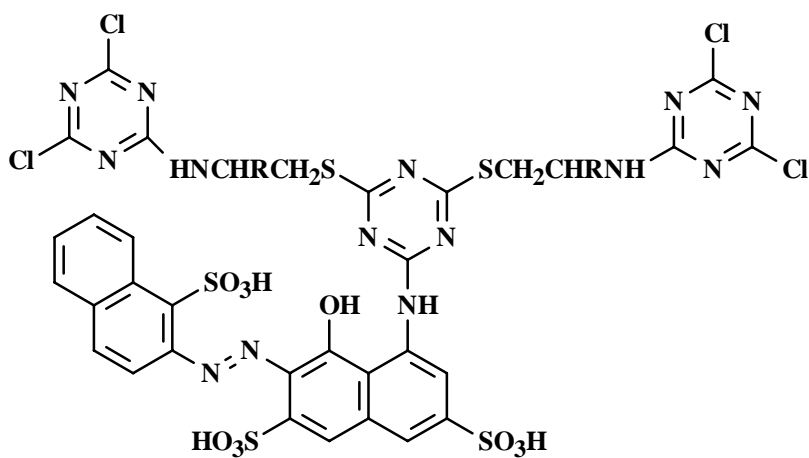


Figure 2.23  Types 1 (R = CO$_2$H) and 2 (R = H) Teegafix red dyes.
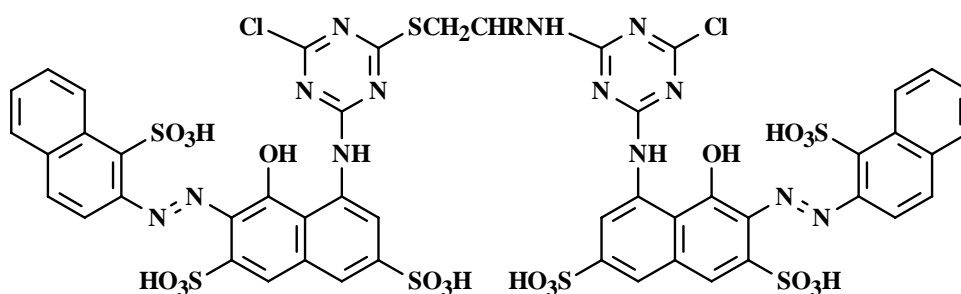


Figure 2.24  Types 3 (R = CO$_2$H) and 4 (R = H) Teegafix red dyes.
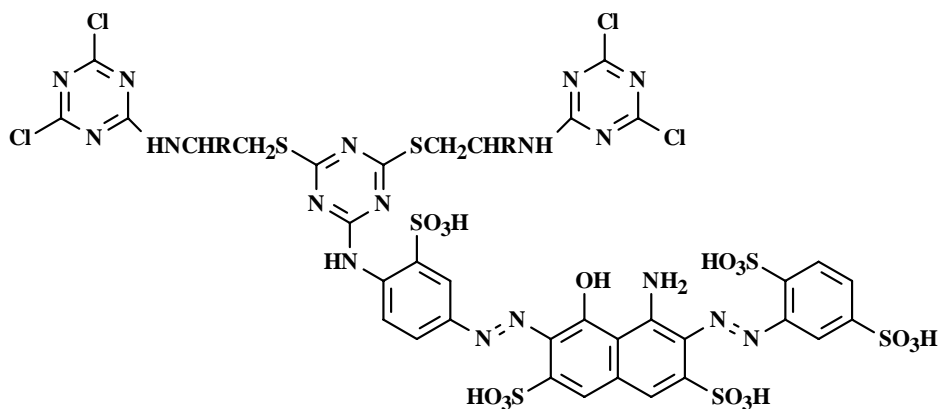
Figure 2.25   Types 1 (R = CO₂H) and 2 (R = H) Teegafix blue dyes.
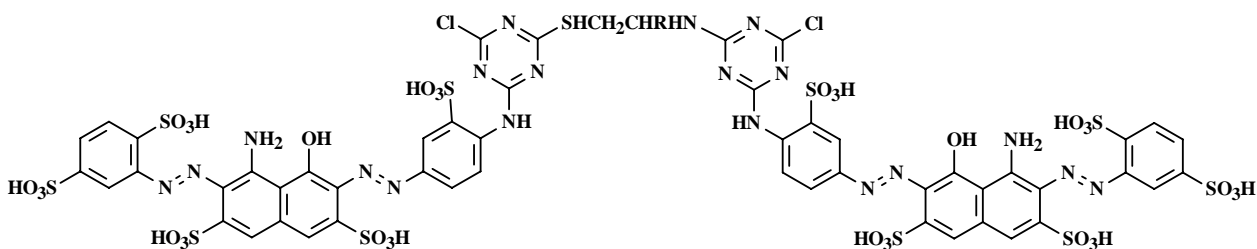


Figure 2.26   Types 3 (R = CO₂H) and 4 (R = H) Teegafix blue dyes.

## 2.4.5 Linking Groups

Linking groups are used in the synthesis of the reactive dyes to connect or link the reactive moiety to the chromogens.  There are several linking groups outlined in the patent literature, including -NR-, -C(O)NR-, NRSO₂-,  -(CH₂)ₙ-, and –SO₂-(CH₂)ₙ-  (In these notations R can be either H or a C1-C4 alkyl, which can be substituted by a number of groups and n= 1-4).  In the present study, the linking group were, -NH-CH₂-CH₂-S- and –NH-CH(CO₂H)-CH₂-S.

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## 2.4.6 Leaving Groups

Leaving groups (such as chlorine or fluorine) are the portion of the reactive dye that is substituted during the reaction of the dye with a substrate.  Leaving group(s) are replaced by a nucleophilic group that is located on the surface of the substrate.  The covalent bonds formed during this reaction are responsible for holding the dye on the substrate that is being dyed.  Most often the reactions leading to the replacement of these groups are carried out at a pH>8 when cellulosic substrates are employed.  This pH level allows the concentration of cellulosate anions to be sufficient for reaction with the leaving group.  The leaving group in the dyes in this study was –Cl (chloro).

# 3. Experimental Methods and Procedures

## 3.1 General Information

These experiments were conducted with three commercially available dichlorotriazine fiber reactive dyes, and four different homobifunctional dye types. The commercially available dyestuffs obtained (Procion® MX-8B, Procion® Yellow MX-3R, and Procion® MX-2G) from DyStar were purified by removing additives, which included salt. The homobifunctional reactive dye types (1-4) were synthesized at North Carolina State University and provided for these studies. These dyes were also purified of salt and other impurities.

The structures of the dyes vary according to the number of reactive groups, the number of chromogens, and the linking moiety. Types 1 and 2 have four reactive groups and one chromogen. Types 3 and 4 have only two reactive groups and two of the same chromogens. The linking moiety has either a hydrogen (–H) or carboxyl group (–COOH ).

There were two types of fabrics used in this project for the exhaustion equilibrium experiments and laboratory dyeings. Equilibrium exhaustion experiments were conducted on 100% cotton white woven crocking squares weighing on average $1.20 \pm 0.5$g were used for each of the exhaustion experiments. A 100% plain weave cotton fabric weighing approximately 5.52 oz/yd$^2$ (156.6 g/m$^2$) before processing was used for the laboratory dyeing experiments. Prior to these experiments, the fabric was desized, scoured, and bleached. The fabric was then cut into 9 in x 11 in rectangles that weighed $10.00 \pm 0.01$g. The chemicals used during

the exhaustion equilibrium and dyeing experiments were sodium chloride (referred to as salt) and deionized water. Sodium carbonate and sodium hydroxide were used as alkali during the laboratory dyeing experiments. Stock solutions of 100 g/L sodium carbonate and 100 g/L of sodium hydroxide were used in the laboratory dyeing experiments. Triton X-200 was used during the washing off procedure following the dyeing step. Table 3.1 lists the chemicals and the suppliers.

Table 3.1    Chemical list and suppliers.

| Chemical | Supplier |
|---|---|
| Sodium chloride – A CS Grade | Fisher Scientific (S271-3) |
| Sodium hydroxide NF/FCC Pellets – A CS Grade | Fisher Scientific (S320-1) |
| Sodium carbonate Anhyrdrous – ACS Grade | Fisher Scientific (S263-1) |
| Triton X-200 | Union Carbide (89543) |

## 3.2    Dyeing Procedures

Equilibrium exhaustion experiments were conducted to determine the apparent affinity of a dye by bringing the dyebath to equilibrium with 1.20 ± .05g of cotton substrate. In this se of experiments dye exhaustion was conducted without the addition of alkali. In a second set of experiments, a laboratory dyeing was performed with the addition of an alkali fixation step.

### 3.2.1 End-of-process Dyebath Analysis Procedures

Absorbance and dye concentrations were determined for each solution using a Cary 3E UV-Visible Spectrophotometer. Standard calibration curves, including a

high and low range ( $r^2$ > 0.9900), were obtained for each dye in deionized water. After the equilibrium exhaustion and dyeing procedures were completed, the fabric was removed from the solution, the dyebaths were mixed thoroughly, and 5 mL aliquots were taken from each. The aliquots were allowed to cool to room temperature and 1mL was diluted in 3 mL using deionized water. The dyebath samples were placed in disposable polystyrene cuvettes (Fisher Scientific) with a 10mm light path, to conduct spectral analyses.

## 3.2.2 Equilibrium Exhaustion Procedure

The equilibrium exhaustion experiments were conducted in 50 mL Erlenmeyer flasks using shaker baths. These studies were conducted at either 60°C (Dubnoff Metabolic Shaking Incubator) or 90°C (Boekel Grant ORS200) and using speed of 100 orbital revolutions per minute. Five woven cotton squares weighing a total of 1.20 g were placed in a single empty Erlenmeyer flask, and sufficient dyebath was added to give a bath ratio of 40:1. The flasks were then covered with lids and placed in the shaker baths where they remained for 48 h. The temperature of the 60°C shaker bath was gradually cooled to 30°C after 2 h. The temperature of the 90°C shaker bath remained constant for the entire 48 h. The fabric samples were then removed and washed under running tap water for 1 min and then placed flat on paper towels to dry. There was very little color transfer to the paper towels during the drying process. The flasks containing the remaining dyebaths were sealed with paraffin and kept at room temperature for subsequent analysis.

### 3.2.2.1 Dye Exhaustion studies for Commercial, Types 1, 2, and 3 Dyes

There were five dyeings conducted at each of the four different salt concentrations employed. The baths contained 1% (owf) dye with salt concentrations of either 0 g/L, 10 g/L, 40 g/L, or 70 g/L.  These solutions were added to the Erlenmeyer flasks at the beginning of the dyeing process.

### 3.2.2.2 Dye Exhaustion studies for Type 4 Dyes

The exhaustion of type 4 dyes involved a slower salt addition because of their higher salt sensitivity.  The addition of the salt in a single dose prevented the dissolution of dye resulting in a cloudy solution.  Thus, the addition of salt was conducted as shown in Table 3.2.  The first addition of salt was conducted after the first 24 h period.  Once the addition of salt was complete, the solutions were kept in the shaker bath for 48 h to ensure that equilibrium was reached.

Table 3.2    Addition of salt solution to Type 4 dyes.

| | Final Salt Concentration | | | |
|---|---|---|---|---|
| Time | 0 g/L | 10 g/L | 40 g/L | 70 g/L |
| 0-24 h | 0 g/L | +10 g/L | +10 g/L | +10 g/L |
| 24-48 h | 0 g/L | 0 g/L | +10 g/L | +10 g/L |
| 48-72 h | 0 g/L | 0 g/L | +20 g/L | +20 g/L |
| 72-96 h | 0 g/L | 0 g/L | 0 g/L | 30 g/L |

## 3.2.3 Laboratory Dyeing Procedure

These experiments were conducted using an Ahiba Texomat laboratory dyeing machine with a liquor ratio of 40:1 for the commercial, type 2 and type 4 dyes.  The initial dyebaths were set up for 0.25% and 1.0% (owf) dyeing. Inititally, 200 mL deionized water was added to each Texomat tube.  Then, an appropriate amount of concentrated dye solution was added to each tube via a 25 mL burette. The tubes were then placed into the Ahiba Texomat machine at a temperature of 30°C.  Ten gram cotton samples were wet out with water and then padded at 100% wpu.  The fabric samples were then mounted on Ahiba sample holders and placed in the baths to agitate.

The temperature was increased to 90°C at the maximum rate of rise and held for 5 min.  The baths were then cooled to the desired dyeing temperature (30°C, 60°C or 90°C) at the maximum rate of cooling and held for 10 minutes.  Appropriate amounts of 25% salt solution were then added to the tubes in two doses spaced 1 minute apart.  Dye exhaustion was continued for 15 min before alkali was dosed over a 15 min time period.  After the final addition of alkali, dyeing was continued for

30 min.  The fabric was then removed immediately from the baths and 5 ml of the

dyebath was placed in a sealed container for subsequent analysis.  Table 3.3

outlines the basic dyeing procedure for the experiments.


Table 3.3      Dyeing procedure outline.

| Step | Description | Time (mins) | Temperature (Celsius) |
|------|-------------|-------------|-----------------------|
| 1 | Load the Texomat with Fabric and Dyebath | 0 | 30 |
| 2 | Heat at Maximum Rate of Rise | 15 | 90 |
| 3 | Run | 5 | 90 |
| 4 | Held or Cooled to Dyeing Temperature Maximum Rate of Cooling | 0-90 | 30, 60, or 90 |
| 5 | Run | 10 | 30, 60, or 90 |
| 6 | Add ½ of the Salt Solution to Dyebath | 1 | 30, 60, or 90 |
| 7 | Add remaining Salt Solution to Dyebath | 1 | 30, 60, or 90 |
| 8 | Run | 15 | 30, 60, or 90 |
| 9 | Add ¼ of the Alkali Solution to Dyebath | 5 | 30, 60, or 90 |
| 10 | Add ¼ of the Alkali Solution to Dyebath | 5 | 30, 60, or 90 |
| 11 | Add ½ of the Alkali Solution to Dyebath | 5 | 30, 60, or 90 |
| 12 | Run | 30 | 30, 60, or 90 |


## 3.2.2.1 Temperature

Dyeings with the commercial and type 2 synthesized dyes were conducted at

30°C and 60°C, while the type 4 dyes were applied at 60°C and 90°C.  These

temperatures were selected because the commercial and type 2 dyes are

dichlorotriazines, in which the second chlorine causes the activation of the ring to a

nucleophilic substitution.  The type 4 dyes are monochlorotriazine, which are slower

reacting due to the lack of any activating group in the triazine structure.

### 3.2.2.2 Salt

Three different salt concentrations were used during the dyeing experiments 0 g/L, 20 g/L, and 40 g/L.  These levels were chosen based on results from preliminary exhaustion experiments.  A saturated sodium chloride solution was added to the tubes in two equal portions during the dyeing procedure, according to the procedure outlined in Table 3.3.

### 3.2.2.3 Alkali

The commercial and type 2 dyes were applied to cotton at a final concentration of 10g/L sodium carbonate. However, the type 4 dyes were applied at a final concentration of 10 g/L sodium carbonate and 1 g/L sodium hydroxide.  Alkali was added in parts (¼, ¼, and ½) over a time interval of 15 min.

### 3.2.3  Washing Procedure

At the end of the dyeing process the fabric samples were washed by stirring them in cold tap water for 2 min and 3 min, successively.  Excess water was removed by blotting and fabric was scoured at 90°C using 0.25 g/L Triton X-200. After 5 min the fabric was rinsed in 90°C water, and excess water was removed by centrifuging.  The fabric samples were dried at 9% power on a Precision Screen Machine Dryer (201-427-5100). Table 3.4 outlines the washing procedure that was used after dyeing.

Table 3.4     Washing procedure.

| Step | Description | Time (min) |
|:---:|:---|:---:|
| 1 | Place fabric in clean cool water and agitate. | 2 |
| 2 | Transfer fabric to clean cool water and agitate. | 3 |
| 3 | Remove excess water. | 0 |
| 4 | Transfer fabric to clean 90°C water with 0.25 g/L of Triton X-200. | 5 |
| 5 | Rinse fabric in clean 90°C water. | 5 |
| 6 | Remove excess water. | 0 |
| 7 | Dry | 3 |

### 3.2.4 K/S Data Collection

To obtain K/S data, the fabric samples from equilibrium and laboratory dyeing procedures were dried and pressed with an iron set on medium high.  The samples were then analyzed using a Datacolor Spectraflash SF600X instrument equipped with SLI-Form® software.  The maximum K/S value was recorded for each fabric sample.

## 3.3     Physical Testing Procedures

The following physical tests were performed on the dyed fabric samples:

1. Color Fastness to Light - AATCC Test Method 16-1998

2. Color Fastness to Water - AATCC Test Method 107-1997

3. Color Fastness to Crocking - AATCC Test Method 8-1996

### 3.3.1 Color Fastness to Light

Colorfastness to light was determined according to AATCC Test Method 16-1998 (AATCC, 2000).  The dyed fabric samples were exposed to a Xenon light source for 20 h and 40 h, using an Atlas 3Sun Hi35 High Irradiance Xenon arc

weatherometer.  Change in color was calculated by evaluating the samples using a Datacolor Spectraflash SF600X equipped with SLI-Form® software.  The color change was also evaluated using an AATCC Gray Scale for Color Change, according to AATCC Evaluation Procedure 1 (AATCC, 2000).  Ratings were assigned to each sample using a scale of 1 (poor) – 5 (excellent). The visual color change assessment was conducted using a Gretag Macbeth Spectralight III instrument with illuminant D65.

### 3.3.2 Colorfastness to Water

Colorfastness to water was evaluated using AATCC Test Method 107-1997 (AATCC, 2000).  The fabric samples were evaluated in the presence of multifiber test fabric No. 10 for a period of 18 h at 38°C.  The multifiber fabric samples were evaluated for color change using the AATCC Gray Scale for Evaluating Staining according to the AATCC Evaluation Procedure 2 (AATCC, 2000).  A rating of 1 (poor) – 5 (excellent) was assigned to each of the six fiber strips on the fabric.

### 3.3.3 Colorfastness to Crocking

Colorfastness to wet and dry crocking was evaluated using the AATCC Test Method 8-1996 (AATCC, 2000).  Color change was assigned by using the AATCC Gray Scale for Evaluating Staining according to the AATCC Evaluation Procedure 2 (AATCC, 2000).  A rating of 1 (poor) – 5 (excellent) was given to each fabric sample.

## 3.4      Computational Procedures

Computation procedures to determine the concentration of dye in solution and in the fiber, percent exhaustion, percent fixation, apparent affinity, and heat of dyeing were conducted on both the equilibrium exhaustion and laboratory dyeing procedures.

### 3.4.1 Determination of Dye in Solution ($c^s$)

To determine the amount of the dye that was in the residual dyebath ($c^s$), a standard Beer-Lambert Law calibration curve was developed for each dye.  Dye solutions had the following known concentrations: 0.00250 g/L, 0.02500 g/L, 0.03125 g/L, 0.06250 g/L, and 0.10000 g/L.  The absorbance of each solution was measured on a Cary 3E UV-Visible Spectrophotometer and linear regression was used to give a calibration model for each dye. The measured absorbances of the residual dyebaths were used with the Beer-Lambert Law regression models to determine the concentration of dye in each solution.

### 3.4.2  Calculation of Dye in the Fiber ($c^f$)

The conservation of mass was used to calculate the concentration of dye in the fiber.  This law indicates that the total amount of dye after dyeing is completed will equal the amount of dye in the fiber plus the amount of dye in solution.

$$c^s_{initial} \, m^s_{initial} = c^f \, m^f + c^s \, m^s$$

Where $m_{initial}$ represents the mass of the initial solution, $m^s$ is the mass of the solution after dyeing, $c^s$ is the concentration of dye in the solution after dyeing, $c^f$ is the concentration of dye in the fiber, and $m^f$ is the mass of the fiber.

### 3.4.3  Calculation of Percent Exhaustion (%E)

The percent exhaustion was calculated for each of the equilibrium exhaustion experiments, using the following equation.

$$\% \ E = [(c^s_{initial} - c^s)/ \ c^s_{initial}] \times 100\%$$

### 3.4.4  Calculation of Percent Fixation (%F)

The percent fixation was calculated for each experimental dyeing, using the following formula.

$$\% \ F = [(c^s_{initial} - c^s)/ \ c^s_{initial}] \times 100\%$$

### 3.4.5 Calculation of the Substantivity Ratio (K)

Substantivity ratios from exhaustion equilibrium studies were calculated by dividing the concentration of dye in the solution by the concentration of the dye in the fiber after dyeing.  The following equation was used to obtain these values.

$$K = c^f / c^s$$

### 3.4.6  Calculation of Apparent Standard Affinity (-Δμ°)

The apparent standard affinity was calculated from K for the exhaustion experiments by using the following equation:

$$-\Delta\mu° = RT\ln K$$

Where R is the gas constant (8.31433 J/mol K), T is the temperature (degrees K) and K is the affinity of the dye for the fiber.

### 3.4.7 Calculation of Apparent Standard Heat of Dyeing (ΔH°)

The apparent standard heat of dyeing was calculated for each dye type using the following equation:

$$-\Delta H°/R = \Delta \ln(K)/ \Delta(1/T)$$

Here, T is the temperature and K is the affinity of the dye for the fiber. The constant R is the gas constant R= 8.31433 J/mol K.

### 3.4.8 Computational Chemistry

Ahmed El-Shafei conducted molecular modeling, for each of the commercial and synthesized dye types. The structures were built using the CAChe graphical editor interface, with the formal and partial charges for the structures assigned where appropriate. "Beautification," a process within the CAChe editor interface provided a starting structure with standard bond lengths, bond angles, and correct configuration of each atom in the structure. The addition of lone pairs of electrons and hydrogen atoms were added when necessary. The equilibrium geometries of the dyes were located in the gas phase and in water using a semi-emperical PM3 parameters. Calculations of the dyes in water were carried out using PM3 with COSMO solvation model at the SCF level in aqueous solution (Klamt, 1993). This was implemented in CAChe Worksystem Pro Version 6.1.12.33 executed on an Intel Pentium® 4-MCPU 2.60 GHz with 766 MB of RAM. COSMO models were used to

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construct a solvent accessible surface area based on a van der Waals radii model.

The computational time for most of the models was 2-3 h for each structure.

# 4. Results and Discussion

## 4.1    *Substantivity Ratio*

The substantivity ratio of reactive dyes for cellulose in aqueous dyebaths is largely determined by the chemical nature of the chromophore and the fiber (Sumner and Taylor, 1967).  Bath ratio, pH, salt and temperature also play an integral role in the substantivity ratio (Sumner, 1963).  The bath ratio of 40:1 and the pH (7 +/- .1) remained constant for the exhaustion experiments.  Substantivity ratios were calculated for each dyeing and were used in determining the apparent standard affinity ($-\Delta\mu°$ ) of the dye for the fiber.

$$-\Delta\mu° = RT\ln K$$

The determination of the substantivity ratio has been used in the exhaustion equilibrium and a similar measure, the fixation ratio, was used in the dyeing experiments to assess the performance of the dyes.  These ratios were determined from the concentration of dye in the fiber and the solution after dyeing.

### 4.1.1 Equilibrium Exhaustion

Equilibrium exhaustion experiments were conducted on all five dye types: Commercial, type 1, type 2, type 3, and type 4.  The goal was to determine which of the four modified structures had the greatest affinity and substantivity for cotton. The factors that were varied in these experiments were temperature and salt concentration.  Four salt concentrations, 0 g/L, 10 g/L, 40 g/L, and 70 g/L, were used to provide a low to high range.  Two temperatures were chosen: 30°C and 90°C.  To ensure that equilibrium was reached in the dyebath, the 30° C bath was initially set

at 60°C and then cooled to 30°C after 2 h.  This reduced the amount of time required for the dyeing to reach an equilibrium between with the dye in the bath and the fiber.

During these experiments it was noticed that the solubility of the type 4 dyes decreased significantly as salt concentration increased.  Therefore, equilibrium exhaustion experiments were conducted over a period of 96 h with an addition of saturated salt solution every 24 h.  The solubility of type 2 dyes was less affected by salt concentrations than type 4, but was affected more than types 1 and 3.  The pH of all dye solutions was 7.0 +/- 0.5 pH units.

The analysis of the dyebath after dye exhaustion was completed allowed $c^s$ and $c^f$ values to be determined (Appendix A).  The corresponding substantivity ratio was then calculated from those values.  Tables 4.1 - 4.3 provide K values for all types of dyes and the experimental conditions.  These results showed that increases in salt concentration in the dyebath increased the substantivity ratio (K).  It is also clear that the substantivity ratio decreased as the temperature of the dyebath was increased.  These data indicate that the use of type 2 dyes led to the largest increase in the K values, compared to the commercial and Teegafix type 1, 3, and 4 dyes.  While type 4 dyes also afforded higher K values than the commercial dyes, the increases observed were not as large as those observed with type 2.  However, the type 4 dyes did have a higher K value than the type 2 dyes at the lower temperature (30°C) at the highest salt concentration (70 g/L).  These results are also illustrated in Figures 4.1-4.3.

Table 4.1    K Values for equilibrium exhaustion of the five red dyes as a function of temperature and salt concentration.

| Dyes | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| R1 | 0.01 | 6.52 | 19.02 | 24.88 | 0.96 | 3.33 | 6.22 | 9.08 |
| R2 | 25.65 | 70.52 | 156.54 | 254.11 | 2.50 | 20.40 | 58.37 | 112.07 |
| R3 | 0.01 | 1.81 | 15.48 | 44.40 | 0.01 | 0.02 | 3.43 | 15.46 |
| R4 | 2.01 | 36.99 | 141.69 | 278.06 | 0.06 | 20.00 | 32.92 | 51.47 |
| Procion® Red MX-8B | 0.32 | 12.50 | 32.93 | 48.37 | 0.04 | 0.71 | 6.95 | 13.42 |

Table 4.2    K Values for equilibrium exhaustion of the five blue dyes as a function of temperature and salt concentration.

| Dyes | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| B1 | 1.66 | 1.96 | 6.24 | 17.47 | 3.67 | 6.21 | 4.94 | 7.33 |
| B2 | 1.66 | 25.89 | 98.12 | 205.57 | 1.28 | 5.50 | 31.40 | 69.50 |
| B3 | 0.00 | 5.40 | 21.20 | 36.34 | 1.06 | 1.80 | 3.34 | 10.37 |
| B4 | 0.03 | 5.27 | 33.04 | 71.96 | 0.03 | 0.03 | 6.29 | 22.70 |
| Procion® Blue MX-2G | 0.06 | 2.23 | 13.80 | 30.40 | 1.46 | 1.70 | 3.18 | 7.10 |

Table 4.3    K Values for equilibrium exhaustion of the five yellow dyes as a function of temperature and salt concentration.

| Dyes | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| Y1 | 0.01 | 4.61 | 11.42 | 10.08 | 24.11 | 25.30 | 27.49 | 38.56 |
| Y2 | 0.46 | 18.92 | 68.41 | 160.96 | 15.39 | 25.17 | 37.54 | 57.73 |
| Y3 | 1.66 | 7.85 | 26.79 | 59.56 | 18.96 | 17.42 | 25.09 | 27.57 |
| Y4 | 0.03 | 18.11 | 65.53 | 127.56 | 7.15 | 15.70 | 25.43 | 36.89 |
| Procion® Yellow MX-3R | 0.02 | 8.01 | 27.66 | 59.05 | 20.42 | 21.02 | 26.38 | 32.09 |
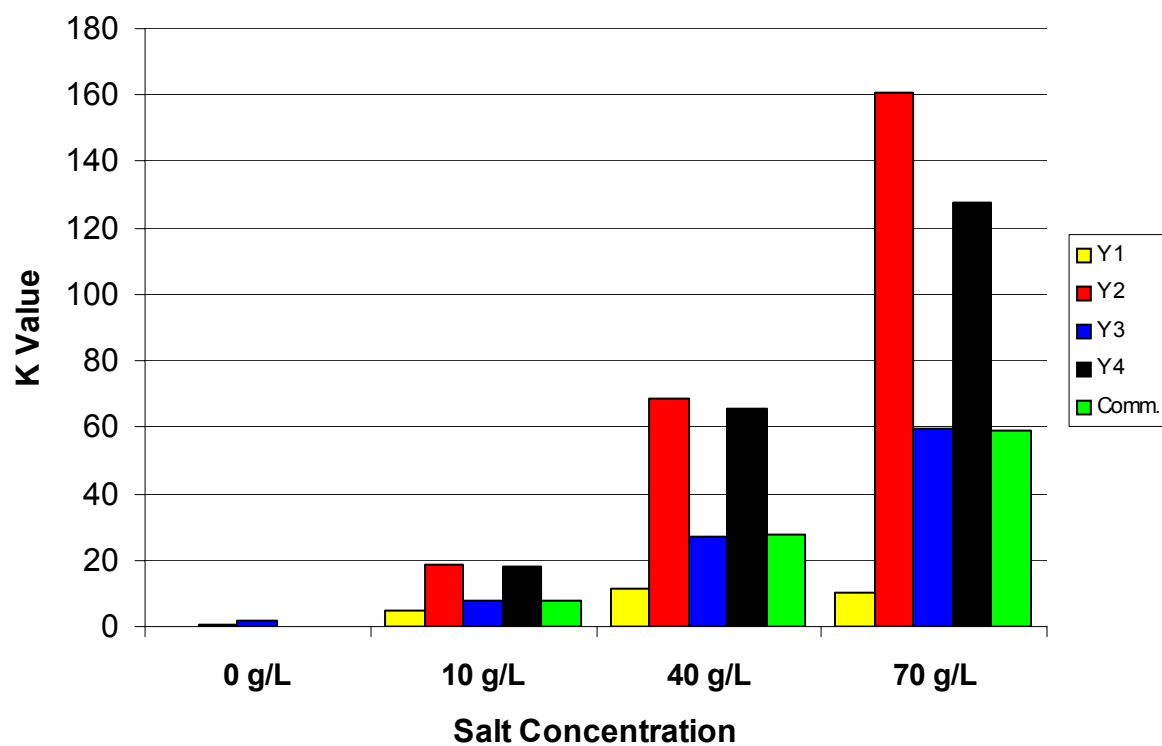
Figure 4.1    K values for exhaustion equilibrium of the five yellow dyes at 30°C.
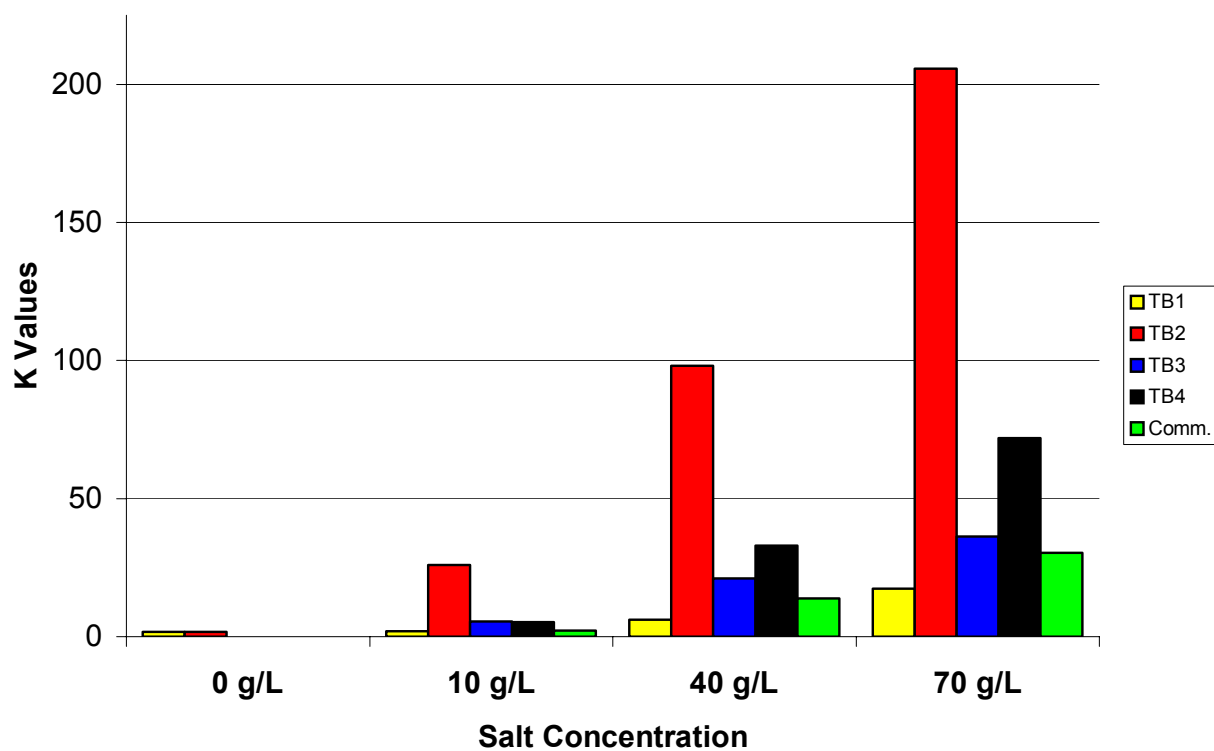
Figure 4.2    K values for exhaustion equilibrium of the five blue dyes at 30°C.
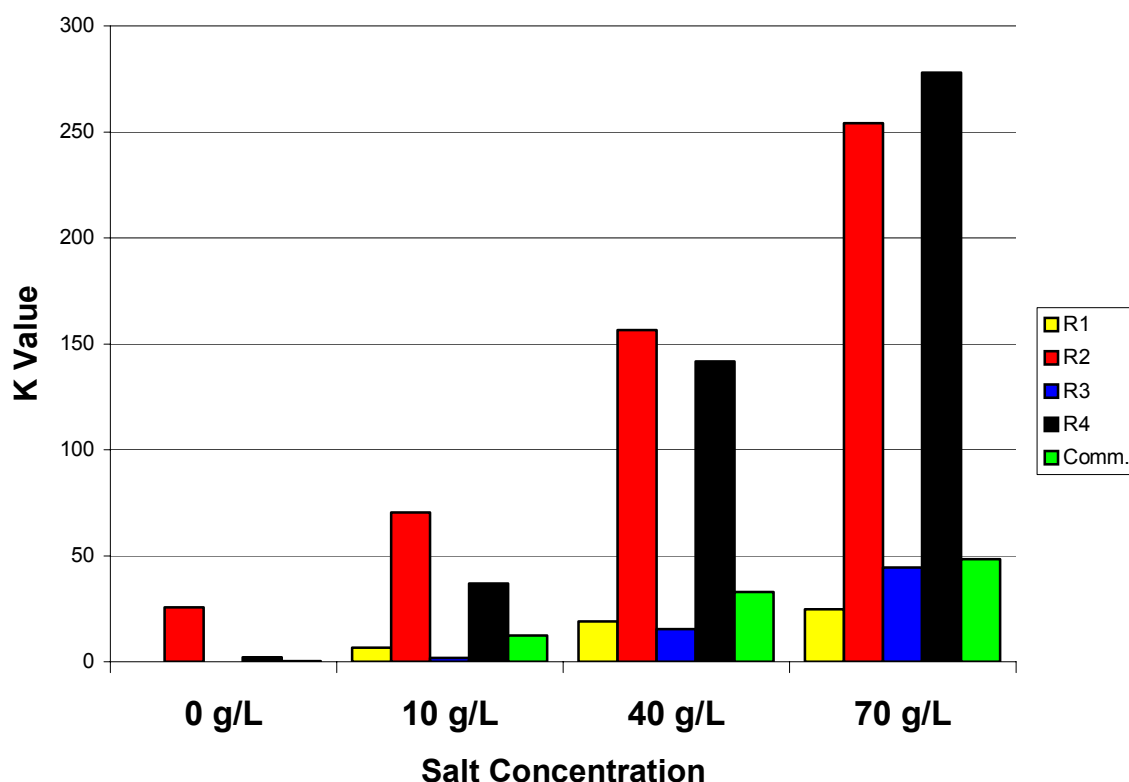
Figure 4.3    K values for exhaustion equilibrium of the five red dyes at 30°C.

In addition to determining K values, percent exhaustion values were determined for each experiment.  The results indicated that percent exhaustion values as a function of dye structure followed the same trends as observed for substantivity ratios. Figures 4.4 – 4.6 show the percent exhaustion values at the lower temperatures. From the results of exhaustion equilibrium experiments, type 2 and type 4 dyes were selected for laboratory dyeing studies, to optimize the dyeing process.
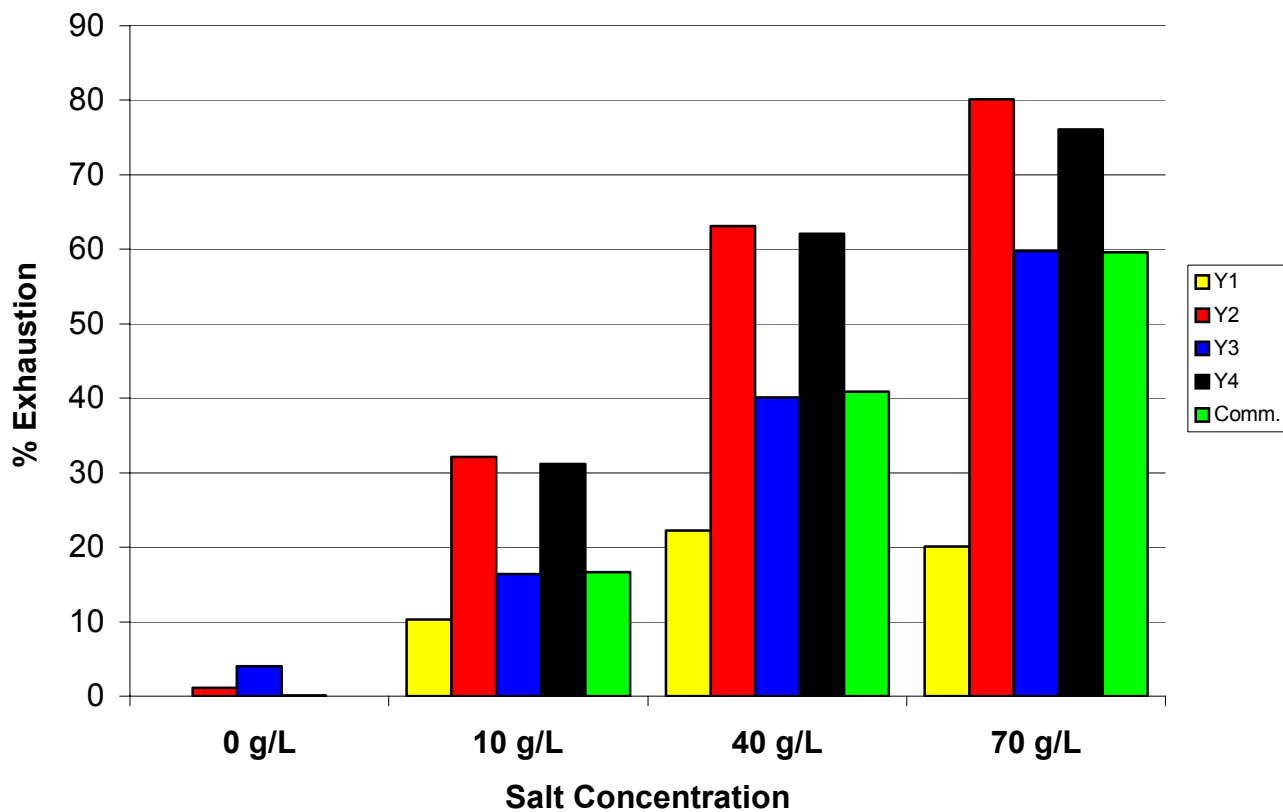
Figure 4.4    Percent exhaustion for exhaustion equilibrium of the five yellow dyes
at 30°C.
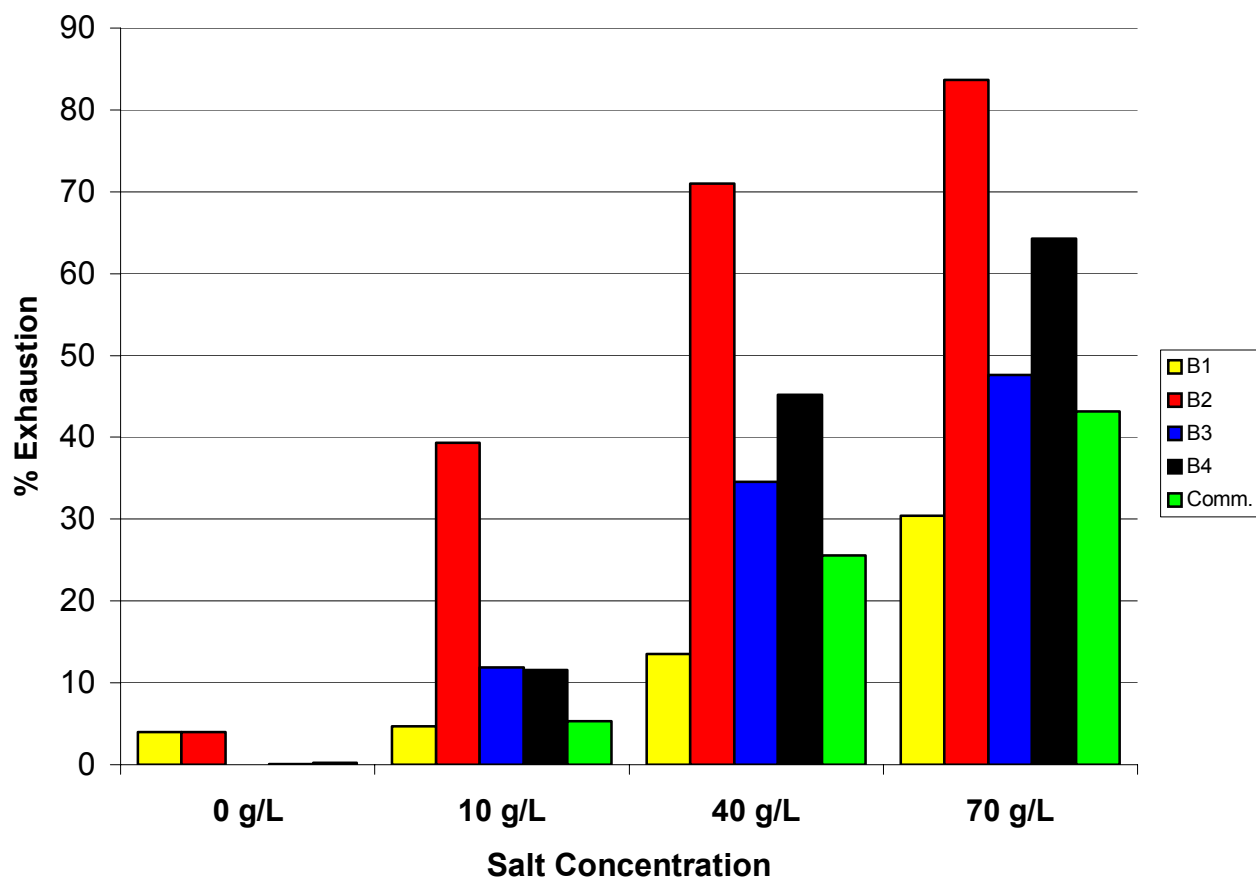
Figure 4.5     Percent exhaustion for exhaustion equilibrium of the five blue dyes at 30°C.
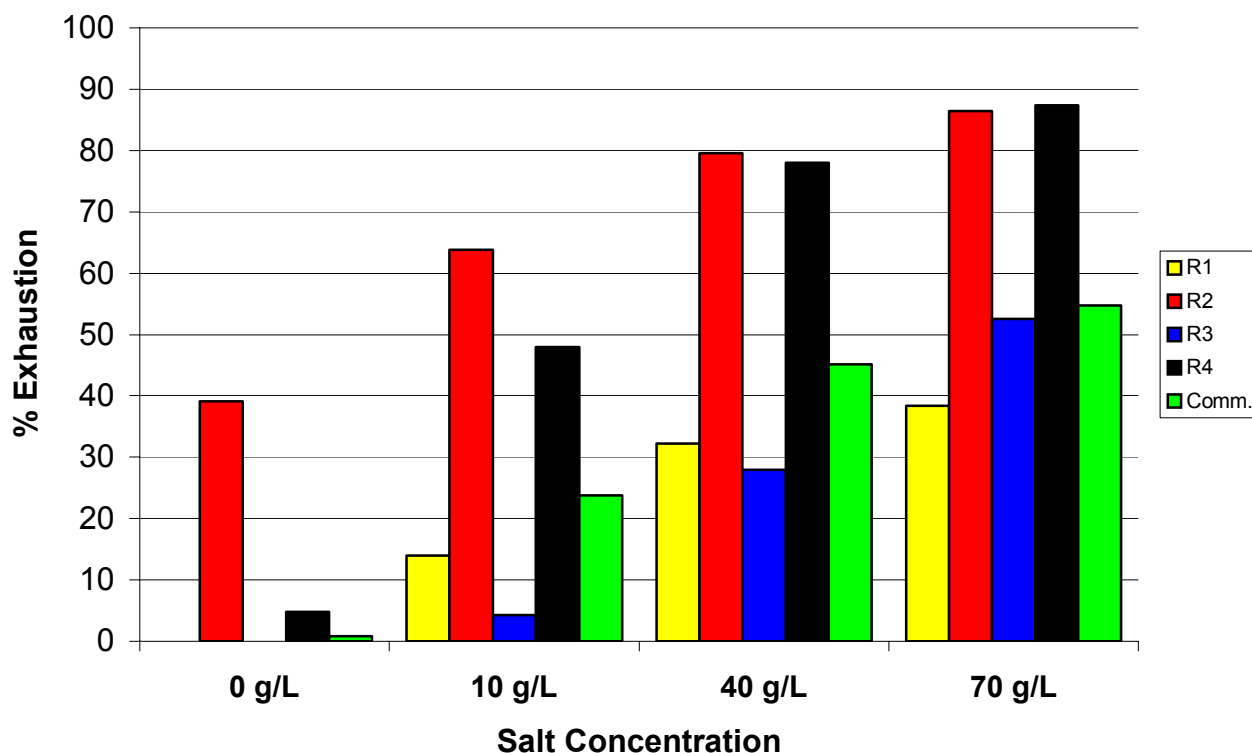
Figure 4.6     Percent exhaustion for exhaustion equilibrium of the five red
dyes at 30°C.

Types 2 and 4 dyes gave higher percent exhaustions than the other dye
types.  The apparent standard affinity calculated values followed the same trend as
the substantivity ratio values for the dye types.  Data from apparent standard affinity
calculations can be found in Appendix A.  The apparent standard heat of dyeing also
followed the same trend as the substantivity ratio values (Appendix A).

Type 2 and 4 structures have simply a proton attached to the –CH- group in
the linking moiety, whereas type 1 and 3 have a carboxyl group in this position.  The
removal of the carboxyl group from these structures affects the water solubility and
planarity of the dye structures.  Results from molecular modeling experiments

indicate that type 2 and 4 structures are more planar, due to the absence of carboxyl groups as determined by the modeling experiments.  The lower water solubility and higher planarity of type 2 and 4 led to increased dye/fiber affinity.

## 4.1.2 Laboratory Dyeings

The laboratory dyeings employed only the type 2 and 4 structures.  In these experiments, salt concentration, shade depths, alkali concentration, and the temperature were varied.  A set of experiments was developed so that the importance of each of these variables could be evaluated for each dye type and color.  Table 4.4 shows the experimental design for the five red dyes (1-36). The same experimental design was employed for the blue (37-72) and yellow (73-108) dyes. The full sets of data are provided in Appendix B.

Table 4.4     Experimental design for the commercial, type 2, and type 4 red dyes.

| Sample No. | Dye | Color | Shade Depth (%) | Salt Conc. (g/L) | Temperature (C) |
|---|---|---|---|---|---|
| 1 | Procion® MX-8B | Red | 0.25 | 0 | 30 |
| 2 | Procion® MX-8B | Red | 0.25 | 20 | 30 |
| 3 | Procion® MX-8B | Red | 0.25 | 40 | 30 |
| 4 | Procion® MX-8B | Red | 1 | 0 | 30 |
| 5 | Procion® MX-8B | Red | 1 | 20 | 30 |
| 6 | Procion® MX-8B | Red | 1 | 40 | 30 |
| 7 | Procion® MX-8B | Red | 0.25 | 0 | 60 |
| 8 | Procion® MX-8B | Red | 0.25 | 20 | 60 |
| 9 | Procion® MX-8B | Red | 0.25 | 40 | 60 |
| 10 | Procion® MX-8B | Red | 1 | 0 | 60 |
| 11 | Procion® MX-8B | Red | 1 | 20 | 60 |
| 12 | Procion® MX-8B | Red | 1 | 40 | 60 |
| 13 | Type 2 | Red | 0.25 | 0 | 30 |
| 14 | Type 2 | Red | 0.25 | 20 | 30 |
| 15 | Type 2 | Red | 0.25 | 40 | 30 |
| 16 | Type 2 | Red | 1 | 0 | 30 |
| 17 | Type 2 | Red | 1 | 20 | 30 |
| 18 | Type 2 | Red | 1 | 40 | 30 |
| 19 | Type 2 | Red | 0.25 | 0 | 60 |
| 20 | Type 2 | Red | 0.25 | 20 | 60 |
| 21 | Type 2 | Red | 0.25 | 40 | 60 |
| 22 | Type 2 | Red | 1 | 0 | 60 |
| 23 | Type 2 | Red | 1 | 20 | 60 |
| 24 | Type 2 | Red | 1 | 40 | 60 |
| 25 | Type 4 | Red | 0.25 | 0 | 60 |
| 26 | Type 4 | Red | 0.25 | 20 | 60 |
| 27 | Type 4 | Red | 0.25 | 40 | 60 |
| 28 | Type 4 | Red | 1 | 0 | 60 |
| 29 | Type 4 | Red | 1 | 20 | 60 |
| 30 | Type 4 | Red | 1 | 40 | 60 |
| 31 | Type 4 | Red | 0.25 | 0 | 90 |
| 32 | Type 4 | Red | 0.25 | 20 | 90 |
| 33 | Type 4 | Red | 0.25 | 40 | 90 |
| 34 | Type 4 | Red | 1 | 0 | 90 |
| 35 | Type 4 | Red | 1 | 20 | 90 |
| 36 | Type 4 | Red | 1 | 40 | 90 |

Three salt concentrations, 0 g/L, 20 g/L, and 40 g/L, were considered in the laboratory dyeings, based on trials that were conducted separately to determine the optimal salt concentration levels.  Concentrations above this range were too high and showed little variation with all other factors being equal.  The temperatures used were dependent on the dye structure.  Monocholorotriazine type 4 dyes were applied at 60°C and 90°C.  The dichlorotriazine dyes (commercial and type 2 dyes) were applied at 30°C and 60°C.  The alkali levels were based on the manufacturer's recommended commercial dyeing procedure.  The amount of alkali used was also dependent on dye structure.  The application of dye monochlorotriazine dyes involved 10 g/L of sodium carbonate, while dicholortriazine dyes were applied using the same amount of sodium carbonate plus 1 g/L sodium hydroxide.

## 4.1.2.1 Fixation Ratio

Unlike the equilibrium exhaustion process, the laboratory dyeings were irreversible, as the addition of alkali to the dyebath cause dye to become covalently bound to the fiber and the dye can no longer desorb.  Therefore, it is not appropriate to use the term substantivity ratio in the assessment of the laboratory dyeings.  However, the ratio of $c^f$ and $c^s$ can still be used to compare the properties of the commercial, type 2, and type 4 dyes.  The latter ratio can also be used to compare the results from exhaustion experiments to those from laboratory dyeings. This ratio will be termed the fixation ratio and derived from the following equation:

$$F_K = c^f / c^s$$

Where the variable $c^f$ represents the concentration of dye that has fixed to the fiber and $c^s$ represents the concentration of dye remaining in the solution. After the dyeings were completed, $c^s$ and $c^f$ values were determined and used to calculate the fixation ratio. Tables 4.5-4.7 provide $F_k$ values for the three dye types and the experimental conditions used.

Table 4.5     $F_K$ values for laboratory dyeings involving yellow dyes (0.25% and 1.00%, owf).

**Procion® Yellow MX-3R**

| Salt | 0.25% | | 1.00% | |
|------|-------|-------|-------|-------|
|      | **30°C** | **60°C** | **30°C** | **60°C** |
| **0 g/L** | 175.52 | 134.22 | 179.78 | 122.10 |
| **20 g/L** | 293.33 | 160.48 | 268.45 | 142.55 |
| **40 g/L** | 416.20 | 203.66 | 346.99 | 179.88 |

**Type 2 Yellow**

| Salt | 0.25% | | 1.00% | |
|------|-------|-------|-------|-------|
|      | **30°C** | **60°C** | **30°C** | **60°C** |
| **0 g/L** | 306.74 | 208.76 | 223.44 | 138.00 |
| **20 g/L** | 704.05 | 268.64 | 417.25 | 239.64 |
| **40 g/L** | 1229.04 | 521.17 | 594.12 | 358.57 |

**Type 4 Yellow**

| Salt | 0.25% | | 1.00% | |
|------|-------|-------|-------|-------|
|      | **60°C** | **90°C** | **60°C** | **90°C** |
| **0 g/L** | 149.39 | 120.98 | 141.42 | 130.04 |
| **20 g/L** | 223.16 | 169.03 | 190.47 | 166.83 |
| **40 g/L** | 329.82 | 258.33 | 251.72 | 213.81 |

Table 4.6    $F_K$ values for laboratory dyeings involving blue dyes (0.25% and 1.00%, owf).

**Procion® Blue MX-2G**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30°C | 60°C | 30°C | 60°C |
| 0 g/L | 3.13 | 112.91 | 120.92 | 113.07 |
| 20 g/L | 168.86 | 135.32 | 153.95 | 127.45 |
| 40 g/L | 201.78 | 161.61 | 184.16 | 137.02 |

**Type 2 Blue**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30°C | 60°C | 30°C | 60°C |
| 0 g/L | 192.1263 | 123.9344 | 150.5125 | 120.0768 |
| 20 g/L | 295.5705 | 211.5091 | 243.6075 | 178.2929 |
| 40 g/L | 435.2852 | 335.3754 | 327.5119 | 224.4104 |

**Type 4 Blue**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60°C | 90°C | 60°C | 90°C |
| 0 g/L | 136.6784 | 104.9275 | 116.3233 | 105.0747 |
| 20 g/L | 159.2032 | 122.8664 | 129.3767 | 134.4287 |
| 40 g/L | 182.618 | 162.5932 | 149.7173 | 142.9491 |

Table 4.7    $F_K$ values for laboratory dyeings involving red dyes (0.25% and 1.00%, owf).

**Procion® Red MX-8B**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30°C | 60°C | 30°C | 60°C |
| 0 g/L | 133.49 | 130.41 | 167.17 | 126.81 |
| 20 g/L | 232.33 | 166.61 | 229.83 | 156.00 |
| 40 g/L | 320.75 | 195.40 | 286.69 | 171.01 |

**Type 2 Red**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30°C | 60°C | 30°C | 60°C |
| 0 g/L | 244.74 | 209.50 | 198.32 | 173.13 |
| 20 g/L | 607.67 | 605.99 | 342.56 | 367.00 |
| 40 g/L | 1023.83 | 1552.36 | 429.70 | 581.50 |

**Type 4 Red**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60°C | 90°C | 60°C | 90°C |
| 0 g/L | 199.01 | 152.16 | 179.25 | 142.68 |
| 20 g/L | 350.63 | 238.71 | 258.60 | 182.17 |
| 40 g/L | 451.16 | 305.78 | 333.83 | 290.36 |

It was found that the highest fixation ratio was observed with the type 2 dyes. The type 4 dyes showed higher $F_k$ than the commercial dyes, but did not reach the levels obtained with the type 2 dyes. Optimal fixation of yellow and blues dyes was observed at 30°C, 0.25% (owf), and 40g/L salt. The type 2 red dyes had the highest $F_k$ value at 60°C, 0.25% (owf), and 40g/L salt. It also must be noted that the type 2 red dyes had the higher $F_k$ value than the other dye types and colors. Figures 4.7-4.9 show the Fk values of the 0.25% (owf) dyeings with respect to the different salt concentrations and temperatures.
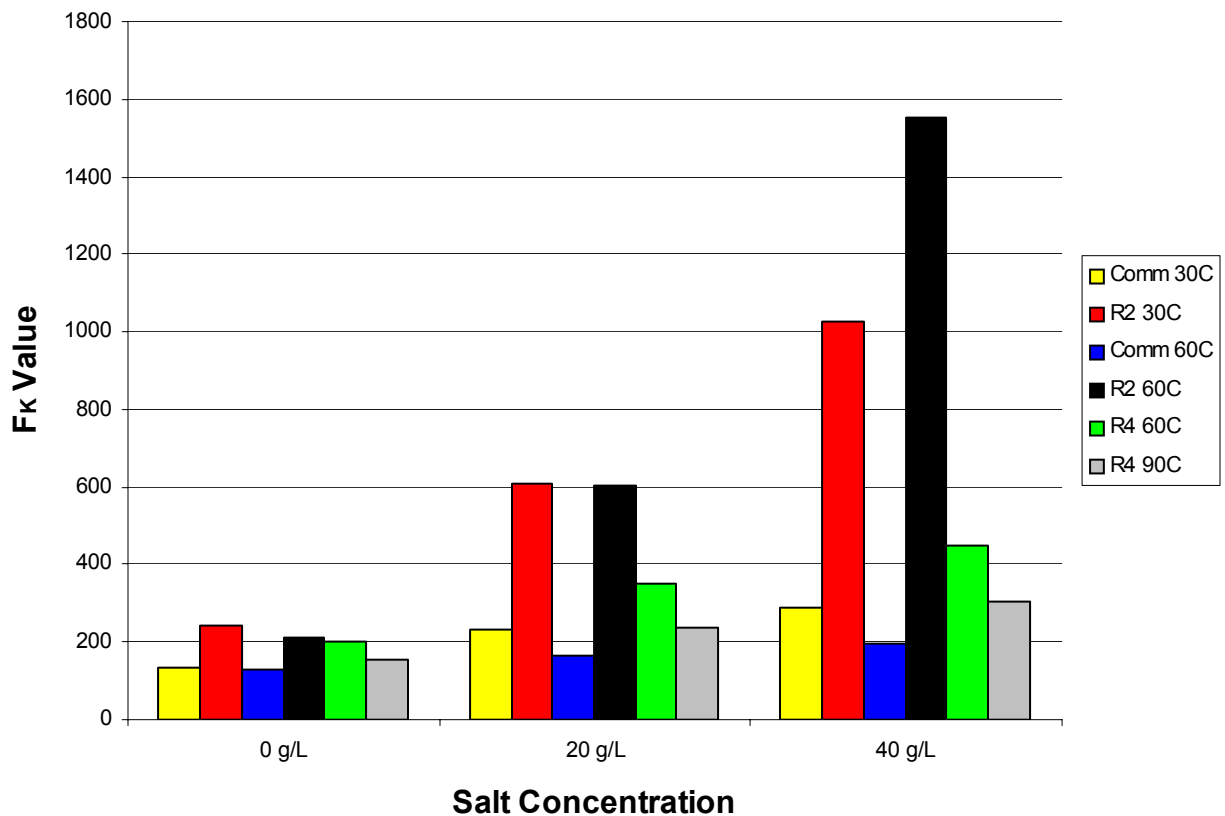


Figure 4.7    $F_K$ values for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 red dyes at different salt concentrations.
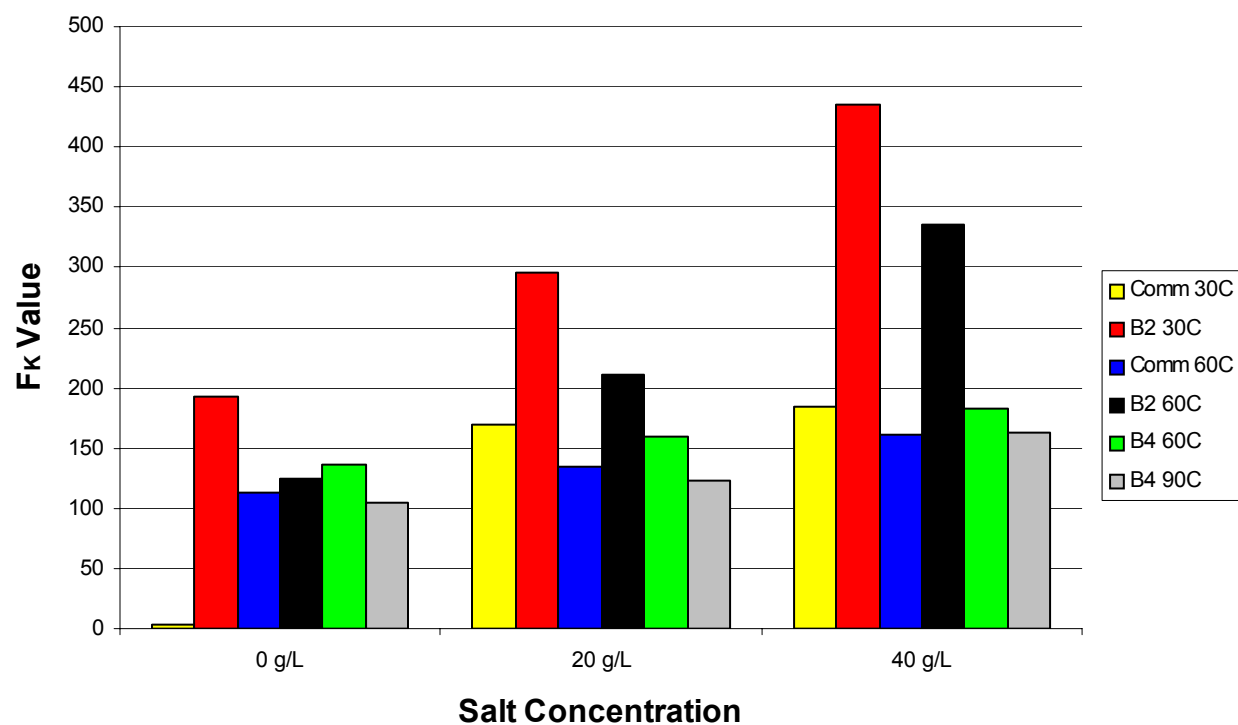
Figure 4.8    $F_K$ values for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 blue dyes at different salt concentrations.
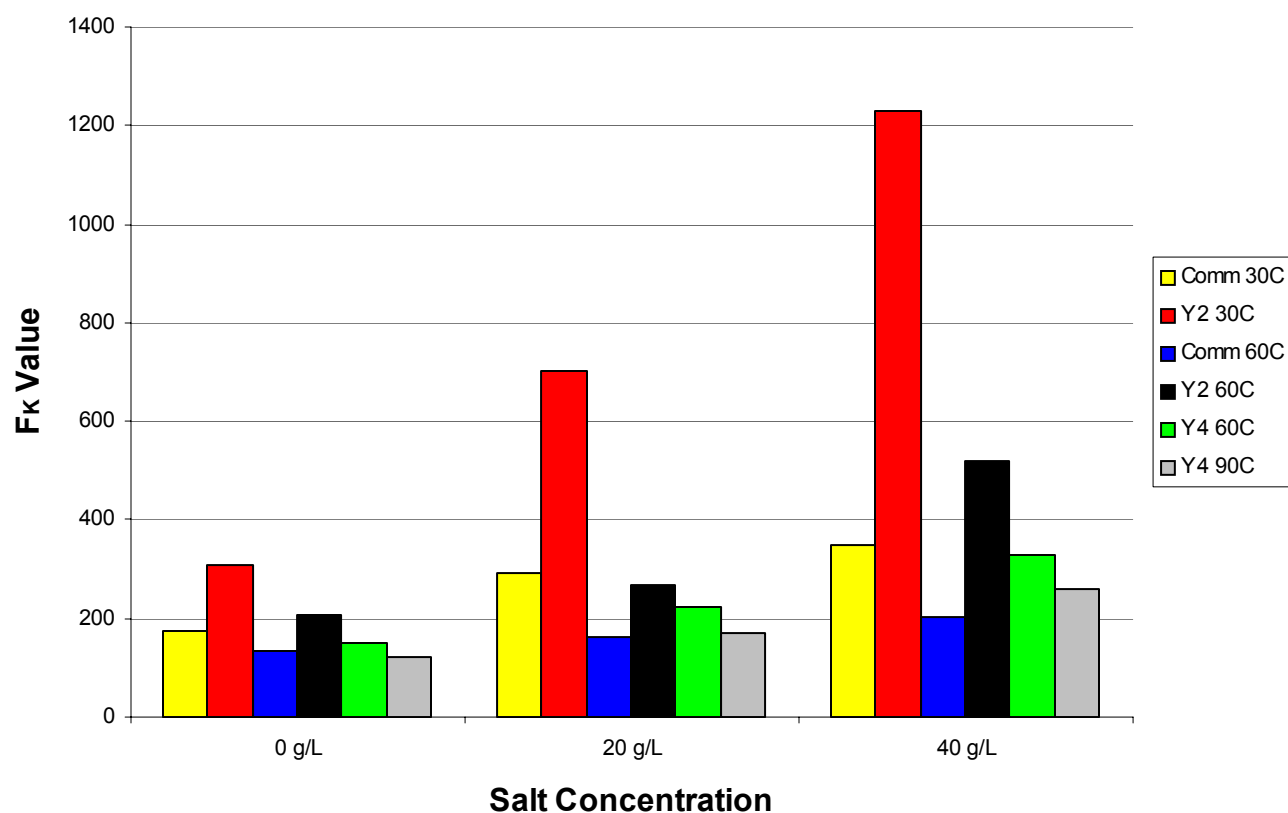
Figure 4.9    $F_K$ values for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 yellow dyes at different salt concentrations.

Results from exhaustion equilibrium and laboratory dyeings show similar increases in substantivity ratios and fixation ratios for the type 2 dyes.  The percent fixation was calculated for the each of the laboratory dyeings (Appendix B).  Figures 4.10-4.12 show the percent fixation for the 0.25% (owf) laboratory dyeings.

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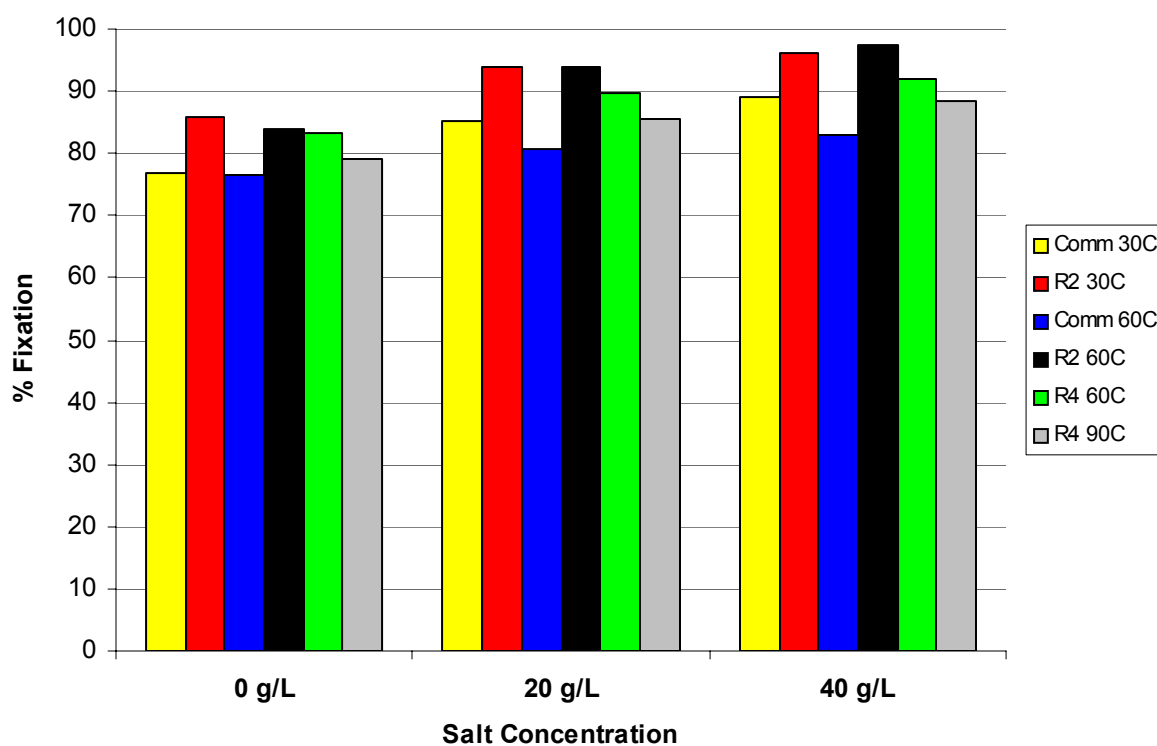
Figure 4.10    Percent fixation for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 red dyes at different salt concentrations.
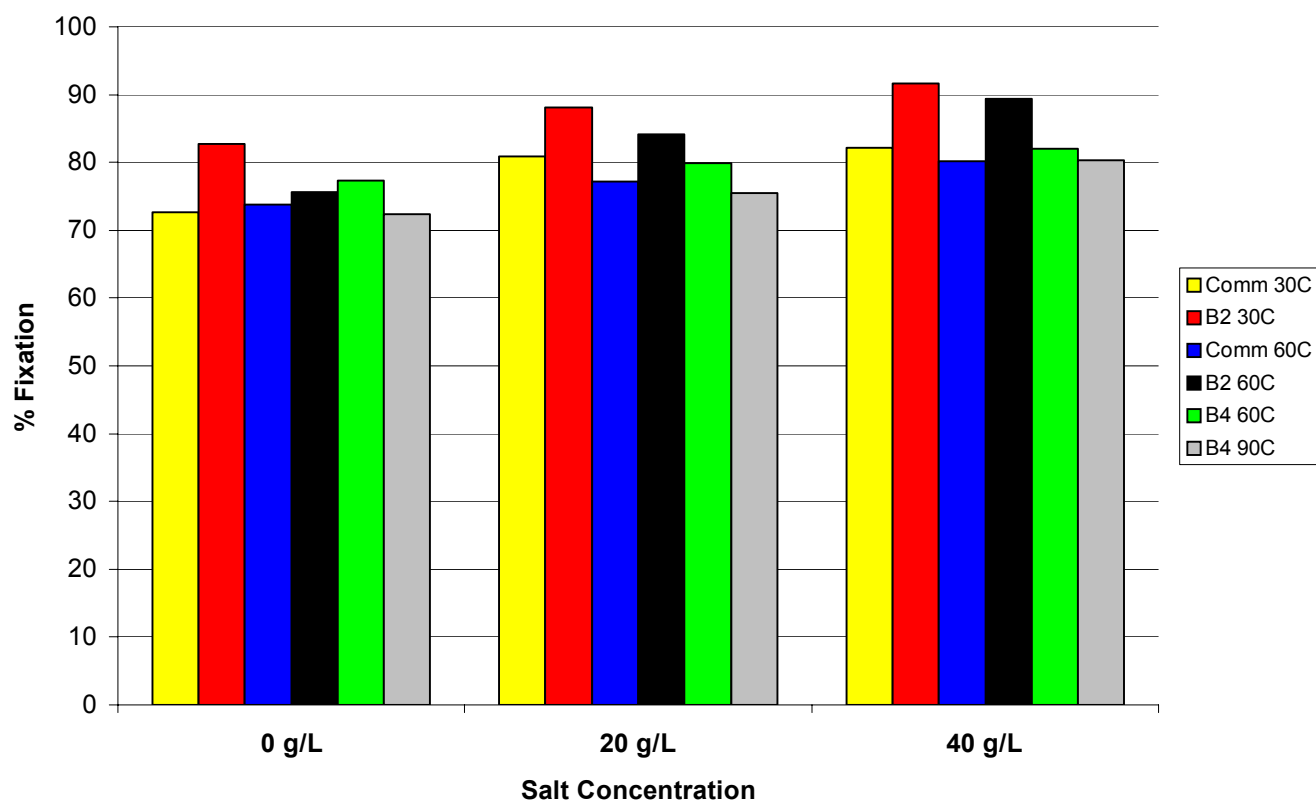
Figure 4.11    Percent fixation for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 blue dyes at different salt concentrations.
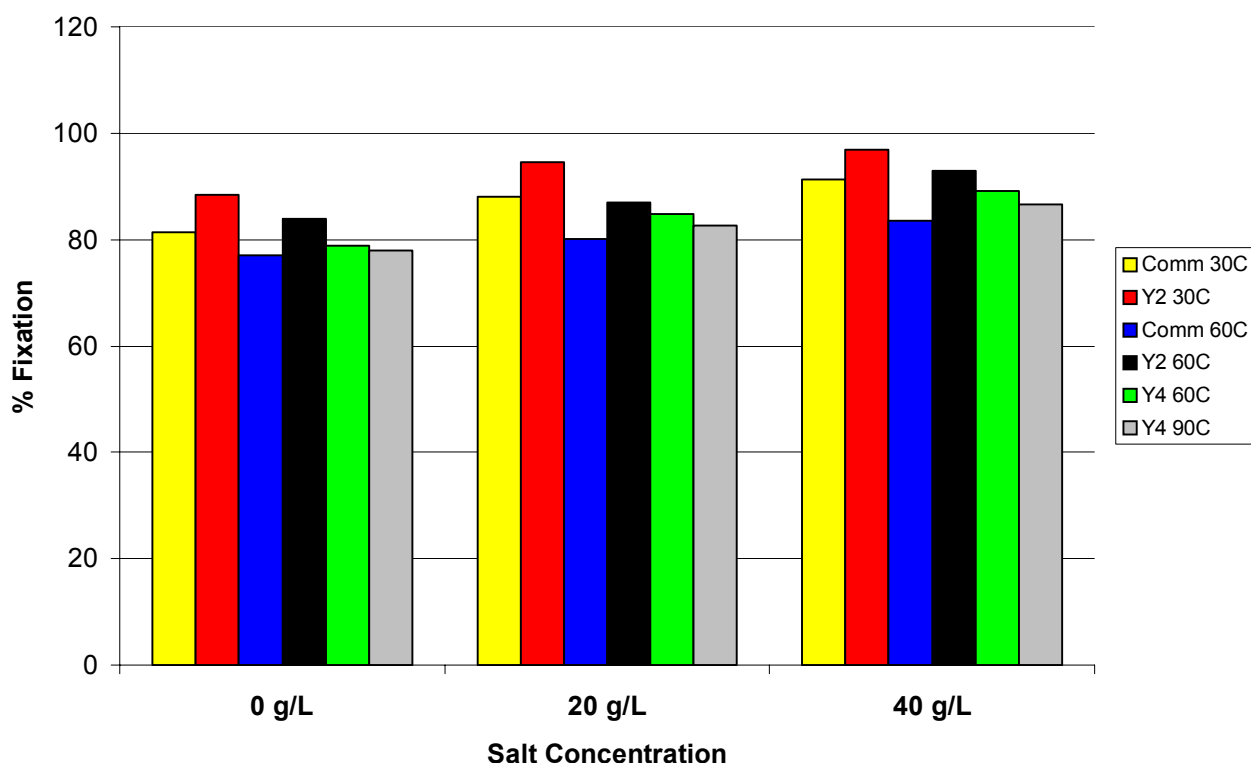
Figure 4.12    Percent fixation for laboratory dyeings at 0.25% for the commercial, type 2 and type 4 yellow dyes at different salt concentrations.

## *4.2     K/S Data*

Ideally, K/S values are linearly related to the concentration of dyes in a solid substrate.  Equation 4.1 can be applied to dyed substrates in which the scattering of light is due only to the substrate and not to dye concentration.

$$K/S = K_f/S_f + K_d/S_f[D]$$

where $K_f$ and $K_d$ are the light absorption coefficients for the fiber and the dye and $S_f$ is the scattering coefficient of the fiber.  The concentration of dye in the fiber is represented by [D] in the above equation (McDonald, 1997).

K/S data were recorded on dyed fabrics obtained from equilibrium exhaustion and laboratory dyeing experiments. The resulting K/S values were compared and used to validate the substantivity ratio values.

## 4.2.1 Equilibrium Exhaustion

K/S measurements were taken on 100% cotton crocking squares dyed with the Teegafix dyes.  The K/S values were consistent with the substantivity ratios that were reported in the previous section.  The highest K/S values were obtained from type 2 and type 4 dyes.  As expected, K/S values increased as salt concentration increased in the dyebath.   When the temperature of the dyebath increased there was also a decrease in the K/S values.  The K/S data were taken into consideration when determining which dyes would be used in the laboratory dyeing studies. Figure 4.13-4.15 provides the K/S values obtained from equilibrium exhaustion experiments.
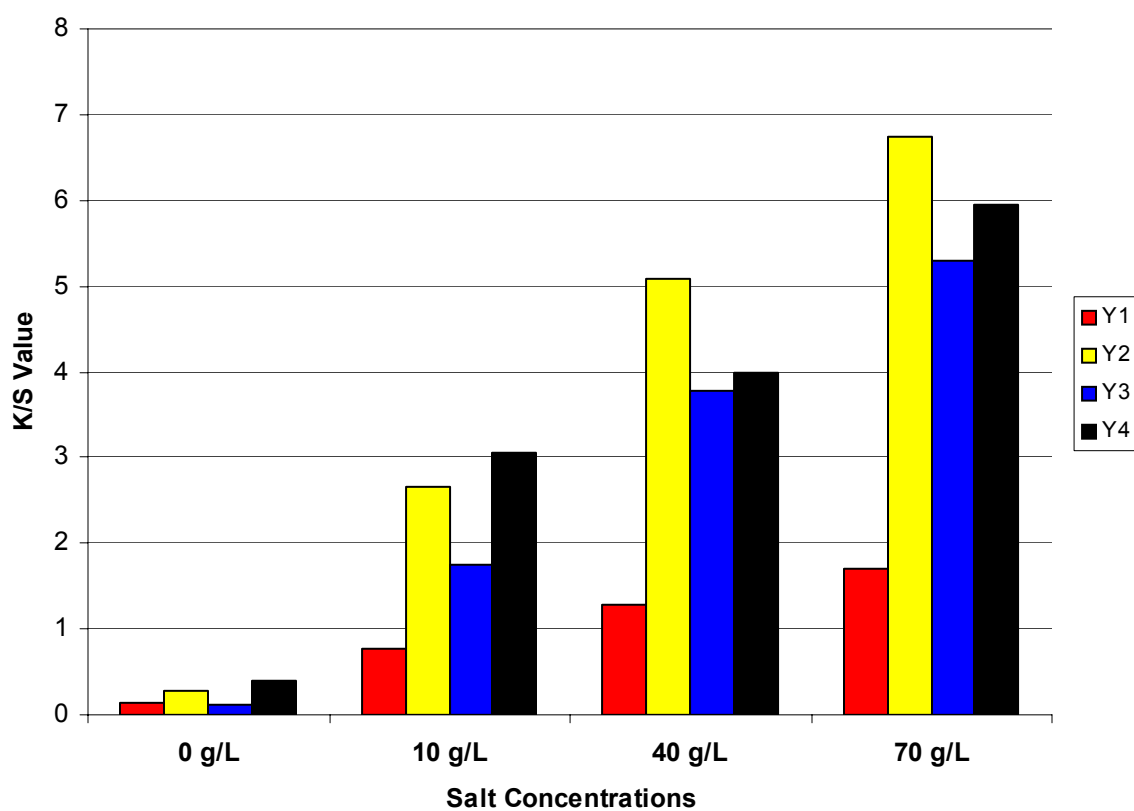
Figure 4.13   K/S values for exhaustion equilibrium of the Teegaifx yellow dyes at 30°C.
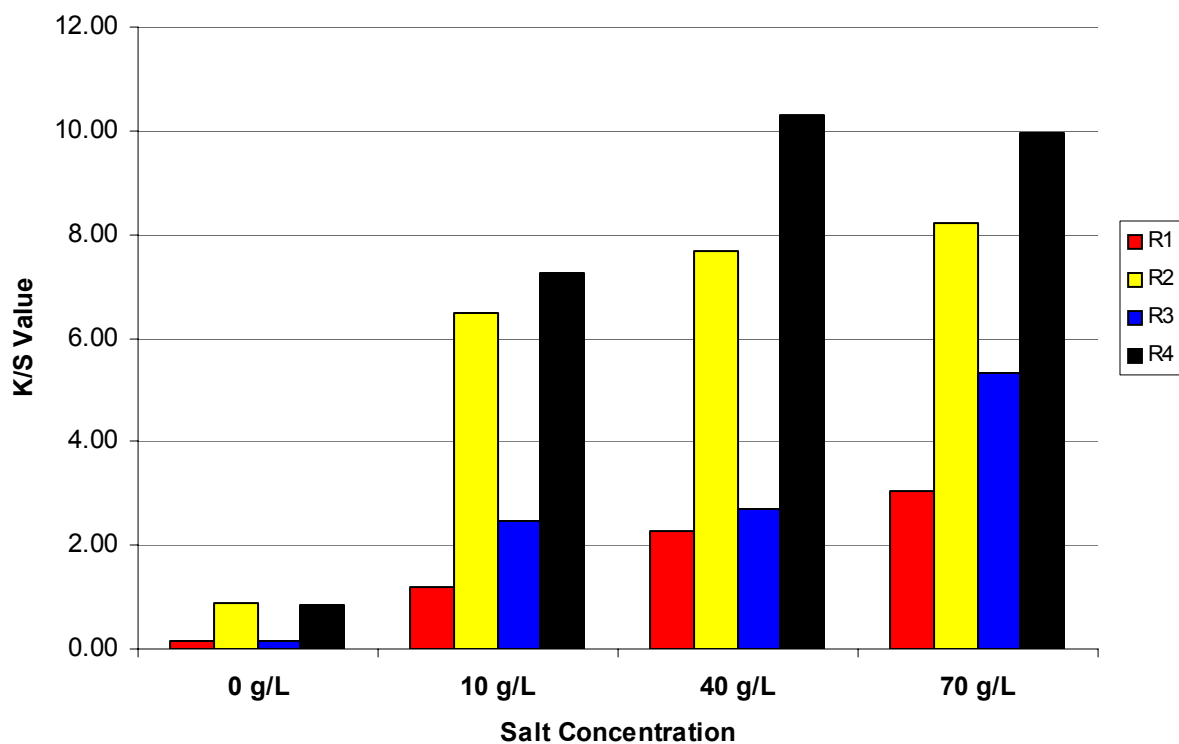
Figure 4.14   K/S values for exhaustion equilibrium of the Teegafix red dyes at 30°C.
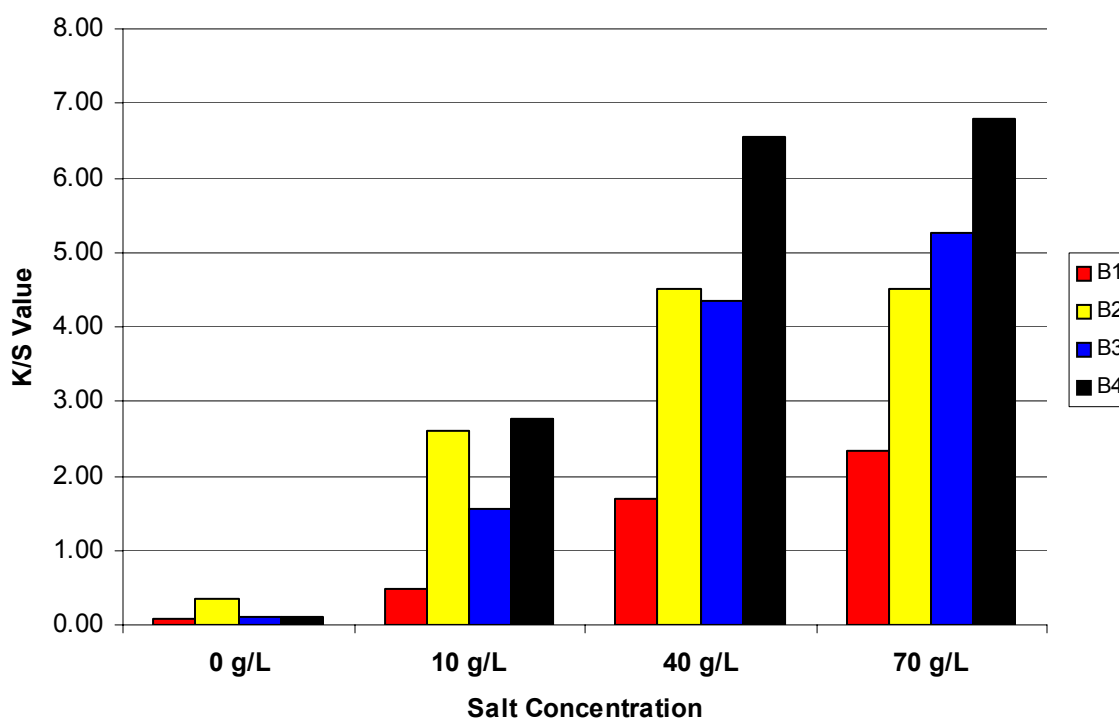
Figure 4.15   K/S values for exhaustion equilibrium of the Teegafix blue dyes at 30°C.

## 4.2.2 Laboratory Dyeings

K/S data were recorded on fabric samples from each of the laboratory dyeings.  Type 2 dyes gave the highest K/S values, which correlates with the trends observed with the $F_k$ values.  The highest K/S values were obtained at 40 g/L salt. The yellow and blue dyes gave the highest K/S values at 30°C and 1.00% dye (owf). The red dyes gave the highest K/S values at 60°C temperature and at the 1.00% dye (owf).  The red dyes also gave the highest values when compared to the other dye types and colors.  This was consistent with the results obtained in the

substantivity and affinity experiments.  K/S values from laboratory dyeings are

presented in Figures 4.16-4.18.
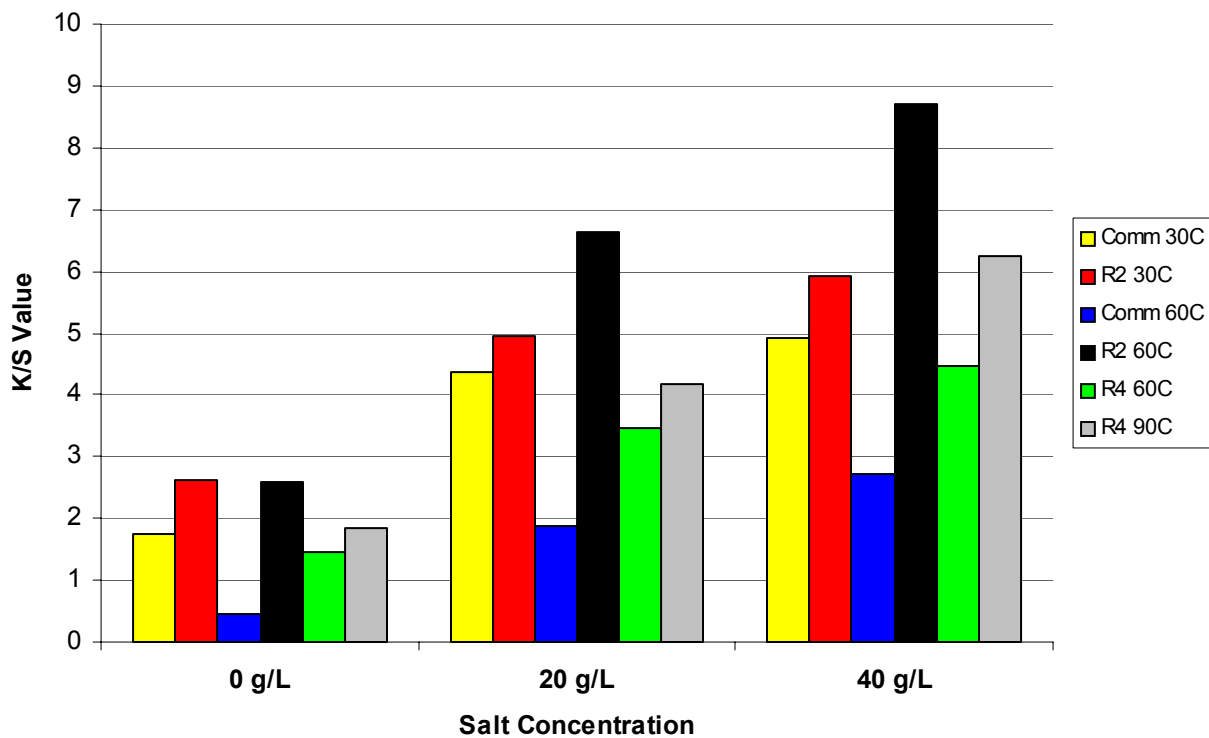


Figure 4.16   K/S values for the commercial, type 2 and type 4 red dyes at 1.00%
(owf) at  the seperate salt concentrations.
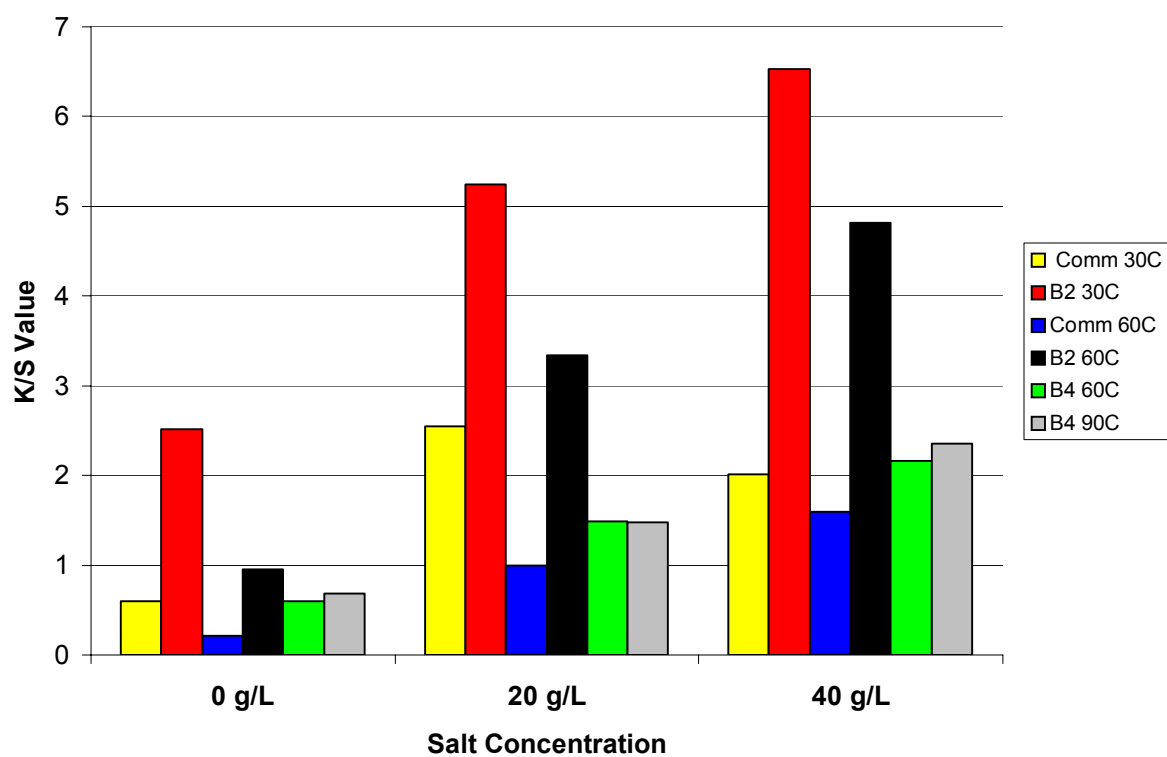
Figure 4.17    K/S values for commercial, type 2, and type 4 blue dyes at 1.00% (owf) at the separate salt concentrations.
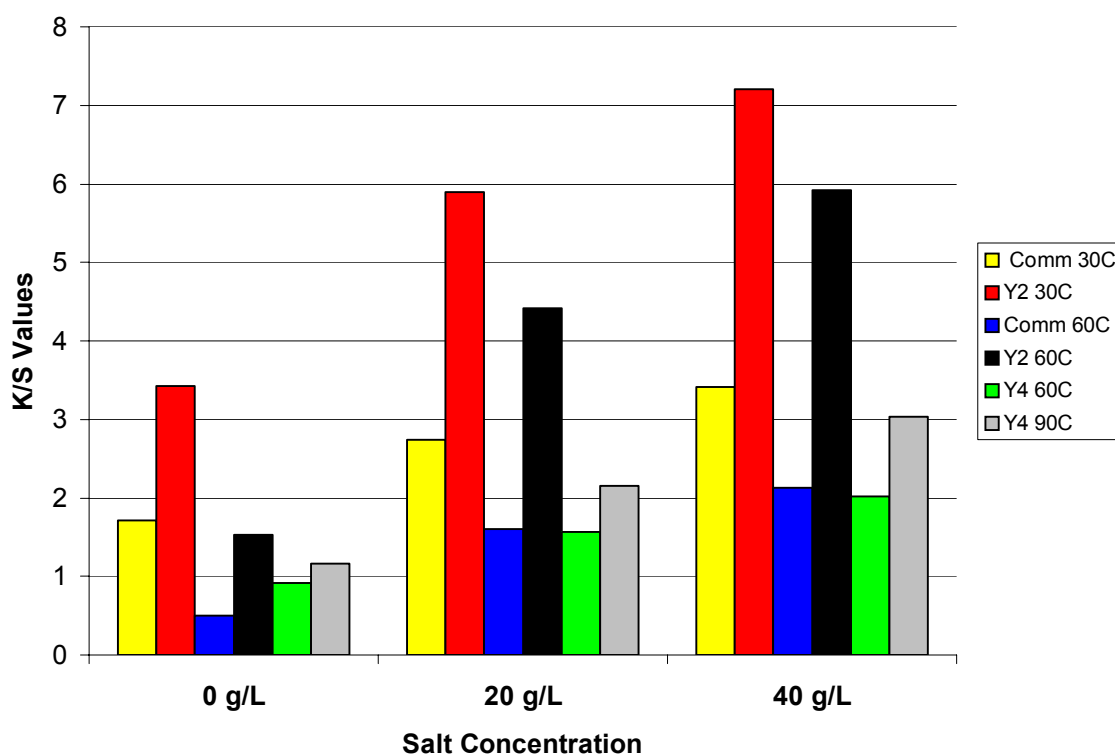
Figure 4.18   K/S values for commercial, type 2, and type 4 yellow dyes at 1.00% (owf) at the separate salt concentrations.

## *4.4      Apparent Standard Affinity and Heats of Dyeing*

The physical principles of the dyeing process are concerned with the influences of the temperature, pressure, concentration, and electrical potential on the chemical interactions between dye and fiber.  Knowing these principles and factors it is possible to determine the optimal dyeing process.  The dyes used in this study were compared in the equilibrium exhaustion experiments and evaluated as a function of substantivity ratio, apparent standard affinity, and heat of dyeing.  The percent fixation was calculated for the laboratory dyeings.

## 4.4.1 Equilibrium Exhaustion Experiments

The data that were collected from the equilibrium exhaustion experiments led to results for the substantivity ratio, apparent standard affinity, and the heats of dyeing.

The apparent standard affinity ($-\Delta\mu^\circ$) is a measurement of the tendency of the dye to move from the solution to the fiber. It can be defined as the difference of the standard chemical potentials of the dye in solution and in the fiber (Broadbent, 2001). Equation 4.2 was used to calculate the standard affinity for each of the equilibrium exhaustion dyeings:

$$-\Delta\mu^\circ = RT \ln (K)$$

where R ( $=8.3144$ J mol$^{-1}$ K$^{-1}$) is the gas constant, T is temperature in degrees Kelvin and K is the substantivity ratio. To obtain a high K value, the standard chemical potential in solution must be greater than in the fiber. When K>1, the value for the standard affinity ($-\Delta\mu^\circ$) will be positive (Broadbent, 2001).

The standard affinity values for various dyes were determined for two different temperatures and the four salt concentrations. Figures 4.19-4.22 show the standard affinity values obtained at the lower temperature and the different salt concentrations.
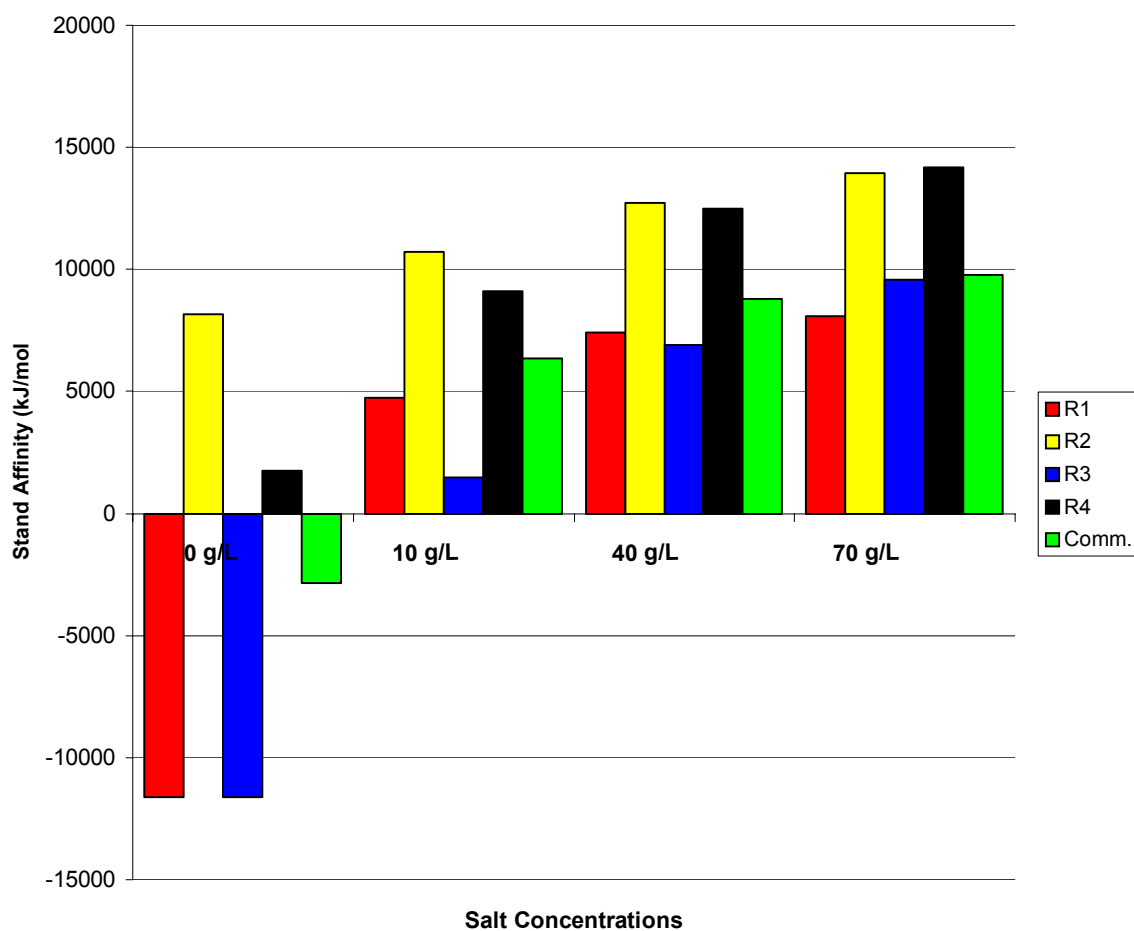
Figure 4.19    Apparent standard affinities for the five red dyes in equilibrium
exhaustion experiments at 30°C.
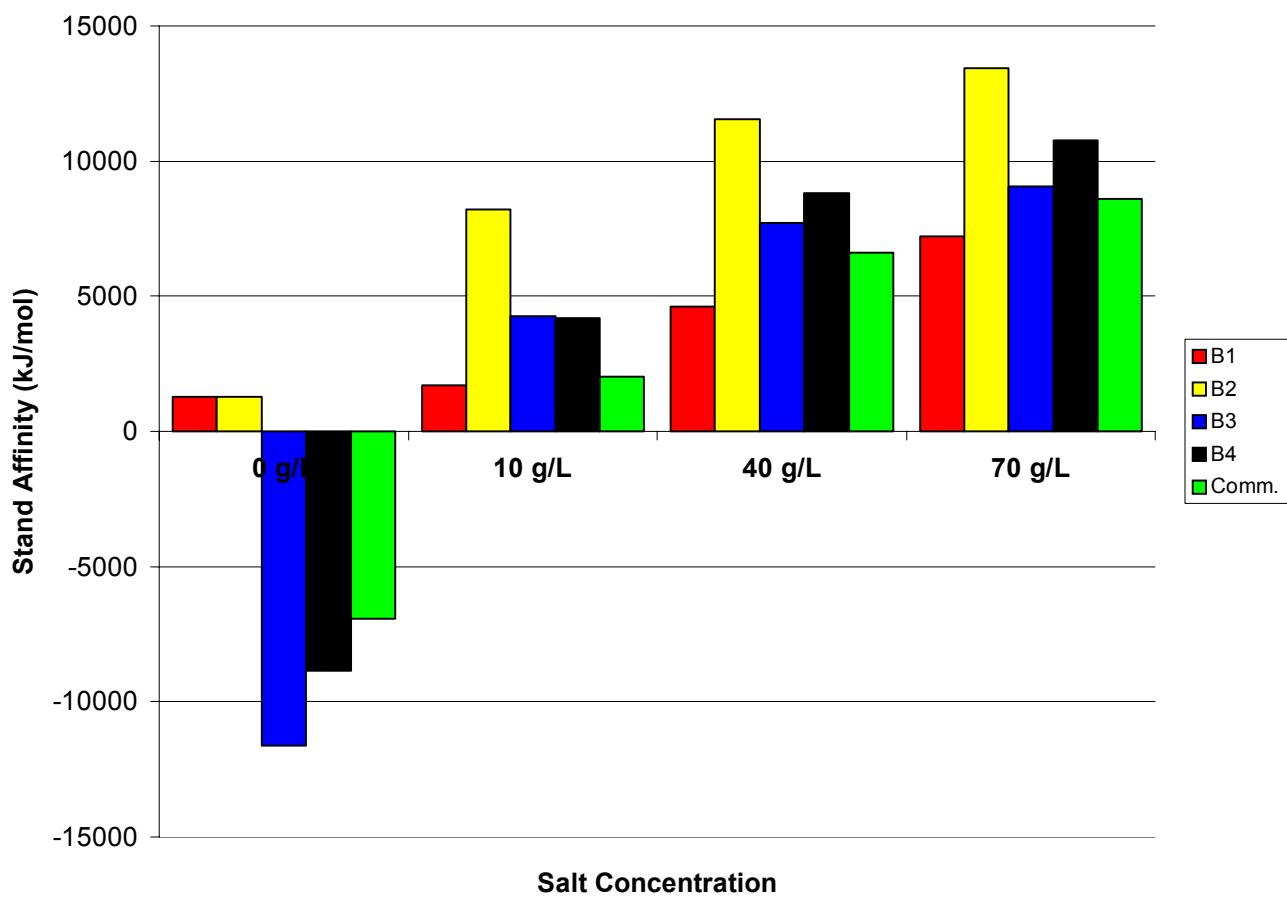
Figure 4.20    Apparent standard affinities for the five blue dyes in equilibrium exhaustion experiments.
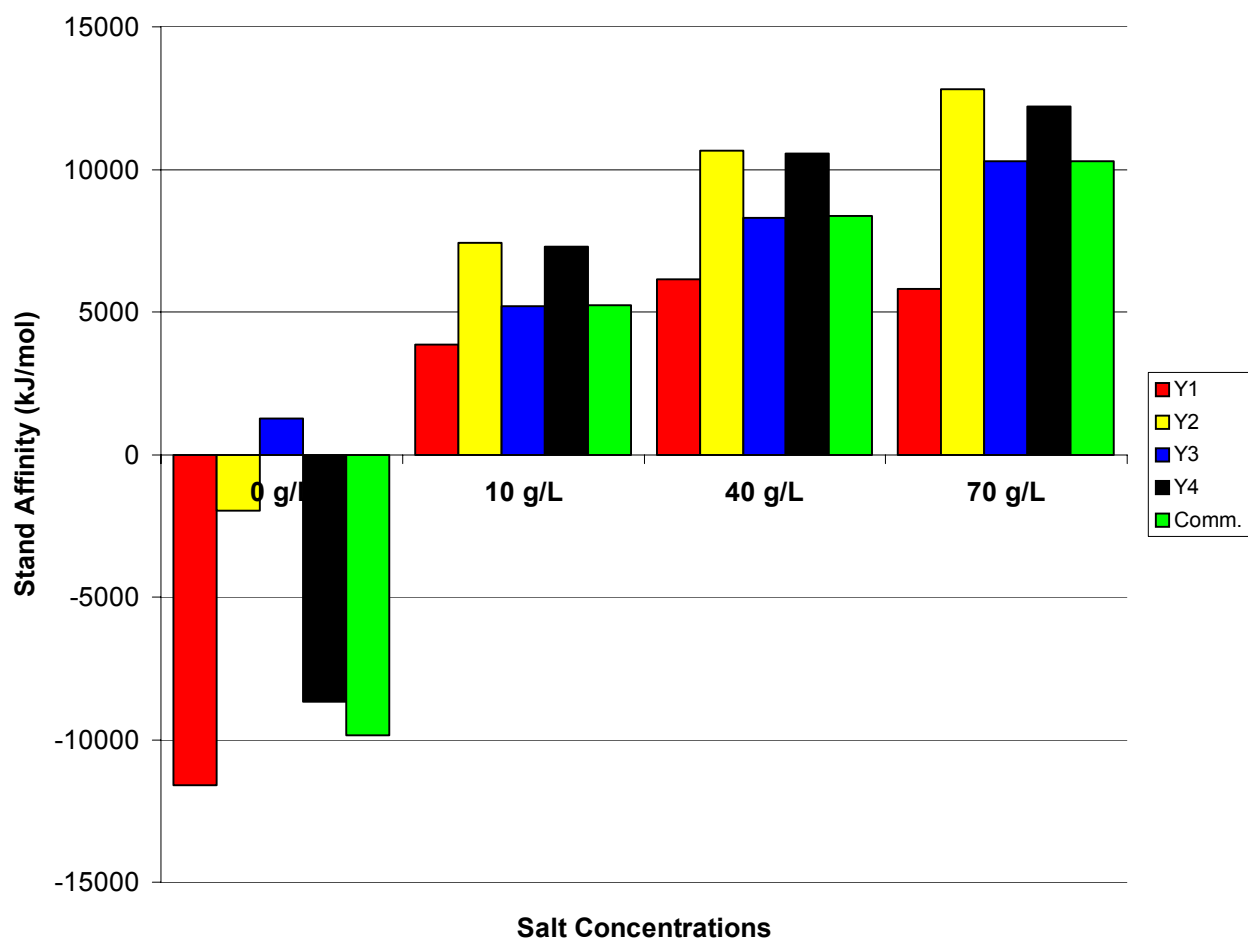
Figure 4.21    Apparent standard affinities for the five yellow dyes in equilibrium exhaustion experiments.

The results indicate that increased salt concentrations resulted in increased affinity of the dye for the fiber.  However, the effect of the salt at 90°C was much less than at 30°C.  The increase in the affinity and K values was much greater as the salt concentrations were increased at 30°C but at 90°C the increase in salt concentrations did not have the same effect on affinity.  This trend was seen with all of the dyes.

When cotton is placed in pure water it develops a negative zeta potential, which can repel a dye anion and thus decreasing dye exhaustion due to like-charge repulsion at the fiber surface.  The negative charge (negative zeta potential) at the fiber/water interface is due to hydrogen bonding that occurs between the fiber and the water (Cook, 1994).  The addition of salt or electrolyte to the dyebath increases the ionic strength and reduces the surface potential.  Reducing the surface potential or zeta potential by the addition of salt to the dyebath increases the exhaustion of the dye into the fiber (Johnson, 1989).

Reduction of the zeta potential is only a minor reason for the addition of salt to the dyebath.  This is evident from the amounts of salt required to achieve higher levels of exhaustion (Johnson, 1989).  Results from the present exhaustion experiments in (Figure 4.4-4.6) show that the higher salt concentrations gave higher dye exhaustion, although only low levels are needed to offset the zeta potential of the fiber.  This indicates that with reactive dyes the most effective salt concentrations used in dyeing are much higher than the amounts required to offset the negative zeta potential.  Therefore, it is believed that the presence of salt in the dyebath not only reduces the zeta potential, but also disrupts H-bonds between water molecules to facilitate dye-fiber interactions.

The idea that salt acts as a disruptor is supported by the present results from exhaustion equilibrium experiments.  At the lower temperature, 30°C, the salt is more effective because the water has higher level of hydrogen bonding.  At the higher temperature, 90°C, salt has a smaller effect because the water has a much lower level of extent of hydrogen bonding.

The role of temperature in the equilibrium exhaustion experiments can be examined by evaluating the heat of dyeing. The standard heat of dyeing (or change in enthalpy), $\Delta H°$, is a thermodynamic quantity that is important when trying to describe the dyeing process. It provides a convenient description of the temperature sensitivity of the dye equilibrium. Most dyeing processes are exothermic, as the value of the heat of dyeing is negative (-$\Delta H$). Therefore, raising the temperature causes less dye to be absorbed by the fiber (Johnson, 1989).

The dyeing process is exothermic ($\Delta H° < 0$) because of the release of energy when the dye binds to the dye site in the fiber. However, during the dyeing process there are additional steps that absorb heat, or are endothermic. These steps include the removal of the water of hydration from both the dye and dye sites in the fiber. For the standard heat of dyeing to be negative, the release of energy when dye binds to a dye site must be greater than the amount required to remove water from the dye ion and dye site.

The standard heat of dyeing was investigated for the equilibrium exhaustion experiments to determine the role of temperature in the exhaustion of the dye on the fiber. When examining the standard heat of dyeing values located in the Appendix A, it was determined that the experiments conducted at the lower salt concentrations were not exothermic reactions endothermic rather than exothermic. However, the heats of dyeing for experiments conducted at the higher salt concentration levels (40 g/L and 70 g/L) were exothermic. The presence of salt in the dyebath helps in the dehydration of both dye sites in the fiber and dye molecules by disrupting the hydrogen bonds to the water, making dye-fiber interactions more exothermic. When

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salt is not present in the dyebath the heat required to dehydrate the dye and fiber is much higher than the heat released from binding the dye to the fiber.

At higher salt concentrations the different dye types had decreased affinity as the dyeing temperature was increased. These decreases were seen in the heats of dyeing at the highest salt concentration (70 g/L). The plot of ln(K) as a function of $1/T$ had a slope of $-\Delta H^\circ/R$. These results showed that the heats of dyeing or enthalpy were negative and the dyeings process was exothermic. Therefore, when the temperature was increased during these dyeings, the affinity of the dyes decreased.
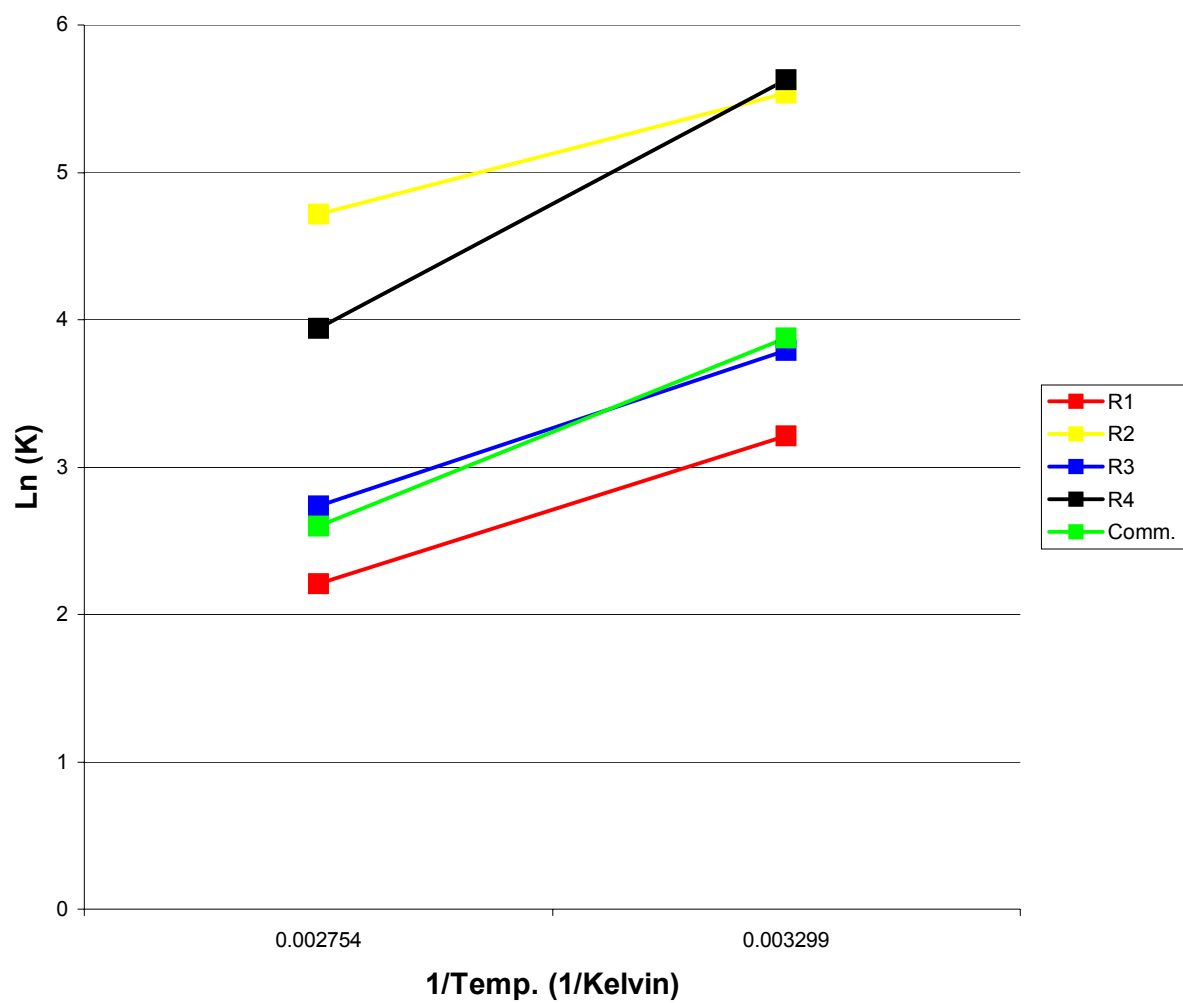
Figure 4.22 Temperature dependence of equilibrium constant for the five red dyes.
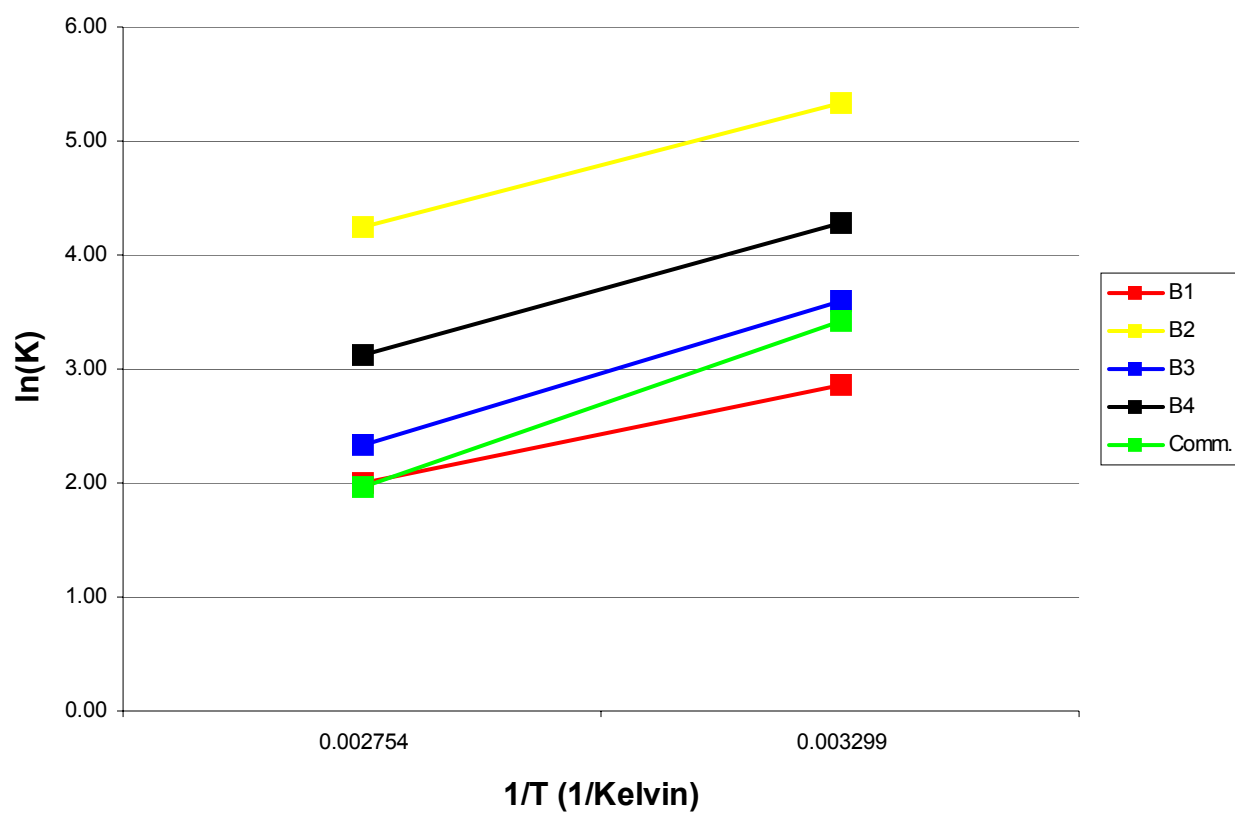
Figure 4.23   Temperature dependence of equilibrium constant for the five blue dyes.
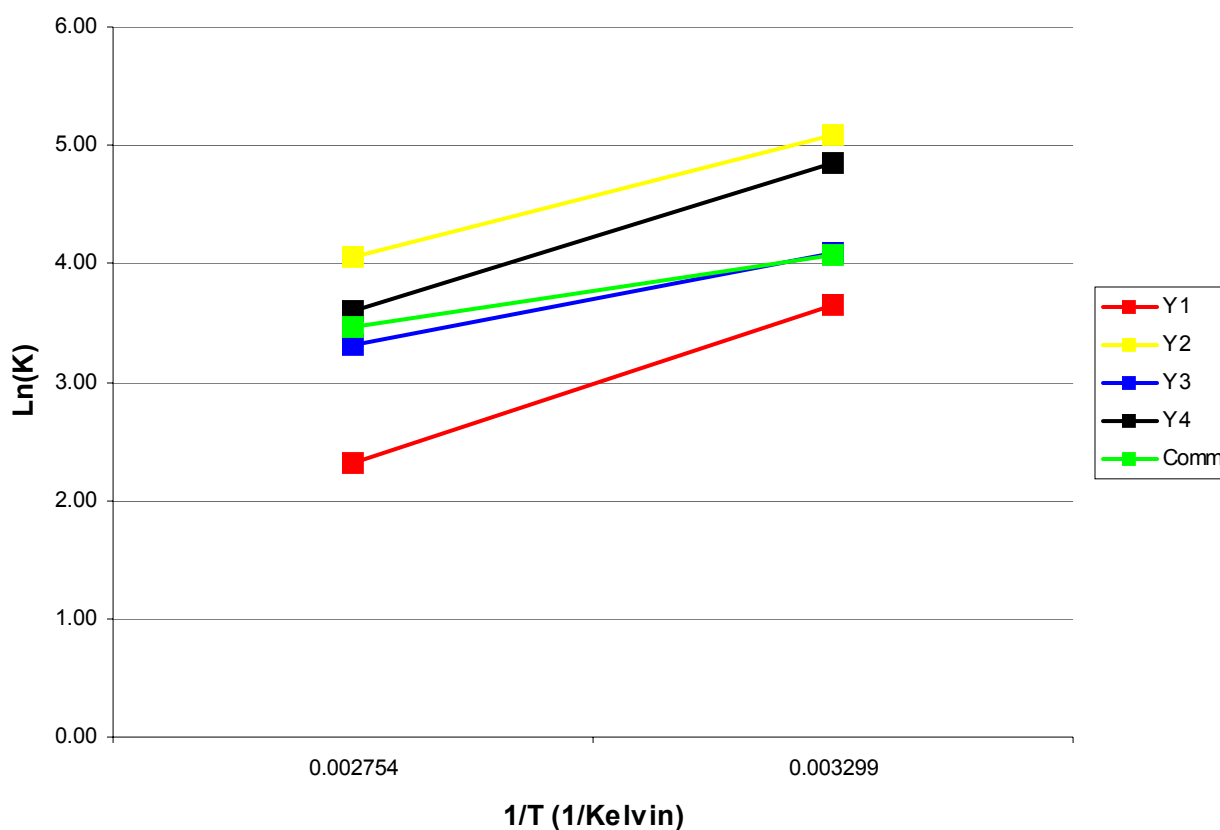
Figure 4.24   Temperature dependence of equilibrium constant for the five yellow dyes.

When examining the different dyeing conditions and dye structures it was apparent that the type 2 and type 4 dyes exhausted at a much higher level than the commercial dyes.  Both types appeared to exhaust well at different salt concentrations and temperature levels employed. Both types also had higher affinity values than the commercial dyes and this increase caused exhaustion to increase.

## 4.4.2  Laboratory Dyeings

Laboratory dyeings were conducted on a time-limited basis with the addition of alkali.  Therefore, dyebath exhaustion was not at equilibrium unlike the exhaustion equilibrium experiments.  This means that neither the standard affinity values nor the heats of dyeing are appropriate to characterize the laboratory dyeings.  Instead, these dyeings were evaluated based on the fixation ratios and the percent fixation values.

Substantivity and fixation ratios play a key role in the fixation efficiency of fiber reactive dyes on cellulosic fibers.  The following equation indicates that the ratio, $c^f / c^s$, must be increased to increase the fixation efficiency.

$$\text{Fixation Efficiency} = [c^f / c^s]\ S/L\ \sqrt{[D/k'_H\ R_F\ ([CellO\text{-}]/ [OH\text{-}])}$$

S represents the surface factor for the fiber, which includes the shape and the surface to volume ratio of the fiber.   This variable is a function of the fiber used during the dyeing process.  L represents the bath ratio and is dependent on the application conditions.  The ratio of the reactions of the dye with the fiber ($k_F$) and the dye with water ($k_H$) is represented by the variable $R_F$, which is dependent on the dye structure.  Generally, the value for $R_F$ is 1.0 if the pH is in the normal fixation range (pH 9.5-11).  D is the diffusion coefficient and is a property of the dye structure.  The diffusion of dye into the fiber depends on the size and affinity of the dye molecule.  The variable, $[CellO\text{-}]/ [OH\text{-}]$ is the a ratio of the concentration of ionized cellulose and the concentration of hydroxide ions.  It is approximately equal

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to 30 but depends on the pH of the application process.  The k'$_H$ variable is the rate of dye hydrolysis, which depends on dye structure rather than the fiber (Preston, 1986).

The ratio, c$^f$ / c$^s$ (K), is one of the main parameters that can be affected by the structure of the dye.  Increasing the ratio by modification of the dye structure results in an increase in fixation efficiency.  This increase is one of the variables that can be controlled in the equation to gain better fixation efficiency.  This ratio has a large impact on fixation efficiency and was the main measure for assessing the performance of dyes used in the laboratory dyeing experiments.

Results from laboratory dyeings showed that the higher salt concentrations increased the fixation ratio. Also the higher temperatures tended to decrease the fixation ratio and percent fixation was lower than in the case of lower temperature dyeings.  There was an increase in percent fixation for the modified dye types when compared to the commercial dye structures.  The increase in fixation ratios for the type 2 and type 4 dyes structures indicated that the fixation efficiency for these dye types was increased when compared to the commercial dye types.


## 4.5      Structures and Reactivity

The structure of the dye molecule plays an important role in the affinity of the dye for the fiber.  Dye structures that are more planar tend to have higher affinity for the cellulosic fibers (Johnson, 1989).  The basis for increase affinity can be seen when comparing the type 1 and 3 structures to the type 2 and 4 structures.  The dye structures that have only protons (types 2 and 4) located on the –CH– the bridging

moiety are more planar than those containing the carboxyl groups (types 1 and 3) in that location.  This can be seen when looking at the molecular geometry of the optimized forms of the yellow dye structures (Figure 4.25-4.28) in the gas phase.
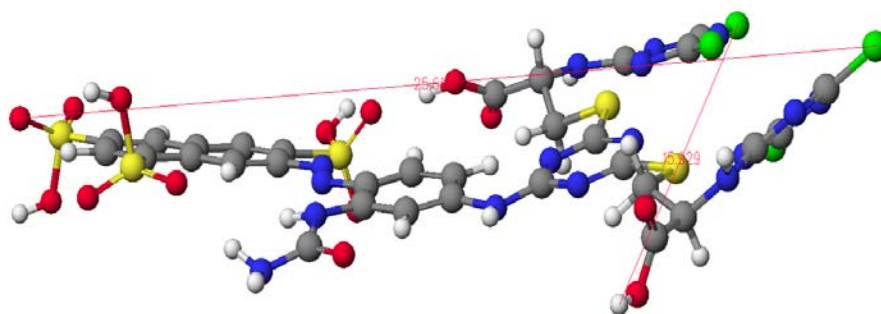


Figure 4.25   Type 1 Yellow Dye Structure
(Horizontal Axis = 25.619 Å Vertical Axis = 15.929 Å)
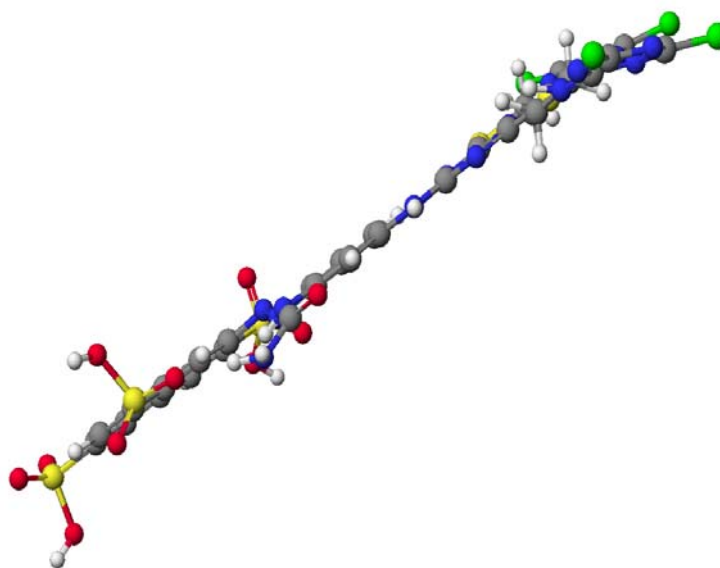


Figure 4.26    Type 2 Yellow Dye Structure
(Horizontal Axis = 26.661 Å Vertical Axis = 20.655 Å)

It is apparent that carboxyl group that is located on the bridging group on the type 1 structure has an adverse effect on planarity.  The type 2 structures have both triazine rings and the rest of the structure coplanar in nature.  Whereas, the type 1 structure shows that the triazine rings are not coplanar.
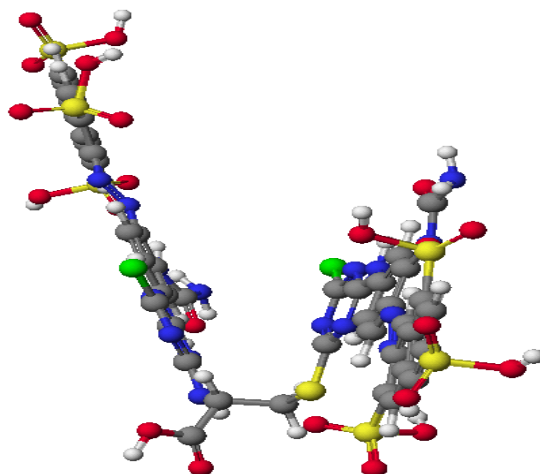
Figure 4.27: Type 3 Yellow Dye Structure
(Horizontal Axis = 37.059 Å)
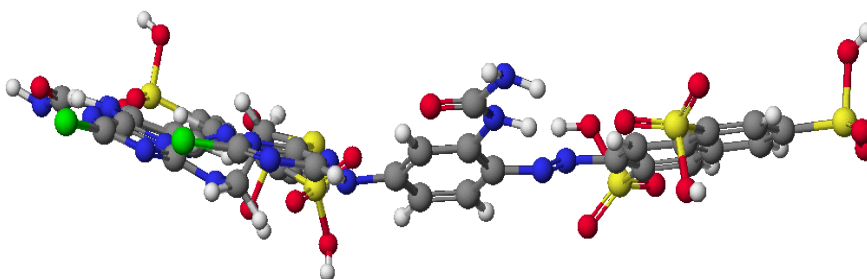


Figure 4.28: Type 4 Yellow Dye Structure
(Horizontal Axis = 31.601 Å)

The addition of a carboxyl group on the type 3 yellow dye structure shows the effects

on the geometry of the molecule.  In the type 3 structure shows that the two halves

of the molecule lie in different planes.  The type 4 structure is much more planar

than the type 3 structure.  When comparing all four types it is evident that the type 2

structure has a much higher degree of planarity.  Therefore, it would be expected

that the type 2 structure would have a much higher affinity for the fiber.  The same

results were found when examining the type 1 and 2 structures for the red and blue dyes (El-Shafei, 2005).

The presence of water solubilizing groups on the dye structures could also affect dye affinity.  The presence of an additional carboxyl group on the dye structures would increase the solubility of the dye in water.  With this in mind, type 1 and 3 structures should have higher water solubility than type 2 and 4 structures. This was apparent when preparing the dye solutions, as type 2 and 4 structures required more time to dissolve than the other two types of dye structures.  The increase in the water solubility of the type 1 and 3 dye structures could cause the dye to remain in the dyebath rather than exhaust onto the fiber.  This would increase the amount of dye in the solution, and decrease the percent exhaustion.

The reactivity of type 1 and type 2 dyes was much higher than the type 3 and type 4 dyes.  The two dichlorotriazine structures located on the type 1 and 2 structures are reactive towards the fiber at room temperature in the presence of sodium carbonate.  The second chlorine atom located on the ring structure enhances activation of the ring to nucleophilic substitution.  It is well known that the monochlorotriazines require much higher temperatures and stronger alkali to react with cellulose (Broadbent, 2001).

## *4.6 Physical Testing*

The following types of physical testing were conducted in samples from the

laboratory dyeings:

1. Color Fastness to Light - AATCC Test Method 16-1998

2. Color Fastness to Water - AATCC Test Method 107-1997

3. Color Fastness to Crocking - AATCC Test Method 8-1996

### 4.6.1 Color Fastness to Light

The color fastness to light testing was completed on fabrics obtained from the

laboratory dyeings utilizing the commercial, type 2 and type 4 dyes.  The physical

testing was conducted for 20 and 40 h and the resultant fabrics were evaluated both

visually and instrumentally.  Results from the instrumental readings suggested that

for the majority of the color fastness tests, type 2 dyes outperformed both the

commercial and the type 4 dyes.  This was evident from data from the red, blue and

yellow dyes.  Comparison of the color change for different dyes show that the yellow

dyes were affected the least. Red dyes showed the most significant color change.

The $\Delta E$ values for the red dyes averaged 2.79 after 20 h of exposure and 4.82 after

40 h of exposure. Yellow dyes $\Delta E$ values averaged 1.12 after 20 h of exposure and

1.81 after 40 h of exposure.  From the light fastness tests it was determined that

there were no significant differences or trends in the color fastness to light of the

modified dye types.  These results can be seen in the tables and graphs in the

Appendix C.

### 4.6.2  Color Fastness to Water

Color fastness to water was conducted on all of the samples from laboratory dyeings.  The tests were conducted with multifiber test fabric.  The multifiber fabric was composed of acetate, cotton, nylon, polyester, Dacron, and wool. There was a slight color change seen on most of the fibers in the multifiber fabrics.  The nylon fiber strips experienced the largest color change. The multifiber fabrics were compared for all of the samples to assess the color fastness to water.  There were no apparent trends in the results obtained from these tests.  The gray scale values for the dyes ranged from a 4.5 – 2.5 for the multifiber fabrics.  The average gray scale values for the red dyes on the multifiber fabrics were 4.1 for the commercial dye, 3.8 for the type 2 dye, and 3.4 for the type 4 dye.  The average gray scale values for the blue dyes were 3.7 for the commercial dye, 3.6 for the type 2 dye, and 3.1 for the type 4 dye.  The yellow dyes had average gray scale values of 4.3 for the commercial dye, 3.9 for the type 2 dye, and 3.7 for the type 4 dyes.  These results suggest that were no significant differences between the performance of the commercial dyes and the type 2 dyes.  The type 4 dyes typically did not perform as well as either the commercial or type 2 dyes.  The specific results from wet fastness testing are found in the Appendix C as tables and graphs.

### 4.6.3  Color Fastness to Crocking

Crockfastness testing was conducted on each of the samples from laboratory dyeings. Both wet and dry crocking tests were completed on the fabric samples. Most of the gray scale values obtained were between 4 and 5, with a few ratings

being lower.  Examining the crocking test results showed no apparent trends based on dye type or color.  Tables and graphs with the crock fastness data are located in the Appendix C.

# 5. Conclusions

The dye application and fastness properties of chlorotriazine Teegafix dyes based on yellow, red, and blue chromogens were evaluated in this study.  Based on results from equilibrium exhaustion experiments it is evident that the type 2 and type 4 Teegafix dyes employing cysteamine as the bridging group had appreciably higher affinity for cotton than either the corresponding commercial dyes or the type 1 and type 3 Teegafix dyes derived from cysteine.  When comparing the four types of dyes, the key difference is the presence of a carboxyl group in the bridging moiety of the dyes derived from cysteine.

The different chromogens used in the synthesis of the Teegafix dyes affected the affinity of the dyes for cotton.  The Teegafix red dyes had greater affinity for cotton than the Teegafix blue and yellow dyes.  Among the commercial dyes, the yellow dye generally had higher affinity than the blue and red dyes.  However, the commercial red dye had higher affinity in the absence of salt at the lower temperature employed.  The molecular size of the dyes was dependant mostly on the number of chromogens on the dye structure.  Dye types 1 and 2 had one chromogen while types 3 and 4 had two chromogens located on the dye.  When comparing the affinity of type 1 and type 3 dyes, the larger type 3 dyes tended to have higher affinity for cotton.  However, when evaluating the affinity of the type 2 and type 4 dyes the smaller type 2 dyes tend to have a higher affinity.

The equilibrium exhaustion and laboratory dyeing studies were used to evaluate the affinity of the dyes at different temperatures and salt concentrations.

The lower dyeing temperatures increase the affinity of the commercial and the Teegafix dyes, while the higher temperatures decrease dye affinity. Affinity also increased when the commercial and Teegafix dyes were applied at higher salt concentrations.

In laboratory dyeing studies, the effects of temperature, salt and alkali on the application of type 2 and type 4 Teegafix dyes to cotton were assessed. It can be concluded that the type 2 dyes, which have one chromogen and two dichlorotriazine groups, have higher affinity for cotton than the bis-monochlorotriazine-based Teegafix dyes. A key advantage associated with the Type 2 dyes is that they are more reactive at lower temperatures. Also, the salt concentration required to achieve the highest fixation ratios for the laboratory dyeing was 40 g/L, which is lower than the suggested concentration for the commercial dyes used.

With the aid of results from molecular modeling studies it was shown that the Teegafix dyes having higher affinity for the cotton fiber also had more planar structures. In this regard, structures having a carboxyl group on the bridging group were non-planar and had lower fiber affinity. The fastness properties of the dyed fabrics suggest that the Teegafix dyes are comparable to the commercial dichlorotriazine reactive dyes. This was the case for light-, wet-, and crock fastness.

The results of this study suggest that the conversion of the commercially available dichlorotriazine reactive dyes to the corresponding Teegafix dyes is advantageous and merits further study that would lead to commercialization. In this regard, the properties of Teegafix forms of heterofunctional bireactive dyes should be investigated.

# 6. Recommendations for Future Work

This research focused on the development of an optimal dye application process for a series of new homobifunctional fiber reactive dyes.  The results indicated that the type 2 modified dyes had greater in affinity for cotton than the corresponding commercial fiber reactive dyes.  Further work in this area should focus on dyeings utilizing the type 2 dyes on production scale dyeing equipment. With the large scale dyeing it would be possible to re-evaluate the physical properties, after conducting on a more uniform washing procedure.

To determine the exact role of water solubility in the increased affinity of the type 2 and type 4 dyes it would be interesting to replace the existing hydrogen atoms located on the bridging group with a methyl group or some other bulky side group. The addition of a methyl or bulky group would result in the same non-planar structure as the carboxyl group, but would not affect the water solubility of the structure.  By determining the affinity of the resultant structures, the effect of water solubility could be clarified.

The reactivity of the dye structures also needs to be investigated in further detail.  This research focused on the affinity of the dye for the fiber mainly. However, the role of reactivity would be useful in the analysis of the efficiency of fixation.  Conducting a series of experiments that evaluate the reactivity of the type 2 and type 4 structures would be beneficial to the large-scale optimal dye application process.

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# Appendix A
# Exhaustion Equilibrium Experiments

Table A1      Red dyes: Concentration of dye in the solution (g/L) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| R1 | 0.240 | 0.215 | 0.169 | 0.154 | 0.244 | 0.231 | 0.216 | 0.204 |
| R2 | 0.152 | 0.090 | 0.051 | 0.034 | 0.235 | 0.166 | 0.102 | 0.066 |
| R3 | 0.240 | 0.239 | 0.180 | 0.118 | 0.240 | 0.240 | 0.230 | 0.180 |
| R4 | 0.238 | 0.130 | 0.550 | 0.031 | 0.250 | 0.164 | 0.137 | 0.109 |
| Comm. | 0.248 | 0.190 | 0.137 | 0.113 | 0.249 | 0.246 | 0.213 | 0.187 |

Table A2      Red dyes: Concentration of dye in the fiber (g/kg) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| R1 | 0.01 | 1.40 | 3.22 | 3.84 | 0.24 | 0.77 | 1.35 | 1.85 |
| R2 | 3.91 | 6.38 | 7.97 | 8.64 | 0.59 | 3.38 | 5.93 | 7.37 |
| R3 | 0.01 | 0.43 | 2.79 | 5.26 | 0.01 | 0.01 | 2.79 | 5.26 |
| R4 | 0.48 | 4.81 | 7.80 | 8.74 | 0.02 | 3.33 | 4.52 | 5.63 |
| Comm. | 0.08 | 2.38 | 4.52 | 5.47 | 0.01 | 0.17 | 1.48 | 2.51 |

Table A3      Percent exhaustion for red dyes at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| R1 | 0.00 | 14.00 | 32.20 | 38.40 | 2.40 | 7.70 | 13.50 | 18.50 |
| R2 | 39.10 | 63.80 | 79.60 | 86.40 | 5.90 | 33.80 | 59.30 | 73.70 |
| R3 | 0.00 | 4.30 | 27.90 | 52.60 | 0.10 | 0.10 | 7.90 | 27.90 |
| R4 | 4.80 | 48.00 | 78.00 | 87.40 | 0.20 | 33.30 | 45.20 | 56.30 |
| Comm. | 0.80 | 23.80 | 45.20 | 54.70 | 0.10 | 1.70 | 14.80 | 25.10 |

Table A4    Standard affinity value for red dyes at different temperatures and salt concentrations.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| R1 | -11608 | 4726 | 7424 | 8101 | -103 | 3032 | 4607 | 5561 |
| R2 | 8178 | 10727 | 12737 | 13958 | 2310 | 7601 | 10251 | 11895 |
| R3 | -11608 | 1496 | 6905 | 9561 | -11608 | -9861 | 3107 | 6902 |
| R4 | 1772 | 9102 | 12486 | 14185 | -7091 | 7551 | 8813 | 9934 |
| Comm. | -2856 | 6366 | 8808 | 9777 | -8113 | -863 | 4887 | 6545 |

Table A5    Heats of dyeing for red dyes at the different salt concentrations.

| Dye | 0 g/L | 10 g/L | 40 g/L | 70 g/L |
|---|---|---|---|---|
| R1 | 127.764 | -18.808 | -31.287 | -28.215 |
| R2 | -65.172 | -34.72 | -27.614 | -22.915 |
| R3 | 0 | -126.11 | -42.183 | -29.531 |
| R4 | -98.433 | -17.22 | -40.787 | -47.218 |
| Comm. | -58.382 | -80.282 | -43.545 | -35.889 |
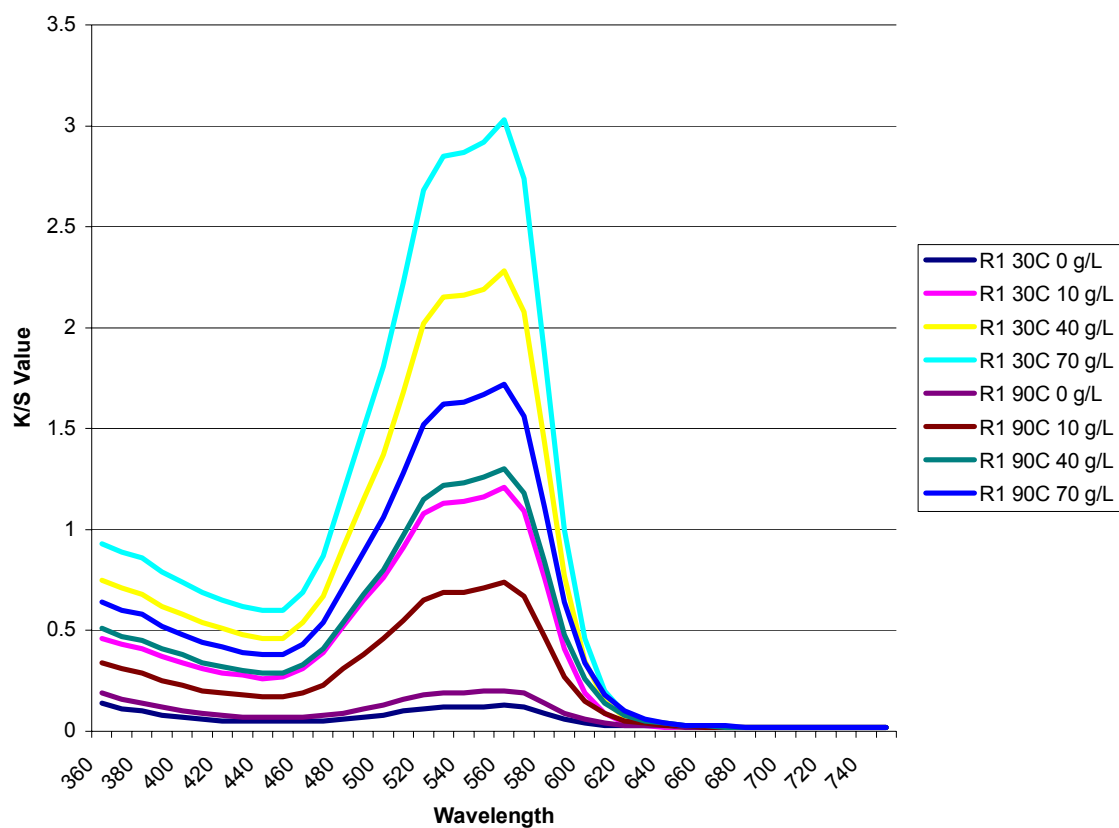
Figure A1    K/S values for equilibrium experiments involving type 1 red dye.

Figure A2    K/S values for equilibrium experiments involving type 2 red dye.

Figure A3    K/S values for equilibrium experiments involving type 3 red dye.

Figure A4    K/S values for equilibrium experiments involving type 4 red dye.

Table A6    Blue dyes: Concentration of dye in the solution (g/L) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| B1 | 0.240 | 0.238 | 0.216 | 0.174 | 0.229 | 0.216 | 0.223 | 0.211 |
| B2 | 0.240 | 0.152 | 0.072 | 0.041 | 0.242 | 0.220 | 0.140 | 0.091 |
| B3 | 0.249 | 0.022 | 0.163 | 0.131 | 0.244 | 0.239 | 0.231 | 0.198 |
| B4 | 0.249 | 0.221 | 0.137 | 0.089 | 0.249 | 0.249 | 0.216 | 0.159 |
| Comm. | 0.249 | 0.237 | 0.186 | 0.142 | 0.241 | 0.240 | 0.232 | 0.212 |

Table A7    Blue dyes: Concentration of dye in the fiber (g/kg) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| B1 | 0.40 | 0.47 | 1.35 | 3.04 | 0.84 | 1.34 | 1.10 | 1.55 |
| B2 | 0.40 | 3.93 | 7.10 | 8.37 | 0.31 | 1.21 | 4.40 | 6.35 |
| B3 | 0.01 | 1.19 | 3.46 | 4.76 | 0.26 | 0.43 | 0.77 | 2.06 |
| B4 | 0.01 | 1.17 | 4.52 | 6.43 | 0.01 | 0.01 | 1.36 | 3.62 |
| Comm. | 0.02 | 0.53 | 2.56 | 4.31 | 0.35 | 0.41 | 0.74 | 1.51 |

Table A8    Percent exhaustion for blue dyes at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| B1 | 4.00 | 4.70 | 13.50 | 30.40 | 8.40 | 13.40 | 11.00 | 15.50 |
| B2 | 4.00 | 39.30 | 71.00 | 83.70 | 3.10 | 12.10 | 44.00 | 63.50 |
| B3 | 0.00 | 11.90 | 34.60 | 47.60 | 2.60 | 4.30 | 7.70 | 20.60 |
| B4 | 0.10 | 11.60 | 45.20 | 64.30 | 0.10 | 0.10 | 13.60 | 36.20 |
| Comm. | 0.20 | 5.30 | 25.60 | 43.20 | 3.50 | 4.10 | 7.40 | 15.10 |

Table A9  Standard affinity values for blue dyes at different temperature and salt conditions.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|---|---|---|---|---|---|---|---|---|
| TB1 | 1277 | 1696 | 4615 | 7210 | 3276 | 4603 | 4026 | 5021 |
| TB2 | 1277 | 8202 | 11560 | 13424 | 622 | 4297 | 8688 | 10691 |
| TB3 | -11608 | 4249 | 7698 | 9056 | 141 | 1480 | 3042 | 5895 |
| TB4 | -8839 | 4189 | 8816 | 10778 | -8839 | -8839 | 4634 | 7870 |
| Comm. | -6929 | 2022 | 6615 | 8606 | 954 | 1337 | 2914 | 4940 |

Table A10  Heat of dyeing for blue dyes at the salt concentrations.

| Dyes | 0 g/L | 10 g/L | 40 g/L | 70 g/L |
|---|---|---|---|---|
| B1 | 22.19 | 32.29 | -6.54 | -24.31 |
| B2 | -7.28 | -43.36 | -31.89 | -30.36 |
| B3 | 130.47 | -30.75 | -51.71 | -35.10 |
| B4 | 0.00 | -144.68 | -46.44 | -32.29 |
| Comm. | 87.54 | -7.60 | -41.11 | -40.72 |
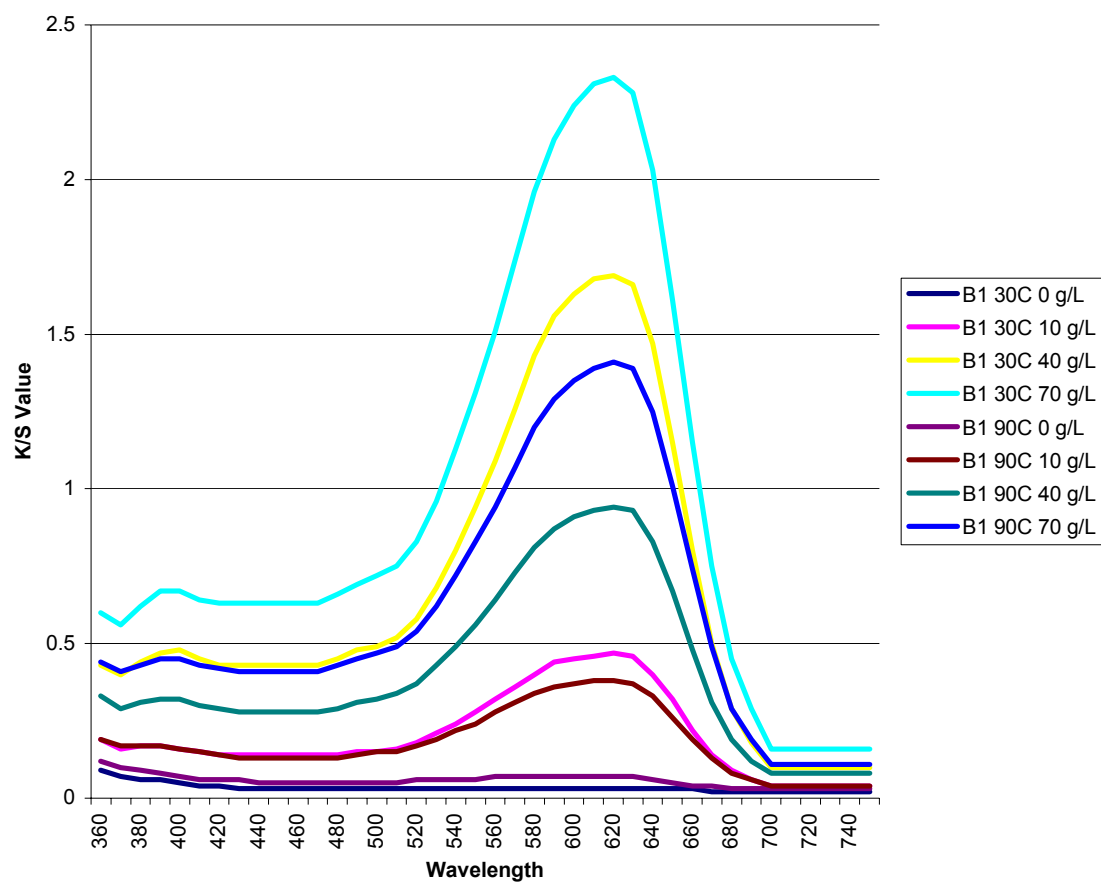
Figure A5    K/S values for equilibrium experiments involving type 1 blue dye.
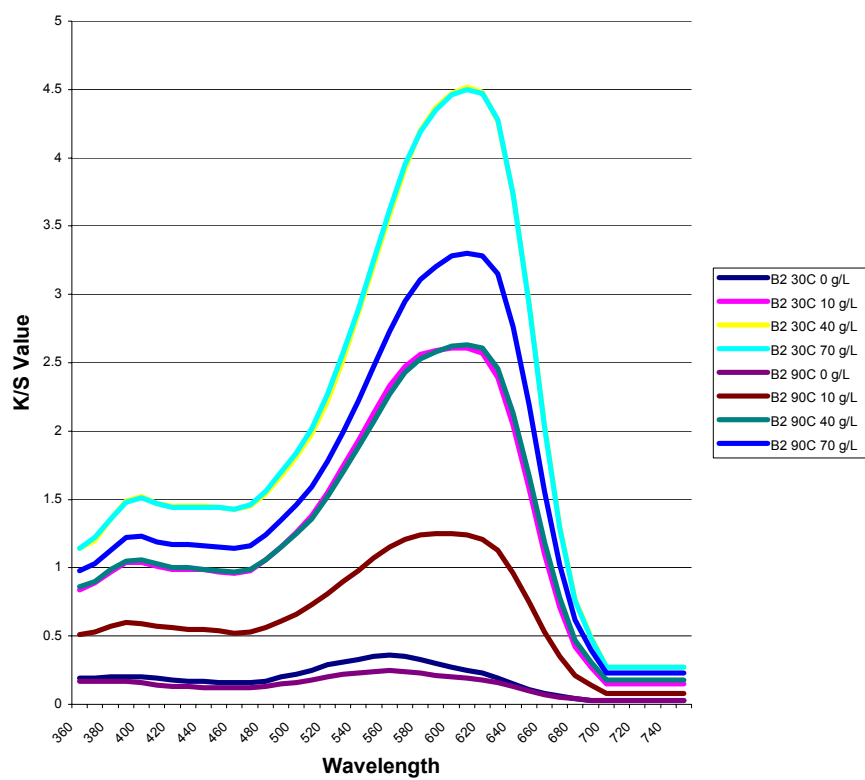
Figure A6    K/S values for equilibrium experiments involving type 2 blue dye.
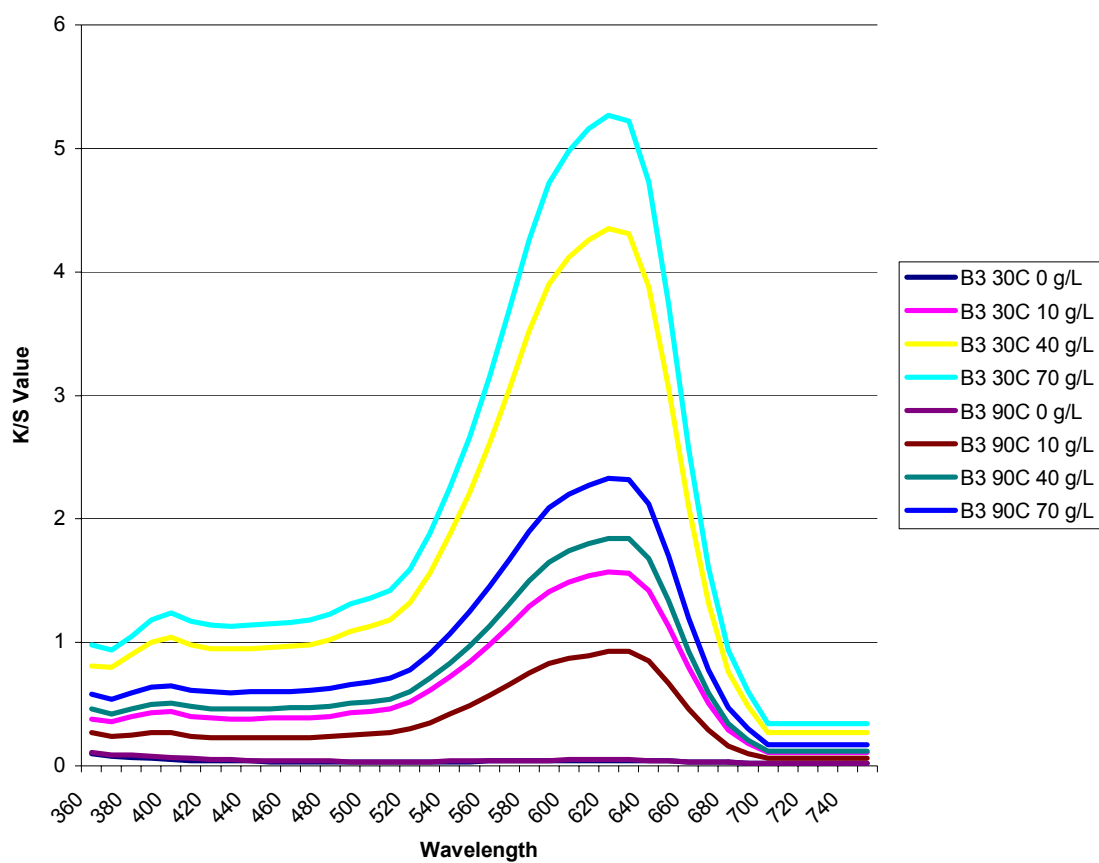
Figure A7    K/S values for equilibrium experiments involving type 3 blue dye.
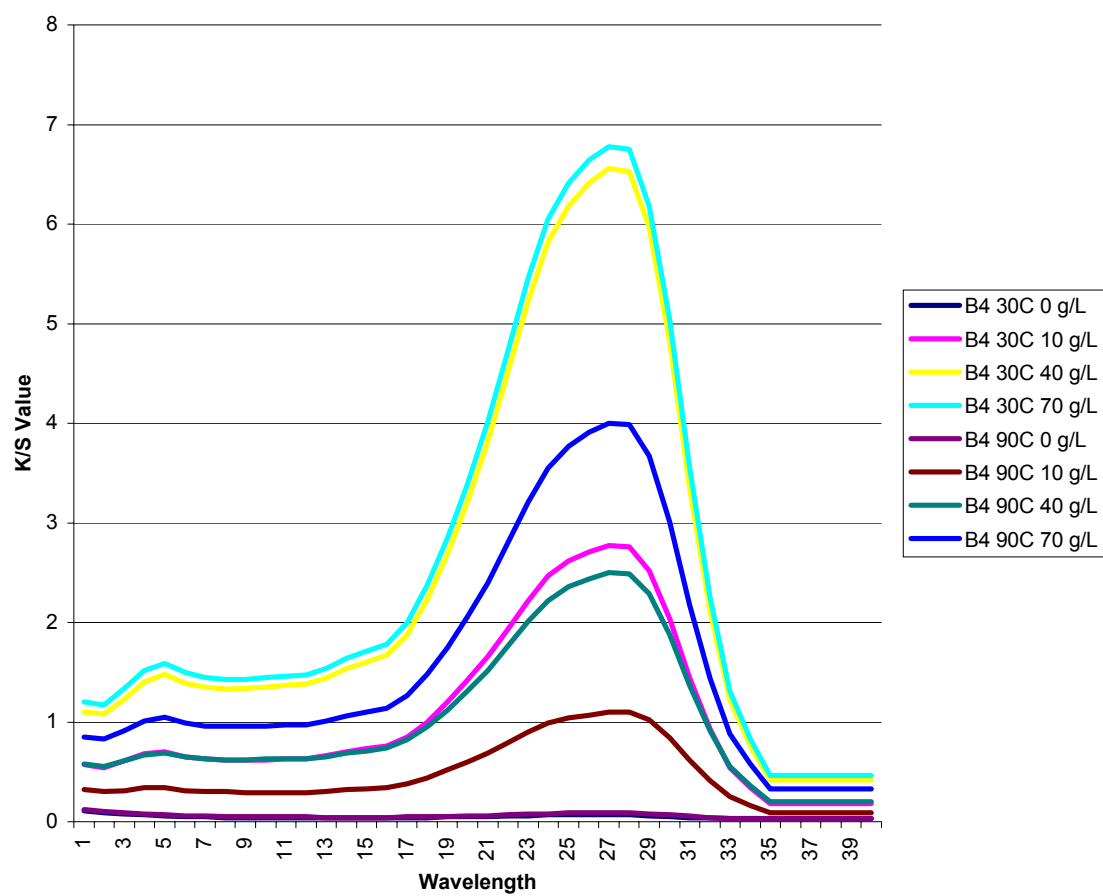
Figure A8     K/S values for equilibrium experiments involving type 4 blue dye.

Table A16    Yellow dyes: Concentration of dye in the solution (g/L) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| Y1 | 3.76 | 3.88 | 4.07 | 4.91 | 0.01 | 1.03 | 2.22 | 2.00 |
| Y2 | 0.11 | 3.21 | 6.31 | 8.01 | 2.78 | 3.86 | 4.84 | 5.91 |
| Y3 | 0.40 | 1.64 | 4.01 | 5.98 | 3.22 | 3.03 | 3.85 | 4.08 |
| Y4 | 0.01 | 3.12 | 6.21 | 7.61 | 1.52 | 2.82 | 3.89 | 4.80 |
| Comm. | 0.00 | 1.67 | 4.09 | 5.96 | 3.38 | 3.45 | 3.97 | 4.45 |

Table A17    Yellow dyes: Concentration of dye in the fiber (g/kg) at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| Y1 | 0.156 | 0.153 | 0.148 | 0.127 | 0.249 | 0.224 | 0.194 | 0.200 |
| Y2 | 0.247 | 0.170 | 0.092 | 0.050 | 0.181 | 0.153 | 0.129 | 0.102 |
| Y3 | 0.240 | 0.209 | 0.150 | 0.100 | 0.170 | 0.174 | 0.154 | 0.148 |
| Y4 | 0.249 | 0.172 | 0.095 | 0.060 | 0.212 | 0.179 | 0.153 | 0.130 |
| Comm. | 0.249 | 0.208 | 0.148 | 0.101 | 0.166 | 0.164 | 0.150 | 0.139 |

Table A18    Percent exhaustion for yellow dyes at the different temperatures and salt levels.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|------|------|------|------|------|------|------|------|
| Y1 | 0.00 | 10.30 | 22.20 | 20.10 | 37.60 | 38.80 | 40.70 | 49.10 |
| Y2 | 1.10 | 32.10 | 63.10 | 80.10 | 27.80 | 38.60 | 48.40 | 59.10 |
| Y3 | 4.00 | 16.40 | 40.10 | 59.80 | 32.20 | 30.30 | 38.50 | 40.80 |
| Y4 | 0.10 | 31.20 | 62.10 | 76.10 | 15.20 | 28.20 | 38.90 | 48.00 |
| Comm. | 0.00 | 16.70 | 40.90 | 59.60 | 33.80 | 34.40 | 39.70 | 44.50 |

Table A19    Standard affinity values for yellow dyes a different temperature and salt concentrations.

| Dye | 30°C 0 g/L | 30°C 10 g/L | 30°C 40 g/L | 30°C 70 g/L | 90°C 0 g/L | 90°C 10 g/L | 90°C 40 g/L | 90°C 70 g/L |
|------|-----------|-------------|-------------|-------------|-----------|-------------|-------------|-------------|
| TY1 | -11608 | 3852 | 6138 | 5824 | 8022 | 8143 | 8353 | 9206 |
| TY2 | -1957 | 7411 | 10651 | 12807 | 6891 | 8130 | 9138 | 10223 |
| TY3 | 1277 | 5192 | 8288 | 10302 | 7416 | 7203 | 8122 | 8360 |
| TY4 | -8676 | 7301 | 10542 | 12221 | 4958 | 6941 | 8156 | 9094 |
| Comm. | -9861 | 5245 | 8368 | 10280 | 7603 | 7676 | 8249 | 8743 |

Table A20    Heats of dyeing for yellow dyes at the salt concentrations.

| Dye | 0 g/L | 10 g/L | 40 g/L | 70 g/L |
|------|-------|--------|--------|--------|
| Y1 | -217.99 | -47.658 | -24.592 | -37.556 |
| Y2 | 98.2581 | 7.98979 | -16.798 | -28.702 |
| Y3 | 68.1744 | 22.3235 | -1.8385 | -21.564 |
| Y4 | 151.411 | -3.9973 | -26.499 | -34.728 |
| Comm. | 193.942 | 27.006 | -1.3263 | -17.071 |
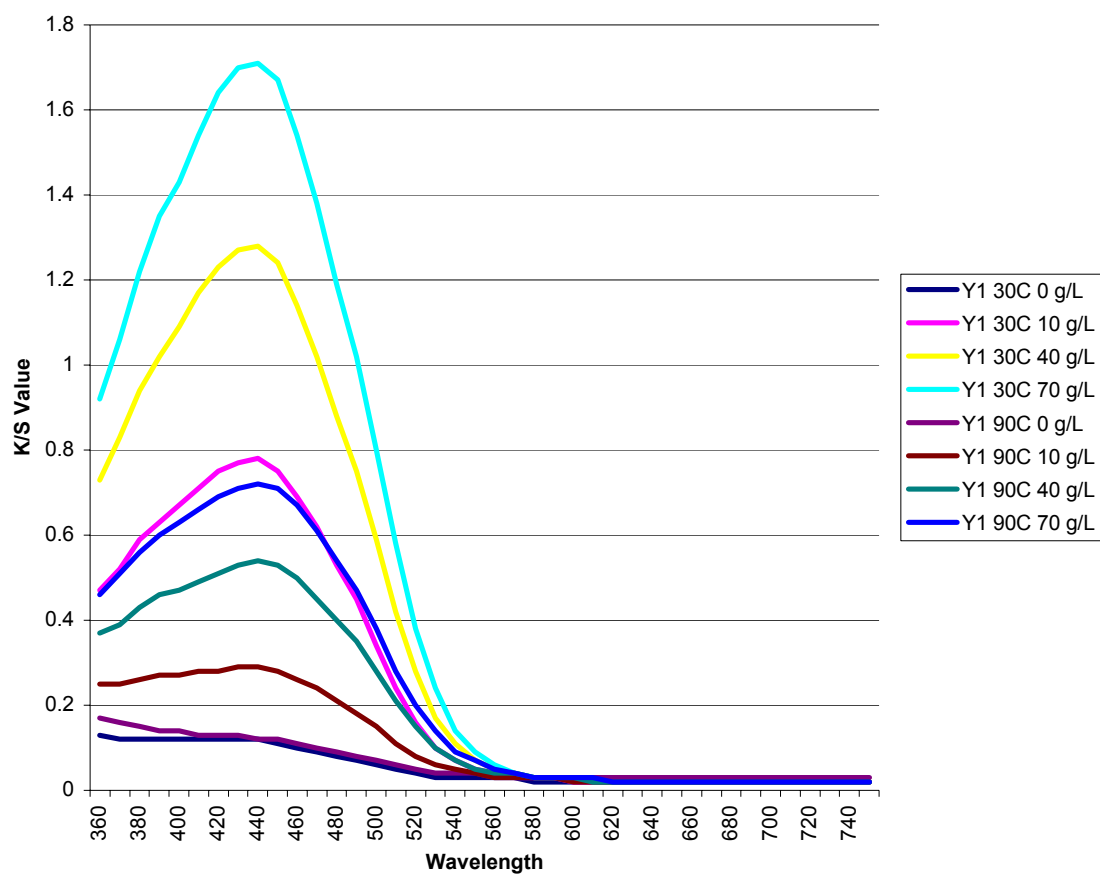
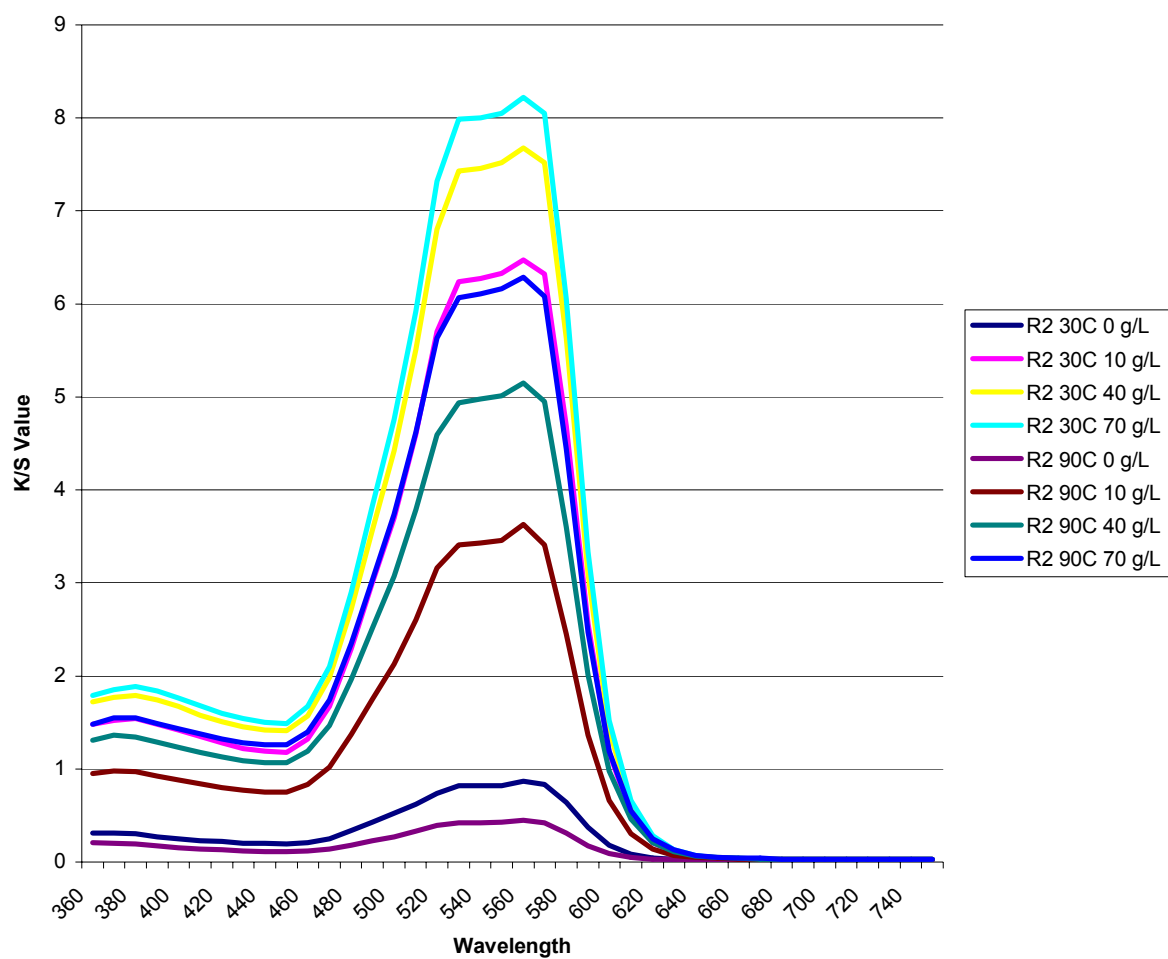Figure A10    K/S values for equilibrium experiments involving type 1 yellow dye.
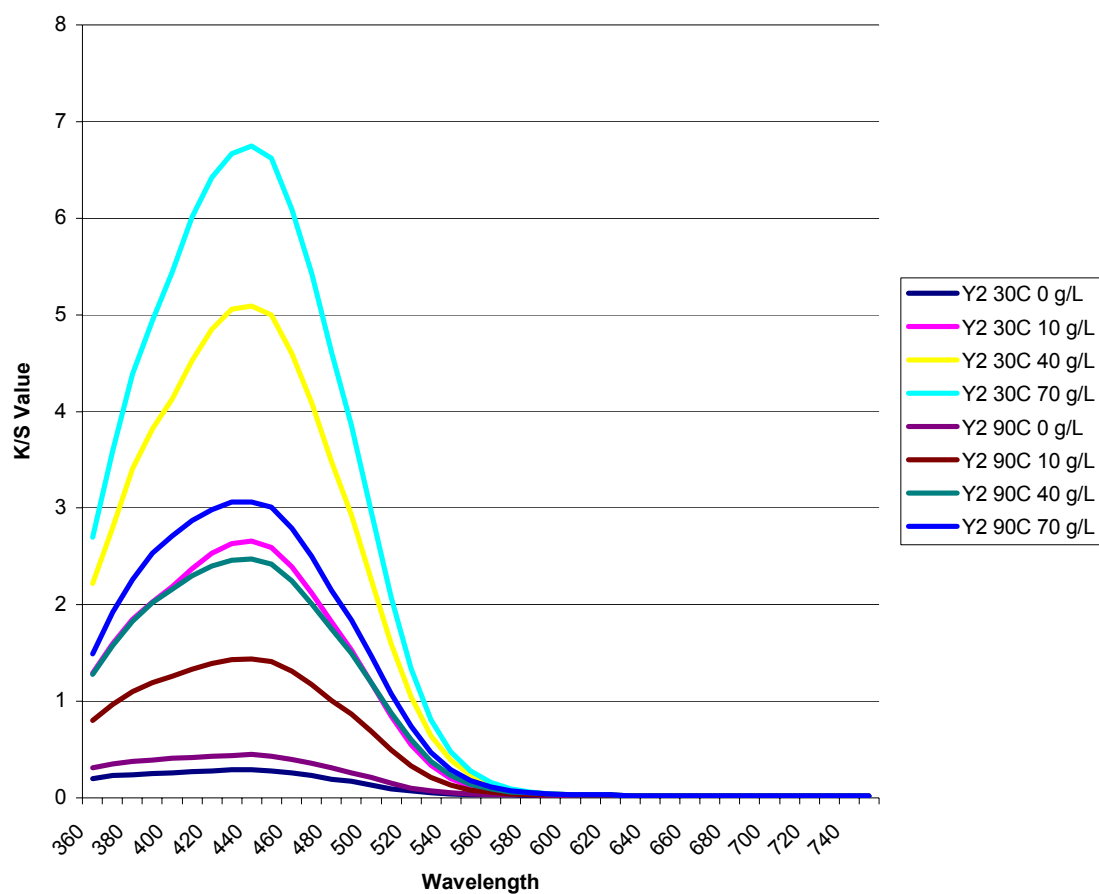
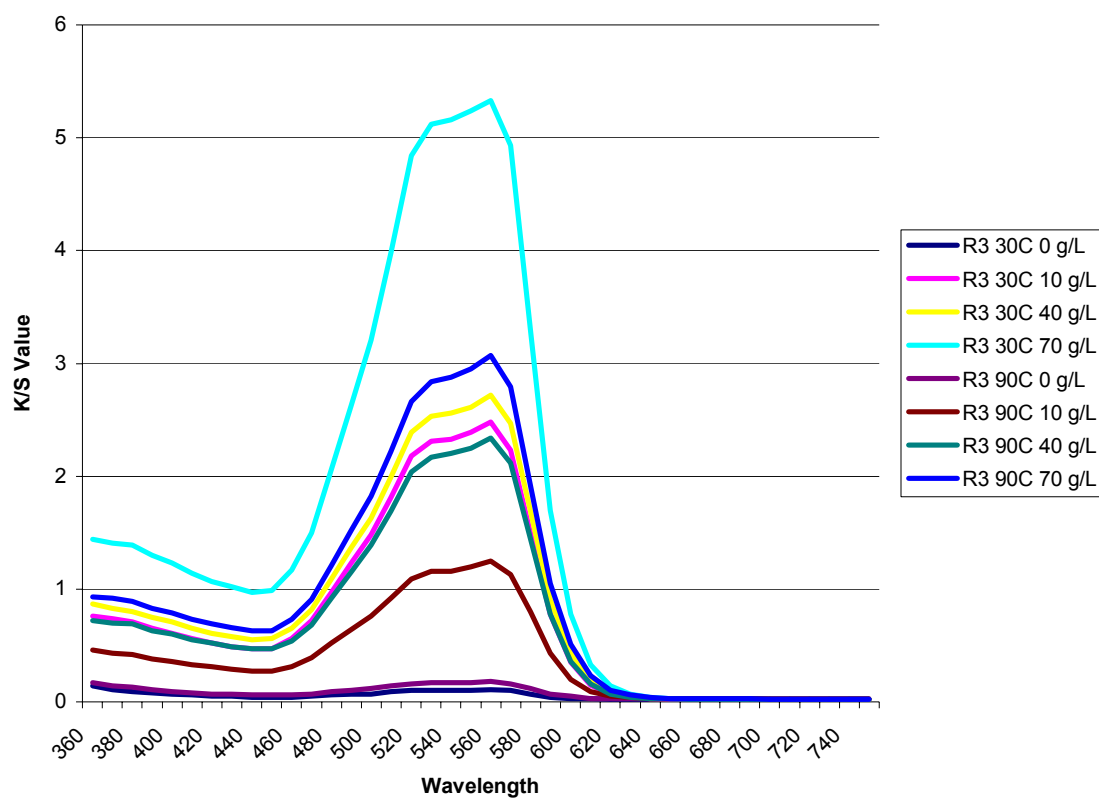Figure A11    K/S values for equilibrium experiments involving type 2 yellow dye.

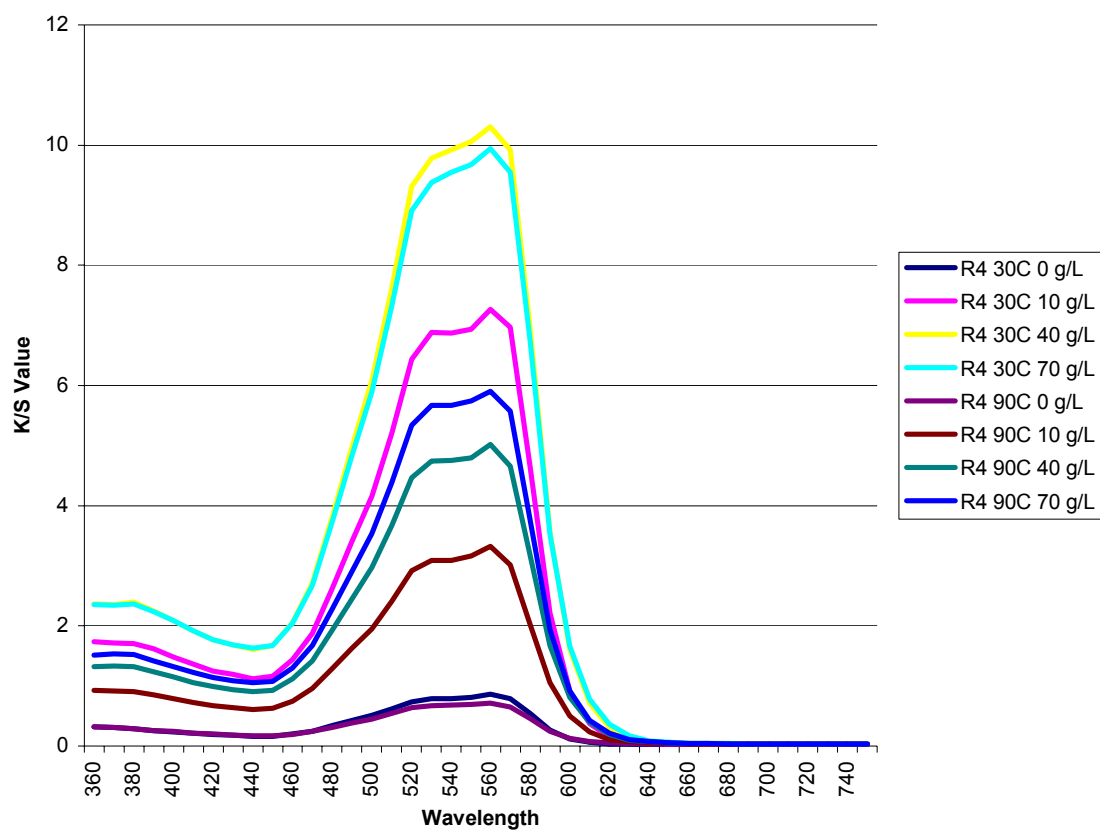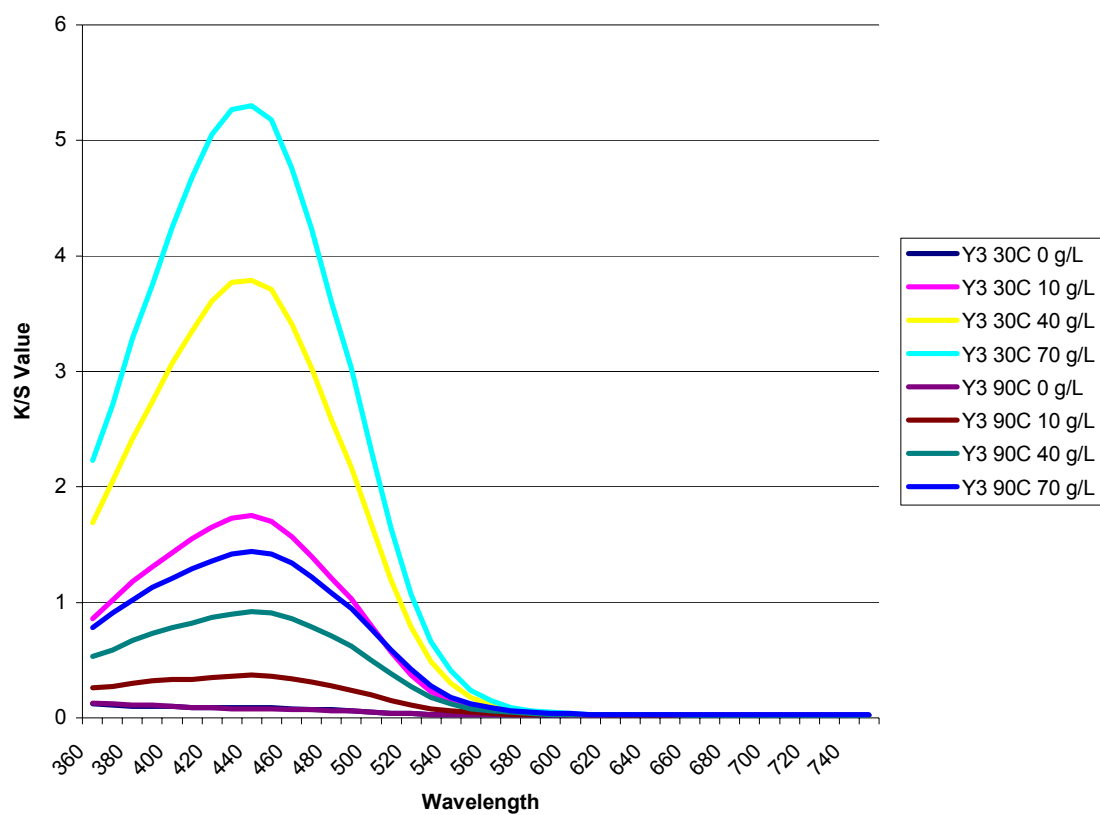Figure A12    K/S values for equilibrium experiments involving type 3 yellow dye.
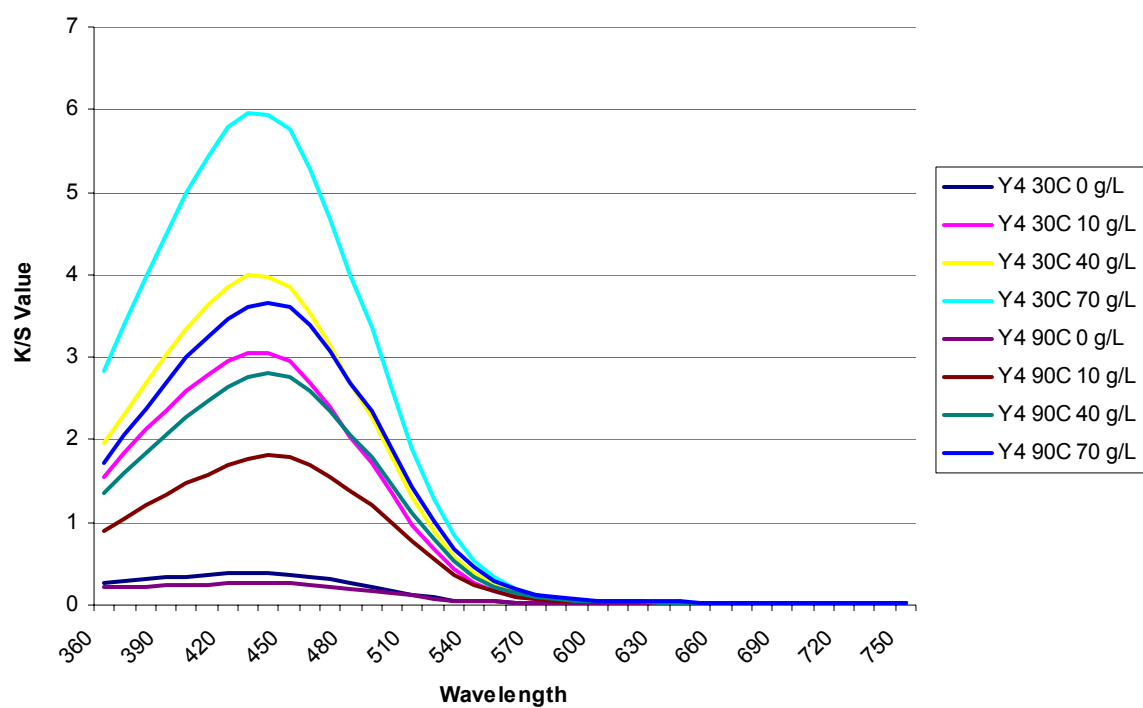
Figure A13    K/S values for equilibrium experiments involving type 4 yellow dye.

**Appendix B**
**Laboratory Dyeing Experiments**

Table B1    Commercial red dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Commercial Red**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 0.001441 | 0.001467 | 0.004827 | 0.005995 |
| **20 g/L** | 0.000918 | 0.001210 | 0.003706 | 0.005102 |
| **40 g/L** | 0.000693 | 0.001062 | 0.003061 | 0.004739 |

Table B2    Commercial red dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Commercial Red**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 0.19 | 0.19 | 0.81 | 0.76 |
| **20 g/L** | 0.21 | 0.20 | 0.85 | 0.80 |
| **40 g/L** | 0.22 | 0.21 | 0.88 | 0.81 |

Table B3    Percent fixation for commercial red dye at the different dye depths, temperature and salt levels.

**Commercial Red**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 76.94 | 76.53 | 80.69 | 76.02 |
| **20 g/L** | 85.31 | 80.64 | 85.18 | 79.59 |
| **40 g/L** | 88.91 | 83.01 | 87.76 | 81.04 |

Table B4    Type 2 red dye: Concentration of dye in the solution (g/L) at
            the different dye depths, temperatures and salt levels.

**Type Red 2**

|          | 0.25%    |          | 1.00%    |          |
|----------|----------|----------|----------|----------|
| **Salt** | **30C**  | **60C**  | **30 C** | **60C**  |
| **0 g/L**   | 0.000878 | 0.001002 | 0.004196 | 0.004692 |
| **20 g/L**  | 0.000386 | 0.000387 | 0.002614 | 0.002457 |
| **40 g/L**  | 0.000235 | 0.000157 | 0.002129 | 0.001609 |

Table B5    Type 2 red dye: Concentration of dye in the fiber (g/kg) at the different
            dye depths, temperatures and salt levels.

**Type Red 2**

|          | 0.25%   |         | 1.00%    |         |
|----------|---------|---------|----------|---------|
| **Salt** | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L**   | 0.21 | 0.21 | 0.83 | 0.81 |
| **20 g/L**  | 0.23 | 0.23 | 0.90 | 0.90 |
| **40 g/L**  | 0.24 | 0.24 | 0.91 | 0.94 |

Table B6    Percent fixation for type 2 red dye at the different dye depths,
            temperature and salt levels.

**Type Red 2**

|          | 0.25%   |         | 1.00%    |         |
|----------|---------|---------|----------|---------|
| **Salt** | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L**   | 85.95 | 83.97 | 83.22 | 81.23 |
| **20 g/L**  | 93.82 | 93.81 | 89.54 | 90.17 |
| **40 g/L**  | 96.24 | 97.49 | 91.48 | 93.56 |

Table B7     Type 4 red dye: Concentration of dye in the solution (g/L) at
             the different dye depths, temperatures and salt levels.

**Type Red 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| **0 g/L** | 0.001046 | 0.001301 | 0.004561 | 0.005474 |
| **20 g/L** | 0.000640 | 0.000897 | 0.003349 | 0.004501 |
| **40 g/L** | 0.000509 | 0.000723 | 0.002675 | 0.003027 |

Table B8     Type 4 red dye: Concentration of dye in the fiber (g/kg) at the different
             dye depths, temperatures and salt levels.

**Type Red 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| **0 g/L** | 0.21 | 0.20 | 0.82 | 0.78 |
| **20 g/L** | 0.22 | 0.21 | 0.87 | 0.82 |
| **40 g/L** | 0.23 | 0.22 | 0.89 | 0.88 |

Table B9     Percent fixation for type 4 red dye at the different dye depths,
             temperature and salt levels.

**Type Red 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| **0 g/L** | 83.26 | 79.18 | 81.76 | 78.10 |
| **20 g/L** | 89.76 | 85.65 | 86.60 | 82.00 |
| **40 g/L** | 91.86 | 88.43 | 89.30 | 87.89 |

Table B10    Design of experiments for red dyes.

| No. | Dye | Color | Shade Depth (%) | Salt (g/L) | Temp. (C) |
|-----|-----|-------|------|------|------|
| 1 | Procion® Red MX-8B | Red | 0.25 | 0 | 30 |
| 2 | Procion® Red MX-8B | Red | 0.25 | 20 | 30 |
| 3 | Procion® Red MX-8B | Red | 0.25 | 40 | 30 |
| 4 | Procion® Red MX-8B | Red | 1 | 0 | 30 |
| 5 | Procion® Red MX-8B | Red | 1 | 20 | 30 |
| 6 | Procion® Red MX-8B | Red | 1 | 40 | 30 |
| 7 | Procion® Red MX-8B | Red | 0.25 | 0 | 60 |
| 8 | Procion® Red MX-8B | Red | 0.25 | 20 | 60 |
| 9 | Procion® Red MX-8B | Red | 0.25 | 40 | 60 |
| 10 | Procion® Red MX-8B | Red | 1 | 0 | 60 |
| 11 | Procion® Red MX-8B | Red | 1 | 20 | 60 |
| 12 | Procion® Red MX-8B | Red | 1 | 40 | 60 |
| 13 | T2 | Red | 0.25 | 0 | 30 |
| 14 | T2 | Red | 0.25 | 20 | 30 |
| 15 | T2 | Red | 0.25 | 40 | 30 |
| 16 | T2 | Red | 1 | 0 | 30 |
| 17 | T2 | Red | 1 | 20 | 30 |
| 18 | T2 | Red | 1 | 40 | 30 |
| 19 | T2 | Red | 0.25 | 0 | 60 |
| 20 | T2 | Red | 0.25 | 20 | 60 |
| 21 | T2 | Red | 0.25 | 40 | 60 |
| 22 | T2 | Red | 1 | 0 | 60 |
| 23 | T2 | Red | 1 | 20 | 60 |
| 24 | T2 | Red | 1 | 40 | 60 |
| 25 | T4 | Red | 0.25 | 0 | 60 |
| 26 | T4 | Red | 0.25 | 20 | 60 |
| 27 | T4 | Red | 0.25 | 40 | 60 |
| 28 | T4 | Red | 1 | 0 | 60 |
| 29 | T4 | Red | 1 | 20 | 60 |
| 30 | T4 | Red | 1 | 40 | 60 |
| 31 | T4 | Red | 0.25 | 0 | 90 |
| 32 | T4 | Red | 0.25 | 20 | 90 |
| 33 | T4 | Red | 0.25 | 40 | 90 |
| 34 | T4 | Red | 1 | 0 | 90 |
| 35 | T4 | Red | 1 | 20 | 90 |
| 36 | T4 | Red | 1 | 40 | 90 |
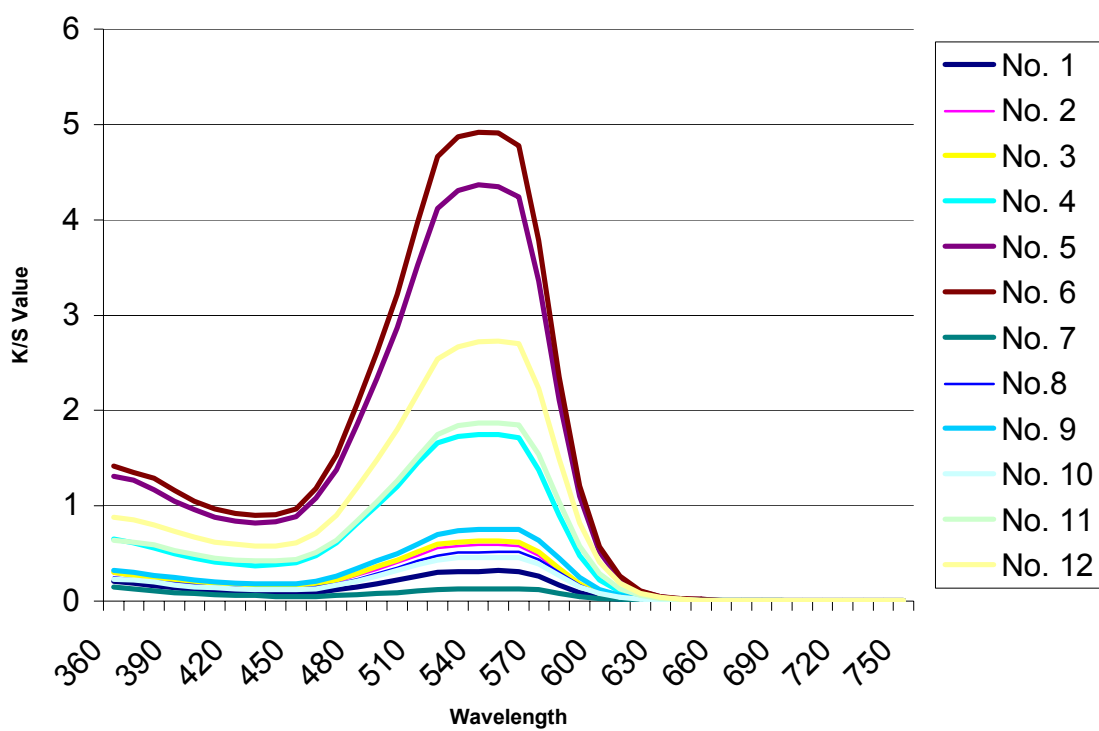
Figure B1    K/S values for samples 1-12 obtained from laboratory dyeings utilizing the commercial red dye.
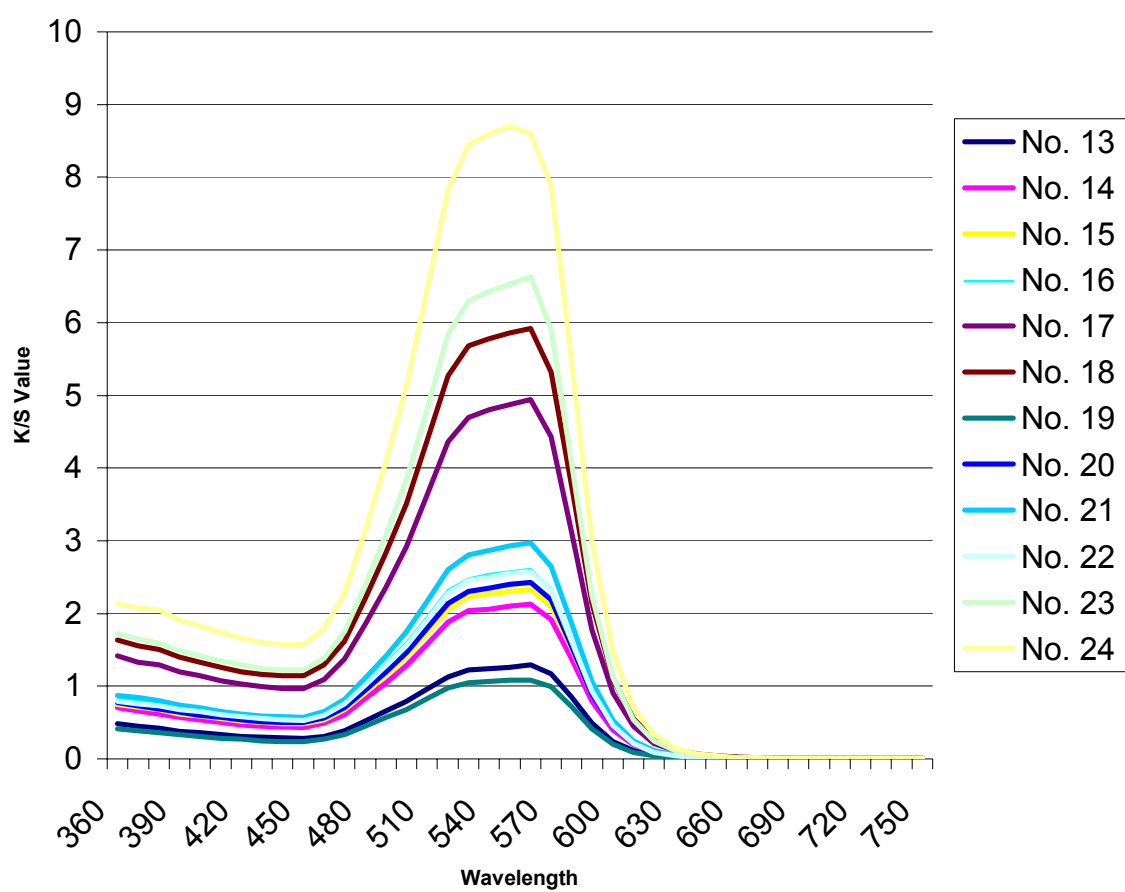
Figure B2    K/S values for samples 13-24 obtained from laboratory dyeings
utilizing the type 2 red dye.

Figure B3    K/S values for samples 25-36 obtained from laboratory dyeings utilizing the type 4 red dye.

Table B11    Commercial blue dye: Concentration of dye in the solution (g/L) at
             the different dye depths, temperatures and salt levels.

**Commercial Blue**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.005796 | 0.001635 | 0.006214 | 0.006533 |
| 20 g/L | 0.001197 | 0.001426 | 0.005156 | 0.005972 |
| 40 g/L | 0.001034 | 0.001240 | 0.004461 | 0.005649 |

Table B12    Commercial blue dye: Concentration of dye in the fiber (g/kg) at the
             different dye depths, temperatures and salt levels.

**Commercial Blue**

| Salt | 0.00 | | 0.01 | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.02 | 0.19 | 0.75 | 0.74 |
| 20 g/L | 0.20 | 0.19 | 0.79 | 0.76 |
| 40 g/L | 0.21 | 0.20 | 0.82 | 0.77 |

Table B13    Percent fixation for commercial blue dyes at the different dye depths,
             temperature and salt levels.

**Commercial Blue**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 72.60 | 73.84 | 75.14 | 73.87 |
| 20 g/L | 80.85 | 77.18 | 79.38 | 76.11 |
| 40 g/L | 83.46 | 80.16 | 82.16 | 77.40 |

Table B14   Type 2 blue dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Type Blue 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| Salt | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.001077 | 0.001525 | 0.005249 | 0.006247 |
| 20 g/L | 0.000745 | 0.000994 | 0.003526 | 0.004581 |
| 40 g/L | 0.000526 | 0.000666 | 0.002721 | 0.003782 |

Table B15   Type 2 blue dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Type Blue 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| Salt | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.21 | 0.19 | 0.79 | 0.75 |
| 20 g/L | 0.22 | 0.21 | 0.86 | 0.82 |
| 40 g/L | 0.23 | 0.22 | 0.89 | 0.85 |

Table B16   Percent fixation for type 2 blue dyes at the different dye depths, temperature and salt levels.

**Type Blue 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| Salt | 30C | 60C | 30 C | 60C |
| 0 g/L | 82.77 | 75.60 | 79.00 | 75.01 |
| 20 g/L | 88.08 | 84.10 | 85.90 | 81.68 |
| 40 g/L | 91.58 | 89.34 | 89.12 | 84.87 |

Table B17    Type 4 blue dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Type Blue 4**

|          | 0.25%    |          | 1.00%    |          |
|----------|----------|----------|----------|----------|
| **Salt** | **60C**  | **90C**  | **60 C** | **90C**  |
| **0 g/L**  | 0.001415 | 0.001725 | 0.006397 | 0.006893 |
| **20 g/L** | 0.001255 | 0.001535 | 0.005904 | 0.005733 |
| **40 g/L** | 0.001123 | 0.001234 | 0.005271 | 0.005466 |

Table B18    Type 4 blue dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Type Blue 4**

|          | 0.25%   |         | 1.00%   |         |
|----------|---------|---------|---------|---------|
| **Salt** | **60C** | **90C** | **60 C**| **90C** |
| **0 g/L**  | 0.19 | 0.18 | 0.74 | 0.72 |
| **20 g/L** | 0.20 | 0.19 | 0.76 | 0.77 |
| **40 g/L** | 0.21 | 0.20 | 0.79 | 0.78 |

Table B19    Percent fixation for type 4 blue dyes at the different dye depths, temperature and salt levels.

**Type Blue 4**

|          | 0.25%   |         | 1.00%   |         |
|----------|---------|---------|---------|---------|
| **Salt** | **60C** | **90C** | **60 C**| **90C** |
| **0 g/L**  | 77.36 | 72.40 | 74.41 | 72.43 |
| **20 g/L** | 79.92 | 75.44 | 76.38 | 77.07 |
| **40 g/L** | 82.03 | 80.26 | 78.92 | 78.14 |

Table B20    Design of experiments for blue dyes.

| No. | Dye | Color | Shade Depth (%) | Salt (g/L) | Temp. (C) |
|---|---|---|---|---|---|
| 37 | Procion® Blue MX-2G | Blue | 0.25 | 0 | 30 |
| 38 | Procion® Blue MX-2G | Blue | 0.25 | 20 | 30 |
| 39 | Procion® Blue MX-2G | Blue | 0.25 | 40 | 30 |
| 40 | Procion® Blue MX-2G | Blue | 1 | 0 | 30 |
| 41 | Procion® Blue MX-2G | Blue | 1 | 20 | 30 |
| 42 | Procion® Blue MX-2G | Blue | 1 | 40 | 30 |
| 43 | Procion® Blue MX-2G | Blue | 0.25 | 0 | 60 |
| 44 | Procion® Blue MX-2G | Blue | 0.25 | 20 | 60 |
| 45 | Procion® Blue MX-2G | Blue | 0.25 | 40 | 60 |
| 46 | Procion® Blue MX-2G | Blue | 1 | 0 | 60 |
| 47 | Procion® Blue MX-2G | Blue | 1 | 20 | 60 |
| 48 | Procion® Blue MX-2G | Blue | 1 | 40 | 60 |
| 49 | T2 | Blue | 0.25 | 0 | 30 |
| 50 | T2 | Blue | 0.25 | 20 | 30 |
| 51 | T2 | Blue | 0.25 | 40 | 30 |
| 52 | T2 | Blue | 1 | 0 | 30 |
| 53 | T2 | Blue | 1 | 20 | 30 |
| 54 | T2 | Blue | 1 | 40 | 30 |
| 55 | T2 | Blue | 0.25 | 0 | 60 |
| 56 | T2 | Blue | 0.25 | 20 | 60 |
| 57 | T2 | Blue | 0.25 | 40 | 60 |
| 58 | T2 | Blue | 1 | 0 | 60 |
| 59 | T2 | Blue | 1 | 20 | 60 |
| 60 | T2 | Blue | 1 | 40 | 60 |
| 61 | T4 | Blue | 0.25 | 0 | 60 |
| 62 | T4 | Blue | 0.25 | 20 | 60 |
| 63 | T4 | Blue | 0.25 | 40 | 60 |
| 64 | T4 | Blue | 1 | 0 | 60 |
| 65 | T4 | Blue | 1 | 20 | 60 |
| 66 | T4 | Blue | 1 | 40 | 60 |
| 67 | T4 | Blue | 0.25 | 0 | 90 |
| 68 | T4 | Blue | 0.25 | 20 | 90 |
| 69 | T4 | Blue | 0.25 | 40 | 90 |
| 70 | T4 | Blue | 1 | 0 | 90 |
| 71 | T4 | Blue | 1 | 20 | 90 |
| 72 | T4 | Blue | 1 | 40 | 90 |
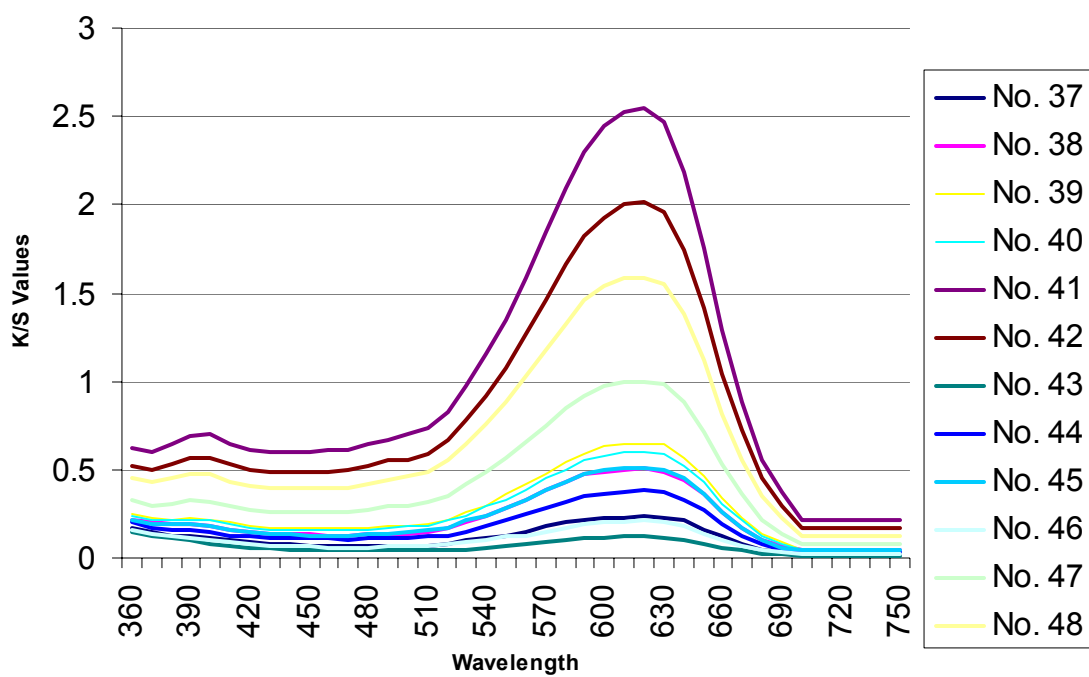
Figure B4    K/S values for samples 37-48 obtained from laboratory dyeings utilizing the commercial blue dye.
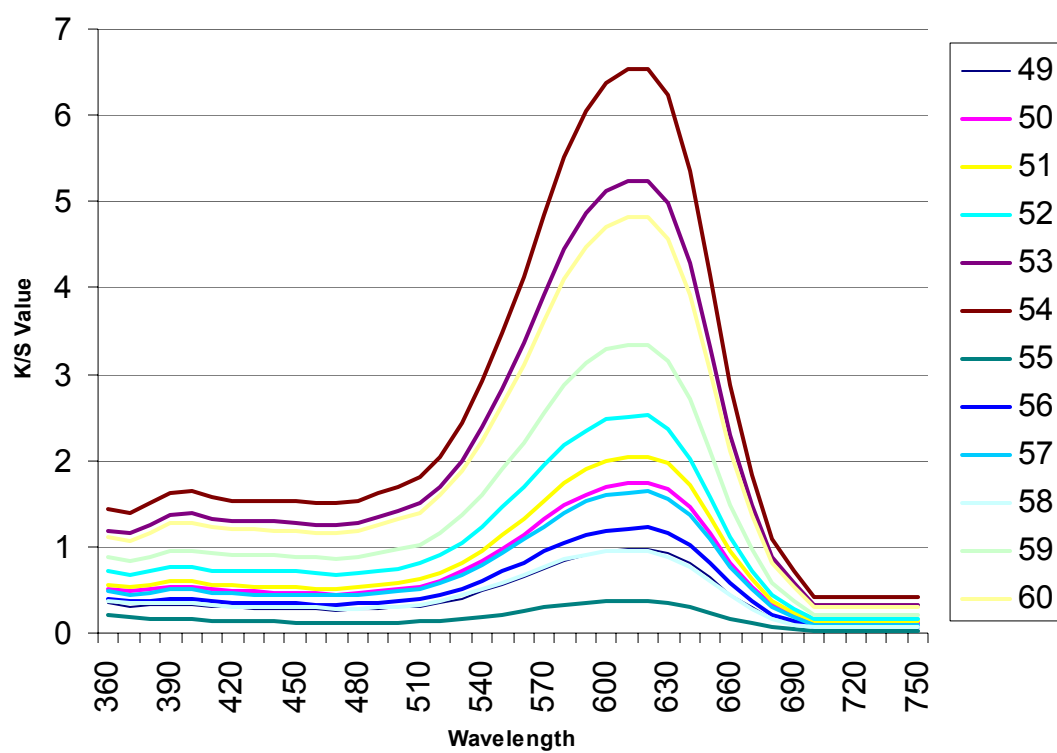
Figure B5     K/S values for samples 49-60 obtained from laboratory dyeings
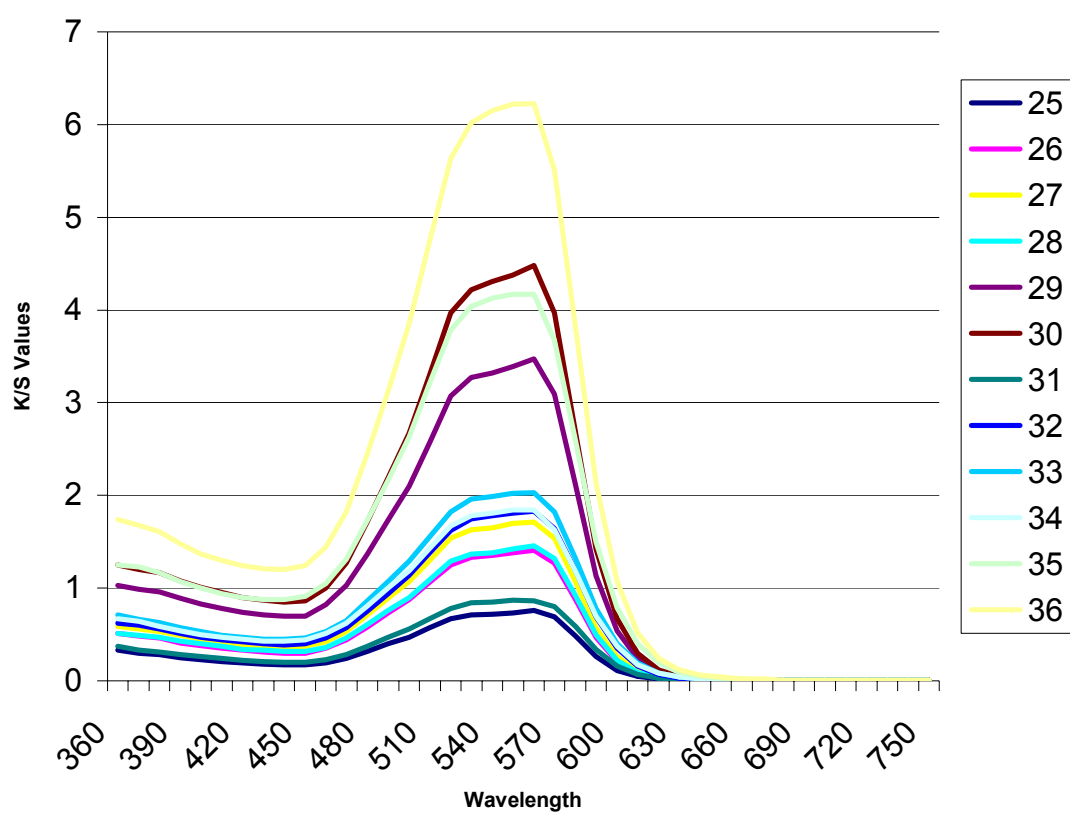utilizing the type 2 blue dye.
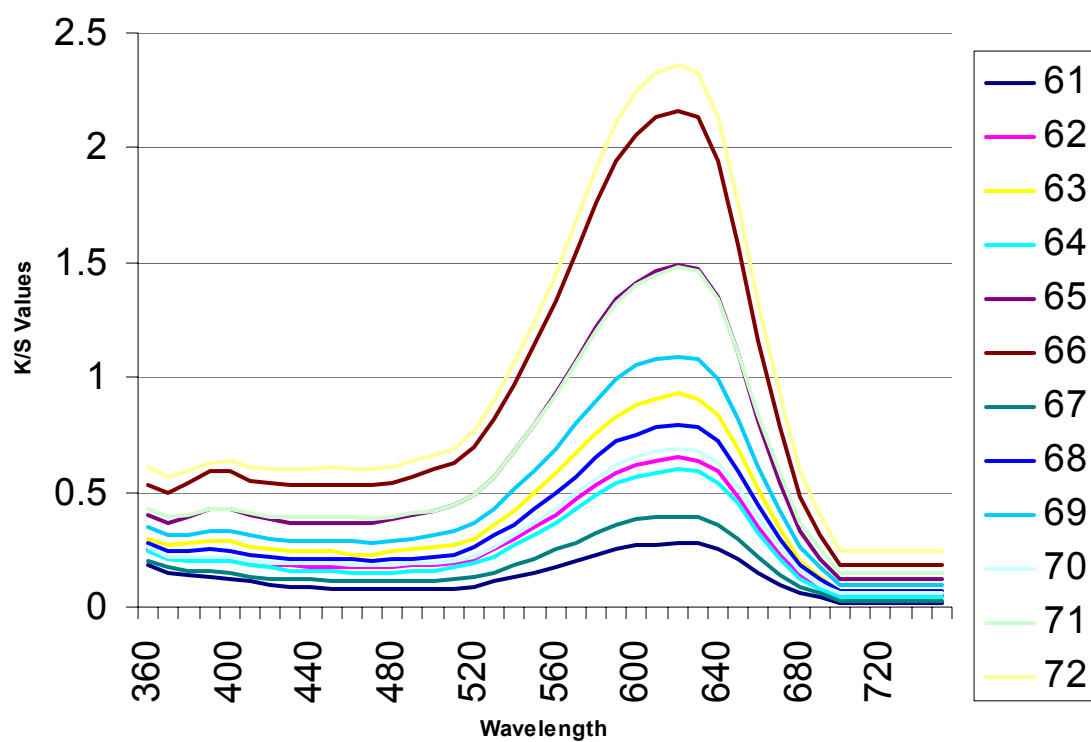
Figure B6    K/S values for samples 61-72 obtained from laboratory dyeings
utilizing the type 4 blue dye.

Table B21    Commercial yellow dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Commercial Yellow**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.001160 | 0.001435 | 0.004550 | 0.006169 |
| 20 g/L | 0.000750 | 0.001247 | 0.003242 | 0.005478 |
| 40 g/L | 0.000548 | 0.001026 | 0.002584 | 0.004548 |

Table B22    Commercial yellow dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Commercial Yellow**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 0.204 | 0.193 | 0.818 | 0.753 |
| 20 g/L | 0.220 | 0.200 | 0.870 | 0.781 |
| 40 g/L | 0.228 | 0.209 | 0.897 | 0.818 |

Table B23    Percent fixation for commercial yellow dye at the different dye depths, temperature and salt levels.

**Commercial Yellow**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 30C | 60C | 30 C | 60C |
| 0 g/L | 81.44 | 77.04 | 81.80 | 75.32 |
| 20 g/L | 88.00 | 80.05 | 87.03 | 78.09 |
| 40 g/L | 91.23 | 83.58 | 89.66 | 81.81 |

Table B24    Type 2 yellow dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Type Yellow 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| **Salt** | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 0.000721 | 0.001005 | 0.003796 | 0.005618 |
| **20 g/L** | 0.000336 | 0.000810 | 0.002187 | 0.003576 |
| **40 g/L** | 0.000197 | 0.000446 | 0.001577 | 0.002509 |

Table B25    Type 2 yellow dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Type Yellow 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| **Salt** | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 0.221 | 0.210 | 0.848 | 0.775 |
| **20 g/L** | 0.237 | 0.218 | 0.913 | 0.857 |
| **40 g/L** | 0.242 | 0.232 | 0.937 | 0.900 |

Table B26    Percent fixation for type 2 yellow dye at the different dye depths, temperature and salt levels.

**Type Yellow 2**

|  | 0.25% | | 1.00% | |
| --- | --- | --- | --- | --- |
| **Salt** | **30C** | **60C** | **30 C** | **60C** |
| **0 g/L** | 88.46 | 83.92 | 84.82 | 77.53 |
| **20 g/L** | 94.62 | 87.04 | 91.25 | 85.70 |
| **40 g/L** | 96.85 | 92.87 | 93.69 | 89.96 |

Table B27    Type 4 yellow dye: Concentration of dye in the solution (g/L) at the different dye depths, temperatures and salt levels.

**Type Yellow 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| 0 g/L | 0.001320 | 0.001553 | 0.005512 | 0.005881 |
| 20 g/L | 0.000950 | 0.001196 | 0.004339 | 0.004835 |
| 40 g/L | 0.000676 | 0.000838 | 0.003428 | 0.003940 |

Table B28    Type 4 yellow dye: Concentration of dye in the fiber (g/kg) at the different dye depths, temperatures and salt levels.

**Type Yellow 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| 0 g/L | 0.197 | 0.188 | 0.780 | 0.765 |
| 20 g/L | 0.212 | 0.202 | 0.826 | 0.807 |
| 40 g/L | 0.223 | 0.216 | 0.863 | 0.842 |

Table B29    Percent fixation for type 4 yellow dye at the different dye depths, temperature and salt levels.

**Type Yellow 4**

| Salt | 0.25% | | 1.00% | |
|---|---|---|---|---|
| | 60C | 90C | 60 C | 90C |
| 0 g/L | 78.88 | 77.95 | 75.15 | 76.48 |
| 20 g/L | 84.80 | 82.64 | 80.86 | 80.66 |
| 40 g/L | 89.18 | 86.29 | 86.59 | 84.24 |

Table B30     Design of experiments for yellow dyes.

| No. | Dye | Color | Shade Depth (%) | Salt (g/L) | Temp. (C) |
|---|---|---|---|---|---|
| 73 | Procion® Yellow MX-3R | Yellow | 0.25 | 0 | 30 |
| 74 | Procion® Yellow MX-3R | Yellow | 0.25 | 20 | 30 |
| 75 | Procion® Yellow MX-3R | Yellow | 0.25 | 40 | 30 |
| 76 | Procion® Yellow MX-3R | Yellow | 1 | 0 | 30 |
| 77 | Procion® Yellow MX-3R | Yellow | 1 | 20 | 30 |
| 78 | Procion® Yellow MX-3R | Yellow | 1 | 40 | 30 |
| 79 | Procion® Yellow MX-3R | Yellow | 0.25 | 0 | 60 |
| 80 | Procion® Yellow MX-3R | Yellow | 0.25 | 20 | 60 |
| 81 | Procion® Yellow MX-3R | Yellow | 0.25 | 40 | 60 |
| 82 | Procion® Yellow MX-3R | Yellow | 1 | 0 | 60 |
| 83 | Procion® Yellow MX-3R | Yellow | 1 | 20 | 60 |
| 84 | Procion® Yellow MX-3R | Yellow | 1 | 40 | 60 |
| 85 | T2 | Yellow | 0.25 | 0 | 30 |
| 86 | T2 | Yellow | 0.25 | 20 | 30 |
| 87 | T2 | Yellow | 0.25 | 40 | 30 |
| 88 | T2 | Yellow | 1 | 0 | 30 |
| 89 | T2 | Yellow | 1 | 20 | 30 |
| 90 | T2 | Yellow | 1 | 40 | 30 |
| 91 | T2 | Yellow | 0.25 | 0 | 60 |
| 92 | T2 | Yellow | 0.25 | 20 | 60 |
| 93 | T2 | Yellow | 0.25 | 40 | 60 |
| 94 | T2 | Yellow | 1 | 0 | 60 |
| 95 | T2 | Yellow | 1 | 20 | 60 |
| 96 | T2 | Yellow | 1 | 40 | 60 |
| 97 | T4 | Yellow | 0.25 | 0 | 60 |
| 98 | T4 | Yellow | 0.25 | 20 | 60 |
| 99 | T4 | Yellow | 0.25 | 40 | 60 |
| 100 | T4 | Yellow | 1 | 0 | 60 |
| 101 | T4 | Yellow | 1 | 20 | 60 |
| 102 | T4 | Yellow | 1 | 40 | 60 |
| 103 | T4 | Yellow | 0.25 | 0 | 90 |
| 104 | T4 | Yellow | 0.25 | 20 | 90 |
| 105 | T4 | Yellow | 0.25 | 40 | 90 |
| 106 | T4 | Yellow | 1 | 0 | 90 |
| 107 | T4 | Yellow | 1 | 20 | 90 |
| 108 | T4 | Yellow | 1 | 40 | 90 |
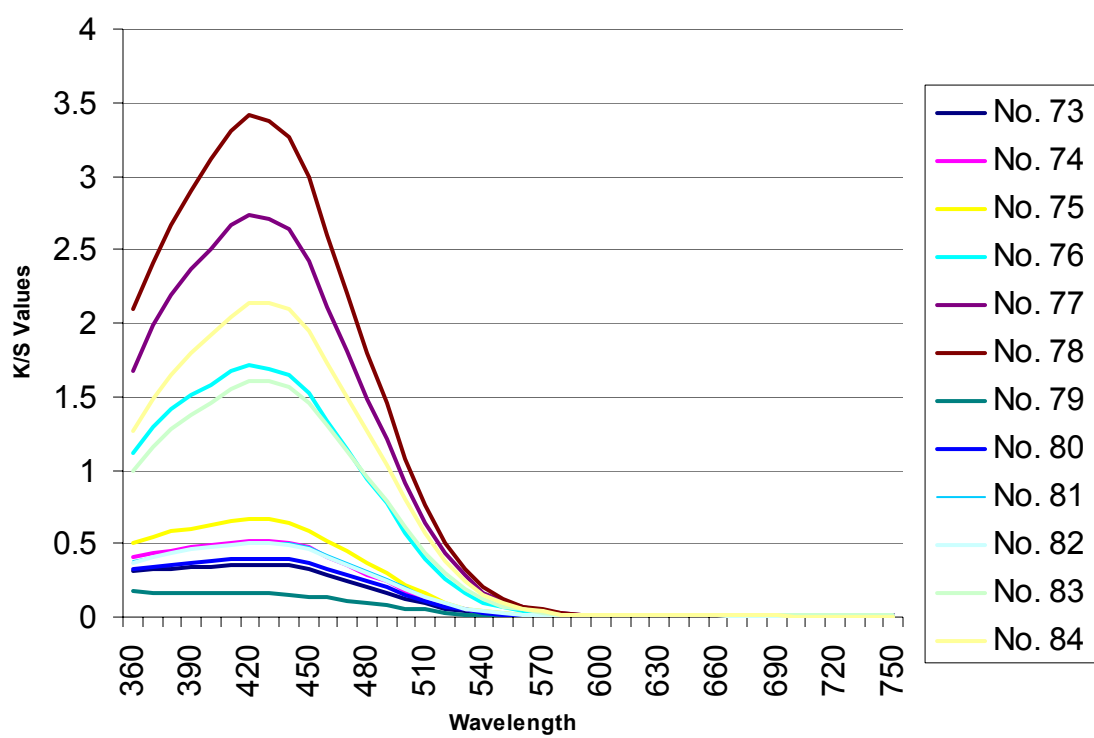
Figure B7    K/S values for samples 73-84 obtained from laboratory dyeings
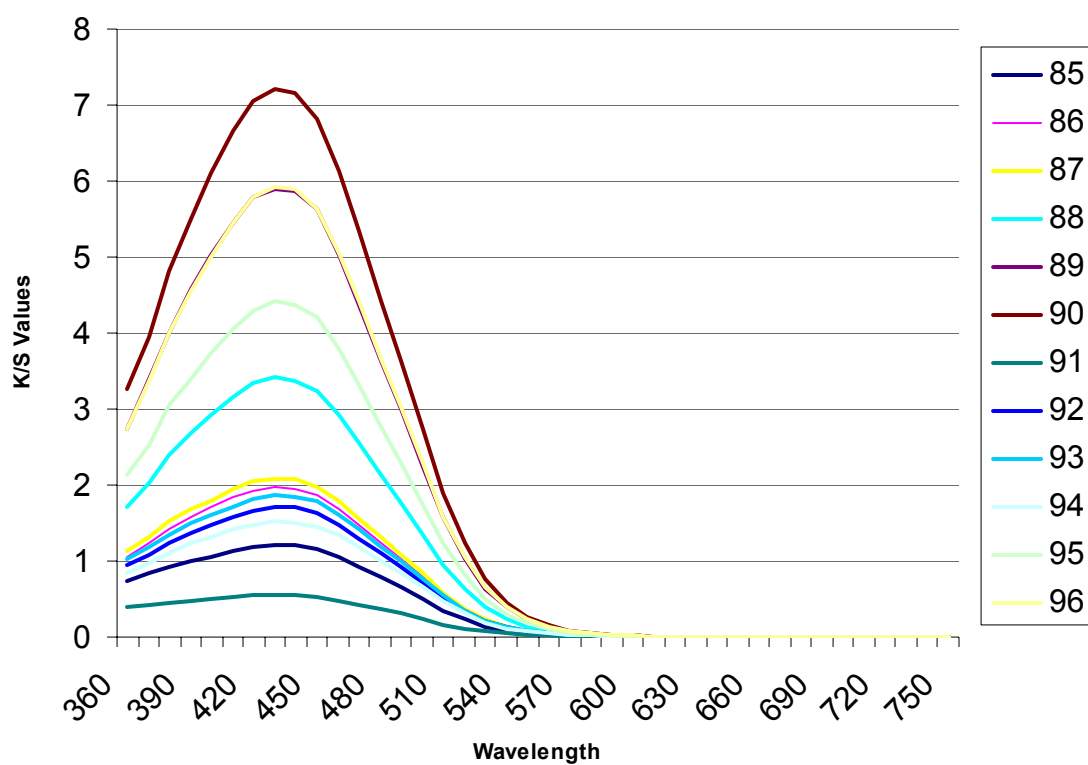utilizing the commercial yellow dye.

Figure B8    K/S values for samples 85-96 obtained from laboratory dyeings
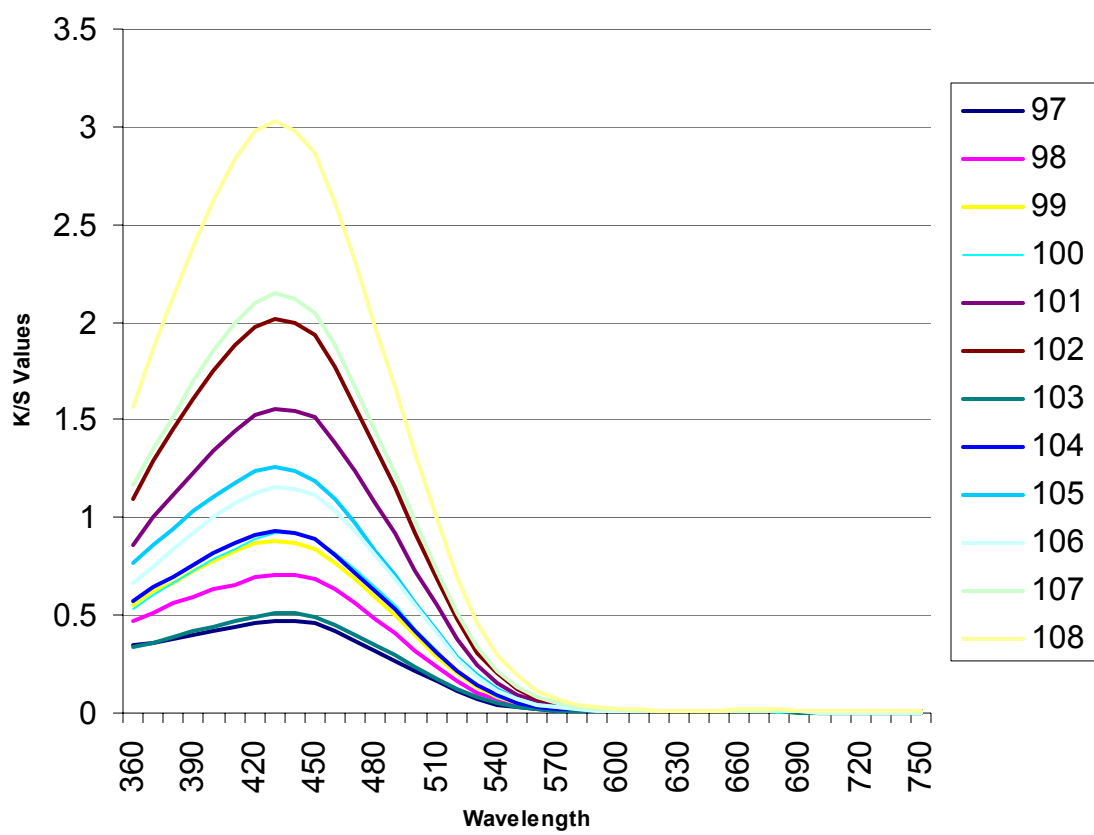utilizing the type 2 yellow dye.

Figure B9     K/S values for samples 2 obtained from laboratory dyeings
                  utilizing the type 4 yellow dye.

# Appendix C
# Physical Testing

Table C1    Fastness data for red dyes.

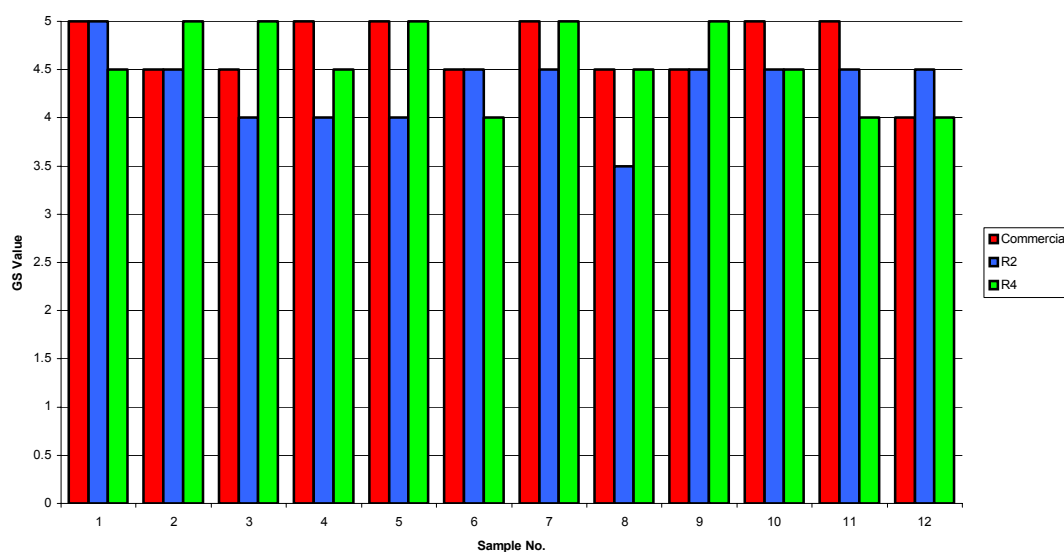| Sample No.* | Crocking | | Wet Color Transfer | | | | | | Light Fastness | | Light Fastness | |
| | Dry | Wet | Ace-tate | Cotton | Nylon | PET | Acrylic | Wool | Delta E 20 Hour | Delta E 40 Hour | GS 20 Hour | GS 40 Hour |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 2.14 | 3.83 | 3.5 | 2 |
| 2 | 4.5 | 4.5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 2 | 4.63 | 3.5 | 1.5 |
| 3 | 4.5 | 4.5 | 5 | 4.5 | 4 | 5 | 5 | 4.5 | 2.69 | 4.41 | 3.5 | 1.5 |
| 4 | 5 | 4 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 2.1 | 3.88 | 4 | 2.5 |
| 5 | 5 | 3.5 | 5 | 4 | 4 | 5 | 5 | 4 | 2.66 | 3.69 | 4 | 3 |
| 6 | 4.5 | 3.5 | 5 | 3.5 | 3.5 | 5 | 5 | 4 | 2.08 | 2.98 | 4 | 3 |
| 7 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 4 | 3.2 | 4.05 | 3.5 | 2 |
| 8 | 4.5 | 5 | 5 | 4.5 | 4.5 | 5 | 4.5 | 4.5 | 2.93 | 4.4 | 2.5 | 1.5 |
| 9 | 4.5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 3.15 | 5.07 | 2 | 1.5 |
| 10 | 5 | 5 | 5 | 3.5 | 4 | 5 | 4.5 | 4.5 | 3.36 | 5.66 | 2 | 1.5 |
| 11 | 5 | 4.5 | 5 | 3.5 | 3.5 | 5 | 5 | 4.5 | 2.54 | 5.14 | 3 | 1.5 |
| 12 | 4 | 4 | 5 | 3.5 | 4 | 5 | 4.5 | 5 | 2.46 | 4.43 | 3 | 2 |
| 13 | 5 | 4.5 | 5 | 4.5 | 5 | 5 | 4.5 | 5 | 3.14 | 5.91 | 3 | 1.5 |
| 14 | 4.5 | 4 | 5 | 4.5 | 4.5 | 5 | 4.5 | 5 | 4.1 | 6.56 | 3 | 1 |
| 15 | 4 | 4 | 5 | 4.5 | 4.5 | 5 | 4.5 | 4.5 | 4.31 | 7.94 | 2.5 | 1 |
| 16 | 4 | 4 | 5 | 4 | 4 | 5 | 4.5 | 4.5 | 3.16 | 5.86 | 3 | 2 |
| 17 | 4 | 4 | 5 | 2.5 | 2.5 | 5 | 4.5 | 3.5 | 3.08 | 5.59 | 3 | 1.5 |
| 18 | 4.5 | 4 | 5 | 2.5 | 2.5 | 4.5 | 4 | 4 | 2.87 | 5.42 | 3 | 2 |
| 19 | 4.5 | 4.5 | 5 | 3.5 | 3.5 | 5 | 4.5 | 4 | 3.87 | 5.88 | 2 | 1.5 |
| 20 | 3.5 | 4 | 5 | 4.5 | 5 | 5 | 4.5 | 5 | 3.25 | 5.92 | 3 | 1.5 |
| 21 | 4.5 | 4 | 5 | 3.5 | 3.5 | 4.5 | 4 | 4 | 3.53 | 6.19 | 2.5 | 1.5 |
| 22 | 4.5 | 4 | 5 | 3 | 3 | 4.5 | 4 | 4 | 3.13 | 5.26 | 2.5 | 1.5 |
| 23 | 4.5 | 4 | 5 | 2 | 2 | 4.5 | 4 | 3 | 2.81 | 4.77 | 2.5 | 1.5 |
| 24 | 4.5 | 4 | 5 | 1.5 | 2 | 4.5 | 4 | 3 | 2.36 | 4.41 | 3 | 2 |
| 25 | 4.5 | 5 | 5 | 3 | 3 | 4.5 | 4 | 4 | 3.22 | 5.16 | 1.5 | 1 |
| 26 | 5 | 5 | 5 | 2.5 | 2.5 | 4.5 | 4 | 3.5 | 2.74 | 4.74 | 2.5 | 2 |
| 27 | 5 | 5 | 5 | 2 | 2 | 4.5 | 4.5 | 4 | 2.64 | 4.55 | 2.5 | 2 |
| 28 | 4.5 | 4.5 | 5 | 2 | 2 | 5 | 4 | 3.5 | 2.63 | 4.48 | 2 | 1.5 |
| 29 | 5 | 4.5 | 5 | 1.5 | 1.5 | 4 | 4.5 | 3 | 2.18 | 3.94 | 4 | 3 |
| 30 | 4 | 4.5 | 5 | 1.5 | 1.5 | 4.5 | 4.5 | 3 | 1.78 | 3.6 | 3.5 | 3 |
| 31 | 5 | 5 | 5 | 4 | 4 | 4 | 4.5 | 4.5 | 3.13 | 5.03 | 3 | 1.5 |
| 32 | 4.5 | 4.5 | 5 | 4 | 4 | 5 | 4.5 | 4.5 | 2.11 | 3.73 | 3 | 2 |
| 33 | 5 | 5 | 5 | 2.5 | 2.5 | 5 | 4.5 | 3.5 | 2.74 | 4.63 | 4 | 2 |
| 34 | 4.5 | 4.5 | 5 | 3 | 2.5 | 5 | 4.5 | 4 | 2.49 | 4.28 | 4 | 2 |
| 35 | 4 | 4 | 5 | 3 | 4 | 4.5 | 4 | 3.5 | 2.04 | 3.94 | 4 | 3 |
| 36 | 4 | 4 | 5 | 2 | 2 | 4 | 3.5 | 3 | 2.11 | 3.62 | 4 | 3.5 |

* See Table B10

Figure C1    Colorfastness to dry crocking for red dyes.
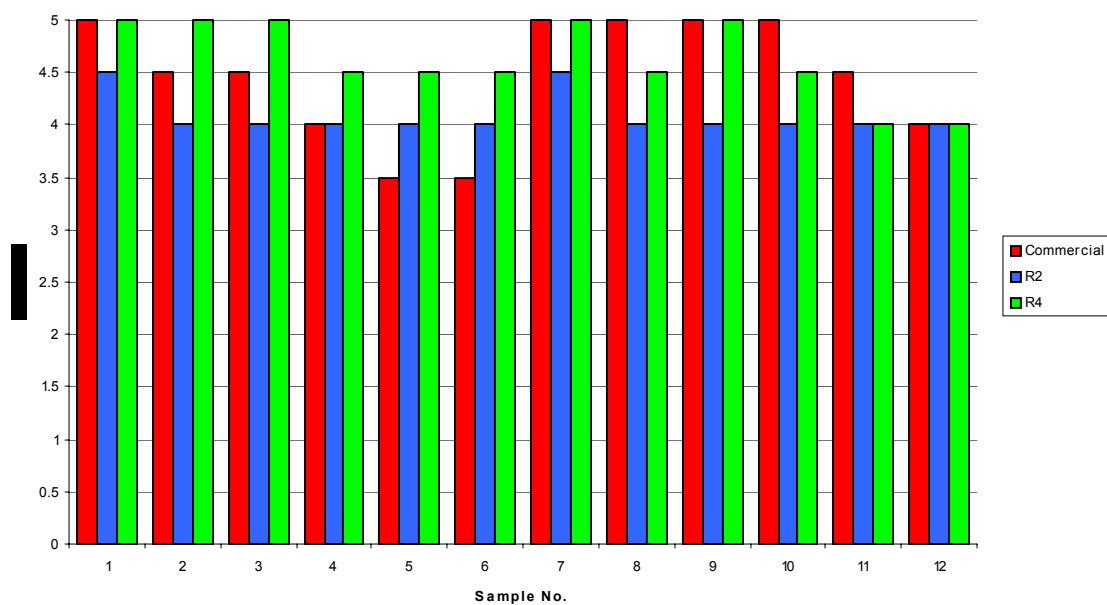


Figure C2    Colorfastness to wet crocking for red dyes.
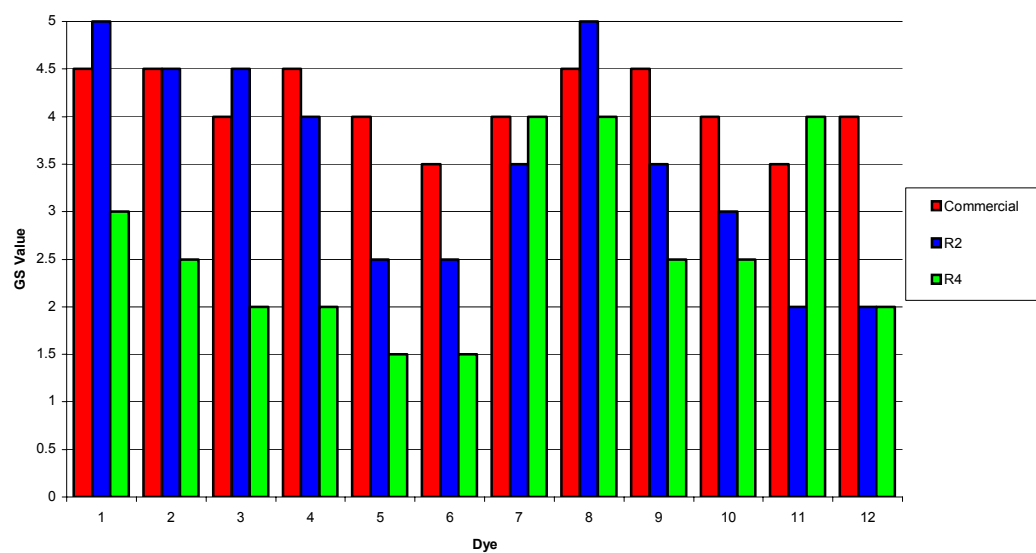
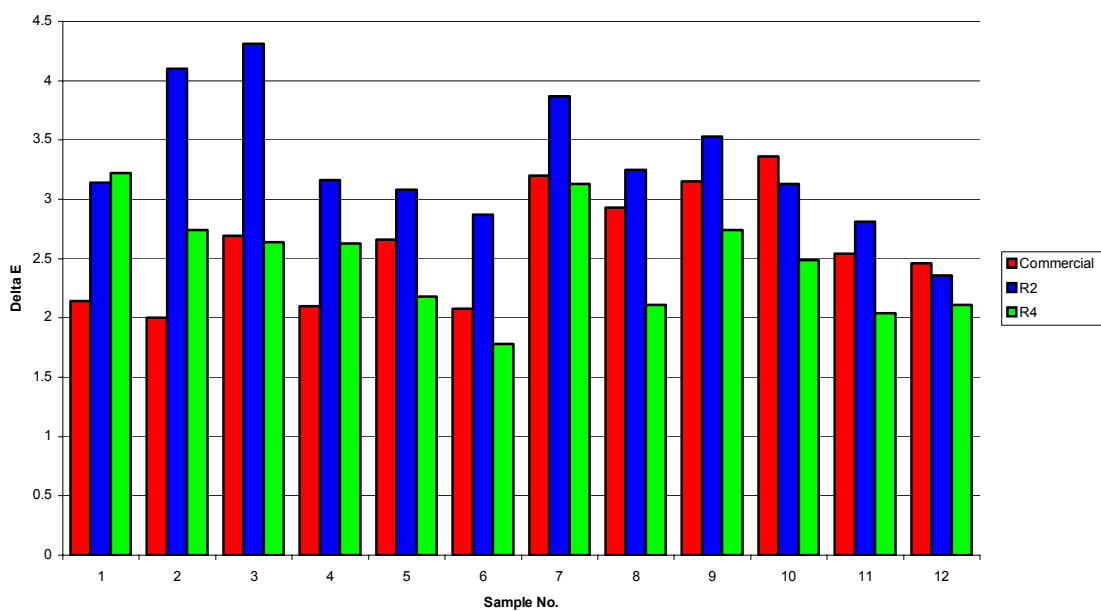Figure C3    Colorfastness to water for red dyes.



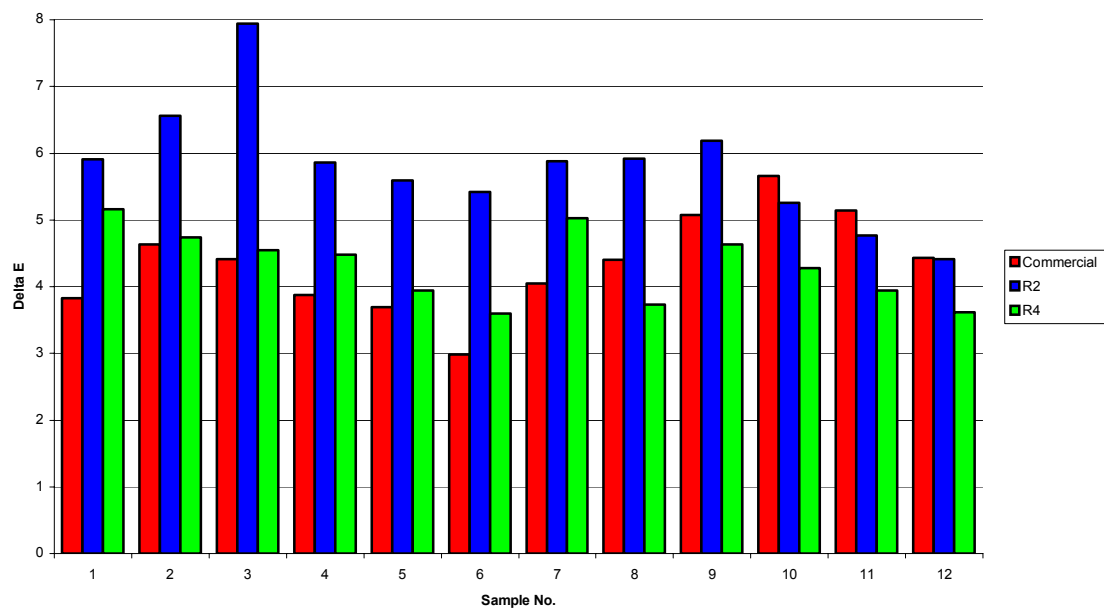Figure C4    Colorfastness to light at 20 h for red dyes.

Figure C5    Colorfastness to light at 40 h for red dyes.

Table C2    Fastness data for blue dyes

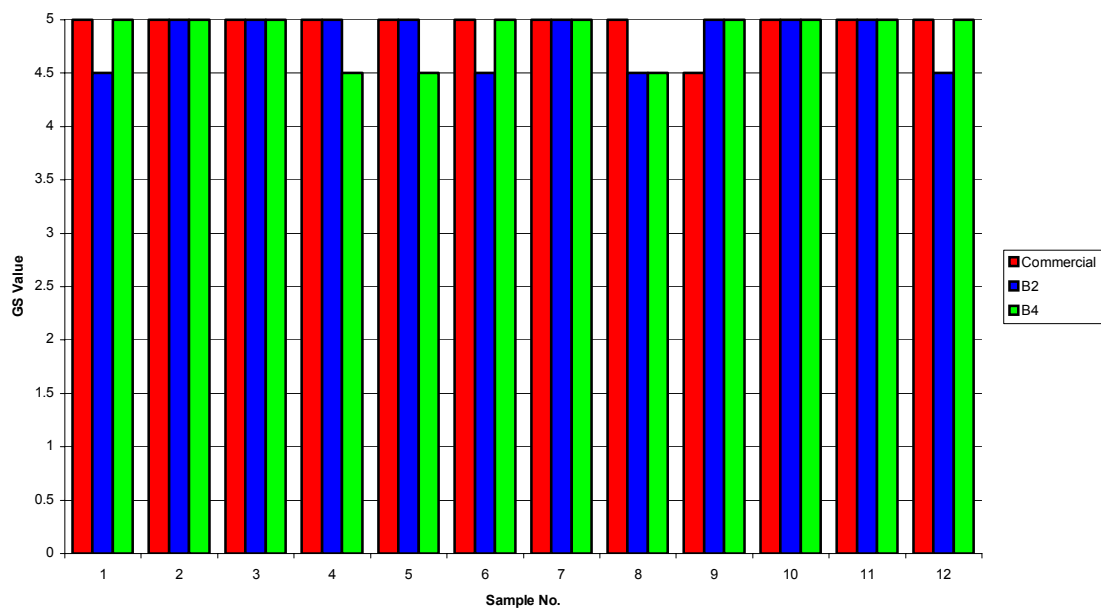| Sample No.* | Crocking | | Wet Color Transfer | | | | | | Light Fastness | | Light Fastness | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Dry | Wet | Ace-tate | Cotton | Nylon | PET | Acrylic | Wool | Delta E 20 Hour | Delta E 40 Hour | GS 20 Hour | GS 40 Hour |
| 37 | 5 | 5 | 5 | 4.5 | 4 | 5 | 5 | 4.5 | 3.36 | 3.5 | 3.5 | 3 |
| 38 | 5 | 5 | 5 | 4.5 | 4 | 5 | 5 | 4.5 | 2.48 | 4.3 | 3 | 1.5 |
| 39 | 5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 2.57 | 4.22 | 2.5 | 1.5 |
| 40 | 5 | 4.5 | 5 | 5 | 4.5 | 5 | 5 | 4.5 | 2.18 | 3.97 | 3 | 1.5 |
| 41 | 5 | 4.5 | 5 | 4 | 3.5 | 4.5 | 4.5 | 4 | 2.23 | 3.67 | 3.5 | 2 |
| 42 | 5 | 5 | 5 | 3.5 | 3.5 | 4.5 | 4.5 | 4 | 2.04 | 3.7 | 3.5 | 2 |
| 43 | 5 | 5 | 5 | 4.5 | 4 | 5 | 5 | 4 | 1.3 | 2.24 | 4 | 2.5 |
| 44 | 5 | 5 | 5 | 4 | 3.5 | 5 | 4.5 | 4 | 2.37 | 3.83 | 3.5 | 2.5 |
| 45 | 4.5 | 5 | 5 | 4 | 3 | 5 | 4.5 | 4 | 2.51 | 4.21 | 3.5 | 2 |
| 46 | 5 | 5 | 5 | 4 | 3 | 4.5 | 4.5 | 3.5 | 2.7 | 3.88 | 3 | 2 |
| 47 | 5 | 5 | 5 | 4 | 4 | 5 | 4.5 | 4 | 2.54 | 4.25 | 3 | 2 |
| 48 | 5 | 4.5 | 5 | 4 | 3 | 5 | 4.5 | 4 | 2.87 | 4 | 3 | 2 |
| 49 | 4.5 | 4.5 | 5 | 4 | 4 | 5 | 5 | 4.5 | 3.35 | 5.33 | 3 | 1.5 |
| 50 | 5 | 4 | 5 | 4 | 3.5 | 4.5 | 4.5 | 4 | 2.92 | 4.77 | 3 | 1.5 |
| 51 | 5 | 4.5 | 5 | 4 | 4 | 5 | 4.5 | 4.5 | 2.29 | 4.32 | 3.5 | 2 |
| 52 | 5 | 4 | 5 | 4.5 | 4 | 5 | 4.5 | 4.5 | 2.64 | 4.93 | 3.5 | 2 |
| 53 | 5 | 3.5 | 5 | 4.5 | 4.5 | 5 | 4.5 | 4 | 2.24 | 4.02 | 3.5 | 2.5 |
| 54 | 4.5 | 3.5 | 5 | 3.5 | 3 | 5 | 4.5 | 4 | 1.56 | 3.59 | 4 | 3 |
| 55 | 5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 2.42 | 3.89 | 3 | 2.5 |
| 56 | 4.5 | 4.5 | 5 | 4.5 | 4 | 4.5 | 4.5 | 4 | 2.24 | 4.34 | 3.5 | 2 |
| 57 | 5 | 4 | 5 | 4 | 3.5 | 4 | 4.5 | 4 | 2.28 | 4.46 | 3.5 | 2 |
| 58 | 5 | 5 | 5 | 4 | 3.5 | 4.5 | 4.5 | 4 | 2.04 | 4.43 | 4 | 2 |
| 59 | 5 | 4.5 | 5 | 3.5 | 3 | 4 | 4.5 | 3.5 | 2.12 | 3.79 | 4 | 2.5 |
| 60 | 4.5 | 4 | 5 | 4 | 2.5 | 4 | 4.5 | 4 | 2.04 | 3.56 | 3.5 | 2.5 |
| 61 | 5 | 5 | 5 | 4.5 | 3.5 | 4.5 | 4.5 | 4 | 2.13 | 3.78 | 3 | 2 |
| 62 | 5 | 5 | 5 | 3.5 | 2.5 | 4.5 | 4.5 | 4 | 2.24 | 4.43 | 3.5 | 1.5 |
| 63 | 5 | 5 | 5 | 3.5 | 2.5 | 4.5 | 4.5 | 4 | 2.47 | 3.98 | 3.5 | 2 |
| 64 | 4.5 | 5 | 5 | 3 | 2.5 | 4.5 | 4.5 | 4 | 2.33 | 4.22 | 3.5 | 1.5 |
| 65 | 4.5 | 5 | 5 | 2.5 | 2 | 4 | 4.5 | 3.5 | 2.32 | 3.96 | 3.5 | 2 |
| 66 | 5 | 5 | 5 | 3.5 | 2.5 | 3.5 | 3.5 | 3 | 2.3 | 4.05 | 3.5 | 2 |
| 67 | 5 | 5 | 5 | 4.5 | 4 | 5 | 4.5 | 4 | 3.35 | 4.8 | 3 | 1.5 |
| 68 | 4.5 | 5 | 5 | 4 | 4 | 5 | 4.5 | 4 | 3.05 | 4.6 | 2.5 | 1.5 |
| 69 | 5 | 5 | 5 | 4 | 3.5 | 4.5 | 4.5 | 4 | 2.6 | 4.07 | 3 | 2 |
| 70 | 5 | 5 | 5 | 4 | 4 | 4.5 | 4 | 4 | 2.96 | 4.54 | 2.5 | 1.5 |
| 71 | 5 | 4.5 | 5 | 4 | 4 | 4.5 | 4.5 | 4 | 2.47 | 4.1 | 3 | 1.5 |
| 72 | 5 | 4.5 | 5 | 3 | 2.5 | 4 | 4 | 3.5 | 2.64 | 4.18 | 3 | 1.5 |

*See Table B20

Figure C6      Colorfastness to dry crocking for blue dyes.
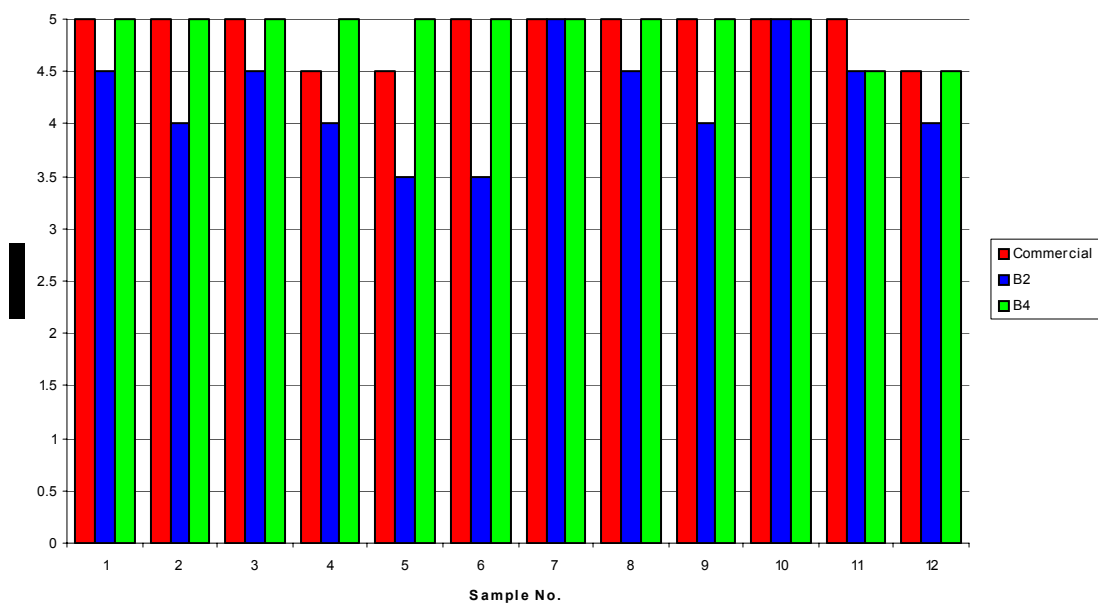


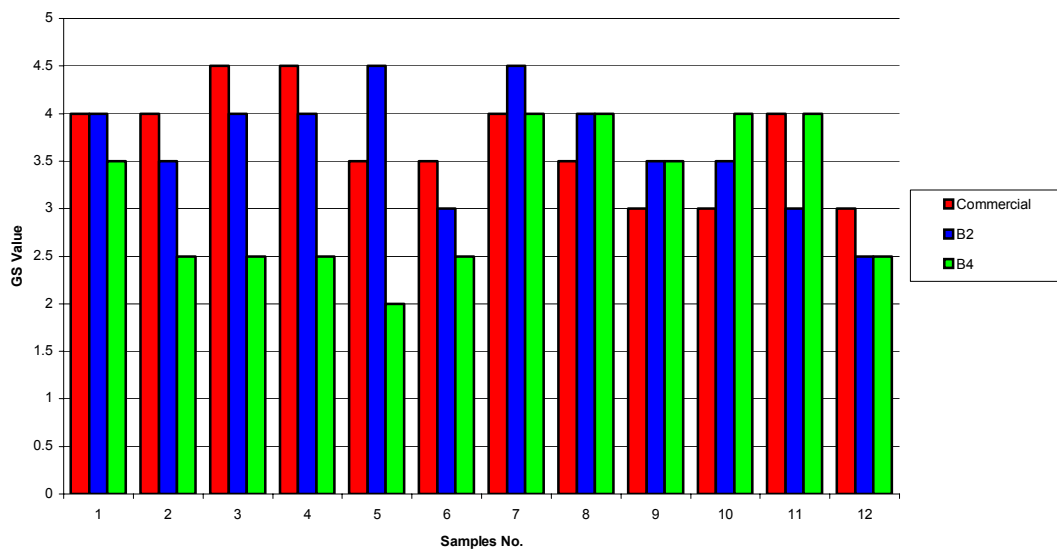Figure C7      Colorfastness to wet crocking for blue dyes.

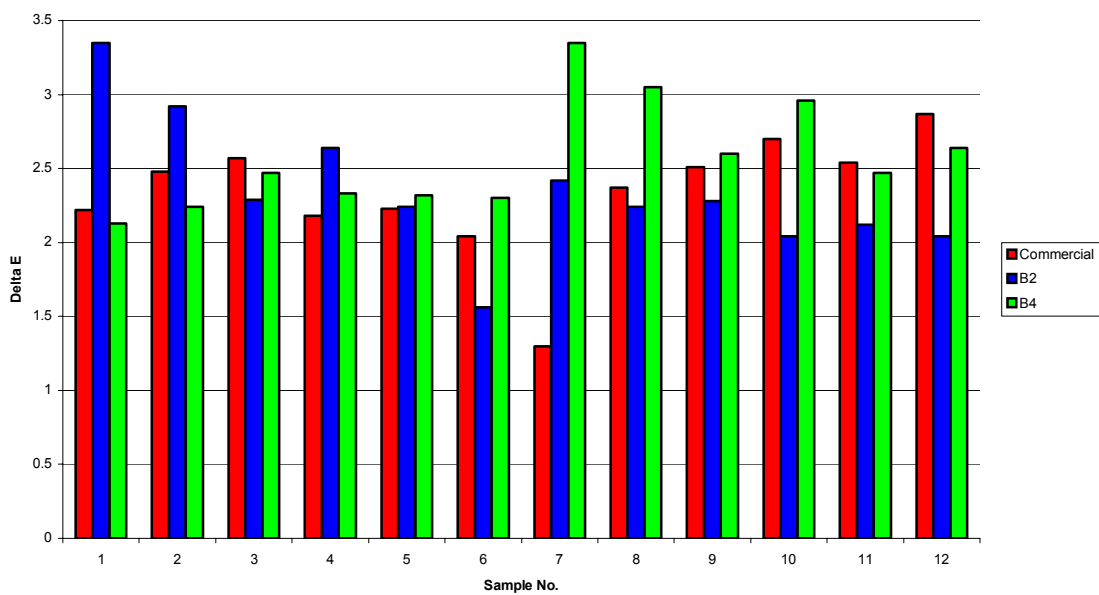Figure C8    Colorfastness to water for blue dyes



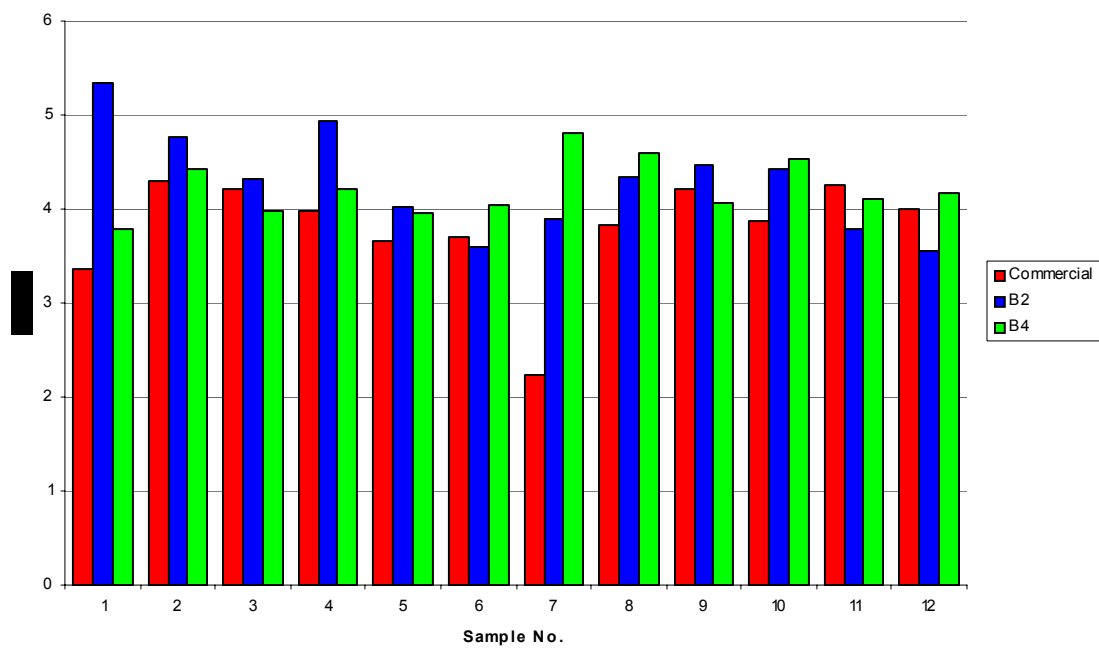Figure C9    Colorfastness to light at 20 h for blue dyes

Figure C10    Colorfastness to light for 40 h at blue dyes.

Table C3    Fastness data for yellow dyes.

| Sample No.* | Crocking | | Wet Color Transfer | | | | | | Light Fastness | | Light Fastness | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Dry | Wet | Ace-tate | Cotton | Nylon | PET | Acrylic | Wool | Delta E 20 Hour | Delta E 40 Hour | GS 20 Hour | GS 40 Hour |
| 73 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 1.1 | 1.19 | 5 | 5 |
| 74 | 4.5 | 4.5 | 5 | 4.5 | 4.5 | 5 | 5 | 5 | 0.51 | 1.56 | 5 | 5 |
| 75 | 4.5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 1.13 | 1.45 | 5 | 5 |
| 76 | 4.5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 5 | 0.57 | 1.17 | 5 | 5 |
| 77 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 4.5 | 0.77 | 1.47 | 5 | 5 |
| 78 | 4 | 4.5 | 5 | 4 | 4 | 5 | 5 | 4.5 | 0.61 | 1.75 | 5 | 4.5 |
| 79 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 4 | 1.25 | 1.5 | 5 | 5 |
| 80 | 5 | 5 | 5 | 5 | 4.5 | 5 | 5 | 5 | 0.39 | 1.1 | 5 | 5 |
| 81 | 4.5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4 | 1.71 | 2.54 | 4.5 | 4.5 |
| 82 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 4.5 | 1.41 | 2.2 | 5 | 4.5 |
| 83 | 4 | 4.5 | 5 | 4 | 4 | 5 | 5 | 4 | 1.14 | 1.82 | 5 | 4.5 |
| 84 | 5 | 4.5 | 5 | 4.5 | 4.5 | 5 | 5 | 4 | 1.07 | 1.79 | 5 | 4.5 |
| 85 | 5 | 4.5 | 5 | 4 | 3.5 | 5 | 5 | 4 | 0.98 | 1.59 | 5 | 4.5 |
| 86 | 5 | 4 | 5 | 4 | 4 | 5 | 5 | 4 | 0.7 | 1 | 5 | 5 |
| 87 | 5 | 4 | 5 | 4.5 | 4 | 5 | 5 | 4.5 | 0.58 | 1.38 | 5 | 5 |
| 88 | 5 | 4 | 5 | 4 | 3.5 | 5 | 5 | 4.5 | 0.68 | 1.28 | 5 | 5 |
| 89 | 4.5 | 4 | 5 | 4 | 3.5 | 5 | 5 | 4 | 1.02 | 1.31 | 5 | 5 |
| 90 | 4 | 4 | 5 | 3.5 | 3 | 5 | 5 | 4 | 1.63 | 1.7 | 5 | 5 |
| 91 | 5 | 5 | 5 | 4 | 3.5 | 5 | 5 | 4 | 1.54 | 2.17 | 4.5 | 4.5 |
| 92 | 5 | 5 | 5 | 4 | 3.5 | 5 | 4.5 | 4.5 | 1.57 | 1.82 | 4.5 | 4.5 |
| 93 | 5 | 4.5 | 5 | 3.5 | 3 | 5 | 5 | 4.5 | 0.85 | 1.84 | 5 | 4.5 |
| 94 | 4.5 | 4.5 | 5 | 3.5 | 3 | 5 | 5 | 4 | 1.3 | 2.12 | 4.5 | 4.5 |
| 95 | 4 | 4 | 5 | 3 | 2.5 | 5 | 5 | 4 | 1.14 | 1.85 | 5 | 5 |
| 96 | 4 | 4 | 5 | 4 | 4 | 5 | 5 | 4 | 1.57 | 2.09 | 5 | 5 |
| 97 | 5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 1.15 | 2.1 | 5 | 4 |
| 98 | 5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4 | 1.3 | 2.23 | 5 | 4 |
| 99 | 4.5 | 5 | 5 | 4.5 | 4.5 | 5 | 5 | 4.5 | 1.49 | 1.98 | 5 | 4.5 |
| 100 | 5 | 5 | 5 | 3 | 2.5 | 5 | 4.5 | 4 | 1.29 | 2.51 | 4.5 | 4 |
| 101 | 5 | 5 | 5 | 3.5 | 3 | 5 | 5 | 4.5 | 1.15 | 2.18 | 5 | 4 |
| 102 | 4.5 | 5 | 5 | 4 | 3.5 | 5 | 4.5 | 4 | 1.38 | 2.33 | 5 | 4 |
| 103 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 5 | 1.69 | 2.56 | 5 | 4 |
| 104 | 4.5 | 5 | 5 | 3 | 2.5 | 5 | 5 | 5 | 1.66 | 1.96 | 4.5 | 4.5 |
| 105 | 4.5 | 5 | 5 | 4 | 3 | 5 | 5 | 5 | 0.15 | 1.06 | 4.5 | 5 |
| 106 | 5 | 5 | 5 | 4 | 4 | 5 | 5 | 5 | 1.7 | 2.65 | 5 | 4 |
| 107 | 4.5 | 5 | 5 | 3 | 2.5 | 5 | 5 | 4 | 1.21 | 1.99 | 4.5 | 4.5 |
| 108 | 4 | 5 | 5 | 3 | 2 | 5 | 5 | 4 | 1.03 | 2.04 | 4.5 | 4.5 |

* See Table B30
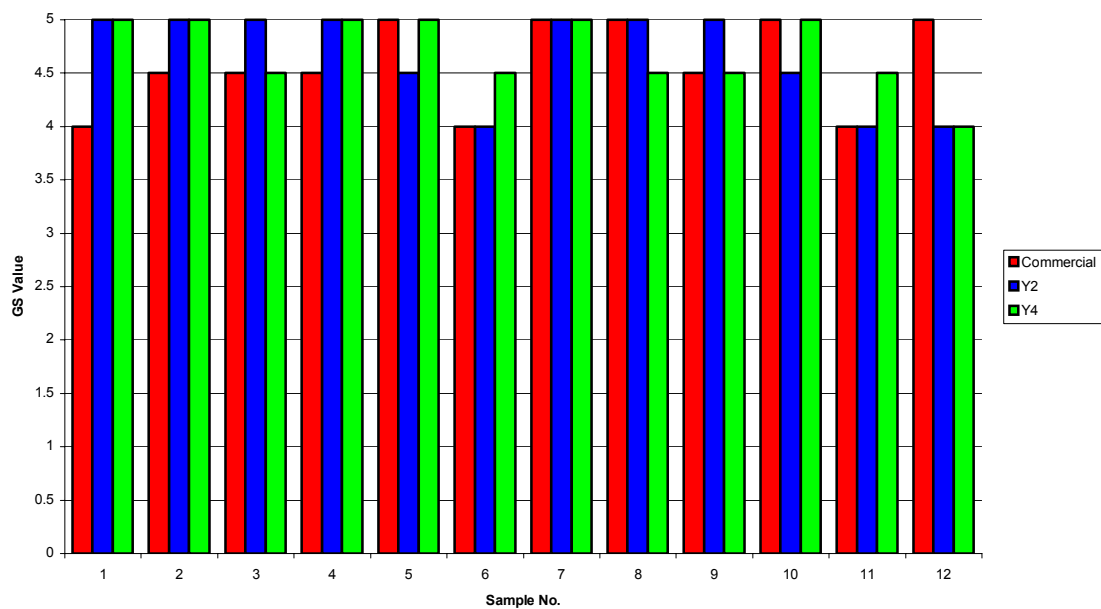
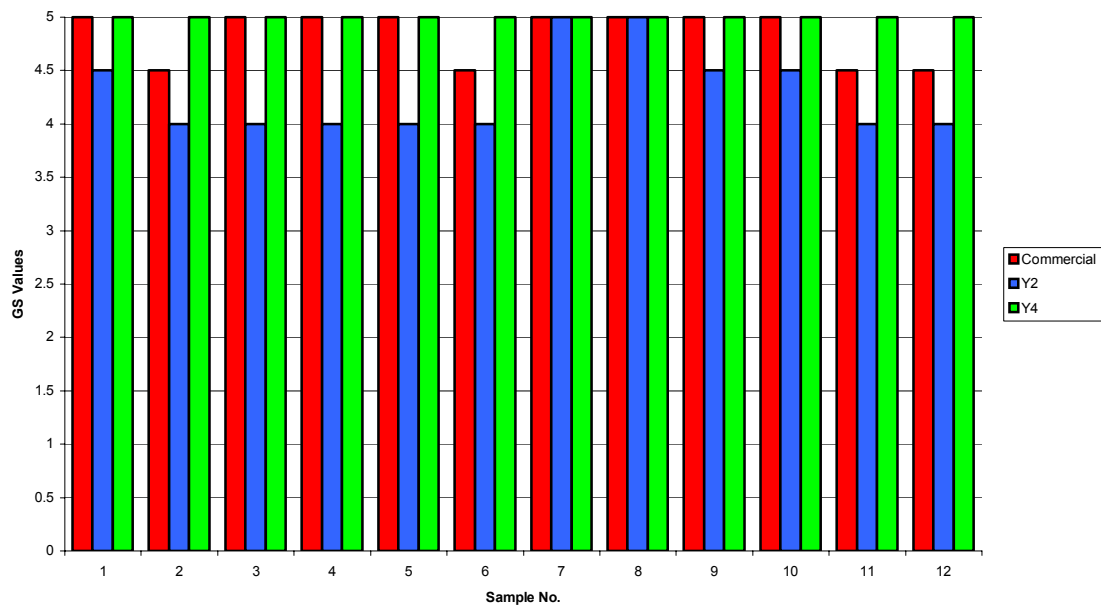Figure C11    Colorfastness to dry crocking for yellow dyes.



Figure C12    Colorfastness to wet crocking for yellow dyes.
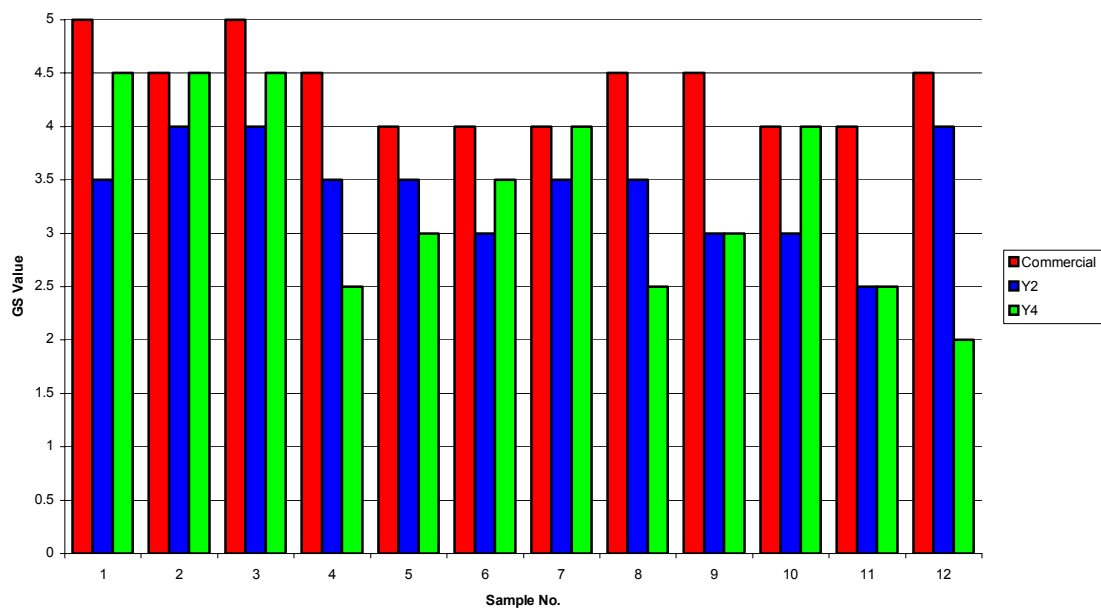
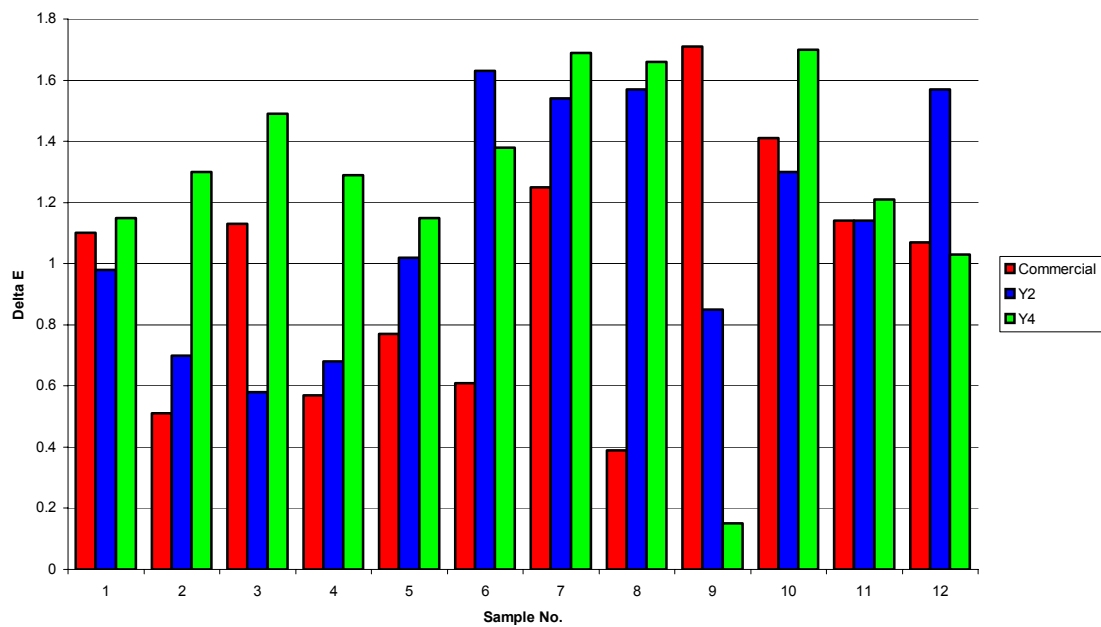Figure C13    Colorfastness to water for yellow dyes
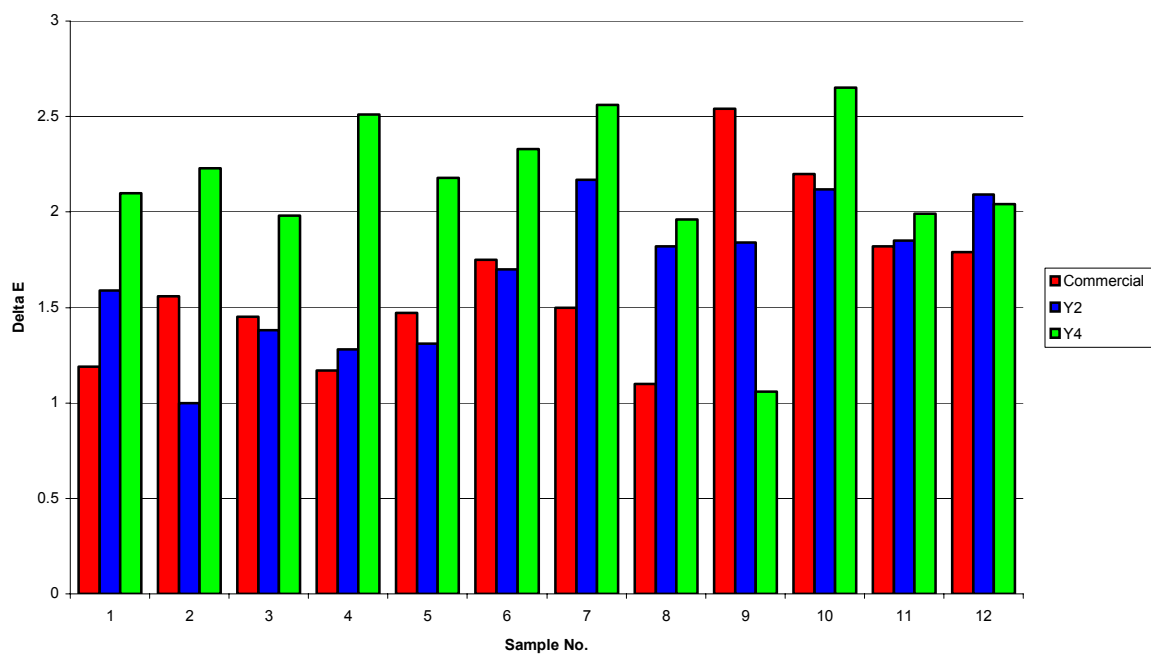


Figure C14    Colorfastness to light at 20 h for yellow dyes.

Figure C15    Colorfastness to light at 40 h for yellow dyes.