KINETICS OF DYEING BEHAVIOR OF COTTON AND MODAL FABRICS WITH REACTIVE DYES

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BONAFIDE CERTIFICATE

Certified that this project report titled **"KINETICS OF DYEING BEHAVIOR OF COTTON AND MODAL FABRICS WIITH REACTIVE DYES"** is the bonafide work of **Miss. V. Veena Sindhuja** who carried out the research under my supervision. Certified further, that to the best of my knowledge the work reported herein does not form part of any other project report or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

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ABSTRACT

Cotton is the mostly used cellulosic fibre from long ago. Since newly developing man-made cellulosic fibre gained importance as they are produced from renewable resources that is from wood pulp. Modal is one such cellulosic fibre produced by new novel process route, with improved property.

Cotton and modal are both cellulosic in nature with same chemical composition. Due to the change in viscose process manufacturing sequence, modal differs in its physical properties. The influence of physical property of modal and cotton on dyeing behaviour was studied.

Cotton and Modal fabrics are dyed with bifunctional reactive dyes. The effect of concentration, temperature and time on modal and cotton was studied by measuring the parameters such as dye affinity, diffusion coefficient, dye uptake and k/s values. Fastness values was also determined.

The results found that dye affinity and diffusion rate of modal is less than cotton. In order to obtain maximum absorption and same shade that of cotton, temperature was increased to 80°C incase of modal/cotton fabrics. Incase, modal dyed separately at recommended dyeing temperature (65 °C), dye concentration is to be increased by 0.5% (o.w.f).

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CHAPTER 1

INTRODUCTION

Cotton has been serviced to mankind for so long that its versatility is almost unlimited and new uses are constantly being discovered. It can be depended on to serve many purposes. Not only cotton a textile in its own right, but some of its byproducts form the base such as viscose rayon which is also cellulosic nature.

The greatest technological break through in rayon is high wet modulus rayon, which is termed as "Modal" by Lenzing. This is also a cellulosic fiber as cotton, but these two fibers differ in percentage of cellulose present and in physical structure. The arrangement of molecular chains in fibers, orientation, and length differs so the performance characteristics related to these aspects also differs. Modal dyed along with cotton fabric using bifunctional reactive dyes and their dyeing behavior is studied by determining its dye affinity, diffusion rate and rate of reaction. The effects of temperature and time periods were studied to determine suitable temperature and time for dyeing of modal fabrics. The k/s values were found to determine the dye strength. With the k/s values the measures to improve the dye absorption rate were taken.

1.1. COTTON AND MODAL FIBER PROPERTIES

Both cotton and modal are cellulosic nature. Due to the changes in the viscose manufacturing process fiber with different property is produced. Because of acid bath of less concentration, there is a slower regeneration and coagulation so that more stretch and greater the orientation of molecules can be achieved, but it retains its microfibrillar structure so its performance is more similar to that of cotton. But due to its higher orientation how the dyeing behavior differs is to be studied.

The difference in the manufacturing process with that of viscose rayon process is as follows,

Purified sheet of cellulose → steeped in NaOH → squeezed → shredding → no aging → crumbs treated with carbon disulfide (39%-50%) to form cellulose xanthate → crumbs +2.8% NaOH to form viscose solution → no aging → solution filtered → pumped to spinnerete and extruded in acid bath of

1% - H_2So_4,

4-6% - Na_2So_4,

Speed - 20-30 m/min

Temperature - 25-35 °C

Stretch – 150-600%

Due to the changes in the bath and stretch% the fibre characteristics also varies.

CHAPTER 2

2.1. FIBRE STRUCTURE

2.2.1. Physical structure:

Dyeing can be defined as the process in the course of which a textile fiber is placed in contact with the solution or dispersion of a dye (Gulrajani etal June1999). This is due to the interrelationship between the molecules. For examining the constitution of textile fibers, characteristic of fibers have to be studied.

Both cotton and modal are cellulosic fibers. Both have same chemical structure but the physical characteristics differ in nature. Generally fibers are made of fibrillar filaments and their molecules are grouped to form linear polymers. An x-ray examination of fibers shows that their molecules are grouped in a regularly shaped crystalline structure i.e., crystalline elements immersed in a substance of an amorphous structure.

Like fibers, dye molecules also have lengthened structure, so for diffusion of dye in to fiber, pore size has to be increased. Generally dyeing is carried out in an aqueous medium and when fiber is immersed in water, it tends to swell to greater or lesser extent depending on the hydrophilic groups present in the molecule. It is obvious to evaluate the size of pores and length of dye molecules. Morton have measured the radius of pores for viscose rayon value ranges about 5 Å (dry state) 20-30 Å (wet state) so values of cellulosic fibers can be imagined within range between 26-100 Å.

2.2.2. Chemical structure

The basic of the chemical composition of all vegetable fibers is cellulose, which is present to a greater or lesser extent modified from cotton to viscose and modal fibers.

As far as their dyeing performance is concerned, all these fibers can be placed in the same group, although there are naturally some difference in general basis of their dyeing behavior. All cellulosic nature fibers such as cotton, modal consists of chain of cellobiose. The repeat unit $(C_6H_{10}O_5)n$ differs from cotton to modal. The repeat unit of cotton is 10,000 whereas for modal is 450-750.

2.2.3 Structural characteristics:

Modal is also cellulosic fiber, which has the same chemical composition and chemical structure as that of cotton except chains are shorter.

In table 1.1, molecular structure (such as density, degree of polymerization, molecular mass) and super molecular structure (crystallinity index, crystalline dimensions, molecular orientation, structure of void, void diameter), which shows difference between modal and cotton fibers. These parameters which significantly influence the water and dye adsorption property of the fibers.

Table 1.1 –Molecular structure

Difraction angle (20)	101	14.7	12.2
	101	20.0	16.6
	002	21.7	22.7
Crystalline dimension (nm)	101	3.1	4.1
	101	3.3	3.3
	002	4.3	4.9

The crystalline structure of modal differs from that of cotton fibers. It has higher molecular mass and degree of polymerization. By x-ray analysis (Tajana Kreze and SonjaMalej August 2003) intensity of crystalline peak of modal and cotton is shown in fig (1.1,1.2)

The intensity of crystalline peak at scattering angle 2θ at (101, 002 101) plane of reflections are seen. The results of wide-angle x-ray scattering of two fibers are as shown in table 1.2.

Table 1.2 –Crystallinity values

Crystalline (%)	70	41
Degree of polymerization	50.7	28.2
Density (g/cm3)	1.55	1.51
Orientation(fn)	0.4	0.7

figure 1.1- scattering curve of cotton

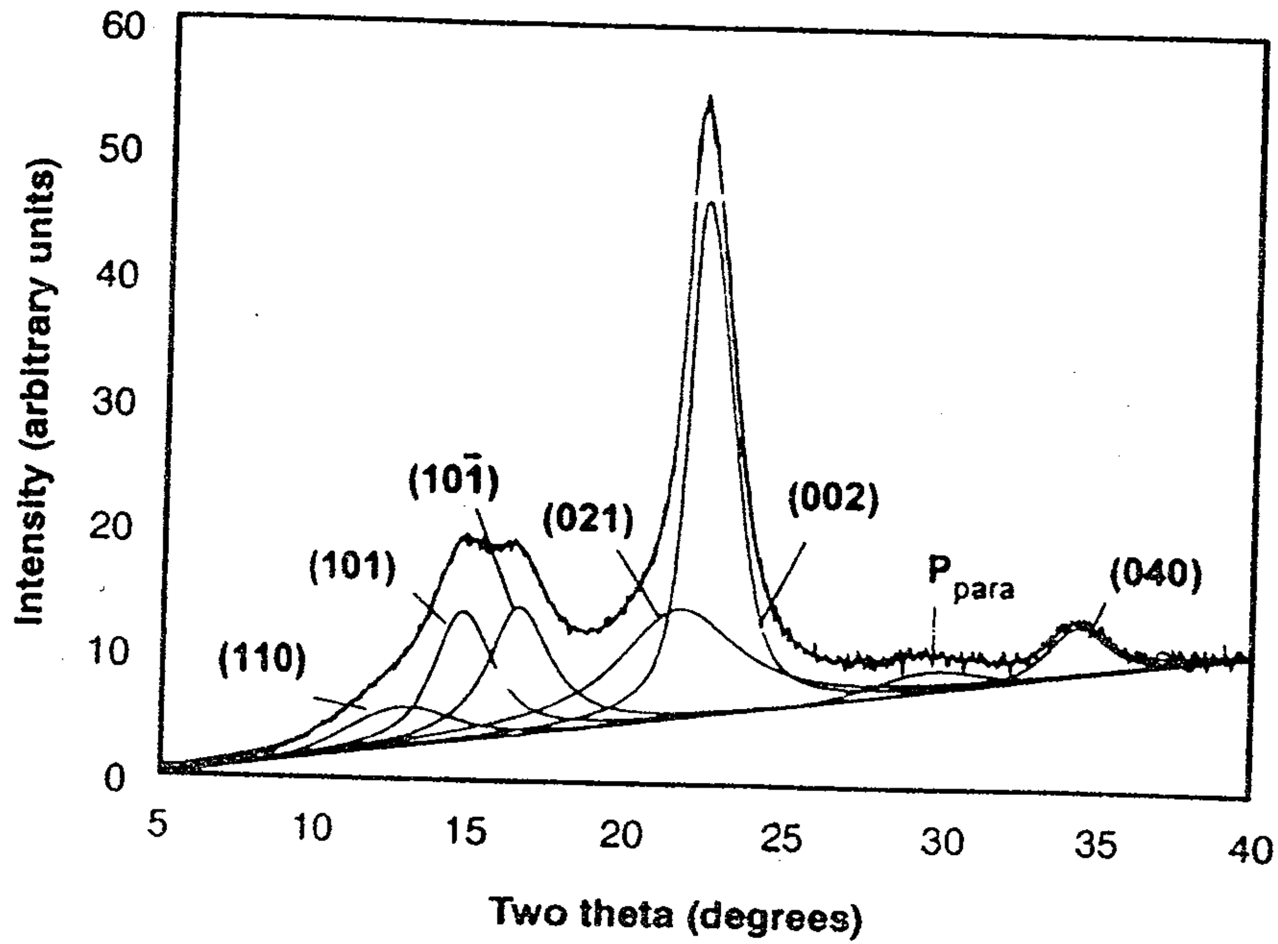
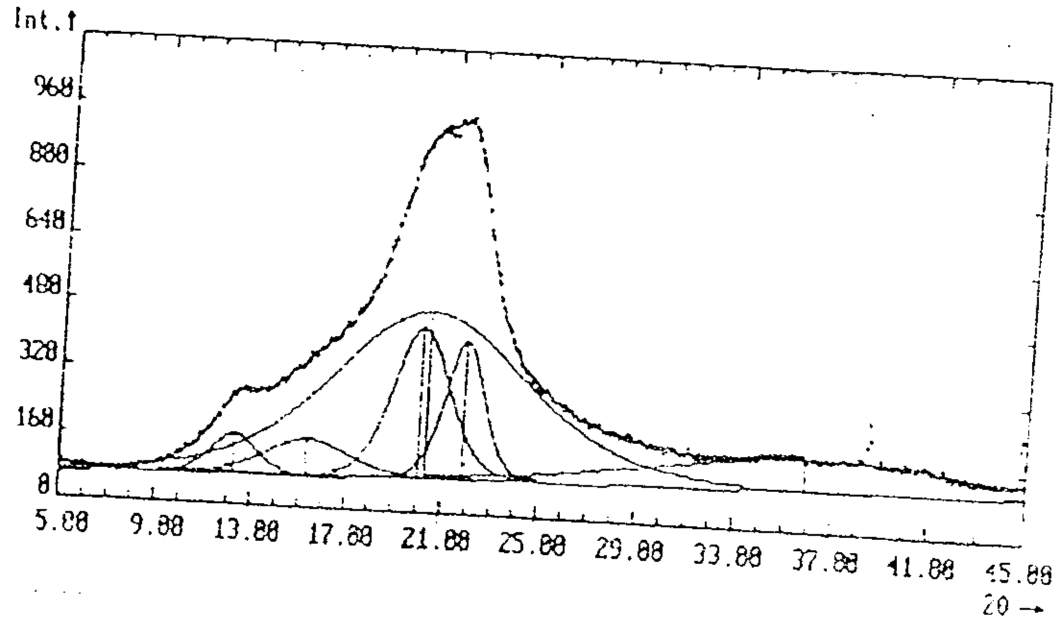


figure 1.2- scattering curve of modal



Difference in crystalline structure i.e., share of crystalline phase, crystalline dimensions, and orientation is different which is varied by high stretch ratio during formation. In modal fiber due to high stretch ratio than in viscose manufacture, orientation is high. Birefringence which is a measure of average orientation increase than that of viscose fiber but lesser when compared to that of cotton. Another important factor to be considered is the void diameters, volume and specific inner surface of the voids in fibers, which are related to water retention value and dye adsorption property. The water retention values of cellulosic fiber are obtained by measuring the amount of liquid water retained by the swollen fibers under defined conditions. Water retention value decreases from viscose to modal and modal to cotton.

Accessible regions (less ordered amorphous regions and void fraction) are as shown in fig(1.3.) The average diameter of voids decreases from viscose fiber to that of modal and cotton. The diameter and retention values are a shown in the table 1.3

Fig 1.3. Amorphous region of Modal and Cotton

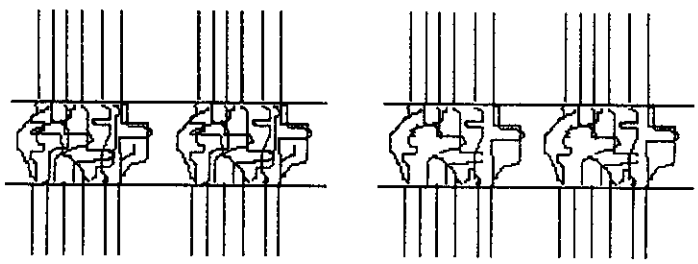


Table1.3-Void diameters

	Cotton	Modal
void dia (nm)	2.0	2.4
void volume (cm3/3)	0.22	0.45
water retention value	52	57.8
hygroscopic property(%)	50	60
swelling in water	35	63

Table 1.4 – General properties

	Cotton	Modal
Tenacity (cn/tex)	24-28	34-36
Wet tenacity(cn/tex)	25-30	20-22
Elong (%)	7-9	12-14
Wet strength	105	60
Fibrillation rate	2	1
Stiffness	57-60	28-75
Moisture regain (%) at 65% R.H	8	12.5
Breaking elong (%)	3-7	9-18
Wet elong (%)	12-14	13-15

Greater the inner surface and small volume of voids in modal indicates different void distributions which have greater diameter, so water retention value is higher for modal than that of cotton, but about 32% lower than viscose fibers. Some of the other general property (D.J. Cole 1999) of modal and cotton regarding its tensile strength and elongation is as shown in Table 1.4.

2.3. THEORY OF CELLULOSIC DYEING WITH REACTIVE DYES

Reactive dyes which are exclusively suitable dye for cellulosic fiber fabrics. These dyes have good affinity for fiber by forming covalent bond with the fiber. In spite of wide range of different reactive groups, their reaction with cellulose they can be divided in to 2 types:

- Reactive dye that form cellulose ester
- Reactive dye that form cellulose ether

For dyeing of cotton and modal fabrics reactive dyes that form cellulose esters which have monochlorotriazine their reaction takes place by means of a nucleophilic replacement mechanism. The cellulosic fiber dyeing with reactive dyes takes place in 3 distinct phases:

(i) Dye absorption by fiber in neutral phase and followed by alkaline liquor for reaction to take place.

(ii) Dye reaction in alkaline liquor with cellulose and water hydroxyl groups.

(iii) Elimination of hydrolysed dye that is not fixed.

The reaction takes place with (–OH) groups in cellulose but as water also contains (–OH) group so the dye is also capable of reacting with the water. Such dye is known as hydrolysed dye, which has lost its ability to form covalent bond with cellulose and therefore have much low affinity and low washing fastness.

The reaction shows dyeing step by step process in which at final phase o dyeing process large quantity of dye has reacted with cellulose or it is hydrolysed. The dye already absorbed during the absorption phase can react with the fiber and covalent bond is formed.

The dye distribution in different process stages is shown in equilibrium of dye bath

External solution   Cellulosic fiber in dye bath

1. Neutral dyeing phase   Dye-Cl   Dye-Cl

Dye /
| \ Fiber
Cl /

2. Intermediate alkaline phase   Dye-Cl

Dye /
| \
Cl /
| Fiber
Dye /
| \
O /

3. Fixation phase   Dye-OH

Dye /
| \
Cl /
| \ Fiber
Dye /
| \
O /

2.3.1. Absorption

The first dyeing phase that takes place in cellulosic dyeing. When fabric to be dyed is added to the dye bath, dye is absorbed by cellulosic chains by secondary type force ad diffuses towards the interior of the fiber. Once equilibrium absorption is reached, alkali is added to dye bath for fixation of dye on to the fabric. The parameters that influence absorption are,

a) Nature of dye

The principle of dye exhaustion is a direct function of its affinity. Reactive dye which have low affinity but have high diffusion coefficient. The reason for this low affinity is due to hydrolysis of dye during dyeing. As affinity is greater in hydrolysed dye, which would be more difficult to eliminate from fiber, so less affinity is suitable. The affinity in turn, is a function of temp, because as this raises affinity decreases, so temperature is selected for good diffusion.

b) Influence of liquor ratio

One of the most important factors in exhaustion of this type of dye is liquor ratio. Its influence can be quantified by determining series of dyeing conditions, distribution constant between fiber and solution. The liquor ratio besides influencing the exhaustion also influences the dye hydrolysis, so in any case the dye yield is improved by working with short liquor ratio.

c) Influence of electrolyte concentration

Neutral electrolytes have a strong influence on reactive dye absorption, so the quantity of salt to be used depends upon the dye concentration and liquor ratio for deeper shades electrolyte concentration must be higher, whereas if liquor ratio is reduced quantity of electrolyte required is less.

d) pH influence

The reactive dye absorption phase takes place at neutral pH and during fixation and exhaustion pH is increased to pH of 11. It has been observed that when pH is over 11, more hydrolysis and reduction in exhaustion.

e) Temperature influence

As in all dyeing process increase in temperature reduces the exhaustion. In case of reactive dyes due to their greater diffusion co-efficient, equilibrium is reached within an hour, when temperature is suitably raised.

f) Influence of fiber

There are marked differences in reactive dye exhaustion on different cellulosic fibers. Depending on the amorphous region and internal volume of the fiber exhaustion, diffusion coefficient varies from fiber to fiber.

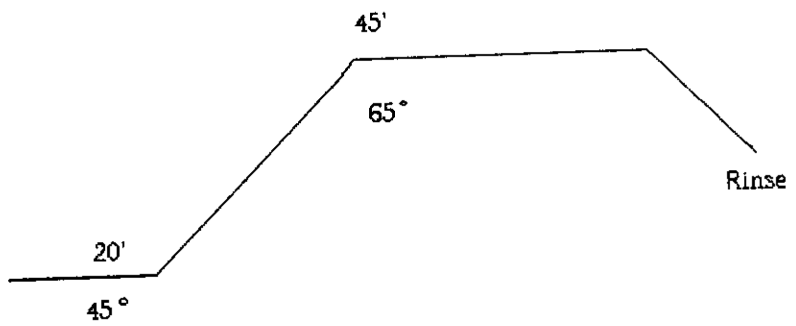
2.3.2 Mechanism of dyeing

Reactive dye is one of the most commonly used dyes for cellulosic fiber. It is exclusively used for cellulosic fiber due to affinity, easily soluble in reduced form and united to fiber by covalent bond formation, so excellent fastness to washing.

Modal and cotton is suitably dyed with reactive dye. The dyeing process is carried out preferably in scoured and bleached fabric. Reactive dye selected is bifunctional dye with good affinity. Before dyeing process is started, the fabric is given pretreatment. The goods are treated with acetic acid for neutral pH and to get high absorbency. Impurities, sizes, and lubricants must be removed.

The dyeing process takes place as follows: The goods have been immersed in dyeing equipment filled with liquor at m:l of 1:10. The required amount of dye solution is added to the bath and suitable amount of salt (common salt or Glauber's salt) is added and the temperature is raised suitably to 45 ^{o}C. The material is worked for about 15-20 minutes for exhaustion purpose. After that temperature is raised suitably after addition of an alkali (sodium carbonate). The material is worked at 65 °C for about 45 min for complete fixation.

Figure 2.1 Process Sequence



During dyeing process the dye reaction takes place between dye and cellulose. The reactive dye reacts with (-OH) group of cellulose for bond formation, water is also having (-OH) group, so the dye also react with water and forms hydrolysed dye. The rate of reaction analysis is as shown in following equations:

Dye –Cl + OH →Dye –OH + Cl

and its rate of reaction V_{H2O} is

$V_{H2O} = K_{H2O}$ [Dye –Cl]s [OH⁻]s

Where, K_{H2O} is the rate constant

[OH⁻]s are dye concentration and hydroxyl ions in solution.

In the same way the reaction with cellulosic ions

Dye –Cl + Cel-O + Dye –O-Cel + Cl^-

Which takes place at a velocity V_{cel}

$V_{cel} = K_{cel}$ [Dye –Cl]$_f$ [Cel-O]

Where, K_{cel} is the rate constant

[Cel-O]$_f$ are dye concentrations and OH groups from fiber.

This relative velocity will depend on three factors such as,

i) Ratio between rate constants: Theoretically there is no great difference between (-OH) group reactivity of cellulose and water. Determination of rate

ii) Relative concentration in fiber and solution: Starting from cellulose dissociation constant and proportion of (-OH) groups in contact with the solution, it is possible to calculate the ion concentration in the cellulose.

iii) Ratio between dye concentration in fiber and solution : This in turn depends on the rate of exhaustion . Dye concentration in fiber is always much more than in the solution. for this ascept to be considered regarding the reaction is the pH so that dye absorption is quick and maximum saving of time.

After dyeing process is completed the dyed fabric is given suitable after treatment. Rinse with cold water and then in hot water for 15 min and neutralize the fabric with acetic acid at pH 5.5–7.5. Then the fabric is given soap treatment with 2 g of soap for 15 min at boil. Then again cold wash and hot wash is given and then finally dried. By this after treatment unfixed dye in the fabric is removed and good fastness is obtained.

2.4. COMPUTER COLOR MATCHING

Color measurement may involve transmittance, reflectance, translucence, fluorescence, radiant energy which one may need a variety of instruments for example reflectometer, spectrocolorimeter, spectrophotometer are most relevant one for the measurement of opaque objects such as textiles. Since from 1990s there has been a rapid improvement in the data storage and speed in PC-AT interfaced with spectrophotometer that modern color system envisage several applications (A.D Sule).

Spectrophotometer most commonly used in color system today are Milton Roy, ACS, data color, hunter lab, Jaypack and Macbeth. In our testing Macbeth color eye 7000 is used. The main saline features are source of PXA (pulsed xenon arc) and dual beam with monochromator and photo detector of SPDA (silicon photo diode array). It is used to measure D65/10° absorb angle and wave length ranges from 350-750 nm.

2.4.1. Principle of working

A spectrophotometer combines the function of spectrometer and photometer. The essential components of spectrophotometer include

a) Source of light (illuminant): The present day color system employ pulsed xenon arc (PXA) lamps for providing and covering visible region. Light from these source is passed through a filter to simulate daylight. PXA lamps were introduced only when miniature photodetector devices with very high response time were available. Arrays of SPDs were used so that measurement could be carried out in fraction of second. The output from PXA lamps is suitably filtered to simulate daylight having color temperature of 6500 K.

b) Way in which a light is made to fall on the object (optics and viewing):

Spectrophotometer employ 2 types of optics like:

Normal optics: Monochromate → Reflect → Photodetect

Reverse optics: Reflect → Monochromate → Photodetect. All earlier modals normal optics has been employed but it was unrealistic when optically whitened sample has to be measured. So reverse optic method is now employed.

a) Method of dispersing the light in to spectrum colors (monochromator).

b) System of detecting the relative intensity of reflector beam (photo detection).

The main features of reflectance spectrophotometer are briefly outlined.

2.4.2 Sample presentation and viewing geometry

One of the factors which influence the measurement of reflectance is the method of sample presentation and viewing geometry. Four type of sample viewing geometry is accepted by CIE. They are,

→ 45/0°

→ 0/45°

→ d/0°

→ 0/d°

Most of the spectrophotometer today employ d/0 geometry with slight difference. Instead of measuring the reflected light 0, 10, angle is selected. This modified geometry is known as d/10.

2.4.3. Monochromatism:

Light emitted by the xenon arc contains radiation of all wave lengths in the visible region. The monochromator breaks the polychromatic light into spectrum of narrow bands. These are 3 types:

1) Prism monochromator.
2) Wedge type filter monochromator
3) Grating monochromators.

These provide wave lengths in band width of 10-20 nm.

2.4.4. Photodetection:

Photosensitive detectors are those which convert the light falling on them in to an electrical signal. These are five types. In Macbeth system, silicon photodiodes are used in which photons increase the conductance across a reverse biased pn junction. The reverse bias creates a depletion layer which reduces conductance of junction to nearly zero. If radiation falls on the depletion layer, holes and electrons are formed which provide current proportional to the radiant power which can be amplified and measured.

2.4.5 Color analysis and parameters in CCM:

All integrated color systems which were economical, popular and useful were developed by Hunterlab. The most useful model from color quality control point of view gives full datas regarding color analysis:

a) XYZ or x, y, z
b) L, a, b and L, c, h

c) Whiteness and yellowness index
d) Color difference (Hunterlab and CIE lab)
e) Averaging of color values measured.
f) Batch correction.
g) Shade matching (555 shade) for sorting.

In Macbeth color eye 2000 version, which offered a useful color quality control system. This model which could measure the reflectance at only 16 wave lengths but could be interfaced with a minicomputer, thus it was possible to compute x, y, z values only CIE illuminant 2 ° but also other illuminants example D6500, CWF, TL84. Thus Macbeth system was an improvement over Hunterlab system. This system is so accurate of about 0.15 CIE. This enables to get the reflectance data to be transformed in to L, a, b values.

Datas obtained: The software used in color system deals with
i) Color quality control.
ii) Recipe prediction.
iii) Reflectance data measurement.
iv) Color specification.
v) Color difference.
vi) Shade passing.
vii)Shade sorting.
viii) Dye strength.
ix) Fastness evaluation.

These values are obtained to analyze the color of the sample. Due to the increase in the speed of the computer, these data's can be obtained at faster speed. Further trends in the field of color measurement, communication, and management indicate very high level of automation technique.

Lightness, Chroma, and Hue

As mentioned earlier color can be specified in these dimensions. In CIE LAB system, L is the measure of lightness (if l is 0 it is perfect black sample and l is 100 it is perfect white sample). Color is represented partially on 2 dimensional plot of a and b with 4 quadrant. Hue is quantified by angler measure H is given by 0-360 ° circle. In which yellow occupies 70-105 ° and red 350-35 ° and blue 195-285 °. However, the most scientific color order system is Munsell system which classifies color 3 dimensionally. It is based on equal perception of color according to hue, value and Chroma in which hue is actual appearance of color and value is lightness of color ranging from white to black and Chroma is the saturation value of the color.

Hue is expressed as a combination of a number and a letter. For example 5R or 10 BG, where the numbers are from 1-10 and letter represent 10 Hues. For example red, yellow, etc. Both value and Chroma are expressed in numerical form from 1-10. In Munsell's notation fractions are allowed for value, Chroma and Hue. For example, values for some colors are light brown 5.4 YR, 5.4/4.8, for yellow 9.8 Y, 8.8/9.5, for a bluish grey is 8.9 B, 5.5/0.9.

CHAPTER-3

METHODOLOGY

Study of kinetics of dyeing behavior of modal and cotton fabrics with reactive dye:

The idea and aim of this work is to study about the reactions taking place during process and to determine its dyeing characteristics of both modal and cotton fabrics.

The dyes selected have good solubility, so it is easily soluble in water and forms good dispersion. Then required amount of dye solution is added to the dye bath and temperature is raised to 45 °C and required amount of Glauber's salt is added for exhaustion purpose. Then after 15-20 min sodium carbonate or soda ash is added to the dye bath and temperature raised to 65 °C where both modal and cotton fabric is worked for required period. After dyeing is completed suitable after treatment soaping is given to remove unfixed dye stuff and to improve the fastness property.

3.1. Materials for study:

3.1.1 Dyeing procedure

Preparation of sample: Samples of 100% modal and 100% cotton fabric of 60^s warp and weft yarn is selected for dyeing. The grey fabric is scoured, bleached, and then used for dyeing.

Specification: EPI-90, PPI- 83

Sample weight: Modal -1 g, Cotton – 1 g

Total 145 samples from modal and cotton fabric is selected for dyeing process.

Preparation of dye solution: Reactive dyes of 3 primary colors are selected. They are

Red FN_2 BL

Yellow F N_2R

Blue FNG.

These were used for experiments, 1 g of dye stuff is taken pasted with cold water and makeup with hot water. To avoid loss of yield through hydrolysis pH should be slightly acid to neutral. Glauber's salt is used for exhaustion and soda ash is used as fixing agent.

3.1.1 Dyeing procedure

Standard samples of 1 g modal and cotton each is placed in the beaker containing dye liquor and placed in sample dyeing machine.

The dye solution is pipette out according to the weight of sample to maintain 0.5%, 1%, and 2% shades. Material to liquor is maintained at 1:10 and required amount depending on depth of shade is added to the dye bath for exhaustion.

The temperature is set at 45 °C for about 15-20 min for exhaustion. Then required amount of soda ash is added to dye bath for fixation. The dye bath temperature is raised by 7 °C/min at 65 °C for required period the sample is dyed.

For determining the temperature and time effect, the dye bath is set at different temperature and time durations. After addition of alkali, the temperature range varies from 40 °C, 50 °C, 65 °C, and 80 °C.

Then time variation by 0.5% depth at 30, 40, 45, and 60 minutes
1% depth at 45, 60, and 75 minutes
2% depth at 60, 75, and 90 minute's
duration the fabric samples are dyed. After dyeing suitable after treatment is given.

Soaping: After dyeing the dyed samples is treated with 2 g/l soap solution at boil. This treatment removes any unfixed dye in the fabric.

Neutralizing and rinsing: The sample is given cold and hot wash, then neutralizing with acetic acid solution. Then again the samples are thoroughly washed with cold water and hot water. Then the sample is dried.

3.2. Study of kinetics with the following parameters

3.2.1. Dye affinity

According to Jose Cegarra and John Wiley affinity is an intrinsic property of matter in virtue of which the body tends to react with one another. Affinity of dyeing is determined by the equation.

$$-\mu^{o} = RT \ln \frac{(D)\phi\ (Na)\phi^{Z}}{(D)\sigma\ (Na)\ \sigma^{z}\ V^{z+1}} \qquad (2.1)$$

Where,

(D) ø is dye uptake of the fiber (g ion/kg)

$(Na)\phi^{z}$ is Na ion concentration in the fiber (g ion/kg)

$(D)\sigma$ is dye concentration in residual solution (g ion/L)

$(Na)\ \sigma^{z}$ is Na ion in residual solution (g ion/L)

Z is number of Na ion in dye molecule

V is effective volume in term of molecules of dyeing for the fiber

R is gas constant (1.99 x 10^{-3} cal/deg)

T is absolute temperature.

In the above mentioned equation (2.1.), - μ^{o} is a measure of tendency of dye to move from its standard state in the solution to the standard state in the fiber that is it is the quantitative measure of affinity of dye for that of the fiber.

3.2.2. Dye uptake

By Medley and Holdstock (1999), the rate of dye uptake progressively decreases throughout the dyeing process in proportion to the concentration. Measurement and control of parameter Q been proposed by

$$Q = \frac{2(C1-C2)}{(C1+C2)\ (t1-t2)} \qquad (2.2)$$

where,

t_1 and t_2 are time interval of dyeing

c_1 and c_2 are concentration of dye in the liquor.

3.2.3. Dye diffusion

In order to obtain dye diffusion into the fiber Jose Cegarra determined the diffusion of dyeing in a steady state and non steady state. But dyeing of textile fiber majority comes under nonsteady state, since majority of process dye is fixed as a function of time and distance from the separation surface between substrate and dye bath. The kinetics of absorption, diffusion are expressed in grams of dye absorbed per kg of material as percentage of exhaustion to the initial dye that is

$$\frac{Mt}{M} \times 100 \qquad (2.3)$$

Where, Mt is the quantity of dye absorbed in time t

M is the initial quantity of dye

To obtain diffusion coefficient Vaidya and Datya explains under nonsteady state where the concentration gradient is not constant and decreases steadily during dyeing.

Diffusion coefficient "D" is given by equation (2.4)

$$D = \frac{0.0632 \times r^2}{(t)_{1/2}} \qquad (2.4)$$

where,

t is time

r is radius of the fiber

3.2.4. Chemical potential of dye in fiber

Jose Cegarra has examined the chemical potential of dye in the solution to analyze the activity of dye in the diffused state which is given by equation (2.5)

$$\mu_f = \mu_o + RT \ln (C_f/V) \quad (2.5)$$

where,

C_f is the concentration of dye expressed in moles/kg if dyed fiber

μ_o is the dye affinity

V is the volume of molecules

These are the kinetic measurement to be done for both cotton and modal sample and the difference between them is to be determined.

3.3.Determining the dyeing behavior

3.3.1. Rate of sorption

In a paper presented by Madhavamoorthy and Premalatha (2003), they studied the rate of sorption of TMT fibers and determined the absorption rate. In that broad range of temperature zone was selected and at each stage of dyeing temperature their k/s value was noted and the sorption rate is estimated at which the value is maximum, determined the dyeing temperature of the dyed sample and it was concluded that further increase in temperature, the dye uptake tends to decrease.

3.3.2. Rate of dyeing

The same authors Madhavamoorthy and Premalatha (2003) carried out study on dyeing time up to which the dyeing is to be done. Dyeing is done for different duration of time and its k/s values for those samples were determined and holding time at which the sample is to be retained was determined. By these methods, the dyeing rate and absorption for both modal and cotton were determined and its k/s values are shown in the table.

3.3.3. Reflectance measurement

Reflectance values determined by spectrophotometer. From reflectance value k/s value is calculated by Kubelka-Munk equation (2.6). Lightness, Chroma, and Hue values were also measured.

$$K/S = (1-r_{max})^2/2r_{max} \qquad (2.6)$$

CHAPTER-4

RESULTS AND DISCUSSION

Dyeing behavior of cotton and modal fabrics were determined. For this purpose varying temperature and time period were selected and effect of each parameter was studied at each stage. Then dyeing behavior of modal and cotton to the reactive dye were determined by dye affinity, dye uptake, diffusion co-efficient, chemical potential of dye. These values are listed in Table 4.5. Then k/s value ΔL, ΔH, ΔC were also determined spectrophotometrically and the values are listed in Table 6.1-6.6.

From the results and values obtained, it was evident that modal fabric has less dye affinity, diffusion rate, and dye uptake than that of the cotton fabric. Even though modal fabric has higher amorphous region than that of cotton their dye uptake is low. This is due to the orientation factor,and the fact that due to the more stretch during spinning process, the chains are more parallel to the fiber axis so during dyeing process it is difficult for the dye molecules to get into the structure, so by increasing the temperature, the mobility of chain molecules increases, so dye penetrate thorough the chain easily and dye uptake gets equal to that of cotton.

The dyeing behavior of modal and cotton are investigated at the temperature ranges from 40°c to 80°c. Between the temperature of 40°c and 50°c, modal and cotton did not show maximum absorption. Maximum absorption of cotton was found at the temperature of 65°c, which is the normal dyeing temperature of selected dye. Modal shows less absorption for darker shades, but for pale shades it shows better absorption, at the temperature of 65 ^{o}c. As the dyeing shade increases the dye absorption decreases, so the temperature was raised.

The rate of dyeing was also examined by selecting different time duration(30, 45, 60, 75, 90 min). From the study, it was found that red and yellow dye reached same shade to that of cotton at the same period of time that is 0.5% in 45 minutes and 1% in 60 minutes, 2% in 75 minutes. For blue dye of 2% shade longer time duration of 90 minutes is preferred which shows similar dye absorption to that of cotton and resulted in same K/S value. This may be due to the following reasons:

i) Opening up of cellulose structure

ii) Increasing the accessibility of cellulose structure.

iii) Overcoming of activation energy barrier due to orientation structure. Modal fabric which has emerging market trend can also be dyed as that of cotton with bifunctional reactive dye economically.

4.1 Dyeing Parameters:

The dyeing parameters studied were determined and the values are tabulated as shown in table 4.1.

Table 4.1- Dyeing parameters

Parameter studied	Cotton	Modal
Dye affinity (- μ^{0}) kcal/mol	4.13×10^{-3}	2.1×10^{-3}
Dye uptake (g ion/min)	7.13×10^{-3}	3.9×10^{-3}
Dye diffusion (%)	19.3	11.2
Diffusion co-efficient (cm2/sec)	2.45×10^{-10}	1.59×10^{-10}
Chemicalpotentialof dye in fiber	0.017	0.013

4.2. Fastness properties

The following table 4.2 shows the wash fastness ratings of cotton and modal at different %shade that modal and cotton exhibits good wash and rubbing fastness.

Table 4.2-Fastness properties

Fabric	%shade(o.w.f)	Wash fastness	Rubbing fastness (dry)
Cotton	0.5%	3-4	3-4
	1%	4	4
	2%	3-4	3-4
Modal	0.5%	4	3-4
	1%	4	4
	2%	3-4	3-4

CHAPTER 5

CONCLUSION

Like cotton, modal is also cellulosic fibre, which was also dyed like that of cotton with bifunctional reactive dyes. From the study

- It was found that the recommended dyeing temperature (65°C) for cotton by the dyeing manufacturers is also suitable for modal only for pale shade.
- It was found that for darker shade in modal the ideal dyeing temperature was found as 80 °C.
- Below 80°C in order to produce same shade in modal like that of cotton fabric, it was found that concentration of dye solution should be increased by 0.5% (o.w.f.).
- The reason for low dye affinity is due to the high orientation of molecules in the fibre.

TABLE 1-TEMPERATURE VARIATION

BLUE

TEMP C	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
40	0.5	33	0.68	9.1B	7.1	5.4	38	0.51	7.8B	7.6	3.5
50	0.5	23	1.29	9.9B	6.8	6.3	37	0.54	8.4B	7.3	4.4
65	0.5	24	1.2	9.5B	6.9	6.1	30	0.8	8.5B	7.3	4.3
80	0.5	26	1.1	9.6B	7.0	5.7	35	0.6	8.1B	7.5	4.1
40	1	18	1.9	0.6B	6.4	7.3	24	1.2	9.4B	6.8	5.8
50	1	20	2.0	0.6B	6.3	7.4	22	1.4	9.6B	6.6	6.3
65	1	16	2.2	0.9B	6.1	7.1	20	1.6	9.9B	6.6	6.2
80	1	20	1.6	0.6B	6.4	7.0	25	1.1	9.6B	6.9	5.9
40	2	10	4.1	1.4B	5.5	8.8	17	2.0	0.5B	6.2	7.4
50	2	12	3.2	1.2B	5.6	8.6	16	2.4	0.5B	6.1	7.5
65	2	10	4.1	1.6B	5.4	8.5	15	2.4	0.4B	6.1	7.5
80	2	13	3.3	1.4B	5.6	8.3	17	2.0	0.3B	6.3	7.2

TABLE 2

RED

TEMP *C	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
40	0.5	52	0.28	1.2RP	7.9	3.7	48	0.28	1.4RP	7.7	4.2
50	0.5	46	0.32	1.2RP	7.6	4.8	46	0.36	1.6RP	7.6	4.7
65	0.5	45	0.33	1.3RP	7.1	4.8	44	0.32	1.7RP	7.5	4.8
80	0.5	36	0.56	1.8RP	7.1	6.4	44	0.32	1.7RP	7.5	5.1
40	1	46	0.3	1.5RP	7.3	5.9	38	0.5	1.9RP	7.2	5.9
50	1	40	0.4	0.7RP	7.6	4.5	34	0.6	2.2RP	7.0	6.8
65	1	83	0.7	2.3RP	7.0	6.8	33	0.7	2.4RP	7.0	6.9
80	1	34	0.6	1.8RP	7.0	6.8	34	0.6	2.2RP	7.0	6.9
40	2	29	0.8	2.4RP	6.6	7.9	28	0.9	2.6RP	6.6	8.0
50	2	26	1.1	2.8RP	6.4	8.3	26	1.1	2.8RP	6.5	8.4
65	2	26	1.1	2.6RP	6.6	8.0	26	1.1	2.7RP	6.4	8.4
80	2	27	0.9	2.7RP	6.5	8.2	25	1.1	2.9RP	6.4	8.7

TABLE 3

YELLOW

TEMP *C	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
40	0.5	34	0.64	4.8Y	8.3	3.9	38	0.51	5.6Y	8.2	3
50	0.5	31	0.78	4.5Y	8.2	4.4	36	0.57	2.1Y	8.3	3.4
65	0.5	28	0.93	4.1Y	8.2	4.8	33	0.68	4.6Y	8.2	3.4
80	0.5	32	0.72	4.5Y	8.2	4.4	34	0.64	4.8Y	8.3	3.6
40	1	24	1.2	3.9Y	8.1	5.6	28	0.9	4.2Y	8.1	4.8
50	1	24	1.2	3.6Y	8.0	5.7	32	0.7	4.4Y	8.1	4.0
65	1	21	1.5	3.4Y	8.0	6.4	30	0.8	4.2Y	8.2	4.0
80	1	32	1.4	3.4Y	8.0	6.1	24	1.2	3.7Y	8.1	5.6
40	2	15	2.4	2.7Y	7.8	7.6	18	1.9	3.1Y	7.9	6.9
50	2	15	2.4	2.9Y	7.7	7.5	16	2.2	3.1Y	7.8	7.0
65	2	15	2.4	2.8Y	7.8	7.5	17	2.0	3.2Y	7.9	7.3
80	2	16	2.2	2.9Y	7.8	7.5	16	2.2	3.0Y	7.9	7.3

TABLE 4- TIME VARIATION

RED

TIME (MIN)	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
30	0.5	44	0.35	1.5RP	7.6	4.6	45	0.35	1.7RP	7.5	4.9
45	0.5	48	0.31	1.4RP	7.8	4.1	47	0.29	1.9RP	7.7	4.2
60	0.5	44	0.35	1.5RP	7.5	5.3	42	0.4	1.8RP	7.4	5.5
45	1	37	0.5	1.2RP	7.2	6.2	37	0.5	2RP	7.1	6.2
60	1	35	0.6	1.9RP	7.1	6.5	35	0.6	2.1RP	7.1	6.2
75	1	36	0.5	1.9RP	7.1	6.4	36	0.5	2.2RP	7.0	6.5
60	2	25	1.1	2.9RP	6.4	8.6	26	1.0	3RP	6.4	8.6
75	2	24	1.2	2.9RP	6.3	8.7	25	1.1	2.9RP	6.4	8.7
90	2	26	1.1	2.8RP	6.5	8.3	25	1.1	2.8RP	6.5	8.5

TABLE 5

YELLOW

TIME (MIN)	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
30	0.5	32	0.7	4.4Y	8.3	4.3	36	0.5	3.8Y	8.6	4.0
45	0.5	33	0.7	4.4Y	8.2	4.1	35	0.6	3.9Y	8.3	4.1
60	0.5	30	0.8	4.4Y	8.3	4.3	35	0.6	3.8Y	8.3	3.7
45	1	23	1.3	3.4Y	8	6.1	24	1.2	3.6Y	8.1	5.8
60	1	21	1.5	3.4Y	8.1	6.3	23	1.3	3.5Y	8.1	5.8
75	1	22	1.4	3.4Y	8.0	6.2	23	1.3	3.6Y	8	5.7
60	2	14	2.6	2.5Y	7.7	7.9	16	2.2	2.8Y	7.9	7.6
75	2	14	2.6	2.7Y	7.8	7.9	16	2.2	2.8Y	7.9	7.5
90	2	16	2.2	2.5Y	7.8	7.9	17	2.0	2.9Y	7.9	7.2

TABLE 6

BLUE

TIME (MIN)	SHADE %	R%	K/S	H	V	C	R%	K/S	H	V	C
30	0.5	25	1.1	9.7B	6.7	6.1	32	0.7	8.4B	7.4	4.5
45	0.5	23	1.3	9.9B	6.7	6.5	28	0.9	8.7B	7.1	5.1
60	0.5	25	1.1	9.6B	6.9	5.9	32	0.7	8.5B	7.4	4.6
45	1	16	2.2	2.9PB	6.1	7.7	20	1.6	0.9PB	6.6	6.7
60	1	16	2.2	1.0PB	6.1	7.8	19	1.7	0.1PB	6.5	6.8
75	1	17	2.1	0.9PB	6.1	7.7	14	2.6	0.9PB	6	7.9
60	2	10	4	1.7PB	5.4	8.9	20	1.6	0.1PB	6.6	7.7
75	2	10	4	1.7PB	5.4	8.9	15	2.6	0.7PB	6	7.8
90	2	9	3.8	1.7PB	5.5	8.8	14	2.4	0.8PB	6	7.8

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