

THE EFFECT OF PROCESS CONDITIONS, TIME, TEMPERATURE, AND  
RATES OF TEMPERATURE RISE, ON THE EXHAUSTION  
OF DISPERSE DYE ON POLYESTER YARN  
UNDER HIGH-TEMPERATURE  
DYEING CONDITIONS

by

Fereshteh Zamani

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APPROVED:

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Charles J. Noel

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Mary Ann Zentner

---

Barbara E. Densmore

---

Marjorie J.T. Norton

---

James P. Wightman

May, 1984  
Blacksburg, Virginia

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(ABSTRACT)

The effect of process conditions, temperature, time and rate of temperature rise, on the exhaustion of disperse dye on polyester yarn under High-Temperature dyeing conditions was investigated. Two ply spun type Dacron 54 polyester yarn was dyed with Disperse Red 60 in 0.5 g/l dye bath concentration using an Ahiba Texomat Dyeing Apparatus under High-Temperature Dyeing conditions. The dyeing process design used, consists of three levels of dyeing temperature (105°C, 120°C, 135°C), four levels of holding time (0 min, 15 min, 30 min, 60 min) and two levels of rate of temperature rise (1°C/min, 3°C/min). After the dyeing process, the dye concentration in the yarn was obtained through extraction and measured spectrophotometrically. A factorial analysis of variance (ANOVA) test was used to determine whether or not significant differences existed among dyeing process conditions in regard to the dye uptake of the yarn. If significant differences existed, which parameter of process conditions (temperature, time, rate of temperature rise or their interactions) was responsible.

The results of this study indicated that a three-way interaction of temperature, time, and rate of temperature rise was responsible for the differences in dye uptake of the yarn. The dye uptake of the yarn increased by increasing dyeing temperature from 105°C to 120°C for all levels of holding time and rate of temperature rise. However, increasing dyeing temperature from 120°C to 135°C, did not increase dye uptake of the yarn. The dye uptake of the yarn increased by increasing holding time from zero to 15 minutes for dyeing temperature of 120°C. However, increasing holding time from 15 to 60 minutes, did not increase dye uptake of the yarn. At the dyeing temperature of 120°C, a slower rate of temperature rise resulted in greater dye uptake of the yarn. It can be concluded, that high temperature dyeing of polyester yarn at 120°C for 15 minutes with a rate of temperature rise of 1°C/min was the optimum dyeing process in achieving full exhaustion.

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## Chapter I

### INTRODUCTION

Polyester is a highly crystalline and markedly hydrophobic fiber with no ionic groups in its chemical structure (1), hence unlike the natural fibers and some synthetic fibers cannot be dyed with common ionic dyestuffs under conventional dyeing conditions. Generally, polyester is dyed with disperse dyes, which are nonionic in character, with the help of thermal and/or chemical energy (2). Penetration of fiber by dye with the assistance of thermal energy is achieved by high temperature dyeing techniques and penetration through chemical energy is accomplished by the use of carrier dyeing techniques.

Today, because of the development of versatile high pressure dyeing machinery, polyester materials are mostly dyed under high temperature conditions, especially considering all the drawbacks associated with the carrier dyeing of polyester. Several factors which may encourage the dyeing industry to change from chemical energy dyeing to thermal energy dyeing are (3): 1) environmental regulations against usage of carriers due to their toxicities, 2) saving of the cost of carrier chemicals and recycling machinery, and 3) difficulties of complete removal of carriers from

dyed fiber and the negative influence of retained carriers on the lightfastness and hand of the material. Even though for the dyeing of polyester under high temperature conditions, expensive pressure dyeing equipment is required, based on this equipment's high production capacity and short dyeing cycles, the economical aspect of high temperature dyeing is justified (4).

High temperature dyeing of polyester is based on dyeing above  $100^{\circ}\text{C}$ . High temperatures give rise to higher kinetic energy of the dyestuff molecules and also promote the movement of fiber chain molecules (5). As a result dye molecules can penetrate rapidly into the fiber. High temperature dyeing of polyester can be characterized by its high dyeing yield, rapid dyeing rate and good leveling properties (5).

Practical dyers want to produce colored material with optimum yield, levelness, shade, fastness and reproducibility (6). Hence, in order to achieve these desirable properties, all the variables in a dyeing process must be controlled and one must have a thorough understanding about the influence of each dyeing process factor on the dyeing behavior of the material. Dyeing process factors which may influence dyeing characteristics are: starting temperature, rate of temperature rise, dyeing

temperature, holding time, cooling rate and liquor ratio (7). This study is especially concerned with the effect of dyeing temperature, holding time and rate of temperature rise on the uptake of disperse dye by spun Dacron 54 polyester yarn under high temperature dyeing conditions.

### OBJECTIVES

The objectives of this study are:

1. To determine the effect of dyeing temperature upon the dye uptake of polyester under high temperature dyeing conditions.
2. To determine the effect of holding time at the dyeing temperature upon the dye uptake of polyester under high temperature dyeing conditions.
3. To determine the effect of rate of temperature rise to the dyeing temperature upon the dye uptake of polyester under high temperature dyeing conditions.

Chapter II  
STATEMENT OF PROBLEM

HYPOTHESES

On The basis of the objectives, the following null hypotheses were developed:

H<sub>1</sub>: There will be no differences in the dye uptake of the yarn related to the dyeing temperature.

H<sub>2</sub>: There will be no differences in the dye uptake of the yarn related to the holding time at the dyeing temperature.

H<sub>3</sub>: There will be no differences in the dye uptake of the yarn related to the rate of temperature rise to the dyeing temperature.

ASSUMPTIONS

1. The dyeing procedure is carried out under controlled conditions.
2. The polyester yarn used has uniform dyeing characteristics.

LIMITATIONS

1. Only one type yarn was used.
2. Only one type and concentration of a disperse dye was used.
3. Only one liquor ratio was used.

DEFINITIONS

Exhaustion	Amount of dye taken from dye bath by fiber, yarn or fabric (8).
Affinity	The difference, in gram-calories per gram-molecule, between the chemical potential of the dye in its standard state in the fiber and the corresponding chemical potential in the dye bath (9).
Leveling	The transfer of dyes from more heavily dyed portions to less heavily dyed portions(10).
Time of half-dyeing	The time at which half the dye which will be absorbed at equilibrium is taken up by the fiber(10).

## Chapter III

### REVIEW OF LITERATURE

The literature related to the subject of the effect of process conditions on the exhaustion of disperse dyes into polyester under high-temperature dyeing conditions was searched and is reported under the following headings: Polyester, Disperse Dyeing of Polyester, Carrier Dyeing, and High Temperature/Pressure Dyeing.

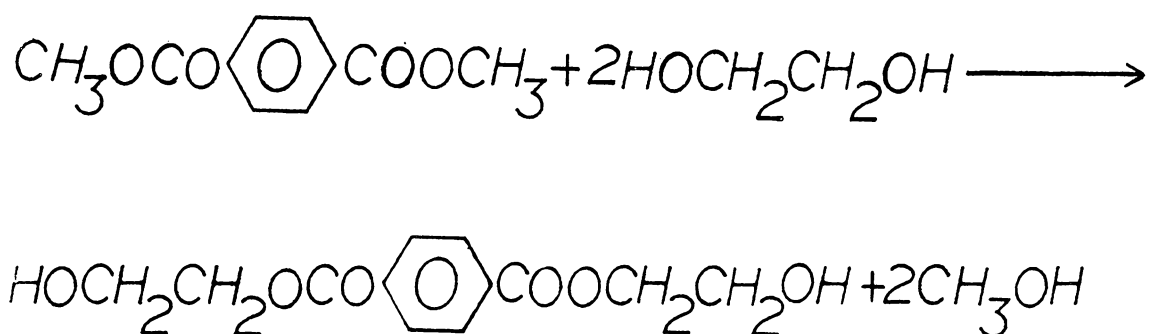
#### POLYESTER (POLYETHYLENE TEREPHTHALATE)

##### History, Synthesis and Fiber Formation

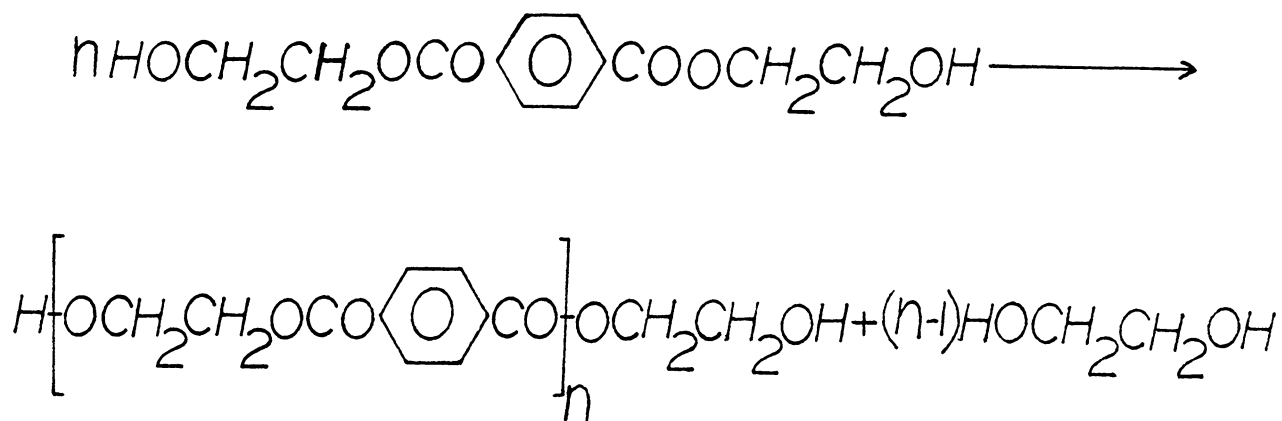
Polyethylene terephthalate is one of the linear, fiber forming polyesters which has received significant commercial attention (11). It was synthesized by Whinfield and Dickson of the Calico Printers' Association, England, in 1941 and then was developed by Imperial Chemical Industries Ltd., in England and by E. I. duPont de Nemours and Co. in the U.S. (11,12,13).

One of the practical ways of producing polyethylene terephthalate (PET) is from dimethyl terephthalate (DMT) and ethylene glycol (EG) with a two stage process (14,15). The first step is a transesterification or ester interchange reaction. DMT and a slight excess of EG are mixed and

reacted in the presence of a catalyst, e.g., sodium or magnesium methoxide or zinc borate, at a temperature of about 150°C-200°C to form bis (betahydroxyethyl) terephthalate or BisHET. The by-product methanol must be removed for completion of the reaction.



The second step is polycondensation of BisHET under high vacuum condition at 260°C-280°C. Then, the by-product ethylene glycol is separated from polyethylene terephthalate polymer.



When the polymerization is complete, the molten polymer is cooled to the form of a solid ribbon and then chipped. Fibers of polyethylene terephthalate are formed by the melt spinning process (11,14). The chipped polymers are melted in an oxygen free atmosphere and extruded through a spinneret into air at room temperature. Polyethylene terephthalate fibers are quite amorphous in this stage; hence, in order to obtain a sufficient amount of crystallinity and orientation, the fibers are drawn (13). The drawing process is carried out at a temperature a little above the glass-transition temperature at 80°C with the stretching of the spun fibers to four or five times their original length. The drawing process imparts several desirable mechanical properties to the fiber including high tenacity, high modulus, and normal extensibility. Staple fibers can be produced by cutting drawn, crimped, and heat set filaments (12).

### Microstructure

Polyester is the generic term for a "manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of an ester of dihydric alcohol and terephthalic acid (TPA)" (16). The elementary chain unit of polyethylene



terephthalate fiber consists of an aromatic benzene group and an aliphatic sequence --  $\text{COO-CH}_2\text{-CH}_2\text{-O-CO}$  -- which are bonded by primary chemical bonds (17). These elementary chain units are arranged repeatedly one after another to form rather long chain macromolecules (18). Each chain repeat unit has a length of 10.75 Angstrom units, slightly less than the length of an extended chain. Therefore the chains are planar (19). Polyethylene terephthalate macromolecules are oriented side by side on parallel planes through their intermolecular bondings (14,17). Intermolecular forces available between the nearest neighbor chains are mostly secondary forces like Van der Waals' bonds and very minor hydrogen bonding at the end groups (17,20). The Van der Waals' forces are relatively weak bonds in comparison with other types of bonds; for example, the strength ratio of bonds (in  $\text{kJ mole}^{-1}$ ) is covalent:hydrogen:Van der Waals = 100:5:1 (17). However, a considerable number of these bonds bring about strong bondings among the neighboring polymer chains (12). The unit cell dimensions of polyethylene terephthalate in crystalline (triclinic) areas (13,19) are:

$$\begin{array}{lll}
 a = 4.56 \text{ \AA} & b = 5.94 \text{ \AA} & c = 10.75 \text{ \AA} \\
 \alpha = 98.5^\circ & \beta = 118^\circ & \gamma = 112^\circ
 \end{array}$$

Aromatic groups and benzene rings in the molecular structure of polyethylene terephthalate are responsible for the stiffness, chemical stability, and high melting point of the fiber due to considerable electronic interaction between neighboring benzene rings. The aliphatic groups, due to the weakness of their Van der Waals' interaction with neighboring chains, are flexible at room temperature (14).

### Morphology

Polyethylene terephthalate fiber has different structural morphologies at the different states of fiber processing (21). The fiber is amorphous-disoriented after extrusion from the spinneret, has an amorphous-oriented morphology after cold drawing, is crystalline-disoriented after heat treatment, and crystalline-oriented after hot drawing. The molecular models suggested for the morphology of polyethylene terephthalate are either the fringed micelle model or the folded chain model (20,22). According to these models, the fiber polymer exists in crystalline and amorphous regions. The amorphous areas are mostly formed by chain folds, free chain ends, and tie molecules and are located on the folds containing surfaces of crystal lamellae, and the remaining amorphous components in the fiber are the crystal defects, i.e., vacancies and kinks (22).

### Thermal Transitions

Polyethylene terephthalate has a heterogeneous fiber structure, consisting of amorphous and crystalline regions; therefore it exhibits two important thermal transitions. One is gradual from 60°C to 100°C and the other is abrupt at 250°C. These are called a second order transition (glass transition) and a first order transition (melting), respectively(23).

There are two secondary transitions for this fiber (18,20). One is below room temperature at about -50°C and the other is above room temperature at about 150°C. The transition at -50°C is due to the change of the aliphatic sequence - COO-CH<sub>2</sub>-CH<sub>2</sub>-OCO - from rigid to flexible, whereas the transition at 150°C is attributed to the breakdown of forces between neighboring benzene rings. The glass transition temperature is therefore somewhere between these two secondary transitions, when the amorphous regions are freely mobile and the fiber becomes noticeably soft and flexible because the polymer chains start rotating around the - CH<sub>2</sub> - CH<sub>2</sub> bonds and the aromatic rings may also rotate around the CO bonds (13). The glass transition temperature varies for polyesters with different degrees of orientation and molecular weight (13,20,23). The higher the molecular orientation and crystallinity, the higher the glass

transition temperature due to the influence of crystallinity on restricting chain movements in the fiber. As a result, fibers with higher drawing and annealing have higher glass transition temperatures. The value of the glass transition temperature of amorphous polyethylene terephthalate is located in the range of 67 - 71°C and the value for the crystalline fiber is in the range of 79 - 81°C (13). The glass transition temperature is an important parameter for the polyester fiber since mechanical properties of the fiber such as extensibility, yield stress, Young's modulus, and shear modulus change suddenly at this temperature (13). The drawing and dyeing take place above this temperature (13). The glass transition temperature can be determined by studying the changes of properties like stiffness, specific volume, dielectric properties, thermal capacity, thermal conductivity, and refractive index with respect to changes in temperature.

Crystallites of the polymer melt over a temperature range. The melting temperature is that above which the crystals cannot exist and the fiber loses its identity and contracts to a molten globule (20,24). The approximate melting range of the fiber is 250 - 267°C (14,20).

### Physical and Chemical Properties

Polyethylene terephthalate fibers depending upon their molecular weight, spinning, and drawing conditions may have various physical and chemical properties (1). According to the literature (25) tensile strength is in the range of 2.5 to 6.0 grams per denier, percent elongation at break is 12% to 15%, percentage elastic recovery 90% to 96% at 2% extension, average stiffness is 8 to 25 grams per denier, average toughness 0.4 to 1.5 g-cm/denier, specific gravity is 1.38 g/cm<sup>3</sup>, and moisture regain is 0.4%. The fiber has good chemical resistance to weak acids and strong acids have little or no effect on the fiber at temperatures below room temperature (12,14,25). However, the alkaline resistance of the fiber is poor (12,14,25). Caustic soda can attack and saponify the fiber. Polyethylene terephthalate fibers have good stability against oxidizing and reducing agents (12,14). The fiber can be swollen by a 0.5% dispersion of chlorobenzene, tetrahydro naphthalenes, methyl salicylate or a 0.3% dispersion of ortho-phenyl phenol in water and can be dissolved by a boiling solution of metacresol or ortho-dichlorobenzene (14).

### Dyeing Properties and Factors Affecting Dyeability

Polyethylene terephthalate fiber is rather difficult to dye because of its low dye diffusion property which results from the fiber's packed and crystalline molecular structure, low swelling, and low moisture absorption characteristics (26). Moreover, the fiber lacks any specific dyeing sites in its chemical structure; therefore, it can be dyed only with nonionic type dyes. In order to alter the dyeability of the fiber, physical or chemical structural changes are required.

Originally, only the less ordered amorphous regions of a polymer structure are accessible to dye and only from these areas can the large dye molecules diffuse into the fiber, while the crystalline region, due to its high molecular orientation cannot permit dye penetration, as is the case with polyester with its partly amorphous and partly crystalline structure (26). As a consequence dyeability can be altered by changing the morphology of the fiber. Dumbleton, Murayama, and Bell (27) investigated the effect of changes in fiber morphology on the dye diffusion behavior. The change in crystallinity of the yarns was accomplished by heat setting at various temperatures. Heat treatment at high temperatures increases the crystallinity which results in decreasing dye diffusion; however, at

temperatures above 180°C, dye diffusion improves due to changes in the crystalline size distribution which reduces the restrictions on segmental mobility in the noncrystalline regions. Furthermore, it is possible to improve dyeability by providing higher mobility of chain segments in the noncrystalline regions (12). Heating the fiber above its glass transition temperature causes thermal agitation of polymer chain segments and as a result, the interpolymer bonds are broken which gives the fiber a more open structure allowing the dye molecules to diffuse in. The change in the size of the pores in the fiber can also affect the dyeability (17). The treatment of polyester with organic solvents acting as swelling agents helps to increase the size of the pores which permits easier diffusion of dye molecules.

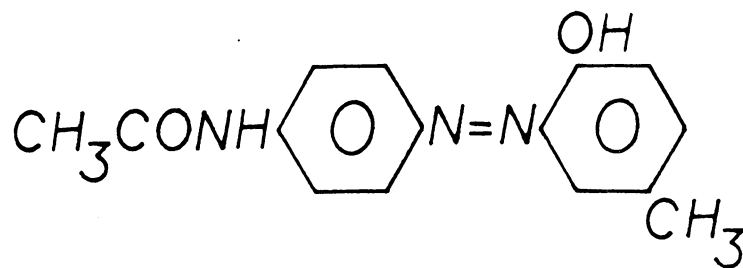
### DISPERSE DYEING OF POLYESTER

#### Disperse Dyes

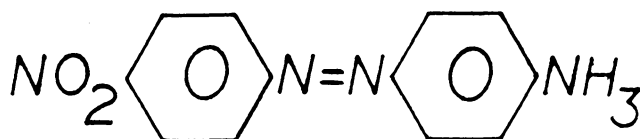
Disperse dyes were defined by the Society of Dyers and Colourists in 1953 as : "a class of water-insoluble dyes, originally introduced for dyeing cellulose acetates, and usually applied from fine aqueous suspensions" (28). These dyes are used for dyeing polyester since no charged groups are available; they have very low solubility in water and are therefore suitable for dyeing hydrophobic fibers.

Disperse dyes have chemical groups such as azo, nitrodiphenylamine or anthroquinone (26,29). Azo dyes cover a wide range of colors: nitrodiphenylamine dyes are in yellows and oranges; and anthroquinone dyes are in orange to greenish-blue colors. Typical chemical structures follow:

Azo

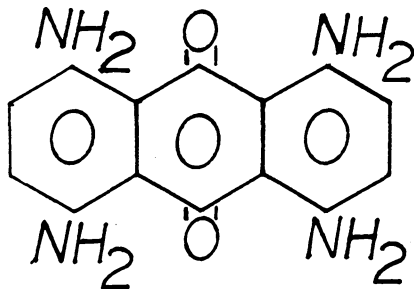


C.I. Disperse Yellow 3



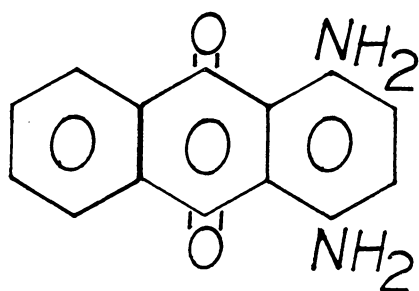
C.I. Disperse Orange 3

Anthroquinone

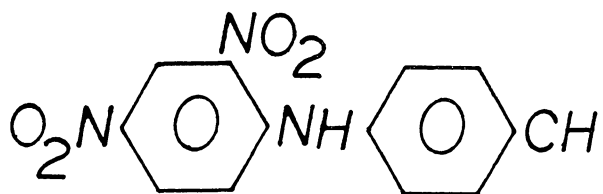


C.I. Disperse Blue 1

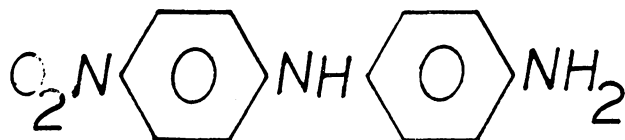




C.I. Disperse Violet 8

Nitrodiphenylamine

C.I. Disperse Yellow 14



C.I. Disperse Yellow 9

### Characteristics of Disperse Dyes

Disperse dyes have a very low solubility in water (3,31,32). Generally, the solubility ranges from 5 - 100 mg/liter (30). Even though these dyes have no charged groups, they have polar substituents like -OH, -CH<sub>2</sub>CH<sub>2</sub>OH, -NO<sub>2</sub> (33). Solubility is a very important factor in dyeing since, in principle, disperse dyes cannot penetrate into the fiber unless they are in the form of monomolecules (31,32,33). Therefore, dye manufacturers add dispersing agents to the dye compounds in order to improve their solubility and dispersion in the dye bath (26,31). The dispersing agent usually used is the sodium salt of a condensate of cresol with naphthalene sulphonic acid and formaldehyde, together with a small amount of sodium alkyl naphthalene sulphonate. During the dyeing, increased solubilities of dyes are achieved by increasing the temperature and also by adding a dispersing agent to the dye bath (31). Higher dye solubility in the bath results in a higher equilibrium concentration in the fiber which yields better bath exhaustion and dye build up (31).

The next important characteristic of disperse dyes is their particle size which is directly related to their solubility behavior. Disperse dyes are usually produced in a fine uniform dispersion with particle size of 0.1 - 1 $\mu$  (31).

Disperse dyes are categorized as high, medium or low energy according to their molecular weights (32,33,34). High energy disperse dyes have molecular weights in the range of 550 - 650 and have low water solubility and dye penetration. However, they have excellent sublimation fastness during heatsetting. Medium and low energy dyes have lower molecular weight, therefore, they have better solubility and diffusion properties and good ability to cover barre but lower sublimation fastness.

Disperse dye behavior and properties may change with the pH of the dye bath (31,35). Alkalinity may influence the shade of the color or it may degrade the dye. Strong acidity of the dye bath may also damage the dye hydrolytically. Almost all disperse dyes are used at a pH around 5.

#### Kinetics of Dyeing

Disperse dyeing of polyester in an aqueous phase is accomplished by transport of dye into the fiber through three steps (3,36,37):

1. Dyes are diffused through the aqueous phase to the surface of the fiber. This step is more rapid than the others because the disperse dye is insoluble in water; therefore the distribution coefficient of the

dye strongly favors the polyester fiber at elevated temperatures as the dye micelles break down into less aggregated units and promote higher vibrational activity. The most efficient way of bringing fresh dye to the fiber surface is to stir, to circulate or agitate the dye bath or the fabric. Dye bath flow carries fresh dye and tends to keep the bath concentration uniform.

2. Dyes are adsorbed on the surface of the fiber. In order to have such a transfer occur driving forces are needed and are hydrophobic in nature.
3. Dyes are diffused within the fiber towards the center. This step is the slowest one due to the mechanical obstruction to movement presented by the network of fiber molecules and the restraining attraction between dye and fiber molecules. The resistance transport factor in the fiber is  $10^5 - 10^6$  times greater than the aqueous phase (38). Diffusion can be achieved by molecular chain movement of the fiber through the assistance of thermal and/or chemical energy to permit dye molecules to position themselves between fiber chain molecules (31). The diffusion of dye molecules into the fiber can be explained by Fick's law.

$$\frac{ds}{dt} = - D \frac{dc}{dx}$$

in which :

$ds$  = amount of dye diffusing across a unit area during time interval  $dt$

$c$  = concentration of dye at point  $x$

$D$  = diffusion coefficient which is the amount of dye diffusing in unit time across a unit area under unit concentration gradient.  $D$  has the units of meters<sup>2</sup> per second.

Raising temperature increases the dye absorption rate. This effect can be expressed by the activation energy of the process which reflects the changes of diffusion coefficient with temperature and is described by equation (14,26):

$$D = D_0 \exp - \frac{\Delta E}{RT}$$

Where:

$\Delta E$  = activation energy

$D_0$  = constant independent of temperature

$R$  = gas constant

$T$  = absolute temperature

The value of the activation energy for the dyeing of polyester with disperse dyes was found to be around 34 kcal/mole (26).

Thermodynamics of Dyeing

Dyeing can be explained by the concept of free energy as the driving force of dye molecules from the dye bath solution into the fiber (14). According to the Gibbs free energy equation:

$$\Delta\mu = \Delta H - T \Delta S$$

Where:

$\Delta\mu$  = change in free energy

$\Delta H$  = change in enthalpy

$\Delta S$  = change in entropy

T = absolute temperature

Enthalpy represents the heat of dyeing and gives information about attractive forces between the dye and the fiber. Entropy measures the movement and randomness of the dye particles. Dyeing equilibrium can be achieved when the free energies of the dye in solution and in the fiber phase are equal. The dyeing of polyester with disperse dye is an exothermic reaction, i.e.,  $\Delta H$  is positive. The affinity of dye transport from the dye bath to the fiber is due to the positive heat of dyeing and the affinity of dye transport inside the fiber is due to the increase in entropy (38).

### Adsorption Isotherm

The adsorption isotherm is a dyeing mechanism parameter which indicates "the amount of dye adsorbed by the fiber against the concentration of the dye in the liquor at constant temperature", which is referred to as the partition coefficient (14). The adsorption isotherm for disperse dyeing of polyester is linear up to the saturation point. This type of adsorption isotherm is known as the Nernst Isotherm (14,26). However, when the dyeing saturation is approached, there are often deviations from the linearity of the iso-therm.

### Mechanism of Dyeing

The diffusion of dye into the fiber depends on the one hand on the geometrical properties of the dye molecules and the intermolecular spaces in the fiber structure, and on the other hand on the intermolecular forces between dye and fiber (39). As mentioned before, polyester has a very closely packed structure with strong polymer-to-polymer bonds which leads to its low dye diffusion properties. Disperse dyes, on the other hand, have very low solubility in the dye bath. Therefore, dye diffusion in the polyester cannot be possible without the dyer being able to change either the diffusion or solubility properties of the dye.

Thermal energy and chemical energy may be used to improve these properties. The free volume concept is used to explain the dyeing mechanism by explaining the changes of the morphology of the fiber with increasing temperature (40).

Below a certain temperature, the polymer chains are frozen into position and the only motions they can undergo are thermal vibrations, but further increases of temperature eventually provide sufficient energy for bond rotation in the backbone of the polymer chain. At this point a whole segment of the polymer chain between two simultaneously rotating bonds changes its position by rotation, until it is hindered from moving further by other polymer molecules. The change in position is referred to as a segmental jump. Such motions may occur only when sufficient free volume has been created to provide a space large enough to accommodate the polymer segment, but, once the segment has moved, the space it has vacated is left for another segment to occupy and the process is repeated through the whole of the polymer structure. Consequently, there is a sudden marked increase in free volume over a narrow temperature range and an associated increase in the segmental mobility, which can be detected by marked changes in the physical properties. The temperature at which this occurs is referred to as the glass transition temperature. In the dyeing process, the dye molecule is adsorbed on a polymer chain and is able to move only when the segmental movement of the adjacent chains is such that a hole is formed of a size sufficiently large to accept the dye molecule and polymer segment together. This situation exists only when the temperature is greater than the glass transition temperature (p.401).

Special dyeing techniques are available for dyeing polyester. The two most important commercial ones are (31,41):



1. Application of disperse dyes at temperatures below the boiling point of water with the assistance of aromatic swelling agents or carriers; this is referred to as carrier dyeing.
2. Application of disperse dyes at temperatures above the boiling point of water without the assistance of carriers; this is referred to as high temperature/pressure dyeing.

### CARRIER DYEING

#### Carrier Characteristics and Mechanism of Actions

The carrier dyeing method is used for the dyeing of polyester when pressure dyeing equipment is not available. As mentioned before, one way to increase the rate and amount of penetration of dye into the fiber is with the use of carriers. All the carriers are aromatic organic compounds of certain hydrocarbons, substituted hydrocarbons, phenols, amino acids, amides, alcohols, esters, ketones, and nitrites (5,42). Carriers are generally water insoluble; therefore, in order to produce a stable emulsion of them in the dye bath, emulsifiers are added (13,43). Some of the commercially available carriers are ortho-phenyl phenol, diphenyl, mono-and dichloro benzenes, benzoic acid, and salicylic acid (39,42). Carriers can increase the diffusion

coefficient of dye penetration from 10 - 100 times. However, the efficiency of the carriers depends largely on the nature of the dye (39). Dyes which diffuse slowly without carrier are accelerated more than those which diffuse rapidly. Several different theories exist about the carrier action mechanism (17,41,42).

1. Swelling - carriers act as swelling agents; hence, the large dye molecules can penetrate more rapidly into the swollen fiber.
2. Increase in water imbibition - carriers with hydrophilic groups like o-phenyl phenol or benzoic acid diffuse rapidly into the polyester. The aromatic part of the carrier forms Van der Waals' forces with a hydrophobic fiber and the hydrophilic part of the carrier attracts water. This results in increased flow of dye into the fiber.
3. Transport Theory - dye and carrier can form a loose combination which can be adsorbed by the polyester more rapidly than the dye itself from the dye bath solution.
4. Increased Solubility of the Dye in the Bath - carriers aid the solubility of disperse dyes in the dye bath by increasing the monomolecular dye particles resulting in faster dye diffusion into the fiber.

5. Increased Availability of Dye from Film - carriers may surround the fiber forming a layer in which the dye particles can dissolve. This phenomenon results in faster penetration of dye particles from the carrier film into the fiber than diffusion from the aqueous dye bath.
6. Liquid Fiber Theory - carriers penetrate the fiber then dissolve and hold the dye particles in the fiber.
7. Increased Sites Accessibility - carriers penetrate into the fiber and form a more open fiber structure with less crystallinity resulting in more space for dye penetration.
8. Lubricity of Fiber Molecules - carriers act like lubricants. They attach to the fiber polymer molecules and break existing crosslinks enabling easier penetration of dye.
9. Loosening of Fiber Structure - small carrier molecules diffuse rapidly into the fiber. This reduces the intermolecular forces of fiber-fiber bonds by forming weaker carrier-fiber bonds. Under thermal vibrations, the weak bonds of carrier-fiber can break and form a number of holes for penetration of dye.

From all these theories, the most accepted is that the action of carrier opens up the internal fiber structure by interrupting polymer-to-polymer bonds, thus resulting in more accessible and porous regions for dye diffusion, therefore acting as a plasticizer which lowers the glass transition temperature of the fiber. Therefore, dyeing is possible at a faster rate and at a lower temperature (3,17,14).

#### Advantages and Disadvantages of Carrier Dyeing

The carrier dyeing technique has several advantages over dyeing without a carrier which are as follows: increase in dyeing rate, increase in diffusion coefficient, ability to obtain deep shades within a reasonable period of time, and minimizing unlevelness. The advantage of this technique over pressure dyeing is the ability to dye the material at temperatures below 100°C without need to use expensive pressure dyeing equipment (34,39,44). However, carrier dyeing has also many disadvantages which include: the extra cost of carrier since it is thrown away after dyeing, difficulty in removing the carrier from the polyester material after dyeing, the remaining residues of the carrier in the fiber lower the light fastness and adversely affect the hand. They may also create unpleasant and harmful fumes

in some situations as volatile carriers are dissipated during heatsetting (3,5,41).

### Carrier Dyeing Application

Carrier dyeing of polyester with loose stock, tow, sliver, spun yarn or continuous filament yarn is carried out at temperatures up to 100°C (17). The bath is prepared with some 0.5 to 2 g/l of an anionic or nonionic dispersing agent and the necessary amount of carrier. The pH is adjusted to 4.5 - 5 by adding ammonium sulphate, acetic acid or formic acid. Then the bath is heated to a selected temperature. The material is treated in the bath for 10 - 15 minutes before the addition of disperse dye. Then the bath is brought to the boil with a heating rate of 1°C/min or so. The dyeing time ranges from 60 - 120 minutes depending on the depth of the shade desired.

### HIGH-TEMPERATURE/PRESSURE DYEING

In the high temperature dyeing method, dyeing takes place at temperatures above 100°C using special pressure dyeing machines. Loose stock, tops, yarns on cheeses or in hanks, and fabrics are dyed with several different high-temperature/pressure dyeing machines which are shown and described schematically in the literature (2,17).

The Longclose pressure-dyeing machine is one of the popular pressure package dyeing machines available (2). This machine is equipped with time/temperature thermostatic control. The yarn packages are supported on perforated stainless steel spindles. The dye liquor is pumped through the perforations and then passes through the yarn package. The dyestuffs must be well dispersed, otherwise the yarn will filter out the dye particles. Advantages of this machinery are: (1) minimal handling of the yarn; (2) low labor cost; (3) low liquor:goods ratio, only 5:1 or 10:1; and (4) less mechanical movement of the yarn minimizing broken filaments.

Fabrics in open width form can be dyed with high temperature/pressure beam dyeing machines and high temperature/pressure jig dyeing machines. Those which are available for high temperature/pressure beam dyeing include the Burlington Hy-Press, Longclose, Bibby, and Barotor beam dyeing machines (2). These machines are equipped with a large beam or several small beams placed horizontally in an autoclave (2,45,46). The beam is a hollow perforated cylinder and closed at both ends. The fabric is wound carefully around the beam with the same degree of density and tension in order to prevent any variation of the shade from beam to beam. The dye liquor flows through the fabric

inside-out and outside-in under high pressure and high temperature. The machine may be equipped with an automatic beam-revolving device which revolves the beam slowly at a constant speed. This gives better dye penetration and also agitates the dye bath which helps to produce level dyeing from end to end of the beam and will also help to dissipate the air bubbles from the layers of the fabric which otherwise might cause light spots in the fabric. The high temperature/pressure beam machines are suitable for light and open weave fabrics since they permit the dye to flow through the layers of the fabric very easily. Advantages of these machines are: (1) elimination of crack marks since the fabric is positioned in open width; (2) fabric does not tangle as is the case with beck type dyeing machines; and (3) a short dye bath which permits savings in dyes and other chemicals.

Dyeing of fabrics in rope form can be carried out in high-temperature/pressure beck or jet dyeing machines (2,17,44). The latest jet dyeing machines are Platt-Longclose, Longclose Ventura Uniflow, Samuel Pegg, Jet Flow BT, Gaston County, and Thies (47). In jet dyeing machines the fabric is fully immersed in the liquor which means that the effective fabric weight is reduced more than 70 percent due to buoyancy; therefore, the fabric is under

less tension (2). The liquor is fed into the bath through jets and circulated by a large pump and the fabric is moved by the circulation of the liquor.

### Characteristics of High Temperature/Pressure Dyeing

The high temperature dyeing process was given serious attention in the late 40's because of the development of new hydrophobic acrylic and polyester fibers (5,48,49). These fibers have slow rates of dye adsorption and diffusion at or below the boiling temperature of water unless carriers are used to loosen and open the fiber structure. However, it was found that these fibers could be dyed even in heavy shades at temperatures above boiling without carriers (48,49). High temperature dyeing can be characterized by its three major advantages over conventional dyeing processes which are faster dyeing cycles, better dye diffusion, and better leveling properties (5). At elevated temperatures above boiling, the fiber molecular chains increase mobility so that the space between fiber molecules gets larger thus introducing a more open fiber structure. At the same time dye molecules at high temperature receive higher excitation, so the motion of the molecules becomes more violent and dye agglomerates break down into dye mono-molecules (48,5). Therefore, dye penetration takes



place faster and easier; and dye can also penetrate into the regions which are inaccessible at 100°C, hence resulting in an increased build-up. High temperature dyeing also introduces better leveling because dye molecules can diffuse into the fiber more easily and can also go back into the dye bath with ease as well (54). In other words, migration improves with increasing dyeing temperature which in turn improves leveling. When dyeing of polyester is done below the boiling temperature, ring dyeing is observed because the rate of accumulation of dye on the surface of the fiber is much faster than the rate of diffusion of dye into the fiber; however, dyeing at temperatures above boiling gives good dye diffusion with a rate closer to that of dye absorption on the fiber surface (50).

From a practical dyeing point of view, there are three basic elements which should be considered; these are (4,51): a) selection of suitable disperse dyes, b) selection of suitable chemical auxiliaries, and c) the establishment of proper dyeing process.

In a system where dye and dye auxiliaries are chosen suitably and are maintained constant, the dyeing characteristics will be a function of the dyeing process.

### Criteria for Dyeing Process

The dyeing process consists of: starting temperature, dyeing temperature, holding time, rate of temperature rise, and liquor ratio.

Starting Temperature (52) - the starting temperature of dyeing should be as high as possible in order for the dye to begin to exhaust as quickly as possible with a desirable speed; too low a starting temperature leads to unnecessary dead time and too high a starting temperature causes dye-stuff to exhaust too rapidly, hence uneven dyeing takes place. The ideal starting temperature for polyester is in the range of 80 - 90°C around its glass transition temperature in water. However, disperse dyes may form aggregates at high temperatures and create a dispersion problem. Starting temperature above 40 - 50°C gives inferior dispersions; therefore, dyeing should commence around 40 - 50°C.

Dyeing Temperature - this refers to the temperature at which the rate of diffusion of dye into fiber begins to be significant. At this temperature, the polymer chains of the fiber reach adequate mobility and the dyestuff is almost completely dispersed (31,55). Generally, in the high temperature dyeing of polyester, dyeing temperature is set at around 130°C. The high dyeing temperature gives rise to

a high dye diffusion rate and a low diffusion time (53,56). Leveling improves with higher dyeing temperature since high temperature allows better migration (53,56,57). It has been shown that small variations in the dyeing temperature results in an influence on the dye yield (52). Dye concentration in the bath influences the dyeing temperature. As the dyestuff concentration increases, the dyeing temperature also increases (55).

    Holding Time - this is the time required for exhaustion and fixation of the dye into the fiber. It is desirable to spend as little time as possible in order to shorten the dye cycle to save time and energy (32). The holding time required for a dyeing process is mainly dependent on dyeing temperature and the depth of shade (58). The higher the dyeing temperature, the less time needed for complete exhaustion. The higher the depth of shade, the longer the time required. However, an adequate dyeing time is required for sufficient migration action in order to obtain reasonable leveling (57). On the other hand, from a practical point of view, reducing the holding time is suggested in order to control the absorption rate during the dyeing cycle (56).

    Rate of Temperature Rise - faster rates of temperature rise produce shorter dye cycles and greater energy savings.

However, the rate of temperature rise is restricted by the liquor circulation of the dye (4). In order to achieve level dyeing, the rate of liquor circulation and the heating rate of the dye bath within a critical exhaustion range of the disperse dyestuff should be synchronized (4,53). Otherwise, too rapid dye strike may occur leading to unlevel dyeing. A practical rate of rise in temperature may fit in a range  $0.9 - 7.5^{\circ}\text{C}/\text{min}$  (4,54). A rapid rate of rise in temperature may be applied before any significant dye exhaustion takes place, usually below 10% exhaustion of the dye bath (55). This way, a shorter dye cycle can be achieved by eliminating dead time and at the same time minimizing the exposure time of the dye dispersion to the dye bath in order to prevent any possibility of dispersion break (55). As the dyeing proceeds, careful control of the rate of temperature rise is necessary during the critical exhaustion interval in which the major portion of the dye in the bath is exhausted at about 80 - 95% (55,54).

Liquor Ratio - this is the ratio of the weight of the dye liquor to the fabric weight. The absorption curve of disperse dyes shifts with the dye concentration, the lower the dye concentration the higher the percentage of exhaustion (51,59).

### Exhaust Dyeing Principles

Conventional exhaust dyeing processes are considered with time/ temperature cycles which are dependent on substrate, dyes and chemicals. They are carried out under one of two principles (60), migration or controlled absorption. The migration principle is based on rapid absorption of dye which results in irregular dye absorption, hence it needs additional time and power to correct the unevenness by the migration of dyes from highly dyed to lightly dyed areas. This action is time consuming and leads to long dyeing cycles. However, in the controlled absorption principle, dye absorption takes place uniformly so there is no need for migration time. Hence, this brings shorter dyeing cycles. A new method of exhaustion dyeing known as Suproma has been developed (60). The Suproma method considers the exhaust behavior of the dyeing cycle in relation to substrate, dyes, chemicals, and machinery. It gains a rapid and short dyeing cycle and level dyeing results. Suproma controlled absorption is accomplished by adjusting the exhaust characteristics of the dyes with the performance capacity of the machine in order to achieve constant exhaustion of dye per contact (one complete circulation of dye liquor through the batch of fabric or yarn).

### Dye Exhaustion Characteristics

The exhaustion curve of dye in substrate is divided into three regions (55,56):

1. Early period of absorption - exhaustion in this region is very low, about 20% or less, and it takes place very slowly. Therefore, no exhaustion control is necessary.
2. Dyeing period - absorption of 20% - 90% of dye takes place in this temperature interval. This region is known as the critical temperature range. In this region the polymer chains of the fiber attain a degree of mobility such that the dye is capable of penetrating the fiber. The critical temperature range, generally lies between  $(T_c - 15)$  and  $(T_c + 15)$ , where  $T_c$  is the temperature corresponding to  $t(1/2)$ , the time of half dyeing (59). The temperature range for polyester is usually in a range of 150 - 250°F which may vary for different concentration and energy level dyes (60). The exhaustion rate is rapid and must be controlled; otherwise, unlevel dyeing is achieved.
3. Diffusing migrating period - the remaining 10% of dyestuff exhausts in this region very slowly. No control of exhaustion is necessary.

Specific Studies on Dyeing Behavior of Polyester Above 100°C

Fern investigated the stability of the polyester and disperse dyes under high temperature conditions (5). Filament polyester yarn was treated for 45 minutes at pH 7.0 (distilled water), 2.8 (lactic acid) and 11.2 (sodium carbonate) at pressures of 10, 30, 50, and 70 lb/in<sup>2</sup> (115 - 160°C). He found no decrease in toughness of the fiber under neutral or acidic conditions up to pressure of 50 lb/in<sup>2</sup>. However, under the mildly alkaline condition, degradation occurred at pressures above 30 lb/in<sup>2</sup>. A group of disperse dyes was heated at a temperature of 135°C for two hours. Then, the optical absorption curves of the unheated and of the heated dye were compared spectrophotometrically. No changes occurred in the optical absorption of most disperse dyes.

Fern also studied the effect of dye bath variables on the dyeing behavior of polyester (5). Terylene yarn was dyed in dye baths with various amounts of dye for 90 minutes at 85, 100, and 120°C. At 120°C, the dye absorption increased linearly, whereas at 85 and 100°C, the fiber was saturated at an early stage. He concluded that the saturation of the fiber at low temperatures results from a saturation of dye on the surface of the fiber, and only a limited quantity of dye can diffuse from the surface into the fiber in a

practical dyeing time. However, an increase in the dyeing temperature results in an increase in the rate of diffusion therefore increasing the amount of dye diffused from the surface into the fiber.

Merian studied the effect of dyeing time and amount of dispersing agent on dyeing behavior of Dacron polyester staple fiber (61). A series of dyeings were produced on the fiber with increasing amounts of dispersing agent and at progressively longer times up to eight hours at 130°C. In the absence of a dispersing agent, the dyeing equilibrium and the maximum exhaustion were obtained after one hour at 130°C, while with 1.00 cc/l dispersing agent, two hours were required for the same result. After these times there were no significant changes in exhaustion. Microscopical examination of fiber cross-sections showed that levelness was already reached after 15 minutes. Therefore, it was not necessary to lengthen the dyeing time in order to bring about level dyeing through migration.

Hadfield and Broadhurst studied the effect of dyeing temperature on the building up and leveling properties of a fast and a slowly diffusing dye (25). The dyeing was carried out in a rotating dyeing machine at temperatures from 85 to 140°C. The results showed that the dye bath exhaustion increased with increasing temperature up to



140°C. Considerable improvement of exhaustion from 120 to 130°C was noted. Slowly diffusing disperse dyes showed greater improvement in exhaustion above 120°C than rapidly diffusing dyes. There was a significant improvement in leveling properties of the yarn as the temperature was raised up to 140°C.

Niwa and Kelly investigated dyeing behaviors at temperatures above 130°C (56). It was concluded that the diffusion rate at 140°C is almost 3 - 3.5 times greater than at 130°C and time required for diffusion is reduced by about one-third. Leveling was also improved by rapid diffusion of dye at 140°C due to the easy absorption and desorption of dye to the fiber.

## Chapter IV

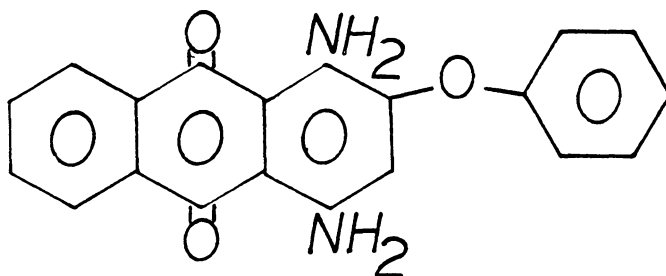
### METHODOLOGY

For this study the following materials and procedures were used:

#### MATERIAL

Two-ply spun Dacron type 54 polyester yarn with a denier of 490 was used in all the experiments. It was purchased from Test Fabrics Incorporated, as ten gram skeins.

The dye used was Disperse Red 60 [CI 60756 (bright bluish red)] which has the following structure:



The dye was used as supplied by its manufacturer (DuPont); it contained dispersing agent. This dye is categorized as a low energy, rapidly diffusing dye (62).

#### PREPARATION OF POLYESTER YARN

Before dyeing, the yarns were scoured in a solution containing 2 g/l nonionic detergent, and 0.5 g/l sodium carbonate for 20 - 30 minutes at a temperature of 75 - 80°C, then rinsed thoroughly in distilled water and air-dried. Yarns were conditioned for 24 hours at 70 ± 2°F and a relative humidity of 65 ± 2%.

#### PREPARATION OF DYE DISPERSION

Four grams of disperse dye and one gram of Triton X-100 (nonionic surfactant) were mixed with 200 ml hot distilled water in a 400 ml beaker. The dispersion was transferred to 1000 ml volumetric flask and was diluted to 1000 ml when cool by adding cold distilled water. Dye dispersion prepared this way had a nominal concentration of four grams per liter.

#### DYEING PROCEDURE

The Ahiba Texomat dyeing machine was used for dyeing the yarns. Each dye bath was made up using 50 ml of dye dispersion and 350 ml of distilled water yielding a total volume of 400 ml. The baths were heated up to 90°C. Then, a ten gram skein of spun Dacron 54 yarn was introduced into each dye bath giving a liquor/material ratio of about 40:1.

The temperature was raised at a specific rate of rise until it reached the specific dyeing temperature. Dyeing was then continued for the specific length of time. The dyeing process designed follows:

Experiment No. 1

Start at 90°C, raise to 105°C at 1°C min<sup>-1</sup>,  
hold 0 minute, cool to 75°C.

Experiment No. 2

Start at 90°C, raise to 105°C at 1°C min<sup>-1</sup>,  
hold 15 minutes, cool to 75°C.

Experiment No. 3

Start at 90°C, raise to 105°C at 1°C min<sup>-1</sup>,  
hold 30 minutes, cool to 75°C.

Experiment No. 4

Start at 90°C, raise to 105°C at 1°C min<sup>-1</sup>,  
hold 60 minutes, cool to 75°C.

Experiment No. 5

Start at 90°C, raise to 105°C at 3°C min<sup>-1</sup>,  
hold 0 minute, cool to 75°C.

Experiment No. 6

Start at 90°C, raise to 105°C at 3°C min<sup>-1</sup>,  
hold 15 minutes, cool to 75°C.

Experiment No. 7

start at 90°C, raise to 105°C at 3°C min<sup>-1</sup>,  
hold 30 minutes, cool to 75°C.

## Experiment No. 8

Start at 90°C, raise to 105°C at 3°C min<sup>-1</sup>,  
hold 60 minutes, cool to 75°C.

## Experiment Nos. 9 - 16

Same as above except dyeing temperature 120°C.

## Experiment Nos. 17 - 24

Same as above except dyeing temperature 135°C.

The experimental design can be visualized as follows:

Dyeing temp.	Rate of temp. rise	Holding Time (minute)			
		0	15	30	60
105°C	1°C min <sup>-1</sup>				
	3°C min <sup>-1</sup>				
120°C	1°C min <sup>-1</sup>				
	3°C min <sup>-1</sup>				
135°C	1°C min <sup>-1</sup>				
	3°C min <sup>-1</sup>				

The order of the twenty-four experiments was randomized using a table of random numbers.

### AFTER TREATMENT

The dye baths were cooled to 75°C, then the yarn skeins were removed and rinsed in water. To remove surface dye, reduction clearing was carried out using a solution containing one gram per liter sodium dithionite and, one gram per liter sodium carbonate for 15 minutes at 70°C. Then, the reduction cleared yarns were rinsed thoroughly with distilled water and air-dried (62).

### ANALYTICAL PROCEDURE

#### Establishing Standard Curve

In order to establish a standard curve for Disperse Red 60, 0.0500, 0.0501, 0.0516, and 0.0518 grams of dye powder were each diluted to 50 ml in separate 50 ml volumetric flasks by adding dimethyl formamide(DMF) solvent. Then, from each of these preparations, several solutions of different dilutions were prepared by measuring 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 ml of each solution and diluting to 10 ml by adding dimethyl formamide in a 10 ml volumetric flask. The absorbance of each solution was determined, using a Bausch and Lomb Spectronic 2000 UV-VIS Spectrophotometer at 520 nm. A Beer's Law plot was drawn spectrophotometrically for each prepared solution. Finally, a composite standard curve was drawn. The resultant composite standard curve had the following equation:

$$Y = .0020 + 8.412X$$

Where:

Y = dye absorbance

X = dye concentration, in grams per liter

### Dye Bath Concentration Before Dyeing

Dye concentration in the bath before dyeing was measured spectrophotometrically. One ml of bath liquor was diluted to 10 ml in a 10 ml volumetric flask by adding dimethyl formamide solvent. As an example, the following calculations were done for the dyeing condition at 135°C for a holding time of 30 minutes with a rate of temperature rise of 1°C min<sup>-1</sup>.

If Y = 0.429 (dye absorbance)

$$Y = 0.0020 + 8.412X$$

$$0.429 = 0.0020 + 8.412X$$

$$X = 0.0508 \text{ mg/ml}$$

Since one ml of 400 ml of the original dye bath was diluted to 10 ml,

Therefore:

$$X = 0.0508 \times 10 \times 400 = 203.0 \text{ mg (dye in original dye bath)}$$

Dye Bath Concentration After Dyeing

Dye concentration in the bath after dyeing was measured spectrophotometrically. Two ml of bath liquor was diluted to 10 ml in a 10 ml volumetric flask by adding dimethyl formamide solvent. As an example, the following calculations were done for the dyeing condition at 135°C with a holding time of 30 minutes with rate of temperature rise of 1°C min<sup>-1</sup>.

If  $Y = 0.0$  (dye absorbance)

$$Y = 0.0020 + 8.412X$$

$$0.0 = 0.0020 + 8.412X$$

$$X = -0.00023 \text{ mg/ml (dye concentration after dilution)}$$

Assumption:  $X = -0.00023 \approx 0.000$

Since 2 ml of 400 ml of the original dye bath was diluted to 10 ml,

Therefore:

$$X = 0.000 \times 10/2 \times 400 = 0 \text{ mg (dye in bath after dyeing)}$$

Dye Concentration in the Yarn

Dye concentration in yarn was obtained through extraction and then measured spectrophotometrically. About 0.05 gram of each yarn was taken randomly from each dyed skein. This



was placed in a test tube and 10 ml of distilled DMF was added. All the test tubes were placed in a shaking water bath for 24 hours at temperature of 64°C. The machine was adjusted for gentle agitation. After 24 hours, the solution from each test tube was emptied into a bottle. Ten ml of DMF was added again to each test tube; these were then extracted in the water bath for an additional 24 hours. After 48 hours, extraction was complete according to testing results. The solution from each test tube was added again to each proper bottle. The solutions were transferred to 50 ml volumetric flasks and were diluted to 50 ml when cool by adding distilled DMF solvent. As an example, the following calculations were done for dyeing condition of 135°C dyeing temperature, 30 minutes holding time and 1°C min<sup>-1</sup> rate of temperature rise.

If  $Y = 0.184$  (dye absorbance)

$$Y = 0.0020 + 8.412X$$

$$0.184 = 0.0020 + 8.412X$$

$$X = 0.0216 \text{ mg/ml (dye concentration in extraction solution after dilution)}$$

Since about 0.05 gram of dyed yarn was extracted and extracted solution was diluted to 50 ml,  
Therefore:

$$0.0216 \times 50 \times 9.736 / 0.0587 = 179.4 \text{ mg (dye in a skein of yarn)}$$

Where 0.0587 and 9.736 are the actual weights in grams of the extracted sample and the entire skein, respectively.

#### Dye Concentration on the Surface of the Yarn

Dye concentration on the surface of the yarn was obtained by simply subtracting dye concentration of bath after dyeing plus dye concentration in the yarn from dye concentration of bath before dyeing. As an example, the following calculations were done for the dyeing condition of 135°C dyeing temperature, 30 minutes holding time, and 1°C min<sup>-1</sup> rate of temperature rise.

$$A = B - (C + D)$$

Where:

A = mg dye on surface

B = mg dye in bath before dyeing

C = mg dye in bath after dyeing

D = mg dye in yarn

Then substituting:

$$A = 203.0 - (0.0 + 179.4) = 23.6$$

### REPLICATION

Three skeins of polyester yarn were dyed for each dyeing process condition. A total of 24 process conditions were tested; therefore, 72 skeins of yarn were dyed. One sample of about 0.05 gram of yarn was analyzed from each dyed skein. A total of 72 samples were analyzed.

### STATISTICAL ANALYSIS

Factorial analysis of variance (ANOVA) was used to test the effects of temperature, time, rate of temperature rise and their interactions on the dye uptake of the yarn, dye left in the bath, and dye on the surface of the yarn.

## Chapter V

### RESULTS AND DISCUSSION

In this chapter, the results of the statistical analyses of the data are presented. Then, the results are interpreted and discussed. Finally, the results are summarized and conclusions are drawn.

#### DATA ANALYSIS

##### Analysis of Variance

Analyses of variance was used to determine whether or not the variables dyeing temperature, holding time, rate of temperature rise, and their interactions had significant effects on the dye uptake of the yarns, dye left in the bath, and dye on the surface of the yarn.

As shown in Table 1, the majority of the data for the dye in the bath after dyeing indicate full exhaustion at dyeing temperatures of 120°C and 135°C. Therefore, ANOVA for this set of data was done for the dyeing temperature of 105°C. Table 2 shows the ANOVA table for the dependent variable, the dye remaining in the bath after dyeing. According to the table, at the dyeing temperature of 105°C, the rate of temperature rise, holding time and the interaction of the two, significantly affect the dye in the bath after dyeing.

TABLE 1

Amount of Dye in the Bath Before and After Dyeing, in the Yarn and on the Yarn for Different Process Conditions.

Temp (°C)	Rate (°C/min)	Holding Time (min)	Amount of Dye (mg)			
			In bath before dyeing	In bath after dyeing	In Yarn	On Surface
105	1	0	201.8	141.9	57.8	2.1
105	1	15	204.4	70.2	132.2	2.0
105	1	30	199.2	30.6	153.6	15.0
105	1	60	199.8	0.0	183.8	16.0
105	3	0	208.3	158.5	48.7	1.1
105	3	15	198.1	97.3	97.4	3.4
105	3	30	197.5	38.9	144.2	14.4
105	3	60	199.5	0.0	174.9	24.6
120	1	0	200.5	16.2	166.3	18.0
120	1	15	202.5	0.0	191.4	11.1
120	1	30	200.9	0.0	174.5	26.4
120	1	60	200.4	0.0	187.1	13.3
120	3	0	200.2	84.6	98.8	16.8
120	3	15	199.4	0.0	184.2	15.2
120	3	30	199.9	0.0	184.7	15.2
120	3	60	200.7	0.0	185.4	15.3
135	1	0	199.9	0.0	172.6	27.3
135	1	15	198.8	0.0	168.1	30.7
135	1	30	200.9	0.0	177.4	23.5
135	1	60	199.7	0.0	182.8	16.9
135	3	0	198.8	0.0	172.8	26.0
135	3	15	200.7	0.0	187.7	13.0
135	3	30	199.2	0.0	177.2	22.0
135	3	60	199.1	0.0	172.6	26.5

TABLE 2

Summary of the ANOVA for the Variable Dye in the Bath After Dyeing, at 105°C.

Source	DF	Mean Square	F-Value	PR>F
Time	3	25473.40	3503.09	0.0001
Rate	1	1019.20	140.16	0.0001
Rate*Time	3	204.66	28.14	0.0001
Error	16	7.27		

R-square	0.998512
Root Mean Square of Error	2.696602

The summary of the ANOVA table for the dependent variable, dye in the yarn, is shown in Table 3. According to the table, all three variables, all two-way interactions and the three-way interaction significantly affect the dye in the yarn.

The summary of the ANOVA table for the dependent variable, dye on the surface of the yarn, is shown in Table 4. According to the table, all the independent variables and their interactions significantly affect the dye on the surface of the yarn except rate of temperature rise and the two-way interaction of rate of temperature rise and temperature.

#### DISCUSSION

On the basis of the results of the statistical analyses for the dye in the bath, dye in the yarn, and dye on the surface of the yarn, it is concluded that these dependent variables are significantly influenced by the three-way interaction of the process condition variables: temperature, time, and rate of temperature rise.

TABLE 3

Summary of the ANOVA for the Variable Dye in the Yarn.

Source	DF	Mean Square	F-Value	PR>F
Temp	2	20058.82	763.80	0.0001
Time	3	12794.38	487.19	0.0001
Rate	1	1771.11	67.44	0.0001
Temp*Time	6	4460.88	169.86	0.0001
Temp*Rate	2	678.95	25.85	0.0001
Time*Rate	3	540.86	20.60	0.0001
Temp*Time*Rate	8	877.58	33.42	0.0001
Error	46	26.26		
R-square	0.989636			
Root Mean Square of Error	5.124620			



TABLE 4

Summary of the ANOVA for the Variable Dye on the Surface.

Source	DF	Mean Square	F-Value	PR>F
Temp	2	1078.12	64.88	0.0001
Time	3	183.99	11.07	0.0001
Rate	1	9.75	0.59	0.4475
Temp*Time	6	210.73	12.68	0.0001
Temp*Rate	2	37.91	2.28	0.1136
Time*Rate	3	121.93	7.34	0.0004
Temp*Time*Rate	6	83.44	5.02	0.0005
Error	46	16.61		

R- square	0.866123
Root Mean Square of Error	4.076374

Effect of the Process Conditions on the Amount of Dye in the Bath After Dyeing

At the dyeing temperature of 105°C, the amount of dye in the bath decreases as the holding time increases from zero to 60 minutes for both rates of temperature rise, 1°C/min and 3°C/min. It is obvious that the longer the yarn stayed in the bath, the greater the amount of dye diffused inside the yarn due to the longer contact time of the yarn with the dye dispersion (Figure 1).

At the 1°C/min rate of temperature rise, more dye left the bath and diffused into the yarn than at 3°C/min, for dyeing temperature of 105°C, for all holding times. This is probably due to the shorter contact time of the yarn with the dye dispersion at the faster rate of temperature rise.

At dyeing temperatures of 120°C and 135°C, complete exhaustion of the bath took place for all the process conditions except for zero holding time at the dyeing temperature of 120°C for both rates of temperature rise (Table 1).

Effect of Holding Time on the Dye Uptake of the Yarn at Different Dyeing Temperatures and Rates of Temperature Rise

The dye uptake of polyester yarn increased significantly with the holding time at the dyeing temperature of 105°C for both 1°C/min and 3°C/min rate of temperature rise (Figure

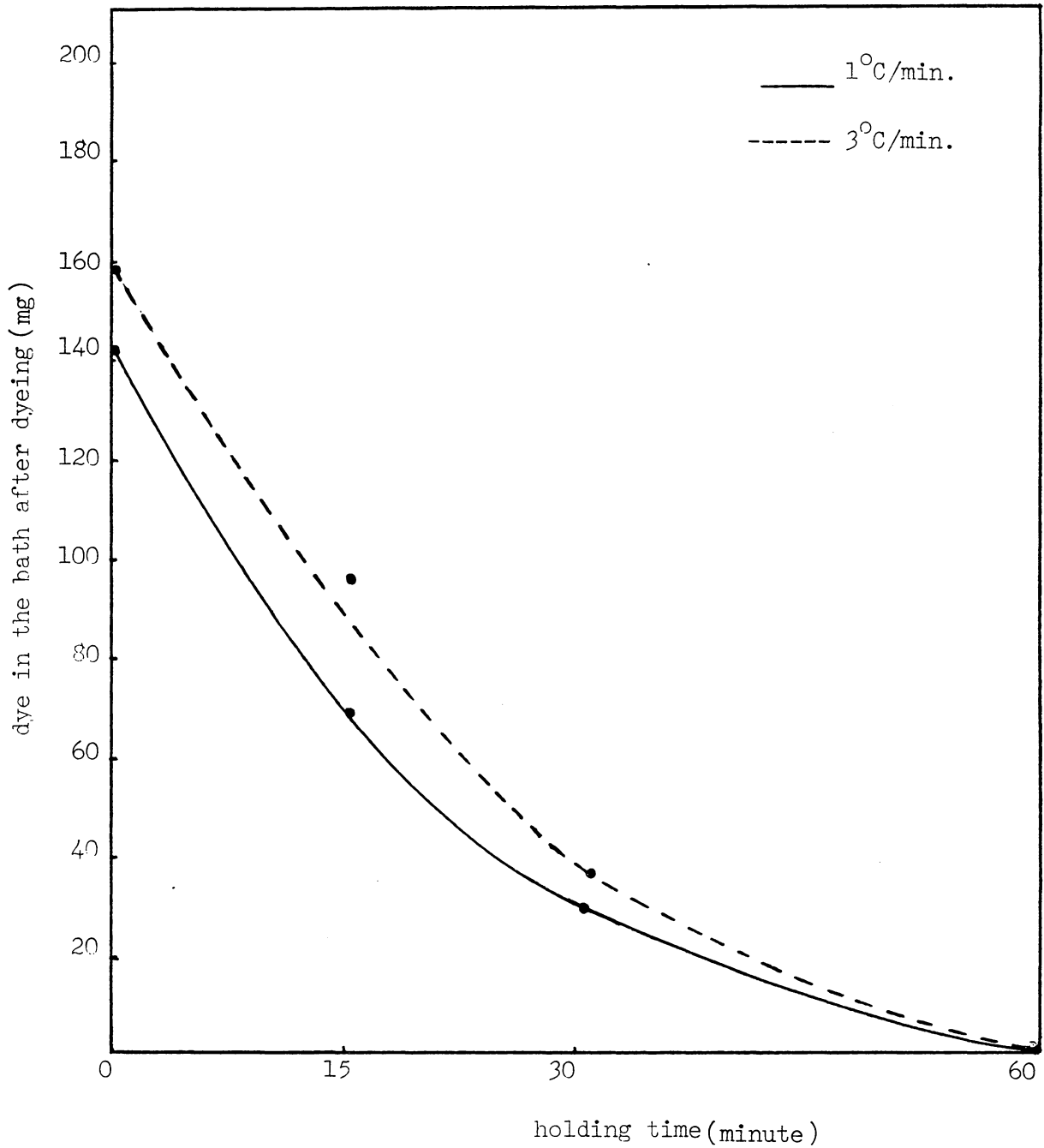


Figure 1: Effect of Holding Time and Rate of Temperature Rise for the Variable Dye in the Bath After Dyeing, at 105°C.

2). In Figure 2, it can be seen that dye diffusion into the yarn increases as the holding time increases, for both rates of temperature rise. This means that the longer holding time gives the opportunity for the longer yarn contact with the dye dispersion, hence higher diffusion takes place. However, the rate of exhaustion of the dye into the yarn decreases as the dye concentration in the yarn increases.

At the dyeing temperature of  $120^{\circ}\text{C}$ , the dye uptake of the yarn increased significantly by increasing the holding time from zero to 15 minutes for both rates of temperature rise (Figure 3). This is due to increasing the yarn and dye dispersion contact as mentioned above for the dyeing temperature of  $105^{\circ}\text{C}$ . However, the dye uptake of the yarn at the dyeing temperature of  $120^{\circ}\text{C}$  did not increase by increasing the holding time above 15 minutes for both rates of temperature rise. This is due to having already achieved full exhaustion at a holding time of 15 minutes. According to the data in Table 1 or Figure 3, the dye uptake even decreased beyond the holding time of 15 minutes. This may be due to the change of the polyester yarn surface by dyeing at a high temperature for prolonged periods of time. It was noted that the yarn surface had a greater amount of protruding fibers and seemed fuzzier after dyeing at high temperatures and with long holding times. Since reduction

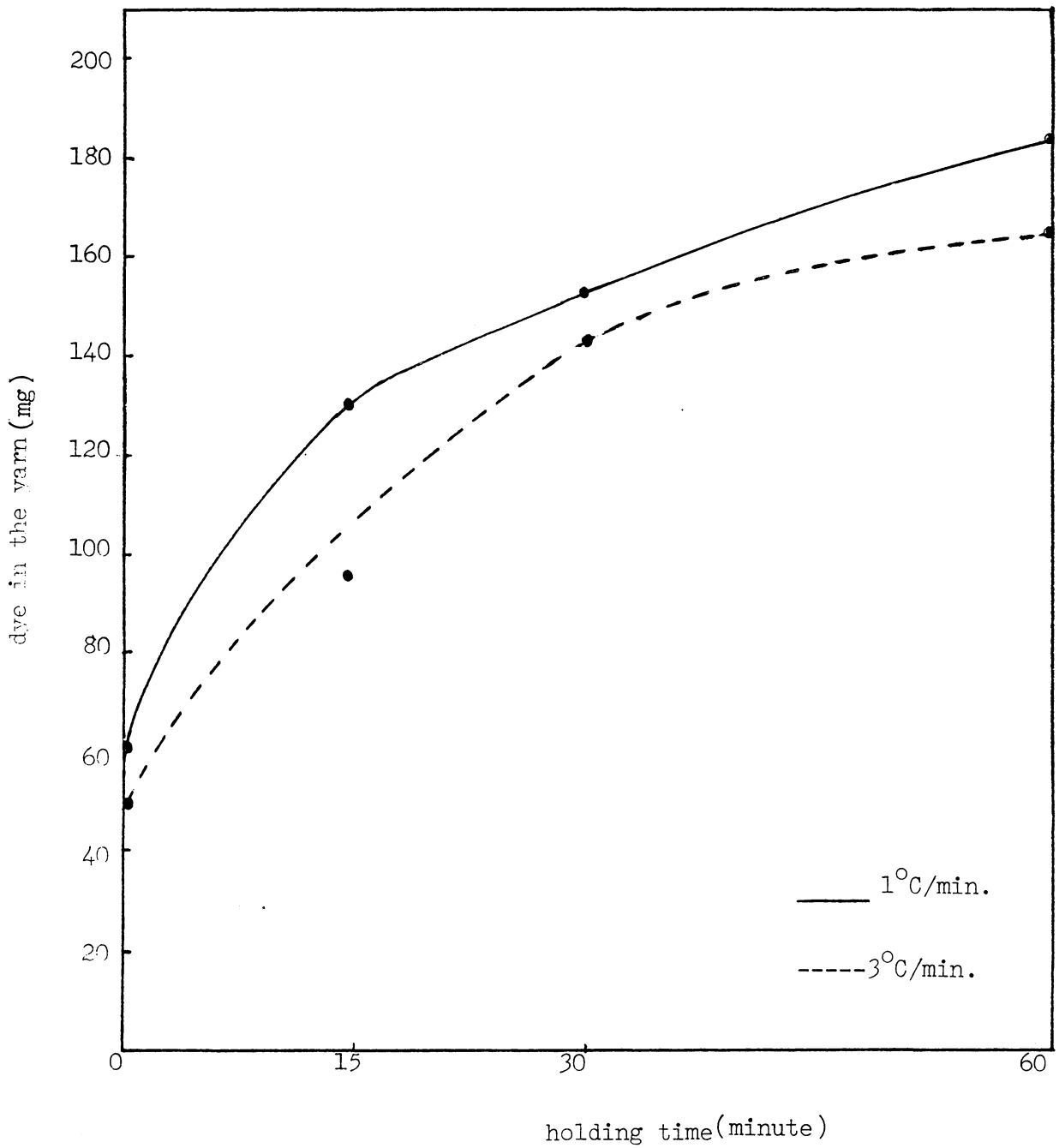


Figure 2: Effect of Holding Time and Rate of Temperature Rise for the Variable Dye in the Yarn, at 105°C.

clearing was done after dyeing, changes of the yarn surface might have caused slight diffusion of the reduction clearing agents into the yarn, removing some of the dye from inside of the yarn in addition to the removal of dye from the surface of the yarn.

Complete dye exhaustion took place at the dyeing temperature of 135°C for all the holding times for both rates of temperature rise. The reason is that the dyeing temperature of 135°C is far above the glass transition temperature of polyester ( $T_g = 85^\circ\text{C}$ ). Therefore, the dye molecules diffused inside the yarn very rapidly in the shortest holding time (zero min). It can be seen from Table 1 and Figure 4 that at the dyeing temperature of 135°C there is the tendency for a slight decrease in the dye uptake of the yarn with increasing the holding time for both rates of temperature rise.

The reason is probably the same as mentioned for dyeing temperature of 120°C, about the change of yarn surface at high temperature dyeing for long holding times and the chance of the diffusion of reduction clearing agents into the yarn and removal of the dye particles from inside of the yarn.

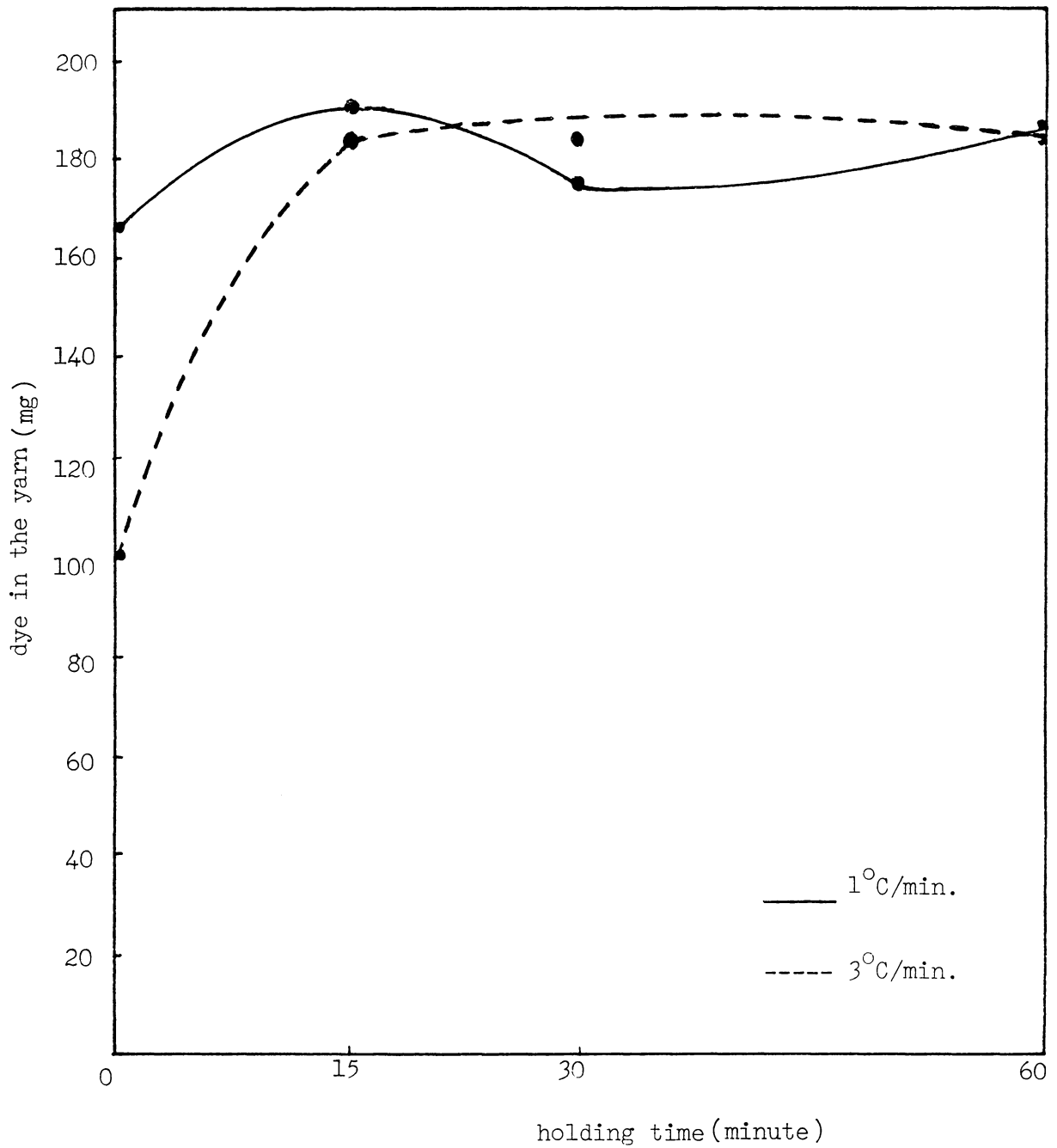


Figure 3: Effect of Holding Time and Rate of Temperature Rise for the Variable Dye in the Yarn, at 120°C.

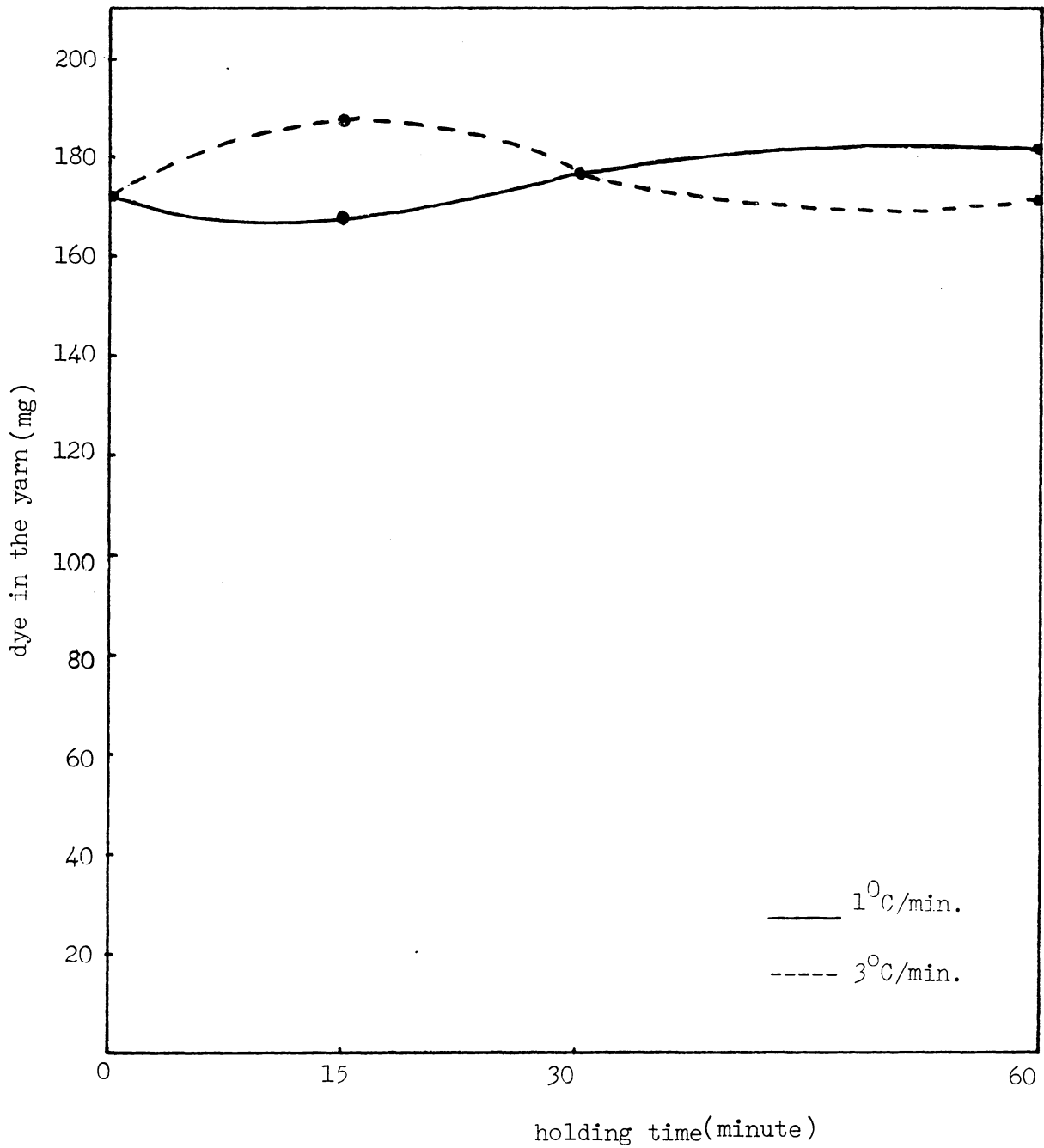


Figure 4: Effect of Holding Time and Rate of Temperature Rise for the Variable Dye in the Yarn, at 135°C.



Effect of Dyeing Temperature on the Dye Uptake of the Yarn at Different Holding Times and Rates of Temperature Rise

The dye uptake of the yarn increased as dyeing temperature increased from 105°C to 120°C for all the levels of the holding time and both rates of temperature rise (Figure 2 and Figure 3). However, the rate increase of the dye uptake slowed down by increasing the holding time and decreasing the rate of temperature rise since at both temperatures, dyeing approached complete exhaustion. Dye uptake of the yarn increased by increasing dyeing temperature due to the increase of the mobility of the polymer chains in the amorphous areas and also due to the increase of the energy of the dye molecules which gave rise to the more rapid diffusion of dye molecules into the yarn.

The dye uptake of the yarn increased by increasing dyeing temperature from 120°C to 135°C only at the zero minutes holding time for both rates of temperature rise (Figure 3 and Figure 4). The reason is that at the higher holding times full exhaustion took place at both 120°C and 135°C dyeing temperature.

Effect of Rate of Temperature Rise on the Dye Uptake of the Yarn at Different Dyeing Temperatures and Holding Times

The rate of temperature rise of 1°C/min gave higher dye exhaustion in the yarn than the rate of temperature rise of

3°C/min at dyeing temperature of 105°C for all the holding time levels (Figure 2). This is due to the longer contact time of the yarn and dye dispersion in the case of 1°C/min rate of temperature rise. It takes three times longer to reach dyeing temperature for rate of temperature rise of 1°C/min than 3°C/min. As can be seen in Figure 2, the influence of the rate of temperature rise on the dye uptake of the yarn decreased as complete exhaustion was approached.

The rate of temperature rise of 1°C/min at 120°C dyeing temperature with holding time of zero and 15 minutes resulted in higher dye uptake in the yarn than rate of temperature rise of 3°C/min (Figure 3). As was mentioned before, this is due to the longer yarn and dye dispersion contact. The rate increase of dye uptake slowed down by approaching full exhaustion. After full exhaustion was achieved, the rate of temperature rise lost its impact on the dye uptake of the yarn.

The rate of temperature rise did not influence the dye uptake of the yarn at a dyeing temperature of 135°C with any level of the holding time (Figure 4). This is due to the complete dye exhaustion at this temperature for both rates of temperature rise and all the holding time levels.

The Effect of the Process Conditions on the Amount of Dye on the Surface of the Yarn

By referring to the chapter on procedure and methodology, the value of dye on the surface of the yarn was measured mathematically by simply subtracting dye in the bath after dyeing plus dye in the yarn from dye in the bath before dyeing. Therefore, all the experimental errors of the mentioned data fall in the data of dye on the surface of the yarn. Also a very small amount of dried dye particles was left on the dye container walls, above the liquor level of the bath due to the evaporation of the dye bath during dyeing.

Keeping all this in mind, the data for the dye on the surface of the yarn showed more surface dye for the higher dyeing temperatures at all the levels of the holding time and both rates of temperature rise (Table 1). This was possibly caused by the change of the yarn surface at high temperatures. High temperature dyeing may cause a rougher and fuzzier yarn surface which in turn results in higher entrapment of the dye particles on the surface of the yarn. On the other hand, at the higher dyeing temperature, the faster and easier dye molecules go back and forth between the yarn and bath. Therefore, the higher temperature may give rise to a higher number of dye molecules available around the yarn for possible entrapment on the surface of the yarn.

### SUMMARY AND CONCLUSIONS

The purpose of this study was to investigate the effect of temperature, time and rate of temperature rise on the dye uptake of the polyester yarn under high temperature dyeing conditions. The results of the dyeing experiments showed that the process conditions, temperature, time and rate of temperature rise had significant impact on the dye uptake of the polyester yarn. Accordingly, all three null hypotheses were rejected.

Below the dyeing temperature of  $120^{\circ}\text{C}$ , dye exhaustion increased with increasing temperature. However, above  $120^{\circ}\text{C}$  dye exhaustion stayed almost the same. At the dyeing temperature of  $120^{\circ}\text{C}$ , dye exhaustion increased with increasing the holding time from zero to 15 minutes for both rates of temperature rise. However, further increase in the holding time above 15 minutes did not increase dye exhaustion for both rates of temperature rise. At the dyeing temperature of  $120^{\circ}\text{C}$  and holding time of 15 minutes, dye exhaustion was improved by decreasing the rate of temperature rise. For the special dye bath concentration and dyeing process design used in this study, the dyeing of polyester yarn at  $120^{\circ}\text{C}$  for 15 minutes with the rate of temperature rise of  $1^{\circ}\text{C}/\text{min}$  is an optimum dyeing process in achieving full exhaustion.

In this study only one dye and one dye concentration was used for the dyeing of polyester yarn. It is very possible that the dye exhaustion is influenced by the dye type and dye concentration. A study covering these two variables would be useful in this respect.

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