

CARRIER CONCENTRATION AND DYE TYPE EFFECT ON CARRIER  
AND DYE UPTAKE OF DACRON TYPE 54 YARN  
IN DISPERSE DYEING OF POLYESTER

by

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(ABSTRACT)

The effect of carrier concentration and dye type on carrier and dye uptake of Dacron type 54 yarn was determined. Disperse Red 60 and Disperse Yellow 54 dyes were used. O-phenyl phenol was used with six different concentrations of this carrier (0, 1, 2, 3, 4 and 5 gm/l). Spun Dacron type 54 polyester yarn of 490 denier weighing ten grams was obtained. Dyeing was done using the Ahiba Texomat dyeing machine. The standard composite curves and equations were established for both dyes as well as the carrier. The dye in the yarn was extracted with dimethyl formamide as a solvent using the Fisher Shaking Water Bath. To measure the dye and carrier uptake of the polyester yarn, the extraction and dye bath solutions were analyzed spectrophotometrically. A two-way factorial Analysis of Variance (ANOVA) was used to test the hypotheses. The first null hypothesis indicating that there will be no difference in the uptake of disperse dye by polyester fiber due to initial carrier concentration was rejected. The second null hypothesis indicating that there will be no difference in the uptake of disperse dye by the polyester fiber due to dye type was also rejected. The third and fourth null hypotheses of no difference in the carrier uptake of polyester fiber

due to initial carrier concentration and dye type respectively were likewise rejected. The results of this study indicated that both carrier concentration and dye type as well as their interaction have a significant effect on dye and carrier uptake of the polyester yarn.

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## I. INTRODUCTION

Polyester fibers have very little affinity for the dyes which are used for the dyeing of cellulose or protein fibers. Disperse dyes are used in dyeing of polyester because of the lack of specific sites and high surface charge (3). Because of high crystallinity and the hydrophobic nature of the polyester polymer, the main difficulty is not lack of dye affinity but a low rate of dye uptake at normal temperatures. The use of high temperature (above 100°C) or carriers is needed to make dyeing possible. Types of chemical compounds used as carriers are phenols, amines, nitriles, aromatic hydrocarbons, esters, alcohols, ketones, etcetra, which are either in emulsion or solution form (37). The level dyeing of polyester fiber with disperse dyes depends on the migration power of the dyes which is affected by the nature and amount of carrier, dyeing time, temperature and shade.

A number of theories on the mechanism of carrier action have been developed and debate on the more correct and practical theories still continues. Basically all the theories about the mechanism of carrier action can be divided into two main categories:

- 1) Those which theorize that the action of the carrier occurs inside the fiber.
- 2) Those which assume that the action of the carrier occurs in the dye bath.

According to some studies (45,50), the mechanism of the carrier action is only reasonable if it increases the diffusion rate of the dye

within the fiber. The concept of a carrier acting in the fiber rather than on the dye has been shown to be sound. It has been shown (45) that: 1) the carrier acts inside the fiber, and 2) without carrier absorption, there is no carrier action.

Carriers may function in different ways once they are inside the fiber. Carriers absorbed in the fiber may accelerate dyeing by plasticization of the polymer. This plasticization causes amorphous polyethylene terephthalate to crystallize and become oriented (23). Once the carrier is inside the fiber structure, it forms carrier-to-polymer Van der Waals' bonds. This plasticizes the fiber by interrupting the cross-linking effect of the polymer-to-polymer bonds and causing larger and more accessible channels and voids (46). This will allow a faster rate of dye diffusion through the fiber structure (23).

Another function of the absorbed carrier is to reduce the attractive forces between polymer molecules. Carrier action decreases the fiber's glass transition temperature ( $T_g$ ), increases segmental mobility, and facilitates faster dye diffusion than when the carrier is absent (41).

Some carriers cause swelling of the fiber and contributes to some degree to an increase in dyeing rate. However, the effectiveness of a compound as a carrier is not solely dependent on its ability to swell the fiber (41).

The theory of "loosening the fiber structure" fits both the requirement of increasing the diffusion rate of the dye and dyeing mechanism. Temperatures under  $100^\circ\text{C}$  are not effective in increasing the number of openings as the segments of the molecules vibrate.

Carriers substitute "chemical energy" for "thermal energy." The carrier is absorbed by the fiber and as a result of fiber molecular vibration, the bonds between fiber molecules weaken, allowing the molecules to separate. At this point, fiber molecule-carrier bonds are formed which are loose and can break as a result of increasing temperatures. The fiber segment vibration results in increasing the number and size of openings in the fiber and causes greater accessibility and increase in diffusion (45).

The diffusion of the carrier into the fiber in most cases brings about a higher rate of dye diffusion and dye uptake. Diffusion of the dye and amount of dye uptake by the fibers are very critical factors in determining the dyeing quality (22). It is necessary to study in detail the mechanism of the action of carrier in the fiber. Equally important is to find the effect of carrier on dye uptake.

The purpose of this study is to determine the effect of carrier concentration and dye type on the uptake of dye and carrier by spun Dacron type 54 polyester yarn in the disperse dyeing of polyester.

## II. STATEMENT OF PROBLEM

### Objectives

1. To investigate the effect of carrier concentration on the uptake of disperse dye by polyester fibers.
2. To investigate the effect of dye type on the uptake of disperse dye by polyester fibers.
3. To investigate the effect of carrier concentration on the uptake of carrier by polyester fibers.
4. To investigate the effect of dye type on the uptake of carrier by polyester fibers.

### Null Hypotheses

- H<sub>1</sub>. There will be no difference in the uptake of disperse dye by polyester fibers due to initial carrier concentration.
- H<sub>2</sub>. There will be no difference in the uptake of disperse dye by polyester fibers due to dye type.
- H<sub>3</sub>. There will be no difference in the uptake of carrier by polyester fibers due to initial carrier concentration.
- H<sub>4</sub>. There will be no difference in the uptake of carrier by polyester fibers due to dye type.

### Assumptions

1. It is possible that factors such as the amount of dye, temperature, volume, and pressure in the dyeing procedure as well as the procedure for finding the standard absorption curves can be kept constant.
2. It is possible to vary the initial concentration of the carrier in the bath as well as the type of the dye used.

### Limitations

1. Spun Dacron type 54 polyester yarn with a constant weight and yarn number was used.
2. Only two dyes were used in the experiments: 1) C.I. Disperse Red 60 and 2) C.I. Disperse Yellow 54.
3. Only one concentration of the dye was used in all cases.
4. Only one carrier (o-phenyl phenol) was used in the experiments.

### Definitions

Standard Curve: A Beer's law plot of absorbance vs. concentration for known concentrations of dye, measured at wavelength of maximum absorbance.

Disperse Dyes: Characterized by a smaller molecular structure than many other classes of dyes. A definition of disperse dyes proposed by the Society of Dyers and Colorists in 1953 (29), calls them: "A class of dyes which are water insoluble, originally introduced for dyeing cellulose acetate and usually applied from aqueous suspensions."

Carrier: "A product added to a dyebath to promote the dyeing of hydrophobic man-made fibers and characterised by affinity for, and ability to swell the fiber." (28). Carriers may also be called "accelerants."

Hydrophilic: Having strong affinity for, or the ability to absorb, water (28).

Hydrophobic: Lacking affinity for, or the ability to absorb, water (28).

Dye Sites: Functional groups within a fiber which provide sites for chemical bonding with the dye molecule. Dye sites may be either in the polymer chain or in chemical additives included in the fiber (28).

Dye Concentration: Amount of dye which exists on the textile material measured as percentage of the weight of the textile material.

Absorption: Attraction and holding of the gases or liquids within the pores of a fiber, filament, yarn, or material (25,28).

Adsorption: Adhesion of gases or liquids to the surface of the substance by capillary condensation. One form is a case of very loose chemical combination, such as dirt sticking to soap (25,28).

Partition Coefficient: Is the distribution of dye between the fiber and the bath at the end of an equilibrium dyeing.  $K = \frac{[\text{Dye}] \text{ on the fiber}}{[\text{Dye}] \text{ in the dye bath}}$  or it is the distribution of carrier between the fiber and the dye bath at the end of equilibrium time.  $K = \frac{[\text{Carrier}] \text{ on the fiber}}{[\text{Carrier}] \text{ in the dye bath}}$  (45).

Exhaustion: During wet processing, the ratio at any time between the amount of dye or substance taken up by the substrate and the amount originally available (28).

Rate of Exhaustion: Is a matter of kinetics and is the speed at which the dyeing system moves towards its equilibrium exhaustion (45).

Affinity: Is measured by the electrical forces, such as hydrogen bonding, etcetra, which binds the dye to the fiber. In the reversible system of disperse dyeing, these forces are responsible for adsorption in the fiber. They must be released for desorption and for further migration of dye within the fiber (28).

Saturation: Is the capacity for maximum absorption of dye and is taken to be the solubility of the dye in the specific fiber (45).

Diffusion: A more or less gradual movement of molecules or ions through a solution or fiber as a result of the existence of a concentration gradient, or repulsive, or attractive forces (28).

Isotherm: Constant temperature line used on graphs of climatic conditions or thermodynamic relations, such as pressure-volume relations at constant temperature (28).

Equilibrium Time: Is reached when dye concentration in both the dye bath and fiber is constant and no more change in the system occurs.

### III. REVIEW OF LITERATURE

The pertinent literature was searched and is being reported under the following headings:

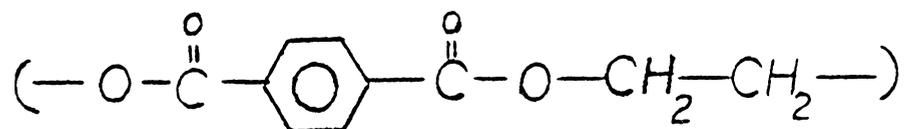
- 1) Polyester Fiber
- 2) Disperse Dyes
- 3) Carrier Dyeing

#### 1. Polyester Fiber (Polyethylene Terephthalate)

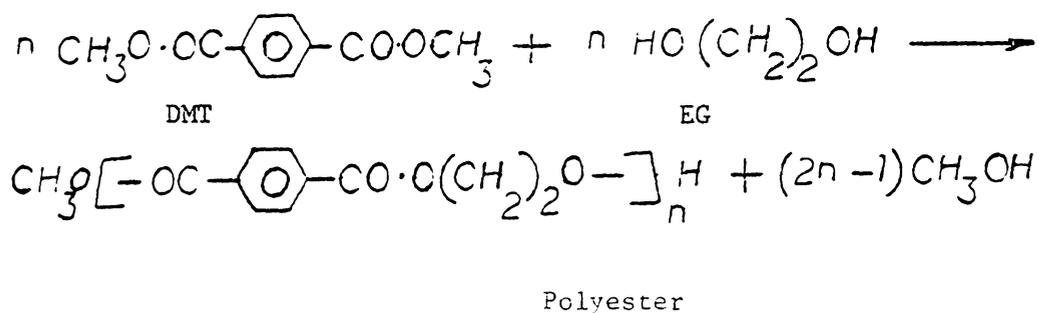
##### History and Preparation

Whinfield and Dickson first investigated the possibility of making a fiber with excellent performance from polyethylene terephthalate (PET) in the early 1940's in England. Their work led to the introduction of "Terylene" polyester fiber in 1950; subsequently the E. I. duPont de Nemours Company commercialized the PET fiber in the United States and shortly after that, polyester production developed rapidly in other parts of the world (22).

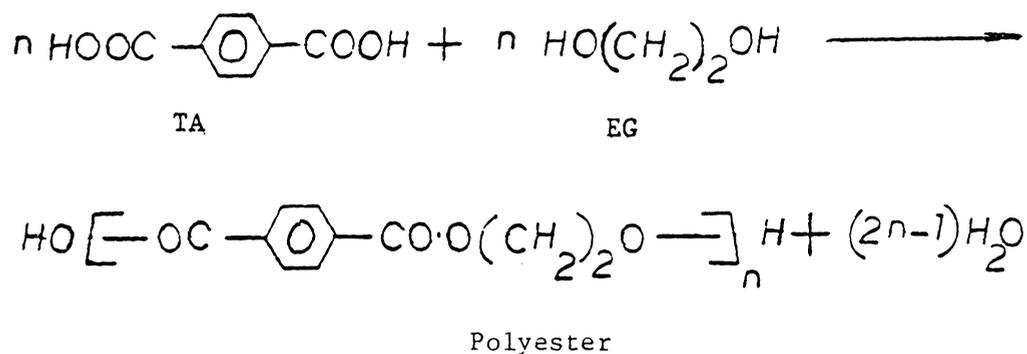
Polyethylene terephthalate (PET) is a linear polyester consisting of repeating ester groups  $-C(=O)-O-$  (6). The repeat unit of PET is



Two different methods are used to produce polyester fiber. One way is to use dimethyl terephthalate (DMT) and ethylene glycol (EG) which can be accomplished through a continuous or batch process.



The second way is to use terephthalic acid (TA) and ethylene glycol (EG) and is usually done by a continuous process.



Zinc, manganese, calcium and lead salts are used as catalyst systems in the dimethyl terephthalate process for transesterification. If the free terephthalic acid is used, a transesterification catalyst is not required but additional pressure and heat are needed for direct esterification with ethylene glycol (6). Each preparation process has advantages and disadvantages.

#### Structure of the Fiber:

As described by P. W. Harrison et al. (2,14), "The repeat unit in polyester fiber is long and consists of alternating units of flexible inert segments and stiff interactive benzene rings (Fig. 1). It is from

this configuration that the similarity to and differences from nylon arise. The main structural difference is that the quenched fiber is noncrystalline and crystallization occurs only on drawing."

The atoms in the macromolecule are bonded to each other by primary chemical bonds, while the cohesion between macromolecules is guaranteed by secondary Van der Waals and hydrogen bonds (35). Intermolecular forces present an important factor in fiber mechanical properties. Their size has an effect on the fiber forming capacity, the crystallinity and the mechanical strength in the fiber (35).

In the simplest structure of polyesters having an even number of atoms, one chemical unit exists per repeat. Polyesters having an odd number of carbon atoms require two chemical units before geometric repetition is observed. The unit cell in this case is rectangular including the carbonyl groups which lie in planes normal to the chain axis [Fig. (2a, 2b), (36)].

According to the works of H. P. Landerl et al. (22) and R. W. Moncrieff (31), a polyester fiber consists of a great number of linear polyethylene terephthalate chains which are extended and parallel to the fiber axis because of drawing. Each chain then, interacts with its neighboring chain along the polymer backbone, by multiple Van der Waals bonds. The dipole-dipole bonds of the ester groups in the polyester fibers are very important in causing the electrostatic bonding forces. Another set of bonds which partially contribute to the bonding energy of the neighboring chains are end group hydrogen bonds. Each of these bonds by itself is weak, but when they are added their effect becomes considerable, especially if the polymer chains are aligned in such a

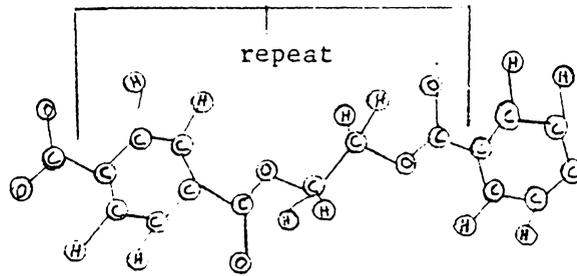


Fig. 1: Polyester (PET).

Source: P. W. Harrison (14)

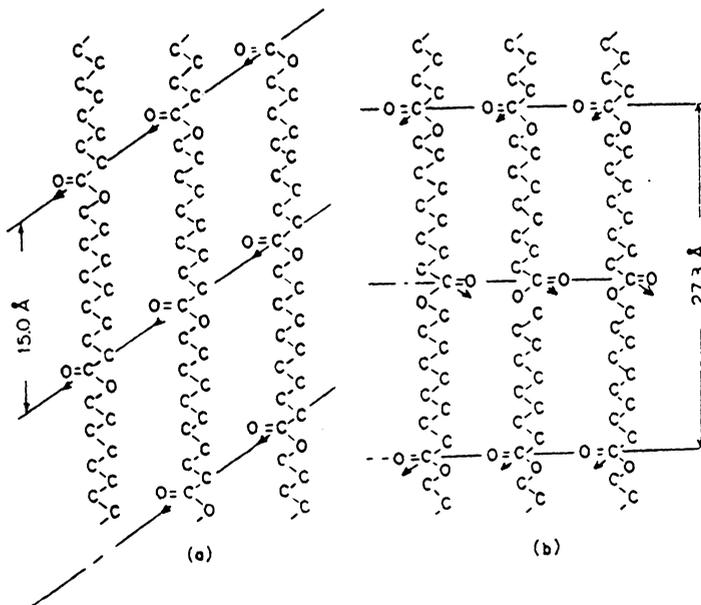


Fig. 2a.

Fig. 2b.

Fig. 2: Chain arrangement in aliphatic polyester with  
 a) even numbers of chain atoms, and  
 b) odd numbers of chain atoms.

Source: R. H. Peters (36).

way as to allow the maximum interaction for a given distance. This is the case for drawn fibers. Because of strong interpolymer bonding, and a rigid polymer backbone due to the benzene rings, the molecules are very closely packed in a zig-zag pattern, so it is difficult for even small molecules of water to get into the fiber. In order for the disperse dye molecule to penetrate into the fiber, the fiber volume must be increased. The way polyester polymer chains are situated with respect to their nearest neighbor, or the polymer-to-polymer arrangements, is known as the orientation of the fiber. Fibers composed of polymer chains with a high degree of regularity and interaction are highly oriented, whereas those which show relatively weaker polymer-to-polymer bonds and have fewer and weaker interactions are known as less oriented fibers. The orientation of polymer chains in a fiber determines the rate of dye diffusion and therefore the overall dyeing rate (22). In a polyester fiber, the crystalline regions are those in which the segments are arranged parallel to each other in a well ordered lattice (45). There are areas with less organization of fiber molecules called amorphous regions. It is in the amorphous region that dye penetration occurs and forces are available to hold the dye molecule. The amorphous regions can be shown as a system of interlocking fiber segments with non-fixed pores between them. The pores are the result of the thermal motion of chain segments where the chain is located between two consecutive intermolecular bonds (45). When the segments are short, the maximum amplitude of these vibrations becomes smaller and therefore the diameter of the pores becomes smaller (45).

In regard to polyester fiber morphology, most of the models include regions of polymer crystallinity surrounded by, or distributed in a less oriented polyester matrix. These regions are not amorphous for a complete lack of orientation is not probable for a drawn fiber. Instead they contain tie molecules, chain ends, chain folds, impurities, voids and polymer kinks. The orientation can change due to the history of manufacturing and processing operations (22). The degree of molecular orientation and crystallinity can change from the surface to the core of fibers. Birefringence studies (2) of Lavsan (polyester from the U.S.S.R.) cross-sectional orientation with respect to drawing show a layered structure with a low-oriented sheath, a highly oriented layer close to the surface, and a great decrease in orientation towards the center of the fiber. Changes in temperature, draw ratio, and the number of drawing stages can modify this layered structure. It is assumed that (36), with higher draw-ratios, the crystals are straight-chain type and are somewhat similar to the fringed micelle crystal concept (2).

When PET fibers are drawn over a heating block (2), the strength is increased with temperatures up to 200°C; further heating causes a decrease in strength. The loss in strength is caused by a loss in amorphous region orientation, an increase in crystallinity, a higher degree of chain folding and a larger lateral crystalline order (2). The effect of tension and temperature on the crystalline polymer texture has been studied (2). As the annealing temperature increases, the chain-folding introduced into the fiber becomes more regular (2).

### Chemical and Physical Properties

The physical and chemical structure of polyester fibers have an important bearing on the diffusion rate of the dye from the fiber surface into the fiber and consequently on the rate of establishing the equilibrium between dye concentration on the fiber surface and inside the fiber.

PET fiber is resistant to attack by weak acid, alkali and normal bleaching agents. It is low in resistance to alkaline substances such as caustic soda which causes the production of soluble products and through saponification, leaving an etched fiber (6). Organic bases and ammonia will be absorbed into the fiber and the subsequent aminolysis will cause a loss in strength. Treatment with methylamine reveals the fiber structure by etching away the amorphous or less ordered regions with no penetration in crystalline regions. Other than this type of degradation which is hydrolytic, PET fibers may degrade by thermal, oxidative and radiation induced reactions (6). Each polymer degradation reaction is accompanied by a decrease in the viscosity and/or molecular weight and an increase in the coloration and number of hydroxylic end-groups (6). Carboxylic end-groups, other than being a result of polymer decomposition, can cause further decomposition of the polyester chain. For example, acid groups catalyze the hydrolysis of ester bonds; this heightens with the increase of temperature (6).

When quenched quickly from the melt, the PET polymer is an amorphous, glassy solid. Differential thermal analysis shows a second order transition temperature at 78°C-80°C, a crystallization endotherm ranging between 125°C and 180°C and a crystalline melting point of

255°C. The polymer is insoluble in most solvents and if the solution of the polymer is needed, powerful solvents such as o-chloro phenol, dichloro acetic acid, difluoro acetic acid and hot meta-cresol are used (6). Polyester fibers usually have a molecular weight of 18,000-25,000. To make highly oriented and well-developed crystalline structured yarns, the just-spun yarn is drawn at temperatures from 80°C - 200°C (6). Table I shows the physical properties of a typical polyester fiber (6).

Polyester fibers have properties such as high crease resistance, initial modulus, shape retention, durable press capacity and durability. Due to these particular properties, they have various end uses (35).

#### Dyeing of Polyester Fiber

Polyester fibers are difficult to dye. The most important reason for this is their enclosed, compact structure, high degree of crystallinity, very low swelling and low moisture absorption. Polyester fibers, unlike nylon and wool, lack free reactive groups in their chains to link-up with dye molecules. Since it is impossible to use conventional dyeing techniques with polyester fibers, new dyeing techniques have been developed (35).

Disperse or nonionic dyes contain no water solubilizing groups and have quite low solubilities in water. The solubility in polyester is much greater. In practice, the disperse dye is suspended or dispersed in a finely milled state. Some small amount of dye dissolves in the water of the dyebath and this dye is then absorbed by the

Table I: Physical properties of PET fiber.

Properties	Range
Tenacity	2.5-6 gm/den
Elongation	12-50%
Elastic Recovery	90-96% at 2% extention
Average Stiffness	8-25 gm/den
Average Toughness	.4-1.5 gm/den
Specific Gravity	1.38
Moisture Regain at 65% RH, 70°F	.4%

Source: Mary E. Carter (6).

fiber. Since the solubility of the dye is greater in the fiber than in the aqueous bath, at the equilibrium, the fiber will be highly dyed with little dye remaining in the dyebath (22).

The main reason for the poor dyeability of polyester fibers is a low diffusion of dye molecules into the fiber. To increase the diffusion rate for short dyeing periods, different methods have been developed (35). The rate of diffusion of the dye into the fiber is too slow even at 100°C. The rate can be increased to a practical level by raising the temperature above the boiling point of the dye bath (use of high temperature) or by the addition of carriers (22). Increases in temperature raise the frequency of vibrations of the fiber molecules as well as the amplitude. The spaces between the molecules open with greater frequency and to greater size with increased temperature. Since dye diffusion depends on the space availability between the molecules, it too increases with the temperature (45).

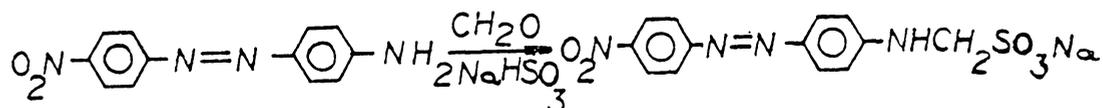
Any change in fiber structure results in a change in dyeability of the fiber (35). This is the reason for different dyeing behaviors of set and unset or modified and standard fibers. The effect of fiber structural changes, such as altered crystalline to amorphous ratios in drawing or changed pore size in the fiber due to swelling, on dyeability depends on accessibility of the fiber to dye (35). The relation between the percentage accessibility (A), and the percentage of crystalline regions in the fiber (K), is given by the equation  $A = (100 - K) + \alpha K$  where  $\alpha$  is a constant related to the size of crystalline portion of the fiber (35).

## 2. Disperse Dyes

### History, Production and General Information

After the introduction of secondary cellulose acetate, disperse dyes were developed to meet the problem of dyeing this fiber. None of the existing dyes which were used for natural fibers were suitable for dyeing secondary cellulose acetate. However, some dyestuffs having simple structures, and without water-solubilizing groups like sulpho groups, can "dye" cellulose acetate just by physical contact with the textile (1,37). A method of application which used water as a medium was devised (1).

The ionamines, which were the earliest invention, were "temporary solubilized" dyes. These dyes were reacted with formaldehyde and sodium bisulphite and solubilized by converting primary or secondary amino groups to N-methane sulphonic acid salts (1,37). This reaction is shown by Peters (37) as follows:



In the dyebath, hydrolysis takes place and the original insoluble dye with low solubility is slowly precipitated in a finely divided form (1, 37). The dye is absorbed by the fiber. Since the rate of hydrolysis differs from one dye to another, ionamines proved to be difficult to apply. However, the invention of these dyes led to the production of fine aqueous dispersions of dyes with low or little solubility which were used to dye hydrophobic fibers (1).

Both the discovery and step by step development of the disperse dyes were performed by several groups such as: Holland, Ellis and co-workers (British Celanese), Baddiley and Shepherdson. To produce dispersions, the manufacturers' precipitation techniques and different forms of milling with surface active agents were used (1).

In the last stage of synthesis of disperse dyes, large particles of dye separate from the mixture. These particles are not suitable for dyeing because they produce uneven dyeing. The introduction of dye into a fiber as a uniform, fine and stable suspension is necessary in order to obtain good dyeing properties and full color yield (37). Therefore the size of the dye particles should be reduced to an ideal average diameter range of .5 - 2  $\mu\text{m}$  or smaller. Also, a dispersing agent should be added to the bath which will hold the dye particles in suspension which will not be affected by hardness of water, temperature or carriers.

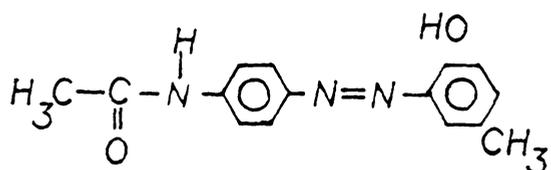
#### Classification and Chemical Structure

Disperse dyes belong to three main classes (37):

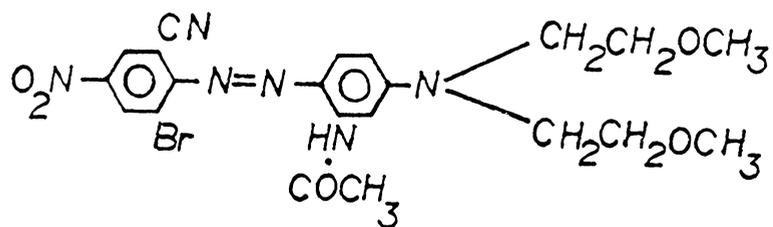
1. Those containing azo groups which are mainly monoazo derivatives with a few disazo groups and can produce a wide range of colors.
2. The nitrodiphenylamine groups which produce yellows and oranges.
3. The anthraquinone group which include  $\alpha$ -amino anthraquinones producing orange to greenish-blue colors.

## 1. Monoazo and disazo dyes

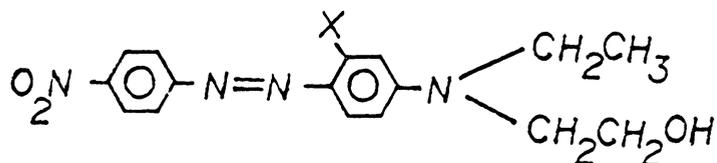
Monoazo dyes are the largest group of disperse dyes with a complete range of properties and hues. These dyes are mainly suitable for acetate and polyester. Many of the monoazo disperse dyes are derivatives of 4-aminophenylazobenzene variously substituted (1). The disazo dyes are not much used in dyeing acetate but are used mostly for triacetate and polyester fibers. In general, the existence of chlorine, bromine and electron-donor groups like  $\text{NO}_2$  or  $\text{CN}$  in the disazo dyes shift the  $\lambda_{\text{max}}$  to longer wavelengths causing deepening of the hue (50). Some examples of mono and disazo dyes are given (50):



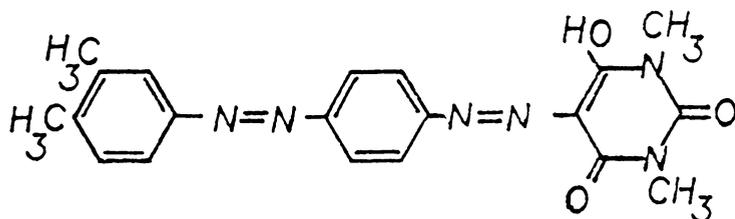
Cibacet Yellow GBA  
C. I. Disperse Yellow 3



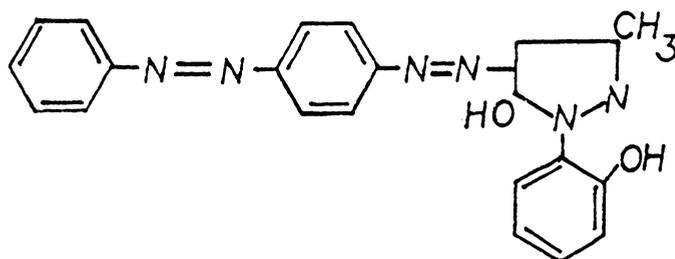
Blue on Polyester



If X = H:  
C. I. Disperse Red 1,  
If X = Cl:  
C. I. Disperse Red 13



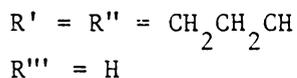
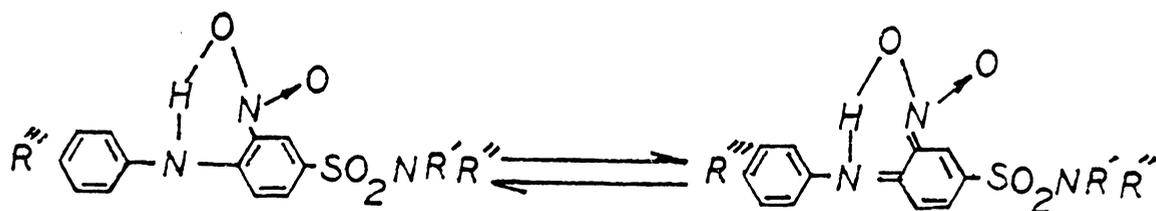
Golden Yellow on Polyester



Orange on Polyester

## 2. Nitrodiphenylamine dyes

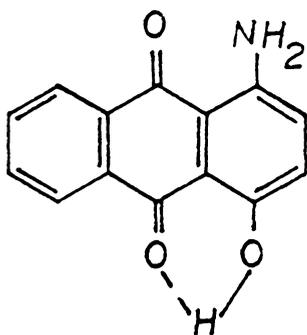
These dyes are suitable for dyeing polyester fibers. Lightfastness is higher when the nitro group is in the 2-position since hydrogen bonding is possible compared to 4-position in which hydrogen bonding is not possible. This is the case in the following dye (1).



Yellow on Polyester

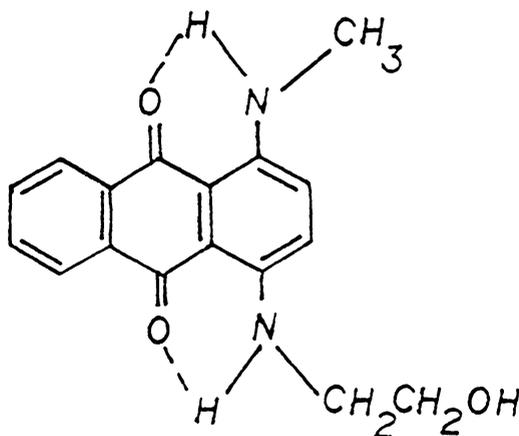
## 3. Anthraquinone dyes

These dyes particularly contribute to the range of violets and blues. One of the earliest dyes having a lightfastness of 6, a sublimation fastness of 5 and a burnt-gas fastness of 3-4 on acetate is (1):



C. I. Disperse Red 15

One of the important acetate dyes, which has a moderate light fastness of 5-6, a good general property but poor burnt-gas fume fastness 1-2, is C. I. Disperse Blue 3 (1):



#### Properties of Disperse Dyes

Disperse dyes suitable for dyeing polyester fibers should have the following basic properties (33,35): "affinity to polyester fibers, levelling properties, color fastness to sublimation, dry cleaning and light, and relative diffusion rate of the dye into the fiber" (33).

Disperse dyes for acetate should have brightness and fastness of shade, good buildup and levelling properties. Some dyes with amino, alkylamino or arylamino groups are sensitive on acetate, and to nitrogen

oxides in the air which leads to deterioration in shade. Dyes which are suitable for the relatively open-structured cellulose acetate, are not suitable for polyester fibers (1). Disperse dyes with more complex structure needing stronger dyeing conditions are used for polyester fibers (1).

Disperse dyes do not have any charged groups but they carry polar groups such as  $-OH$ ,  $-CH_2CH_2OH$ , and  $-NO_2$ . The molecules of disperse dyes should be small. These dyes have a small but, for dyeing purposes, important solubility.

Solubility of the dye increases rapidly with decreasing particle size of the dye (24,46). Naturally, solubility increases as the temperature rises but this dependence on the temperature varies from one dye to another. Dispersing agents used in the preparation of disperse dyes increase the solubility of these dyes several times. As the temperature rises, the solubility effect of dispersing agents decreases; this also depends on the type of dye (24,46).

For disperse dyes solubilization of insoluble dyes quickens the dye transfer. Carriers are usually good solvents for the dye. This feature plays a role but it is not the major one in the carrier-dye relationship (37). Insoluble carriers more likely form a film on the surface of the fiber (39,40). Since disperse dyes dissolve in the carrier, the dyeing rate might increase with the high concentration of dye on the fiber. The high solubility of the dye in the carrier might cause the distribution of the dye in favor of the carrier phase (37).

A study done by Roberts et al. (44) examined the role of water in solvent dyeing of polyester fiber. It is reported in this study that water lowers the glass transition temperature, increases the diffusion coefficient and decreases energy of activation of diffusion and the entropy of activation of diffusion. Also the magnitude of the increase in the diffusion coefficient changes from dye to dye, and for a certain dye, it decreases with the increase in temperature. These results show that the role of water in solvent dyeing is similar to that of a carrier in aqueous dyeing which is plasticizing (44).

The melting behavior of disperse dyes depends on the crystal modification and purity of the products. It is impossible to find the exact melting temperature of any commercial dyes because secondary components and additives included in the dye have an influence on the melting temperature. Purified preparations have been done to investigate the melting temperature of the disperse dyes (24). Most disperse dyes melt under thermosol dyeing and at 130°C, some dyes take the form of an emulsion of melted dye in water, unless they are dissolved. At the dye melting temperature, the enthalpy of the system changes affecting the kinetic and thermodynamic dyeing parameters.

#### Theory and Mechanism of Dyeing

When studying the dyeing process, the laws of dye transfer from the dyebath into the fiber should be emphasized. The theory of the dyeing process includes three stages (35):

1. Dye transfers from a solution or dispersion towards the fiber surface.
2. Dye is adsorbed on the fiber.

3. Dye diffuses from the fiber surface into the fiber.

The first stage has to do with the process by which dye is transferred to the fiber through the liquor. Because of the rapid adsorption of the dye on the fiber surface, the liquor becomes deficient in dye. The speed and ease with which dye reaches the surface depends on the increase in the velocity of liquor flow. Finally the speed of dyeing reaches a limit where resistance to transfer in the liquid has become minimal (37). The second stage usually occurs instantaneously so the dye in the liquid is in equilibrium with the dye adsorbed on the fiber surface (37). The third stage involving dye diffusion into the fiber is very much slower and is extremely important in dyeing. If the dyebath is well stirred so the dye can diffuse to the fiber surface at a greater rate than that with which it diffuses into the fiber, a stage will be developed between the solution and the fiber surface which can be regarded as an equilibrium situation (37).

Dyes can be divided into two groups; first, those which diffuse into the fiber more rapidly than they dissolve in the dyebath and, second, those which dissolve more rapidly in the dyebath than they diffuse into the fiber. Dyes with low solubility and slow diffusion result in large increases of dye uptake with temperature increase. Even though lower solubility results in a lower rate of adsorption, the reverse may not be true since the diffusion rate becomes the controlling factor (37).

Disperse dyeing takes place from a water solution of dye. Higher temperatures affect movement of dye particles and increase mobility of dye in water solution. The forces linking fiber and dye together are

not ionic forces. They are electrical forces such as: hydrogen bonding, Van der Waals' forces and dipole-dipole interaction (45).

### Rate of Dyeing and Diffusion

The most important problem when dyeing polyesters is the low rate of dyeing which is due to slow diffusion of disperse dyes into the polyester fiber (12). The reasons for low dye diffusion into the fiber are relative size of the dye particles and pores on one hand and Van der Waals' forces which bond macromolecular chains of the fiber on the other. To increase the dye diffusion, dyestuffs having smaller dye molecules and certain geometric shapes should be selected so that the dye would get into the fiber easily and bonds between macromolecules of the fiber would be replaced by dye to fiber bonds. Increase in temperature, change in fiber surface and preparation of fine dispersions also influence the diffusion of the dye into the fiber (8,35).

The process of diffusion inside the fiber governs the dyeing rate. The diffusion coefficient is the measure of dyeing rate. The information on the diffusion coefficient is preferred to that on the dyeing rate because the diffusion coefficient is independent of the amount of dye absorbed. Therefore, the diffusion coefficient appears a suitable parameter for comparing rates of different dyes (12).

The low diffusion rates of disperse dyes can be increased (35) by:

1. Pressure dyeing at temperatures above 100°C.
2. Short term dyeing with high temperature (thermosol system).
3. Addition of carriers to the dyebath.

Datye et al. (7) concluded from their study of exhaustion of disperse dye baths that the ratio of the dye concentration in two consecutive dyeings is a good indication of residual concentration of the dye in the dye bath. They also suggested that this ratio can be used to show exhaustion ratings of the disperse dyes.

Using exhaustion curves, diffusion coefficients at 100°C with and without carrier were measured (12). The relation between dye constitution and the diffusion coefficient may be explained assuming that hydrogen bonding is the most important factor in bonding polyester chains and dye molecules together (12). The diffusion coefficients in the presence of a carrier are 10-100 times higher than in the absence of a carrier (12). It has been shown (12) that the dyes which diffuse slowly in the absence of a carrier are accelerated more than those which diffuse rapidly.

#### Isotherm Studies

As quoted by Peters (37), many researchers have obtained the isotherms of disperse dyes. Two types of isotherm exist: linear and curved. However it is shown (37) that if the isotherm is measured when dye is dissolved or solubilized, linear isotherms will be obtained. The major reason for having a curved isotherm is presence of the large dye particles with lower solubility. Curved isotherms are observed especially with insoluble types of dyes. Therefore, when using a dye with the correct solubility, the isotherm is usually linear. According to Peters (37), some other experiments show linear isotherms for dyes up to a point where further amounts of dye in solution do not cause an

increase in the quantity of the dye adsorbed. This point is probably the saturation point for the fiber. However, if the surfactant concentration is increased, linearity or saturation limit does not change, but the slope of the isotherm will be reduced. After the saturation point, the presence of a solid dye increases the partition coefficient in favor of the dye bath but does not affect the amount of dye taken up by the fiber (37). The partition coefficient of a dye is the ratio of the dye concentration in the fiber to that in the bath. It shows that those dyes of highest water solubility exhibit low exhaustion (45).

According to Balmforth et al. (3), "the effect of a carrier on the partition coefficient of a dye primarily depends on the partition coefficient of the dye and the carrier and also on the solubility effect of the carrier on the dye in the fiber and in the dyebath." According to Peters (37), the partition coefficient changes from one solvent to another. However, this property of the dye is related to the solvent solubility parameter. In the case of polyester, the partition coefficient increases as the solubility parameter of the solvent becomes different from that of the fiber. When the solubility parameter for the fiber and solvent are similar, the dye has little preference for the fiber (37).

### 3. Carrier Dyeing

#### Mechanism of Carrier Action

Comprehensive studies have been done (4,30,39,40) about all the different theories of carrier action. Nine different theories have been developed about the mechanism of carrier action:

#### 1. Loosening of the fiber structure:

Fortess and Salvin (10) assumed that the same dyeing mechanism of absorption to the fiber which works for disperse dyes, holds for the carrier as well. Because of the smaller size of carriers compared to disperse dyes, carriers diffuse into the fiber much more rapidly. The dye is absorbed into the fiber by Van der Waals or hydrogen bonding whereby the carrier reduces the intermolecular forces which cause fiber to fiber bonds. Under vibration, opening and closing of fiber structure causes holes to be opened. When the mobility increases in fiber molecule segments, dye diffusion of the dye increases.

#### 2. Swelling:

The theory of swelling of the fiber by the carrier was considered by Waters (50). The swelling of the fiber makes it possible for disperse dry molecules to diffuse into the fiber more rapidly. However, Waters in the same study, mentioned that swelling action is not the only responsible process. Waters suggested that the degree of swelling of the fiber is not directly proportional to carrier effectiveness. Aqueous solubility of the carrier is important in its effectiveness. The main assumption in this case is that contraction or shrinkage is

caused by swelling.

3. Increased site accessibility:

According to Shenai (47), the action of the carrier is to open up the areas of fiber which due to its compact structure, have been un-accessible and difficult to reach. The carrier changes the ratio of amorphous to crystalline areas and as crystallinity is decreased, additional areas would be available for dyeing.

4. Liquid-fiber theory:

According to R. H. Mehra et al. (30), this theory assumes that the action of a carrier is to work as a cofiber inside the fiber. The carrier then dissolves and holds the dye.

5. Increase in water imbibition:

According to Vickerstaff, as mentioned in papers presented at American Association of Textile Chemists and Colorists meetings (39,40), products with hydrophilic groups are diffused very rapidly in polyester. The phenolic part attracts water and the aromatic portion of the molecule has Van der Waals attraction for hydrophobic fibers. As the attraction for water increases, so does the flow of the dye liquor and as a result the dyeing rate increases.

6. Increased solubility of the dye in the bath:

Zimmermann et al. (51) assumed that the carrier causes an increased solubility of the dye in the aqueous environment. Dyeing with disperse dyes is done from a dilute aqueous solution of the dye. Soluble dyes are absorbed by the fiber, whereupon more undissolved crystals of dye

dissolve in the dye bath.

7. Increased availability of dye from fiber:

As quoted by R. H. Mehra et al. (30), Peter and Sumner assumed that the action of water insoluble carriers may be that they surround the fiber with a film. Because of great solubility of dye in different carriers, dyeing can occur faster from the source of dye which is more concentrated in the film than from the dilute aqueous bath.

8. Transport theory:

As quoted by R. H. Mehra et al. (30), Vickerstaff presented a second theory of carrier action which assumes that the carrier and dye form a loose complex. Then this combination is easily absorbed by the fiber in the aqueous bath.

9. Lubricity of fiber:

As explained by R. H. Mehra et al. (30), this theory assumes that the action of the carrier is that of a molecular lubricant. The carrier attaches itself to the polymer molecule of the fiber and destroys the existing cross-linkages.

All the theories mentioned are discussed and criticized (30,39). However, there is not overall agreement about the mechanism of carrier action. Experiments have been conducted to test the validity of various theories (39,40).

The swelling phenomena has been noted in the case of o-phenyl phenol (41). The swelling theory was tested by measurement of swelling which was achieved on Dacron polyester and Arnel triacetate fibers by

the use of various carriers. The result was that some carriers caused some swelling but others (e.g., trichlorobenzene) caused less swelling which seems to demonstrate that the swelling of fibers is not the main action of the carriers (39). Several studies show that while swelling is important, there is no direct relation between swelling power and carrier activity (30,39,41,50).

The water-imbibition theory was also tested by measuring the amount of water which is absorbed by Arnel triacetate and Dacron polyester pretreated with carrier compared to untreated controls. In the case of Dacron polyester, the difference between the water imbibition of carrier treated and untreated control was only slight, whereas in case of Arnel, the water imbibition was the same for both. This experiment gives no support to the water imbibition theory. Also some efficient carriers (trichlorobenzene and biphenyl) have no hydrophilic groups which demonstrates that water-imbibition theory cannot be supported (4,39).

The theory of increased availability of dye from film has been supported by observing the droplets, or surface clouds of carrier on the surface of the fiber (4). However, even though tri-propyl phosphate forms film around some fibers, it is not an appropriate carrier for polyester (4,39).

No correlation existed between the solubility of the dyes in carriers and the efficiency of the carrier. Also suitable reactive groups are absent in many good carriers. Therefore the transport theory was not supported (4,30,39).

It was shown (30,39,40) that carriers which are effective for a particular fiber are absorbed by the fiber at levels as high as 40% of the carrier used. Also it was demonstrated that carriers are held by fibers and are difficult to remove by scouring. Researchers noted that carriers attach themselves to the fiber by electric forces. These results all give evidence for the theory of carrier action inside the fiber (39,40).

The action of a carrier inside the fiber loosens the internal structure of the fiber to increase the opportunity for diffusion of the dye into the fiber. As the fiber interchain bonds break due to thermal agitation, dye diffuses through the holes that had been made. The carrier partially replaces interchain bonds by fiber-carrier bonds. Under the same thermal energy, the increase in number of openings will result in a more permeable fiber and higher dye diffusion (30).

#### Carrier Dyeing Theory

Polyester fibers are usually dyed with disperse dyes which are water insoluble and are applied in an aqueous dispersion form. Three methods are available to increase the rate of dyeing of polyester: 1) carrier dyeing, 2) high temperature, and 3) pad-dry-thermosol. As quoted by Kramirsch (21), E. I. Fisher studied three stages in carrier dyeing: (1) establishment of equilibrium between the surface layer of the fiber and the carrier, water and dye, (2) diffusion of carrier into the fiber, and (3) diffusion of dye into the fiber.

Dyeing of some fibers such as polyester is difficult because of the low rates of dye sorption at temperatures below  $T_g$  (60°C - 80°C).

The absorption which occurs is only due to carrier, which is held in the fiber by capillary forces (5). At  $T_g$  a great amount of bond rotation occurs. The chains of the fiber move apart and the fiber structure becomes more available to the carrier and dyestuff. Fast rates of dyeing can be reached when it is done above  $T_g$  at high temperatures. An alternative method is the use of carriers. The important effects of the carrier is the plasticizing action which results in a reduction in the glass transition temperature (37). However, the study done on effects of a series of amines, alcohols and phenols does not show any correlation between the swelling of the fiber and the lowering of  $T_g$  and therefore with carrier action.  $T_g$  is a very important factor in the dyeability of polyester. This depends on the total thermal and mechanical exposure of the fiber. According to Peters and Ingamells (38), the free volume equation of Williams, Landel and Ferry for the temperature dependence of viscoelastic properties of amorphous polymers predicts the dyeability of acrylic and polyester fibers. This shows that: (1) segmental mobility of the polymer causes the change in rate of dye diffusion, and that (2) carriers act by decreasing  $T_g$  which in fact increases the segmental mobility and causes dye diffusion. The free-volume model explains dyeability above  $T_g$ , whereas, the fiber-pore mechanism is shown to operate below  $T_g$ . Sufficient thermal energy can be provided to the fiber to break any polymer-to-polymer bonds; however, there is a limit to which small amounts of carrier in the bath can decrease  $T_g$ . A carrier can break those polymer-to-polymer bonds where it is energetically favorable to do (22). The theory of the loosening of the fiber structure as the mechanism of carrier action is applicable to

the dyeing mechanism as well as the requirement for an increase in the dyeing rate (45).

The concept of carrier action in the fiber rather than in the dyebath has been shown to be more acceptable (45). Carriers can enter the polyester at a faster rate and at a lower temperature because of their small size (22).

A widely accepted theory (49) shows that carriers act by plasticizing of the internal structure of the fiber. They diffuse into the amorphous segment of the fiber faster than dye (23) and form carrier-to-polymer Van der Waals bonds and interrupt the cross-linking effect of polymer-to-polymer bonds formed by secondary bonds therefore plasticizing the fiber (22,23). This action increases the accessible layer channels, voids and pores in the fiber. As a result dye and water can be diffused into the fiber more rapidly (22). Jean H. Lemons et al. (23) also observed that any solvent which plasticizes the fiber will increase the dyeing rate.

The structure of the hydrophobic fiber is presented as a closely packed bundle of long fiber molecules in the shape of a honeycomb structure. At temperatures below 100°C, the effect of temperature in increasing the number of openings in segments of molecules is little. First, the carrier gets absorbed by the fiber. As a result of vibration in fiber molecules, the bonds existing between the fiber molecules separate. Thus, fiber molecule-carrier bonds are formed and are easy to dissociate under high temperature. As an outcome, when the fiber segments vibrate, the size and number of the holes formed increases resulting in a great accessibility and increase in diffusion rate of the dye (45).

Some researchers assume that a layer of carrier in which the dyestuff is readily soluble is formed around the fiber therefore affecting the distribution of dye concentration in and on the fiber (37).

Findings about the film theory suggest that the carrier is first absorbed on the surface of the fiber and a continuous film is formed. The disperse dye is dissolved in the film. If the carrier does not get diffused into the fiber, a film with the thickness of  $.75 \mu\text{m}$  would be formed on the surface with the concentration of carrier being 10%. The disperse dye in the film has a higher concentration than the dye in an aqueous dispersion. The polarity between fiber and carrier helps the formation of carrier film around the fiber (22).

#### Types of Carriers Used and Characteristics

Typical chemicals used as carriers may be divided into these types: 1) phenolic compounds, such as, ortho and para phenyl phenol; 2) esters or phenolic esters, and 3) halogenated aromatic compounds (4).

An ideal carrier should satisfy the following requirements (30,35): 1) high efficiency, 2) absence of unpleasant odor, 3) nontoxicity, 4) no discoloration or degradation of the fiber, 5) easy to remove, 6) low price, 7) no effect on lightfastness of dyeing, 8) low volatility, 9) uniform absorption by fiber, 10) high stability under dyeing conditions, 11) ease of dispersion in the dyebath and 12) compatibility with the dyestuff.

High molecular weight carriers initially have low solubility in water and therefore a higher carrier efficiency. However, when the molecular weight is increased over an optimum value, the rate of carrier

absorption in the fiber is decreased; and beyond a limit, the carrier action is completely stopped by preventing entry (30,50).

#### Advantages and Disadvantages of Carriers

The advantages of using a carrier in an aqueous dyeing are (31): 1) dyeing is carried out much more rapidly; 2) the dyestuff penetrates the fiber by the use of carrier and the improved penetration of dye gives better fastness (to rubbing); 3) leveling of dye is improved; and 4) fabric can be dyed by this method without the use of pressure. The disadvantages are (31): 1) the goods retain the odor of some of the carriers and have to be washed thoroughly to remove the odor (Biphenyl is odorless.); 2) extra cost is considerable; and 3) the lightfastness of dyeing is badly affected by p-phenyl phenol, o-phenyl phenol and salicylic acid. Monochlorobenzene does not reduce the lightfastness of dyes but it is toxic.

#### Solubility of Carriers

Organic substances which are insoluble in water in temperatures up to 100°C, like biphenyl, which may be applied on fiber from aqueous emulsions, have the best adsorption on polyester. Carriers which exhibit little solubility in water at temperatures up to 100°C, such as p-phenyl phenol and dimethyl terephthalate are applied from aqueous suspensions (35,37).

There is another group of carriers with a melting point below 100°C which are insoluble in water and very efficient. These carriers include compounds such as o-phenyl phenol and methyl salicylate which are applied from aqueous emulsions (35,37).

Different carriers affect the rate of dye uptake to different extents. The water soluble ones require large concentrations in the dyebath, whereas others require only relatively small amounts (37). Water-insoluble carriers shrink PET more than water soluble carriers. Water soluble carriers are more effective on a weight basis as dyeing assistants (41).

Both hydrophobic and hydrophilic carriers act by breaking the interchain bonds in the fiber. However it should be assumed that the mechanism is different in two cases: hydrophilic carriers containing proton donating groups can form hydrogen bonds with carbonyl groups of polyester; however, hydrophobic carriers cannot have attachments of this kind to polyester, but can only have dipole, induction and dispersion forces. Attachment by hydrogen bonds can have a very different effect on the loosening of the bond between neighboring polyester chains from attachment by other intermolecular forces (12). Schuler (46), however, conducted experiments in nonaqueous media, and showed that all carriers are active almost on an equal basis when they are present in the fiber in equimolar concentrations. Therefore, the effect of the carrier appears to depend only on the number of molecules of that carrier absorbed by the fiber but not on their nature. The chemical structure of the carrier becomes important when it comes to distribution of carrier between fiber and water. Glenz, Beckman and Wuder (12) also indicated that the carrier increases the coefficient of diffusion by a factor of 10 - 100 times. Also confirmed was the work done by Schuler (46) showing that in aqueous medium as well as in a nonaqueous one, if equimolar concentrations of different carriers exist

in the fiber, similar effects on the dyeing rate will be achieved. The key is carrier concentration in the fiber.

In general carriers should have good dispersion properties, minimum volatility, low cost and no toxicity. In order to have good dispersion and reduced volatility, hydroxide or other hydrophilic groups can be added to the carrier. Thus the possibility of having complete hydrophobicity is slight; there should be a compromise between hydrophobicity and the other properties of a carrier.

#### Action of the Carrier in the Fiber

For a carrier to function maximally, it should be inside the fiber (37). Salvin (45) studied the effect of carrier concentration on dye exhaustion in polyester dyeing. Results showed that the exhaustion increases as a result of increase in the carrier content in the fiber. Salvin showed that: 1) the carrier acts in the fiber, 2) there is no carrier action occurs without absorption, and 3) if carrier absorbance is reduced, so is the dyeing rate. The effectiveness of a carrier depends on the molar concentration of that used in the fiber.

Thus the function of the carrier is accepted only if it is absorbed by the fiber. Next, we will look at the specific studies done on the swelling and plasticization action of carriers.

F. M. Rawicz et al. (41) studied the swelling effects of polyester fibers after treatment with various carriers in different concentrations in the dye bath. The effect of swelling treatments on the change in physical properties of filament and the effect of certain swelling treatments on the rate of dye uptake were studied. The results show

that the swelling of the fiber changes the mechanical properties and causes partial deorientation of the fiber. As the amount of contraction, which is the measured effect of swelling increases, elongation at break increases, initial modulus decreases, and tenacity based on the denier of the strained fiber increases. From this study, it was concluded that the swelling of fiber persists to some degree after removal of the carrier. Dyeing rate on carrier treated fiber is increased relative to untreated fiber. If the amount of dye used is constant and limited, increase in concentration of the carrier decreases the amount of dye on the fiber in the equilibrium state in favor of the bath.

Jean H. Lemons et al. (23) studied the effect of the carriers on plasticizing PET fiber and the changes in the properties of the fiber which have been caused by plasticization. The results indicate that chemical compounds responsible for plasticizing PET, induce crystallization of amorphous polymers and accelerate dyeing. The mechanism which is used by the carrier to influence the crystallization and rate of dyeing of polyester fiber is to plasticize the amorphous regions of the fiber. Those liquids plasticizing the polymer have cohesive energy densities which are close to that of the polymer and through generalized, non-specific forces interact with polymers. If specific forces are involved, they come from acid-base interactions where the solvent acts as an electron acceptor and the polymer as an electron donor (23). Even though some carriers are solvents and induce crystallinity of the amorphous area (23,27), others such as methyl or phenyl salicylate, show no effect in the crystalline structure, however deorientations may occur (4,5,37).

In a study done by A. H. Brown et al. (5), polyester fibers were pretreated with a carrier and then various washing and solvent extractions were carried out. Pretreated fiber showed an improvement in dye uptake. Also, very little correlation existed between the carrier activity and the orientation or nature of halogen substituents. Compounds with bromo and chloro were the most suitable.

#### Sorption and Isotherm Studies of the Carriers

One difference in characteristics of carriers is their ability to be sorbed. Careful measurements show that the isotherm of the carrier is linear which is the same as in disperse dyes (37). The mechanism of carrier adsorption seems to follow the disperse dyeing mechanism (10).

Carriers do not change the linearity of isotherm of the disperse dyes, however, they change the partition coefficient. As quoted by D. Balmforth et al. (3), Schuler and Remington studied the effect of benzoic acid in different concentrations on the isotherm of a disperse dye on polyester fiber. It was shown that the isotherm was linear and because of the solubility effect of benzoic acid, the partition coefficient will change in favor of the water phase as the concentration of benzoic acid increases. According to D. Balmforth et al. (3), dye uptake increases and then decreases as the carrier concentration is increased. The maximum concentration corresponds to the amount of carrier which is necessary to saturate the system (3).

Partition coefficient for hydrophobic carriers increases with carrier concentration, whereas in the case of a more hydrophilic carrier (benzoic acid), it is reduced (37). The presence of a carrier in the

fiber phase increases the solubility by the amount of dye which can be dissolved in the adsorbed carrier (37). With the assumption that the additional dye in the fiber is dissolved in the adsorbed carrier, the partition coefficient can be estimated. The values are greater if the partition coefficient of dye for the carrier is greater than that for the fiber (37).

C. R. Jin et al. (17) studied the equilibrium partitioning of o-phenyl phenol between polyethylene terephthalate and the bath up to the point of saturation. The results showed that the absorption isotherm of o-phenyl phenol indicates the linear distribution of carrier between the dissolved carrier in the fiber and dissolved carrier in the bath. The contraction of fiber which is known to be linearly dependent on concentration of the adsorbed carrier, is at maximum when the fiber is saturated with carrier.

#### Studies of Carrier Diffusion

Diffusion coefficients have been determined from exhaustion curves. The diffusion coefficients are 10 - 100 times higher when carrier treatments are given with benzoic acid and trichlorobenzene as carriers rather than without a carrier (12). It is interesting to note that the carrier efficiency depends on the nature of the dye. A certain levelling of diffusion rates takes place, i.e., dyes which diffuse slowly without a carrier accelerate more than those which diffuse quickly (12).

R. K. Solanki (42) studied the aspects of diffusion behavior of carriers in polyester fibers using a series of compounds as commercial

carriers. The results show that both the rates of uptake and the equilibrium uptakes were found to vary considerably with variation in the chemical nature of the carrier. The major difference between the diffusion behavior of carriers with that of disperse dyes is that the diffusion coefficient of carriers is very concentration dependent. The apparent diffusion coefficient ( $D_a$ ) increases with the increase of carrier uptake. This is because of the plasticizing action of carriers which reduce  $T_g$  and so an increase in diffusion coefficient occurs.

Solanki (43) also worked on the influence of carriers on diffusion rates of disperse dyes for carrier concentration in the fiber up to .5 mol/kg. The results showed that the chemical nature of the carrier does not affect the effectiveness of different carriers at the same molar concentration in the fiber. However, the particular dye involved is very important in the effectiveness of different carriers. The magnitude of the increase in the rate of diffusion, as a result of presence of carrier, will decrease as temperature increases. The rates of decrease are in relation with the activation energies of diffusion of the dyes in the absence of carrier. Experimentally determined activation energy of diffusion of the dye is reduced by the presence of a carrier. This reduction is related to the decrease in the entropy of activation of diffusion which is caused by the plasticizing action of carriers.

#### Improved Dyeability with Carriers

According to R. A. F. Moore et al. (32), pretreatment of polyester yarns in biphenyl/methylene chloride (biphenyl- $\text{MeCl}_2$ ) solution causes

greater penetration of dye into filaments than when dyeing is done in presence of the same concentration of biphenyl which is added to the dye bath. This may be due to residual methylene chloride in the yarn or solvent-induced structural changes which occur when pretreatment is done. However, pretreatment does not increase the rate of exhaustion of high and medium energy dyes significantly compared to treatment of the filament with carrier added to dye bath.

According to A. Hebeish et al. (15), polyester treated with benzoic or salicylic acid is much more susceptible to dyes than untreated polyester. The pretreatment can change the microstructure of fiber. X-ray analysis shows breakage of intermolecular bonding in the pretreated polyester.

### Summary

Carriers are used to accelerate the rate of dyeing of hydrophobic fibers with disperse dye. Much of the theoretical work that has been carried out on the mode of action of these compounds show that the mechanism is very complex.

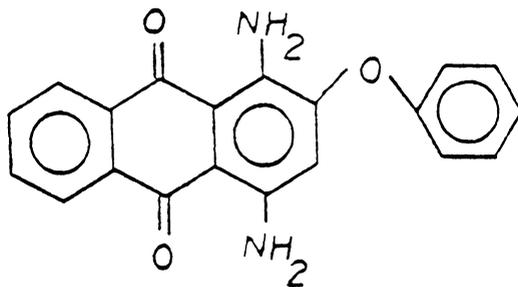
To be effective the carrier must be absorbed by the fiber. Direct correlations between carrier activity and concentrations in the fiber have been shown. The literature indicates that initial carrier concentration and type of dye are important factors in exhaustion of the dye as well as diffusion of the dye into the fiber.

#### IV. EXPERIMENTAL DESIGN

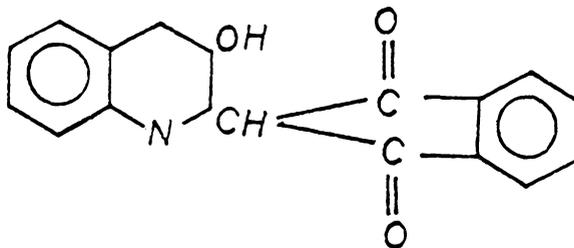
##### Experimental Material

Yarns used in this experiment were spun, two-ply Dacron type 54 polyester with a total denier of 490; each skein weighing 10 grams. Yarns were purchased from Test Fabrics, Incorporated.

The disperse dyes used in this experiment were C. I. Disperse Red 60 and C. I. Disperse Yellow 54. Disperse Red 60 [C. I. 60756] is bright bluish red and has the following anthraquinone structure.



Disperse Yellow 54 [C. I. 47020] is bright yellow. It has the following quinoline structure:



Both dyes contained dispersing agent and were manufactured and supplied by E. I. duPont de Nemours and Company.

O-phenyl phenol was used as a carrier in the dyeing of spun Dacron type 54 polyester yarns. Six different concentrations of o-phenyl

phenol (0, 1, 2, 3, 4, 5 gm/l) were used. The carrier was donated by Sybron Corporation.

### Experimental Method

#### Preparation of the Dye Dispersion

To prepare the dye dispersion 4.000 grams of the dye and 1.000 gram of Triton X-100 (nonionic surfactant) were transferred quantitatively to a 400 ml. beaker using approximately 200 ml. of hot distilled water. This dispersion was transferred quantitatively to a 1000 ml. volumetric flask with cold distilled water. Distilled water was added up to the 1000 ml mark of the volumetric flask, and the dispersion was cooled to room temperature. The nominal concentration of dye was 4 grams per liter.

#### Preparation of the Carrier Dispersion

To prepare the carrier dispersion, 20.000 grams of the carrier was transferred to a 400 ml. beaker and diluted with distilled water to approximately 200 ml. This dispersion was then quantitatively transferred to a 1000 ml. volumetric flask and distilled water was added to the top mark. The nominal carrier concentration was 20 grams per liter.

#### Carrier Treatment Procedure

The Ahiba Texomat dyeing machine was used for carrier treatment of Dacron yarns. All skeins of yarn were conditioned at  $65\% \pm 2\%$  RH and  $70^{\circ}\text{F} \pm 2^{\circ}\text{F}$  for 24 hours before treatment. The arrangement of the dye baths containing different carrier concentrations was randomly

selected using a table of random numbers. Total bath volume was 400 ml. and each bath contained a skein of yarn weighing approximately ten grams. The liquor ratio was 40/1. The treatment started at  $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and the temperature was increased to  $95^{\circ}\text{C}$  at a rate of  $3^{\circ}\text{C}/\text{min}$ . Then the machine ran for an additional 40 minutes at  $95^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The proportions given in Table II were used for carrier treatment. Carrier treatment in the absence of dye was considered as a control for the dyeing process. Two repeats of this treatment were conducted containing 6 skeins of yarn each time.

#### Dyeing Procedure

Dyeing procedure was the same as for the carrier treatment procedure. The concentration of the dyes in the dye bath was kept constant (.5 gm/l). The order of experiments and the arrangement of the dye baths was randomized using a table of random numbers.

The dyeing procedure was repeated twice for each dye. Since there were 12 skeins used in each repeat, the total number of skeins of yarn were 24. The proportions in Table III were used for dyeing process.

#### Establishing the Standard Curves

Standard curves for Disperse Red 60, Disperse Yellow 54 and o-phenyl phenol were established as following: Approximately .0500 gms of the material was weighed and quantitatively transferred into a 50 ml. volumetric flask using dimethyl formamide as a solvent. From the 50 ml. solution, several different dilutions were prepared by taking .1, .2, .3, .4, .5 and .6 ml. and diluting each of them to a volume of 10 ml. with dimethyl formamide. By analyzing each of the dilutions with the

Table II: Proportions for carrier treatment procedure.

number of dyeing bottles	carrier dispersion	distilled water
2	0 ml. $\equiv$ 0 mg. (0 gm/l)	400 ml.
2	20 ml. $\equiv$ 400 mg. (1 gm/l)	380 ml.
2	40 ml. $\equiv$ 800 mg. (2 gm/l)	360 ml.
2	60 ml. $\equiv$ 1200 mg. (3 gm/l)	340 ml.
2	80 ml. $\equiv$ 1600 mg. (4 gm/l)	320 ml.
2	100 ml. $\equiv$ 2000 mg. (5 gm/l)	300 ml.

Source: Reference 34.

Table III. Proportions for dyeing procedure.

number of dyeing bottles	dye dispersion	carrier dispersion	distilled water
2	50 ml. $\equiv$ 200 mg.	0 ml. $\equiv$ 0 mg. (0 gm/l)	350 ml.
2	50 ml.	20 ml. $\equiv$ 400 mg. (1 gm/l)	330 ml.
2	50 ml.	40 ml. $\equiv$ 800 mg. (2 gm/l)	310 ml.
2	50 ml.	60 ml. $\equiv$ 1200 mg. (3 gm/l)	290 ml.
2	50 ml.	80 ml. $\equiv$ 1600 mg. (4 gm/l)	270 ml.
2	50 ml.	100 ml. $\equiv$ 2000 mg. (5 gm/l)	250 ml.

Source: Reference 34.

use of the Bausch and Lomb Spectronic 2000 UV-VIS spectrophotometer and plotting the absorbance values against concentration, Beer's law plot was obtained. This entire process was repeated five times for each of the disperse dyes as well as for o-phenyl phenol using different original amounts of the material each time. The composite standard curve for each material was established from combining all the individual curves and the use of linear regression.

The resulted equation and wave length for Disperse Red 60 were:

$$y = -.0045 + 8.52 [c] \text{ at } \lambda = 519.9 \text{ nm}$$

Since Disperse Yellow 54 and o-phenyl phenol were not completely soluble in dimethyl formamide, a corrected composite curve was established for each of them using linear regression:

$$\text{Disperse Yellow 54: } y = -.0013 + 20.83 [c]$$

$$\lambda = 442.3 \text{ nm}$$

$$\text{o-phenyl phenol: } y = -.0093 + 14.81 [c]$$

$$\lambda = 289.9 \text{ nm}$$

#### Analysis of the Dye and Carrier Concentration Before Dyeing

In order to measure the dye bath concentration, 10 ml. of the before dyeing solution was taken therefore reducing the total volume of the bath to 390 ml. The diluted solution of this sample was then spectrophotometrically analyzed. Since both the dye and the carrier were present in the dye bath, concentrations of both were measured. The dyes were analyzed in the visible spectrum of (400-700) nm, whereas the carrier was analyzed in the spectrum of ultra-violet light (200-400) nm.

For example:

If ABS. Dye =  $y = .430$

since composite curve for  
Disperse Red 60:  $y = -.0045 + 8.52 [c]$

then dye concentration  
after dilution:  $[c] = .051 \text{ mg/ml}$

since 1 ml. of 400 ml. original dye bath was diluted into 10 ml.  
of dimethyl formamide

Therefore, amount of dye in  
original dye bath:  $A = .051 \times 10 \times 400 = 204.00 \text{ mg.}$

If ABS. Dye at 289.9 nm = ABS. carrier and  
dispersing agent =  $y = .346$

since ABS. Dye at 289.9 nm at 0 g/l = ABS. of  
concentration of carrier dispersing agent =  $.058$

then ABS. carrier =  $y = .346 - .058 = .288$

and composite curve for  
o-phenyl phenol:  $y = -.0093 + 14.81 [c]$

Therefore, carrier concentration  
after dilution:  $[c] = .02007 \text{ mg/ml}$

since 1 ml. of 400 ml original dyebath was diluted into 10 ml. of  
dimethyl formamide.

Therefore, amount of carrier in  
original dyebath:  $A = .02007 \times 10 \times 400 = 802.8 \text{ mg/ml}$

A total of 36 samples was examined for the dyes, each repeat containing 18 samples. In the case of the carrier, two repetitions were used, with 18 samples in each. Therefore, a total of 36 samples was used for the carrier.

Analysis of the Dye and Carrier Concentration in the Bath After Dyeing

Dye and carrier concentrations in the bath after dyeing were measured spectrophotometrically. One ml. of the dye bath solution after dyeing was diluted into 25 ml. of dimethyl formamide. For example:

If ABS. = .118

since composite curve for  
Disperse Red 60:  $y = -.0045 + 8.52 [c]$

then dye concentration  
after dilution:  $[c] = .0144 \text{ mg/ml}$

therefore amount of dye in the  
bath after dyeing:  $A = .0144 \times 25 \times 390 = 140.4 \text{ mg}$

and

if ABS. dye at 289.9 nm = ABS. carrier and  
dispersing agent =  $y = .343$

since ABS. dye at 289.9 at 0 g/l = ABS. for  
carrier concentration = dispersing agent = .170

then ABS. of carrier =  $.343 - .170 = .173$

and composite curve for  
o-phenyl phenol:  $y = -.0093 + 14.81 [c]$

Therefore carrier concentration  
after dilution:  $[c] = .01231 \text{ mg/ml}$

and amount of carrier in  
the bath after dyeing:  $A = .01231 \times 25 \times 390 = 120.02 \text{ mg/l}$

A total of 36 samples for the concentration of the dye in the bath and 36 samples for the concentration of the carrier in the bath was obtained.

### Removing the Dye and Carrier on the Surface of the Yarn

The procedure of C. R. Jin et al. for "the removal of the surface dye and carrier" was used. After the yarn sample was removed from the carrier bath, it was washed three times (5, 5, 3 sec.) successively in 50:50 acetone-water mixture at 10°C - 14°C. Then the yarn was dried in the conditioning room until a constant weight was achieved.

### Analysis of the Dye and Carrier Concentration in the Yarn

The dye and carrier in the yarn were extracted using dimethyl formamide and the obtained extraction solution was analyzed spectrophotometrically. The sample yarns which were used for extraction weighed approximately .0500 grams in lengths of 3 cm which were cut randomly from different parts of the skein. Each sample was placed in a test tube and 10 ml. of dimethyl formamide (DMF) was added. Test tubes were placed in Fisher Shaking Water Bath model 129 for 24 hours at a speed setting of 3 with a temperature of ~ 60°C. At the end of 24 hours, the solution was emptied into a bottle, fresh DMF was added to the test tube and the shaking water bath was run for an additional 24 hours. After 48 hours, the extraction was completed. The combined extracts were transferred quantitatively to a 25 ml. volumetric flask and diluted to the mark with DMF. Two ml. of this solution was diluted into 10 ml. DMF. For example:

if           ABS. Dye =  $y = .134$

since        composite curve for  
Disperse Yellow 60:  $y = -.0013 + 20.83 [c]$

then         dye concentration  
after dilution:  $[c] = .0065 \text{ mg/ml}$

Therefore amount of dye in one dyed skein of yarn:  $A = .0065 \times \frac{10}{2} \times 25 \times \frac{9.9705}{.0581} = 161.73 \text{ mg}$

and

if  $\frac{\text{ABS. dye at } 289.9 \text{ nm}}{\text{dispersing agent}} = \frac{\text{ABS. carrier}}{\text{dispersing agent}} = y = .270$

since  $\frac{\text{ABS. dye at } 289.9 \text{ at } 0 \text{ g/l}}{\text{carrier concentration}} = \frac{\text{ABS. for dispersing agent}}{\text{dispersing agent}} = .175$

Then  $\text{ABS. for carrier} = .270 - .175 = .095$

and composite curve for o-phenyl phenol:  $y = .0093 + 14.81 [c]$

Therefore carrier concentration after dilution:  $[c] = .00704 \text{ mg/ml}$

and amount of carrier in one dyed skein of yarn:  $A = .00704 \times 5 \times 25 \times \frac{10.1568}{.0522} =$

171.23 mg

A total of 36 samples for the concentration of the dye in the yarn and 36 samples for the concentration of the carrier in the yarn was used.

#### Analysis of the Dye and Carrier Concentration on the Surface of the Yarn

The amounts of the dye and carrier on the surface of the yarn were obtained using simple formulas:

$$\text{Dye on the surface (mg)} = \text{Dye in the bath before dyeing (mg)} - \left[ \text{Dye in the bath after dyeing (mg)} + \text{Dye in the yarn (mg)} \right]$$

$$\text{Carrier on the surface (mg)} = \text{Carrier in the bath before dyeing (mg)} - \left[ \text{Carrier in the bath after dyeing (mg)} + \text{Carrier in the yarn (mg)} \right]$$

A total of 36 samples for dyes and 36 samples for carrier was obtained.

#### Statistical Analysis

A two-way analysis of variance (ANOVA) was used to test the effects of type of dye and carrier concentration and their interaction.

## V. RESULTS AND DISCUSSION

### Statistical Analysis

A two-way factorial was run to test the effects of independent variables of dye type and carrier concentration and their interaction on each of the following dependent variables: amount of dye in the dye bath, amount of dye in the yarn, amount of dye on the surface of the yarn, carrier in the bath, carrier in the yarn and carrier on the surface of the yarn. The main dependent variables of interest were dye in the yarn and carrier in the yarn. However, since the amount of dye and carrier in the yarn were interrelated with the amount of dye and carrier left in the dye bath as well as the amount of dye and carrier on the surface of the yarn, statistical analysis included all the above variables. The means from the measurements of two repetitions of the dependent variables are given in Table IV.

The results of the statistical analysis indicated that the initial carrier concentration had a significant effect on the amount of dye in the polyester yarn. The first null hypothesis of no difference in the dye uptake of the polyester fiber due to the initial carrier concentration therefore was rejected. The results also showed that the dye type had a significant effect on the amount of dye in the polyester yarn. Therefore the second null hypothesis indicating that there will be no difference in the dye uptake of the polyester fiber due to dye type was rejected. It was observed that both the initial carrier concentration and dye type had an effect on the amount of carrier in the

Table IV: Means from two repetitions of the measurements of dependent variables

Dye type	Initial carrier concentration (gm/l)	Dye in the bath after dyeing (mg)	Dye in the yarn (mg)	Dye on the yarn surface (mg)	Carrier in the bath after dyeing (mg)	Carrier in the yarn (mg)	Carrier on the yarn surface (mg)
No Dye (o-phenyl phenol treatment used as a control)	0	-	-	-	-	-	-
	1	-	-	-	234.18	104.49	61.33
	2	-	-	-	389.40	315.39	95.21
	3	-	-	-	665.44	468.7	65.86
	4	-	-	-	763.78	585.20	251.02
	5	-	-	-	789.65	639.66	570.69
Disperse Red 60	0	133.25	58.93	7.82	-	-	-
	1	108.75	85.68	5.48	127.56	144.24	128.43
	2	41.05	152.94	6.01	276.00	419.28	103.93
	3	36.04	157.72	6.74	401.83	680.97	117.21
	4	17.74	174.42	7.74	436.75	715.00	448.26
	5	11.81	178.45	9.74	583.66	769.44	646.90
Disperse Yellow 54	0	85.45	90.45	21.98	-	-	-
	1	75.19	106.98	17.83	169.14	154.76	76.10
	2	60.22	105.55	30.42	123.52	495.12	181.36
	3	63.34	125.71	10.95	231.10	876.66	92.24
	4	47.00	143.73	9.27	308.65	937.09	354.26
	5	20.74	169.56	9.69	300.05	1032.90	667.06

polyester yarn. The third and fourth null hypotheses therefore were rejected.

Additional results relating to the dye and carrier in the bath and on the surface of the yarn were obtained from the statistical analysis. The results indicated that the initial carrier concentration had an effect on the amount of the dye and carrier in the bath and on the surface of the yarn after dyeing. Whereas dye type had an effect on the amount of carrier in the bath and that of dye and carrier on the surface of the yarn, its effect on the amount of dye in the bath was not significant. The interaction of two factors of initial carrier concentration and dye type also had a significant effect on all the dependent variables tested. It was important to examine the interaction effect rather than looking at each factor separately. All the tests were conducted at .05 level of significance. Table V shows a summary of the analysis of variance table.

#### Interpretation of Results

In case of Disperse Red 60, it was found that as the initial concentration of the carrier in the bath was increased the amount of dye in the yarn increased as well (Table IV and Fig. 3). This caused a decrease in the amount of dye in the bath. The amount of red dye on the surface of the yarn stayed almost constant with increasing initial concentration of the carrier. The highest rate of dye uptake for Disperse Red 60 was observed between the initial carrier concentration of 1 gm/l and 2 gm/l. When the carrier concentration was increased beyond this point, the rate of increase of the amount of red dye in the

Table V: A summary of the analysis of variance

Source	Dye in the bath		Dye in the yarn		Dye on the yarn surface		Carrier in the bath		Carrier in the yarn		Carrier on the yarn surface	
	DF	PR > F	DF	PR > F	DF	PR > F	DF	PR > F	DF	PR > F	DF	PR > F
Carrier Concentration	5	.0001	5	.0001	5	.0003	4	.0001	4	.0001	4	.0001
Dye Type	1	.6489	1	.0001	1	.0001	2	.0001	2	.0001	2	.0001
Carrier Conc. * Dye Type	5	.0001	5	.0001	5	.0001	8	.0001	8	.0001	8	.0114

Level of significance =  $\alpha$  = .05.

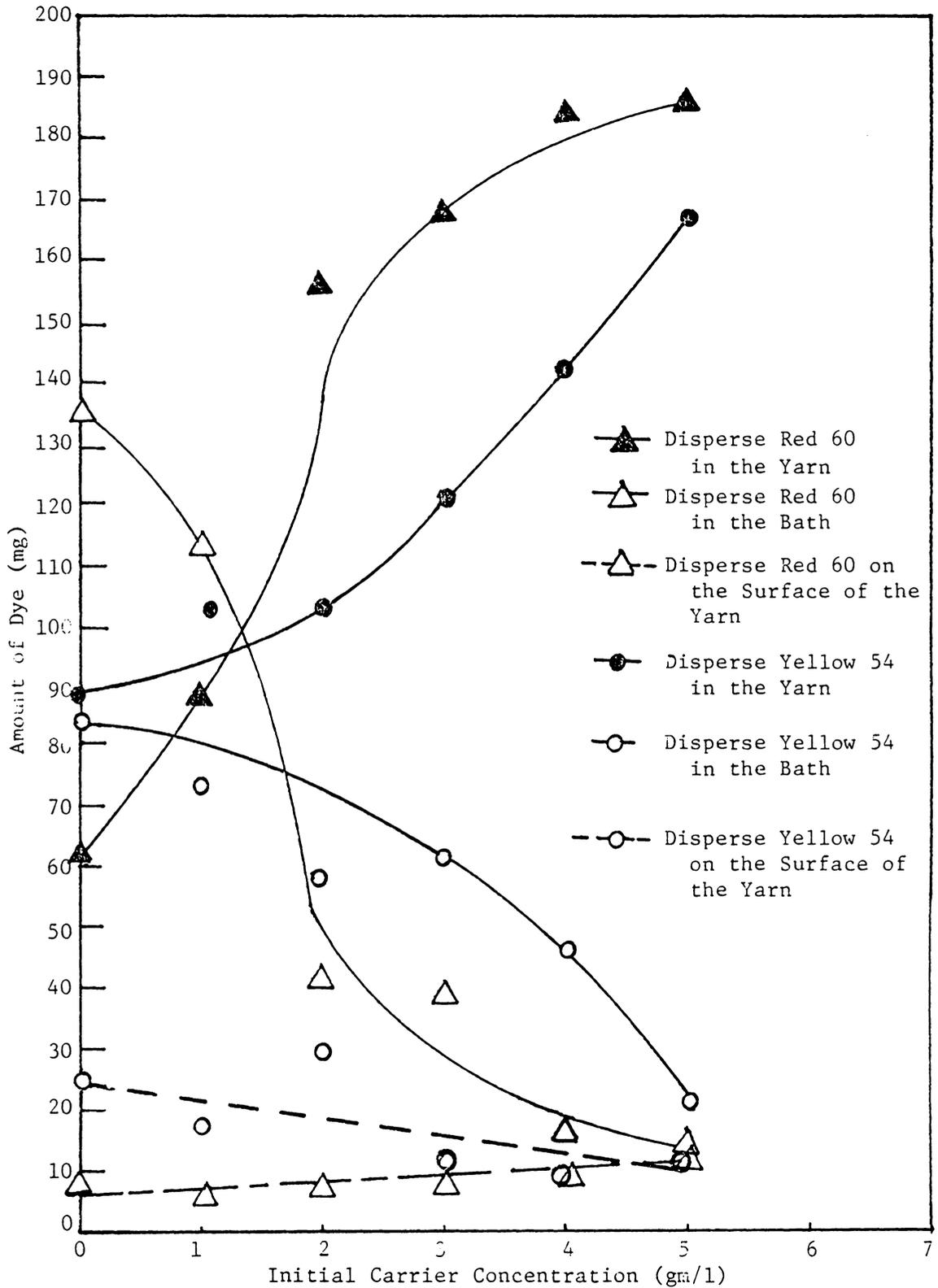


Fig. 3. Effect of initial carrier concentration and dye type on dye uptake of polyester yarn.

yarn was decreased. At the carrier concentration of 5 gm/l, there was very little dye left in the bath. In order to make better sense of changes which occur in the dye bath, a ratio was developed  $\left( K = \frac{\text{mg dye in the yarn}}{\text{mg dye in the bath}} \right)$ . The K ratio does not include the concentration terms and therefore is not the partition coefficient. However, since this ratio is related to the partition coefficient, it is called a pseudo partition coefficient. In Fig. 4, pseudo partition coefficient was plotted against the initial carrier concentration. In case of red dye, at the initial carrier concentrations of 0 and 1 gm/l the K values were very low, .44 and .79 respectively. This meant that there was more dye in the bath than in the yarn. At the carrier concentration of 2 gm/l, the value of K increased to 3.73 meaning that the amount of dye in the yarn was almost four times that in the bath. At carrier concentrations of 3 and 4 gm/l, the value of K was 4.38 and 9.83, which meant that the K ratio increased with the increase of carrier concentration from 2 to 4 gm/l. The value of K at carrier concentration of 5 gm/l increased a great deal. The K value at this concentration was 15.11 which meant the amount of dye in the yarn was 15 times greater than that in the bath. At this point the bath was highly exhausted.

Disperse Yellow 54 behaved differently compared to Disperse Red 60 (Table IV and Fig. 3). As a general trend an increase in the initial carrier concentration caused an increase in the amount of the yellow dye in the yarn and a decrease in the amount of the dye in the bath. The amount of yellow dye on the surface of the yarn was found to be slightly higher in lower concentrations of 0, 1 and 2 gm/l of the carrier. This might be due to the low rate of dye diffusion at those

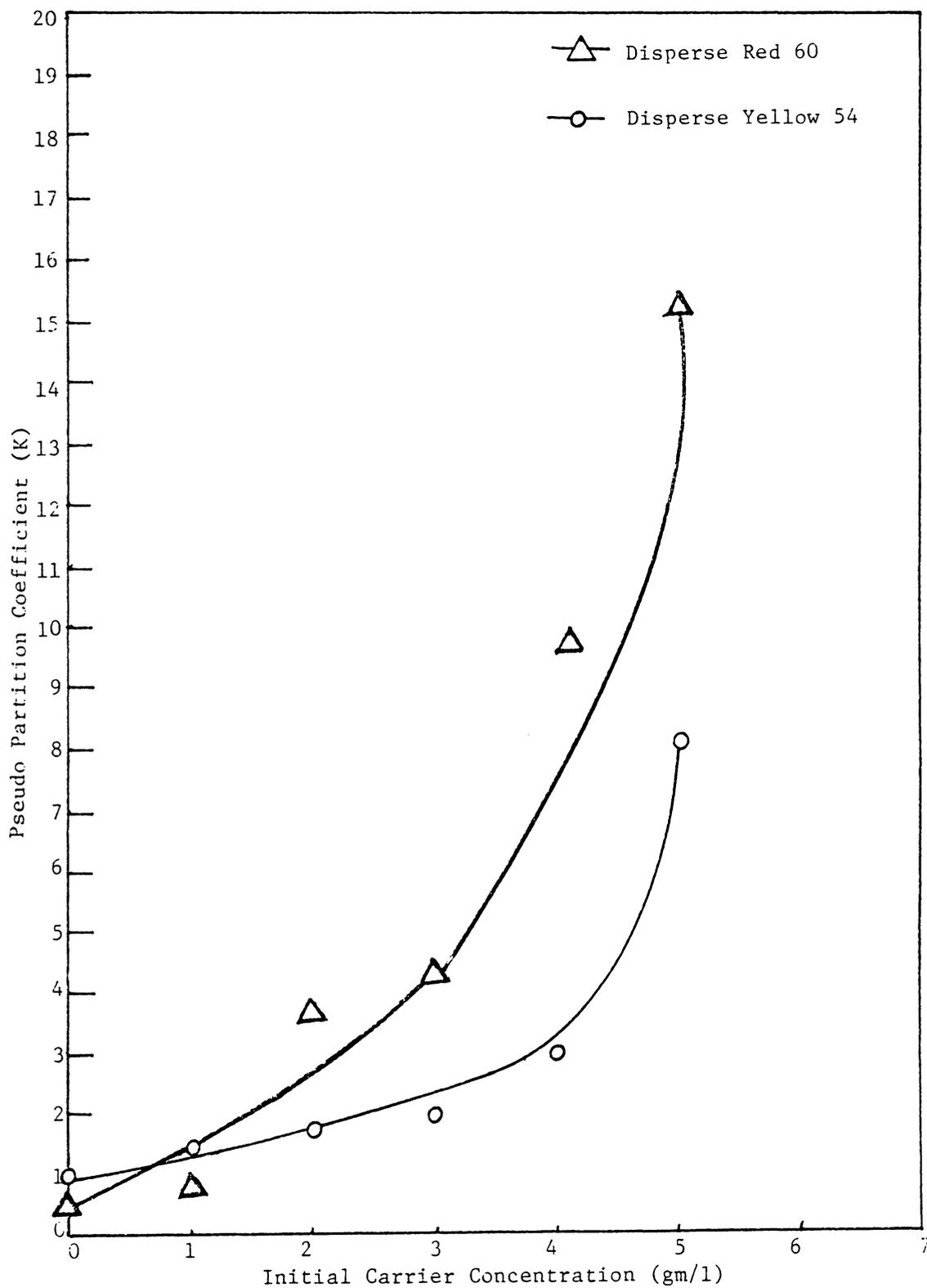


Fig. 4. Effect of the initial carrier concentration on the pseudo partition coefficient (K) for the dyes.

carrier concentrations. The amount of dye uptake of Disperse Yellow 54 at carrier concentrations of 0 and 1 gm/l was higher than that of Disperse Red 60 at the same carrier concentrations. This meant that at the carrier concentrations of 0 and 1 gm/l, the yellow dye was absorbed by the polyester better than the red dye. The rate of increase in the yellow dye uptake stayed constant between carrier concentrations of 1 and 2 gm/l. This rate increased at higher concentrations of carrier (2-5 gm/l). Figure 4 shows that K values for Disperse Yellow 54 at 0 and 1 gm/l are 1.06 and 1.42 respectively which meant that at 0 gm/l of carrier concentration there was almost the same amount of dye in the yarn as dye in the bath. This ratio increased to almost 1.5 at 1 gm/l of the carrier concentration. At the carrier concentrations of 2 and 3 gm/l the K values increased slightly (1.75 and 1.98). Therefore at 3 gm/l, the amount of dye in the yarn was twice that in the bath. At 4 gm/l of the carrier concentration the K ratio was triple the K value at 0 gm/l (3.06). At 5 gm/l of the carrier concentration the K value increased to 8.18 which indicated that the yarn held eight times more dye compared to the dye bath.

The interaction effect of carrier concentration and dye type was significant. Therefore the function of Disperse Red 60 and Disperse Yellow 54 at different initial carrier concentrations was observed (Fig. 4): At 0 g/l of the carrier concentration K value of Disperse Yellow 54 was higher than that of Disperse Red 60. This was also applicable to carrier concentration of 1 gm/l. However, at carrier concentrations higher than 1 gm/l, the K value for Disperse Red 60 increased and was higher than the K value for Disperse Yellow 54 at

every single carrier concentration. At carrier concentrations of 2 and 3 gm/l, the K value for Disperse Red 60 was twice that of Disperse Yellow 54. At carrier concentration of 4 gm/l, the ratio of K value for Disperse Red 60 to that of yellow was around 1.5. This ratio became nearly 2 at carrier concentrations of 5 gm/l. It was concluded that at carrier concentrations between 2-5 gm/l, the dye uptake of polyester yarn for Disperse Red 60 was more than that for Disperse Yellow 54. At 0 and 1 gm/l of the carrier concentration, the dye uptake of polyester yarn for Disperse Yellow 54 was more than that for Disperse Yellow 60. Therefore the interaction effect of dye type and carrier concentration showed to be a very important factor in effecting dye uptake of the polyester yarn. At 5 g/l of the carrier concentration, the bath was highly exhausted. As a general trend, the pseudo partition coefficient for both Disperse Red 60 and Disperse Yellow 54 increases with increase in the initial carrier concentration.

After observing the dye uptake of the polyester yarn, the results relating to carrier uptake of the polyester yarn were studied in the presence of Disperse Red 60, Disperse Yellow 54 and no dye.

In case of carrier treatment with no dye present, as the initial concentration of the carrier in the bath was increased, the amount of carrier in the yarn as well as that of the carrier on the surface of the yarn were increased. Therefore, the amount of the carrier in the bath, in the yarn and on the surface of the yarn all increased together (Table IV, Fig. 5). The trend of increase in the amount of the carrier in the yarn, in the bath and on the surface of the yarn was followed for the carrier in presence of Disperse Red 60 and Disperse Yellow 54.

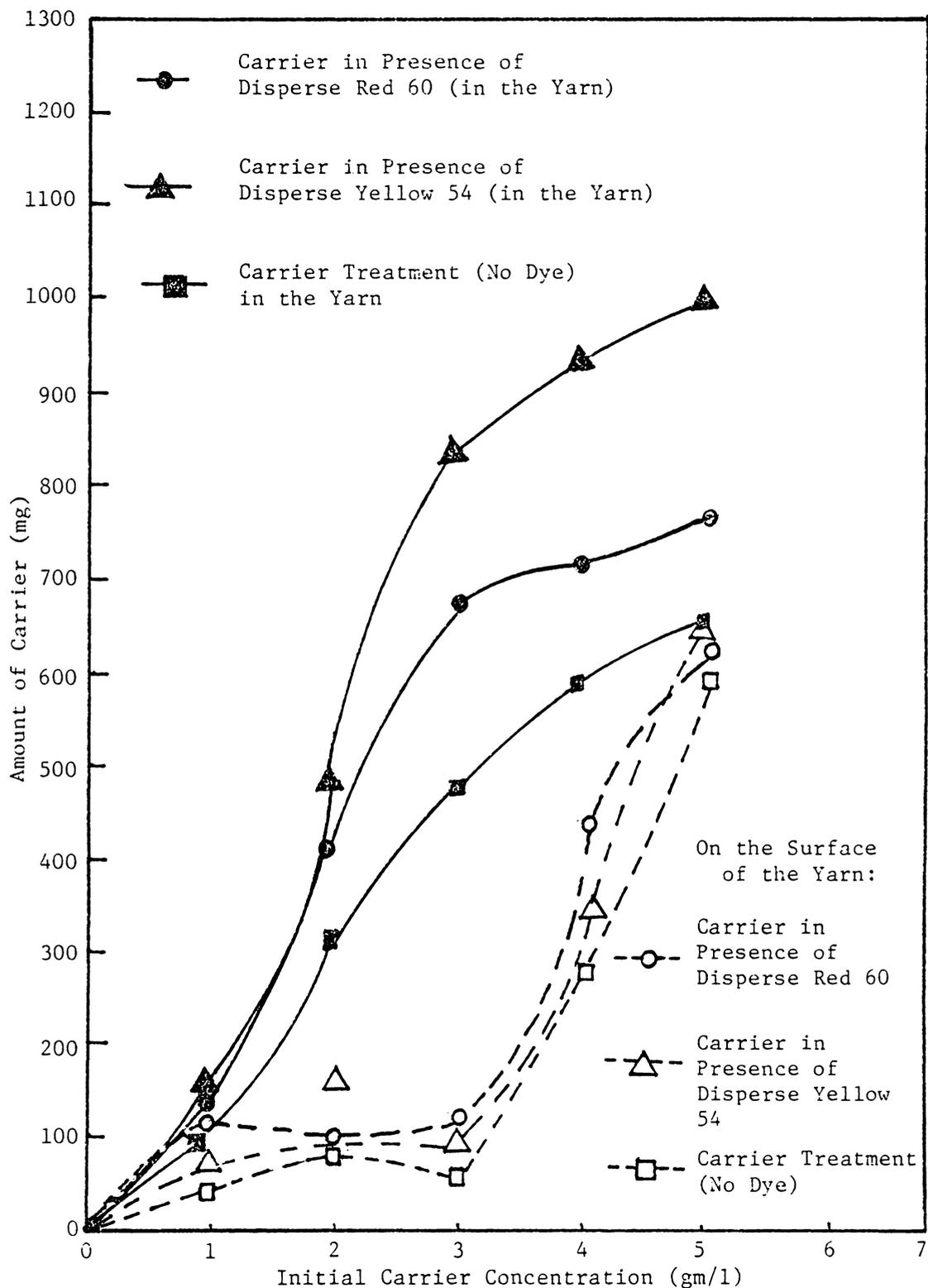


Fig. 5. Effect of the initial carrier concentration and dye type on carrier uptake of polyester yarn.

However comparing the amounts of the carrier uptake by polyester yarns dyed with Disperse Red 60, Disperse Yellow 54 and no dye, it was observed that in all the initial concentrations of carrier, yellow dye had the highest amount of carrier uptake followed by the red dye. The highest rate of the carrier uptake in the presence of both red and yellow dyes occurred between the concentrations of 1 to 3 gm/l of carrier. In the case of both dyes the rate of increase in the amount of the carrier uptake decreased beyond the carrier concentration of 3 gm/l. The data obtained from the amount of carrier on the surface of the yarn was lower for low concentrations of carrier up to 3 gm/l. Beyond this carrier concentration, the amount of the carrier on the surface increased at a very rapid rate.

A  $K'$  ratio  $\left( K' = \frac{\text{mg carrier in the yarn}}{\text{mg carrier in the bath}} \right)$  was established. This ratio does not include the concentration terms and therefore is not the partition coefficient. However, since it is related to the partition coefficient, it is called a pseudo partition coefficient. Examining the plot of pseudo partition coefficient ( $K'$ ) against the initial carrier concentration the following results were obtained (Fig. 6): when there was no dye present, at all the initial carrier concentrations, there was more carrier in the bath than in the yarn. However higher but different  $K'$  values were found in the presence of red and yellow dyes which indicated that the type of dye is an important factor in the carrier uptake of the polyester yarn. The value of  $K'$  for the carrier in presence of Disperse Red 60 was above 1 meaning that there was slightly more carrier in the yarn than in the bath.  $K'$  had its highest values at carrier concentrations of 2, 3 and 4 gm/l showing

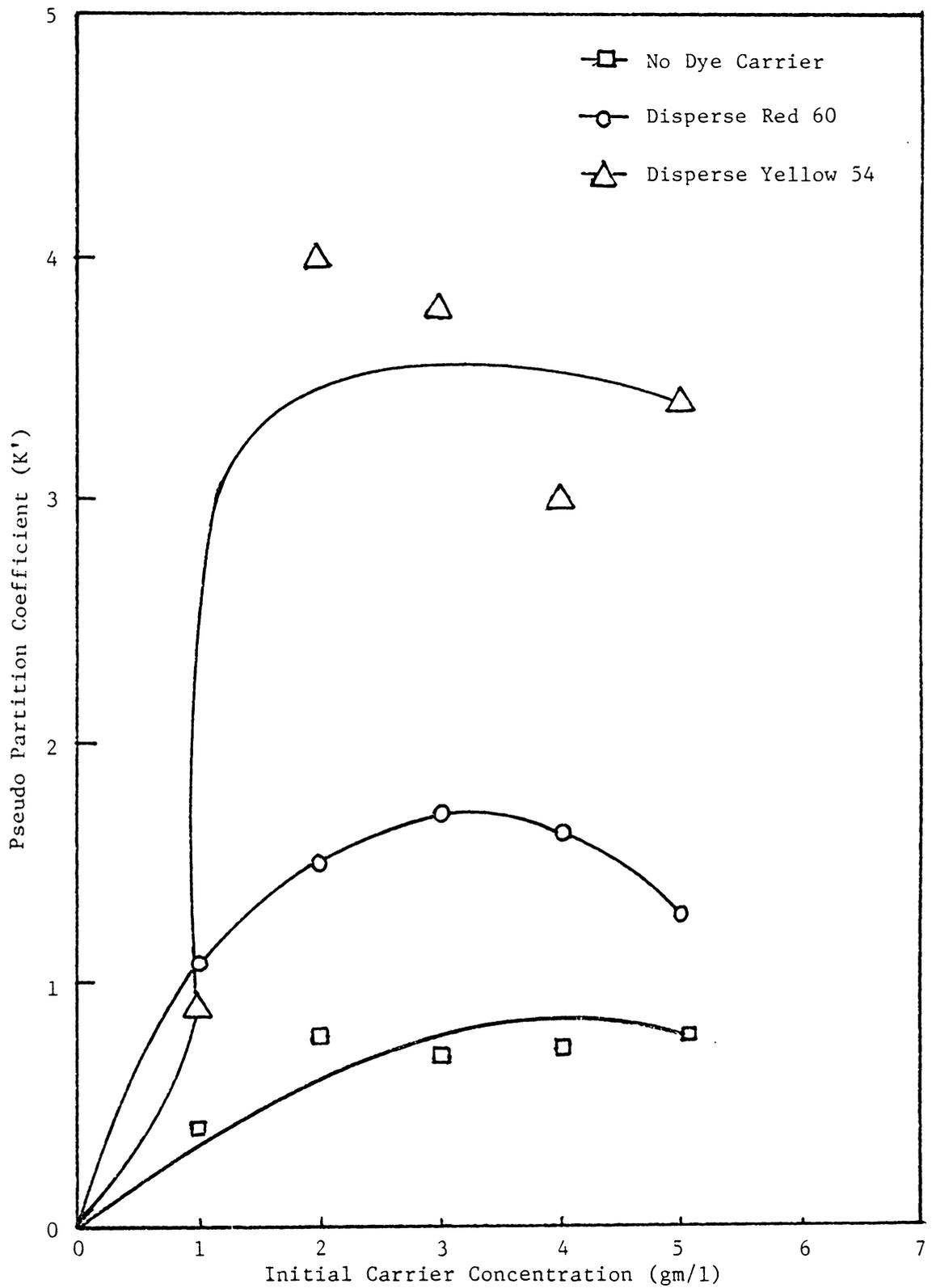


Fig. 6. Effect of the initial carrier concentration on the pseudo partition coefficient ( $K'$ ) for the carrier.

1.52, 1.69 and 1.64 respectively. The behavior of the carrier in the presence of Disperse Yellow 54 was different from when red dye was present. The value of  $K'$  for the carrier in the presence of the yellow dye was .91 at 1 gm/l of the carrier concentration meaning that the amount of the carrier in the yarn and bath were approximately equal. At carrier concentrations of 2, 3 and 4 gm/l the carrier uptake increased rapidly causing high values of  $K'$  (4.00, 3.79 and 3.04) respectively which meant that there were 3 to 4 times more carrier in the yarn than in the bath.

### Discussion

Most of the studies in the literature were based on the assumption that a true equilibrium in dyeing was attained. At low concentrations of carrier (1-9 gm/l) long dyeing times (sometimes days) are required, whereas at high concentrations of carrier (9-14 gm/l) equilibrium is reached after as little time as two hours (41). In the case of this research, since the low concentrations of carrier (1-5 gm/l) were used, achieving the dyeing time would be a time consuming process. According to Cates et al. (41): "When the effects of various carriers on dyeing rate are compared, it is common to determine percent exhaustion of the dyebath after a certain time interval and to consider this as a measure of rate of uptake. Although dyeing 'rates' obtained this way are not strictly comparable, the method has the advantage of convenience." Therefore, for this study, a dyeing time of 40 min. was selected. It was concluded from this research that as the initial carrier concentration in the bath increased, the amount of carrier uptake in the

polyester yarn and dye exhaustion in the bath were increased for both red and yellow dyes. These results were supported by the work done by M. J. Shuler and V. S. Salvin (45,46). The results of the present research also indicated that even though the carrier uptake of the polyester yarn in the presence of the yellow dye was greater than that of red at carrier concentrations of 2-5 gm/l, the amount of dye uptake of the polyester yarn at the same concentration of the carrier was greater for the red dye. From this phenomenon it was concluded that when more than one type of dye was involved the type of dye as well as interaction of the dye type and carrier concentration would be very important factors affecting the amount of dye uptake as well as carrier uptake of polyester yarn. D. Balmforth et al. and M. J. Shuler concluded from their studies (3,46) that in case of some carriers, there is a carrier concentration which gives a maximum uptake of the dye. Any increase beyond this concentration results in a lower dye uptake. This optimum carrier concentration appears to correspond approximately to the amount of carrier necessary to saturate the system of both dye bath and fiber. So if this concentration is exceeded, the carrier forms a film layer at the fiber surface and emulsified droplets in the bath. Depending on the type of the carrier and other factors involved, excess carrier might dissolve the dye, lower its activity and thus reduce the dye uptake. It was concluded from the results of the present research that beyond carrier concentration of 3 gm/l, the amount of surface carrier for both Disperse Red 60 and Disperse Yellow 54 as well as the carrier in presence of no dye was increased a great deal. However, the carrier uptake of the polyester yarn was still increasing with a slower

rate meaning that the yarn was not completely saturated with the dye. The fact that the excess carrier did not return to the bath can be explained by high hydrophobicity of the carrier which made it difficult for the carrier to move towards the dye bath. On the other hand, the dye uptake of the polyester yarn did not decrease after the carrier concentration of 3 gm/l but it kept increasing with a slower rate. This phenomena was different from the results obtained in similar experiments. The difference can be explained by the following factors: different types of dyes were used and the exact equilibrium time was not achieved in this experiment.

If one would want to choose the best condition of the present research for the purpose of practical dyeing, it would be the use of Disperse Red 60 at carrier concentration of 3 gm/l. The reason for this choice was that beyond this concentration a carrier layer would form on the surface of the yarn which was difficult to remove. Also the dye uptake beyond the carrier concentration of 3 gm/l did not increase a great deal. The practical dyer does not always need to reach the full exhaustion to obtain a good quality dyeing. Disperse Red 60 showed a higher dye uptake compared to Disperse Yellow 54.

The random sampling which was done both in dyeing and extraction processes increased the accuracy and precision of the study and gave more meaningful results.

The results of this experiment cannot be generalized to all the disperse dyes and carriers. One factor which could have decreased the internal validity of the study was that dimethyl formamide was not the

best solvent for the yellow dye and o-phenyl phenol.

Since the spectrophotometer was used to measure the absorption of the dyes and carrier, careful measurements should be taken to eliminate the factors which might affect the reliability of the measuring device. For example, temperature, which can change the curve shape and intensity of the absorption maximum, was kept constant for all the samples. Examining the dye bath absorption after dyeing showed that the absorbance for colored dispersing agents (yellowish brown) did not occur at the maximum peak absorption of the dyes. Therefore the presence of dispersing agents did not introduce an error in the dye absorption values.

## VI. SUMMARY AND CONCLUSION

The purpose of this study was to determine the effect of the carrier concentration and dye type on dye and carrier uptake of spun Dacron type 54 polyester yarn in the disperse dyeing of polyester. Three types of dye (control or no dye, Disperse Red 60 and Disperse Yellow 54), one carrier (o-phenyl phenol) and six levels of carrier concentration (0, 1, 2, 3, 4 and 5 gm/l) were used. Spun Dacron type 54 yarn of 490 denier weighing 10 gm was obtained.

Dyeing was done using Ahiba Texomat dyeing machine. A total of 36 skeins was dyed in absence of dye, or in the presence of yellow or red dyes. The total bath volume was 400 ml and each yarn weighed approximately ten gm. Therefore the liquor ratio was 40/1. The concentration of the dyes in the dye bath was .5 gm/l, corresponding to 2% on weight of yarn. The concentrations of the carrier were 0, 1, 2, 3, 4 and 5 gm/l, corresponding to 0 to 20% on weight of yarn. Dyeing started at temperature of  $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and it was increased  $3^{\circ}\text{C}/\text{min}$  until it reached  $95^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The holding time was 40 minutes at  $95^{\circ}\text{C} \pm 2^{\circ}\text{C}$ .

A composite standard curve was established for each dye as well as the carrier. The dye in the yarn was extracted using dimethyl formamide as a solvent. A Fisher Shaking Water Bath model 129 was used for this purpose with the temperature of  $60^{\circ}\text{C}$ . The samples of extraction and dye bath solutions were analyzed spectrophotometrically.

A two-way factorial design was used to test the hypotheses. The first null hypothesis indicating that there will be no difference in the

uptake of disperse dye by polyester fiber due to initial carrier concentration was rejected. Therefore there was a significant difference in the uptake of the disperse dye by polyester yarn using different carrier concentrations.

The second null hypothesis indicating that there will be no difference in the uptake of disperse dye by the polyester fiber due to dye type was also rejected. The result showed that dye type had an effect on the dye uptake of the disperse dye by polyester yarn.

The third and fourth null hypotheses of no difference in the carrier uptake of polyester fiber due to initial carrier concentration and dye type respectively were both rejected. This meant that both carrier concentration and dye type had an effect on carrier uptake of polyester yarn.

### Conclusion

This study indicated that the initial carrier concentration, dye type and their interaction had a significant effect on both carrier and dye uptake of polyester yarn.

### Suggestions for Further Study

In case of this study only one carrier and one concentration of the dye were used. A study covering the effect of carrier type would be informative. Also a study involved with different concentrations of dye would be of interest. The equilibrium time in carrier dyeing is very important. A study of equilibrium time for different concentrations of carriers in the bath is suggested.

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