Solvent Dyeing of Acrylic Fibers.   Process Variables and Mechanisms Based on Rates of Dyeing and Diffusion Studies Using Cationic Dyestuffs

EDWARD A. DUFFY and EDWARD S. OLSON, *Textile Department, Clemson University, Clemson, South Carolina 29631*

Synopsis

Diffusion coefficients of selected cationic dyes are calculated for one aqueous and six organic solvent dye systems.   The concentrations of dyestuffs sorbed by the fibers as functions of dyeing times are plotted for the various dyeing systems.

Results indicate that dye sorption decreases and the diffusion coefficient increases as the concentration of the cosolvent increases.   The results were determined by comparing the Crank and Olofsson equations for diffusion.

INTRODUCTION

Economic advantages of organic solvent process systems make replacing the aqueous system feasible.   Chlorinated hydrocarbons have been shown to be suitable solvents for the various textile wet processes, and their advantages over other organic solvents are numerous.[1,2]

Fabrics have been successfully dyed using organic solvents since 1882,[3] and more recently solvent processing has been utilized to achieve diverse finishes.[1,2,4,5,6]   Substantial insight into the development of important organic solvent processes can be gained from selected publications.[7-16]

In this work acrylic fibers were dyed using cationic dyestuffs from an aqueous system and two organic systems using *m*-xylene or tetrachloroethylene vapor.   The fibers were first padded using a solution of dyestuff dissolved in organic solvents then dyed in an organic vapor.   To better understand the solvent dyeing system, selected factors were studied; these were fiber composition, dyestuff, pad solution, and organic vapor.   Rates of dyeing and diffusion coefficients were calculated using the data obtained from these experiments.

EXPERIMENTAL

Three acrylic fabrics were used in this work' and were dyed in aqueous and organic solvent systems.   Those fabrics dyed in the organic solvent systems were first immersed in a solution of dyestuff dissolved in organic solvents and then padded.   For each fiber and dyestuff, one sample was exposed to tetrachloroethylene vapor and the other was exposed to *m*-xylene vapor.

The organic solvent systems were three different dye solutions, shown in Table I. The primary difference between dye solutions was in the concentration of the tetrahydrothiophene 1,1-dioxide (THTDO). Series I utilized 10% THTDO; series II utilized 20% THTDO; series III utilized 30% THTDO. Series I and III also contained formic acid which was used to incorporate a small amount of acid in the dye system. Series III also contained a surface-active agent.

TABLE I
Composition of Organic Solvent Solutions[21]

Component	Series I	Series II	Series III
Dyestuff	1 g	1 g	1 g
Tetrahydrothiophene 1,1-dioxide (THTDO)	10 cc	20 cc	30 cc
2-Phenoxy-1-ethanol (EPH)	10 cc	10 cc	10 cc
Formic acid	0.5 cc	—	0.5 cc
Dodecylbenzenesulfonic acid (DBSA)	—	—	1.0 cc
Diethanolamine (DEA)	—	—	1.0 cc
Trichloroethylene	79.5 cc	70.0 cc	57.5 cc

C.I. Basic Red 2 was chosen for the comparison between the aqueous and solvent systems. Four dyestuffs were used in the series II solvent system. Comparisons between series I through III were made using C.I. Basic Blue 22 because it was the only dyestuff compatible in all series. The dyestuffs used to dye the three acrylic fabrics are shown in Table II.

TABLE II
Dyestuffs Used in the Dyeing Systems

| Dyeing system	Dyestuff
Aqueous	C.I. Basic Red 2
Series I	C.I. Basic Blue 22
Series II	C.I. Basic Red 2
	C.I. Basic Blue 22
	C.I. Basic Red 14
	C.I. Basic Orange 21
Series III	C.I. Basic Blue 22

Fabrics

The three acrylic fibers used were Acrilan 16, Acrilan 36, and Orlon 75. Table III supplies the fabric, dye site, fiber, and structure data.

Dyestuffs

The dyestuffs used were C.I. Basic Blue 22, C.I. Basic Red 2, C.I. Basic Red 14, and C.I. Basic Orange 21. The structures of the dyestuffs are known, are planar, and each one has one group capable of forming a salt

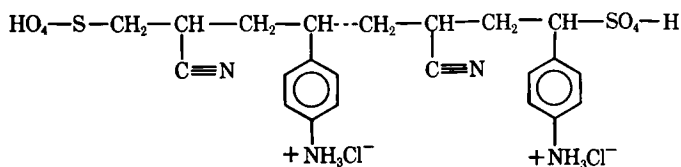## TABLE III
Fiber, Dye Site, Fabric and Structure Data[a][17,18]

Acrilan 16:

$$HO_4-S-[CH_2-CH-]_n-CH_2-CH-[CH_2-CH-]_n-SO_4-H$$
with $C\equiv N$, $COOH$, $C\equiv N$ substituents
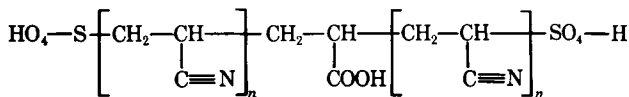
Radius: 1.48 × 10⁻² mm
Density: 1.18 gms/ml
Denier: 2.2
Per cent Acrylonitrile: 99.0

Construction: 47 × 38
Wt/sq yd: 113.7 gms
Micro eq. of dye sites/gm fiber:
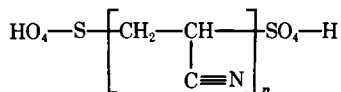Sulfuric Acid = 38.0 ± 1.0
Carboxylic Acid = 14.0

Acrilan 36:

$$HO_4-S-CH_2-CH-CH_2-CH\cdots CH_2-CH-CH_2-CH-SO_4-H$$
with $C\equiv N$, phenyl-$^+NH_3Cl^-$, $C\equiv N$, phenyl-$^+NH_3Cl^-$ substituents

Radius: 1.60 × 10⁻² mm
Density: 1.18 gms/ml
Denier: 2.3
Per cent Acrylonitrile: 96.0

Construction: 47 × 41
Wt/sq yd: 112.8 gms
Micro eq. of dye sites/gm fiber:
Sulfuric Acid = 27.5 ± 1.5
Phenylamine hydrochloride = 450

Orlon 75:

$$HO_4-S-[CH_2-CH-]_n-SO_4-H$$
with $C\equiv N$ substituent

Radius: 1.09 × 10⁻² mm
Density: 1.18 gms/ml
Denier: 2.0
Per cent Acrylonitrile: 99.0

Contruction: 47 × 38
Wt/sq yd: 113.7 gms
Micro eq. of dye sites/gm fiber:
Sulfuric Acid = 49.0 ± 1.0

[a] Obtained from Testfabrics Inc., 55 Van Dam Street, New York, N. Y.

linkage with a fiber acidic group.   The structure of C.I. Basic Red 2 is shown in Figure 1.   The manufacturer has requested that the structures of the other dyestuffs be kept confidential.   The dyestuffs, when received from the manufacturer, were labeled "crude," which was assumed to mean that the purity of the dyestuff was approximately 90%.
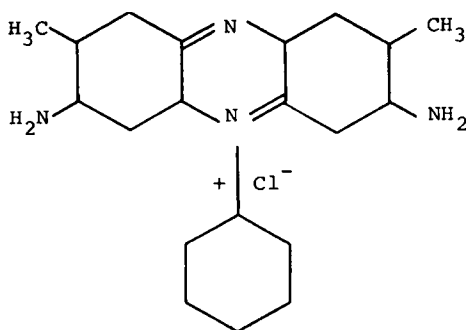

Fig. 1. C.I. Basic Red 2 Structure.

Dyeing

Aqueous. The samples were weighed and framed with 1-mil stainless steel wire in order to prevent creasing in the dye bath. Each dyeing was performed at a liquor ratio of 80 to 1, a pH of approximately 4.6[19,20] adjusted with acetic acid, and the amount of dyestuff added was based on the weight of the fabric. The Acrilan 16 and Acrilan 36 fabrics were dyed using 1.25% dyestuff, but the Orlon 75 fabric was dyed using 2.75% dyestuff. Each sample was entered into the dye solution at the boil and dyed according to the schedule shown in Table IV. At the end of each dye cycle, the sample was removed and repeatedly washed with cold acetone until the washings were clear.

TABLE IV
Dyeing Schedule

Aqueous system	Solvent system
15 min	30 sec
30 min	1 min
45 min	2 min
1 hr	3 min
$1^1/_2$ hr	4 min
2 hr	5 min
3 hr	
4 hr	
5 hr	

Solvent. The dyeing solutions, Table I, were made by first dissolving the dyestuff in THTDO, then EPH was added. When appropriate, the DBSA, DEA, and/or formic acid was added, followed by the addition of trichloroethylene. The unconditioned fabric was submerged in the dye solution for 1 min, padded using a pad air pressure of 50 psi and then placed in the solvent vapor. The solvent had been boiled for 1 hr prior to exposing the fabric in the vapor in order to insure that the vapor system had come into equilibrium with the boiling solvent. After the fabric had been exposed to the vapors for the required time, it was removed and then washed in boiling acetone until the washings became clear.

The organic solvents used to produce the dyeing vapors in this experiment were *m*-xylene and tetrachloroethylene. Table V contains pertinent properties of these organic solvents.

TABLE V
Selected Properties of Organic Solvents Used as Dyeing Vapors

Solvent	Boiling point, °C	Specific heat, cal/g-°C	Dipole moment μ_D ($T = 25$°C)
m-Xylene	139.0	0.385	0.32
Tetrachloroethylene	121.0	0.222	0.00

Solution Studies

The dye liquors from the aqueous dyeings were analyzed using the Spectronic 20 colorimeter, and the concentrations were obtained by applying Beer's law.[22] An aliquot of the dye solution was diluted with water buffered to pH 4.6 and then adjusted so that transmission readings between 20% and 80% were obtained. Transmission readings were converted to optical densities for the Beer's law calculation.

Extraction and Estimation of Dyestuff in Fiber Substrate

After being dyed, the fibers were diluted 100 to 1 with dimethylformamide. The relative speed with which the fibers dissolved was: Orlon 75 > Acrilan 16 ≫ Acrilan 36. These solutions were further diluted in order to obtain transmission readings between 20% and 80%.

The transmission readings of the dyestuffs were obtained using the following wavelengths:

Dyestuff	Wavelength, nm
C.I. Basic Red 2	545
C.I. Basic Blue 22	605
C.I. Basic Red 14	557
C.I. Basic Orange 21	430

Infrared Spectra

An infrared spectrum was obtained in order to determine whether or not THTDO was present in the dyed samples. The fabrics were pulverized in a Wiley mill, mixed with potassium bromide, and a pellet was made from the mixture.

Cross-Sectioning

In order to obtain projector slides of the acrylic fibers, the yarn was mounted, cut, and photographed.[23] Random fibers were selected from each slide, their sizes determined, and the distance the dyestuff had diffused was measured.

DISCUSSION AND RESULTS

The purpose of this work was to measure the rates of diffusion of selected cationic dyestuffs into different acrylic fibers from aqueous and organic systems. This information should provide for better understanding of the solvent dyeing mechanism.

The mechanism of dyeing acrylic fibers from the aqueous system is not completely understood, but probably can be explained by combining two theories: the static pore theory and the free volume theory. Brief explanations of these theories, along with descriptions of the acrylic polymer and fibers, should be valuable aids for determining the solvent dyeing mechanism.

Acrylic Polymer and Fiber

The active dye sites present for cationic dyestuffs in the acrylic fiber are sulfuric acid groups which are derived from the persulfate–bisulfite redox catalyst or from copolymerization with a suitable monomer. Analytic data have been obtained indicating that the sulfuric acid groups are likely to be located at the terminal groups of the polymer.[24-28] Other potential dye sites are carboxyl groups produced by the possible hydrolysis of the nitrile groups pendent to the polymer chain. The carboxyl groups are capable of combining with the dyestuff only at pH's higher than 6.0.[19,20] The process of dyeing acrylic fibers using cationic dyestuffs is essentially an ion exchange equilibrium described by a Langmuir sorption isotherm.[29-31]

Once the cohesive forces exhibited by the acrylic fiber were attributed to hydrogen bonding between the hydrogen on the tertiary carbon and the nitrile group, but studies[32] using nuclear magnetic resonance have discounted this, because the carbon–hydrogen bond of the tertiary carbon is not sufficiently polarizable to permit bonding with the nitrile group. Rather, it is now believed that the strongly polar nitrile groups form a "C≡N dipole pair bond." The bond energy of this dipole–dipole interaction is approximately 8 kcal/mole.[33,34]

Free Volume Theory

The free volume theory of dyeing states that the dyestuff is attracted from solution to the fiber surface and remains there until sufficient thermal energy has been supplied to the system to allow the dyestuff to diffuse into the fiber. When thermal energy is supplied at and above the glass transition temperature of the fiber, the dyestuff diffuses into the fiber by "jumping" from one site to another.

Below the glass transition temperature, the polymer molecules are relatively motionless, and very little, if any, diffusion of dyestuff into the fiber takes place.[35] Once the glass transition temperature is reached, sufficient energy exists in the fiber causing some segments in the polymer to move. These segments, including dye sites, vibrate, but no net translational motion of the center of gravity of the molecule occurs.[36] When an unoccupied dye site and an occupied dye site come into close proximity, a condition exists in which the dyestuff can interchange between these dye sites and thus diffuse through the fiber.[37,38] Rosenbaum[39] calculated that one half of the encounters between an occupied and an unoccupied dye site result in a fruitful exchange of a dyestuff molecule.

In the free volume theory, the activation energy of dyeing is defined as the energy required to form a free volume around the dye site which can accommodate the dyestuff and permit a location change of the incorporated dyestuff molecule.[40,41] Another factor to be considered is the amount of energy needed to overcome the attractive forces between the dyestuff and the dye site to which it is bound. This energy is reported to be very low.[42] Rosenbaum[43,44] reported that the activation energy is not a constant but

is a variable with a maximum value at the glass transition temperature, decreasing with increasing temperature.

The purpose of the solvent, such as water, according to the free volume theory, is to transport the dyestuff from solution to the fiber surface and then to act as a plasticizer. The mode of action of the plasticizer in dyeing is to lower the energy of activation. The plasticizer is sorbed into the fiber and weakens the interpolymer attractive forces.[45-47] In weakening these forces, the plasticizer decreases the energy needed to permit rotational and vibrational motion of the chain segments, and it, therefore, lowers the glass transition temperature of the fiber.[48,49] The concentration of plasticizer in the polymer is more important than the chemical structure of the plasticizer.[50,51,52,53]

Static Pore Theory

The static pore theory states that the dyestuff is attracted from solution to the fiber surface and remains there until higher temperatures are reached. At the higher temperatures, the dyestuff diffuses through the solvent filled canals and attaches itself to dye sites in the polymer.[27,54]

In the static pore theory, the polymer is given a passive role in the act of dyeing because the dyestuff is considered to be the energy absorber. The activation energy defined by this theory is markedly different from that of the free volume theory and is defined as the amount of energy necessary to remove the dyestuff from a dye site within the polymer and return it to the internal solution. This energy of activation is acquired thermally at the glass transition temperature and is considered to have a constant value at all temperatures for polyacrylonitrile polymers.[27]

The solvent plays an integral part in the static pore theory. Not only does the solvent transport the dyestuff from solution to the fiber surface, but it also transports the dyestuff through an internal pore to a dye site in the polymer. An internal pore is not to be mistaken for a free volume, because an internal pore is filled with solvent, whereas free volume is a void between molecules.

Variations in the Solvent System During Processing

The chemical constitution of the organic solvent dyeing solution on the fiber surface varied greatly during the dyeing process. Analysis of the series II dye solution during processing is of major importance in understanding the solvent dye system. The fiber was first submerged in the dye solution for 1 min and was subsequently padded between squeeze rolls in order to insure uniform application. The solution on the fabric surface after padding contained dyestuff, THTDO, EPH, and trichloroethylene. When the fabric was exposed to the solvent vapor, the vapor condensed on the cold fiber surfaces, probably diluting the dye solution. Initially, the condensation was so great that a quantity of dyestuff was flushed from the fiber surface. The quantity of dyestuff flushed from the fiber surface decreased as the temperature of the system increased. At a tempera-

ture of 84°C, the trichloroethylene was evaporated from the dye solution. The fiber temperature then continued to increase until the dyeing temperature, the temperature of the solvent vapor, was reached. The dyeing temperature was assumed to have been reached in approximately 20 sec because the cross sections of the fibers, after being exposed to the vapors for 30 sec, showed only slight dyestuff diffusion. Therefore, the dyeing solution, at the time of actual dyeing, consisted of dyestuff, THTDO, EPH, and solvent vapor.

Analysis of Dyestuff Sorption Curves

The results of the dyeing performed in the aqueous and solvent systems are shown in Figures 3–11. These curves should provide for a better understanding of the contributions made by the various chemicals in the solvent dyeing system.

Figure 2 is a plot of the concentrations of C.I. Basic Red 2 sorbed into the Orlon 75, Acrilan 16, and Acrilan 36 fibers as functions of dyeing times. The graphs show that in each case more dyestuff was sorbed by the fiber after being dyed in the m-xylene vapor than in the tetrachloroethylene vapor. These figures also show that the order of sorption of C.I. Basic Red 2 by the fibers was Orlon 75 > Acrilan 16 > Acrilan 36.

Figure 3 shows that the same order of sorption of C.I. Basic Red 2 in the acrylic fibers occurred when using the aqueous dyeing system as with the solvent systems. This figure demonstrates the classic Langmuir isotherm and illustrates dependency upon the numbers of dye sites available for dyestuff location. Supporting data show that as the dyestuff was sorbed by the fibers, similar amounts of dyestuff moved from the dyestuff solution to the fiber. It is significant that in the aqueous and solvent dyeing trials using C.I. Basic Red 2, the order of fiber dyeing remained the same and that the rate of dyeing in the solvent systems was increased by a factor of 60 times those dyed in the aqueous system.

Figures 4–6 are plots of the concentrations of C.I. Basic Blue 22 sorbed into the Orlon 75, Acrilan 16, and Acrilan 36 fibers as functions of the dyeing times, when using the series I, II, and III solvent systems, respectively. From these data several observations are made pertaining to the amount of dyestuff sorbed, order of the rate of dyeing, order of the amount of dyestuff sorbed, and the influence of the organic solvent vapor. When the results from the series I and II dye trials are compared, it is seen that three dyeings resulted in increased dye usage, two dyeing decreased, and one remained constant. Comparing series II with series III showed that all yields were reduced by approximately 50%. The order of the rates of dyeing was Orlon 75 > Acrilan 16 > Acrilan 36, except for the series I dye trials, which was Acrilan 16 > Orlon 75 > Acrilan 36. Acrilan 36 was the least in all cases. The change in order for Orlon 75 and Acrilan 16 was reversed in series I. No explanation for this reversal is available at this time. Of particular note is that the quantity of dye sorbed was in the same order as that for the rates of dyeing. In all cases, m-xylene improved the rates of dyeing over that of the tetrachloroethylene.
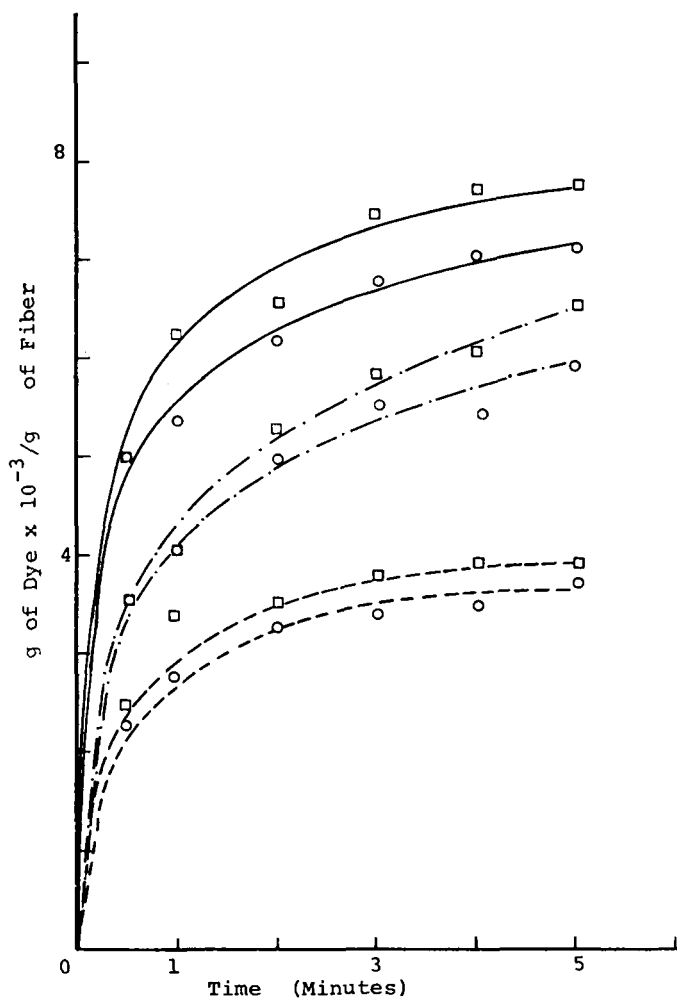
Fig. 2. Series II, concentrations of C.I. Basic Red 2 sorbed into the fibers: (□) *m*-xylene; (O) tetrachloroethylene; (—) Orlon 75; (– ·–) Acrilan 16; (---) Acrilan 36.

Figure 7 is a plot of the concentrations of C.I. Basic Orange 21 sorbed into the Orlon 75, Acrilan 16, and Acrilan 36 fibers as functions of the dyeing times after exposing one sample in *m*-xylene vapor and the second sample in tetrachloroethylene vapor.   From the graph it was determined that in each case more dyestuff was sorbed by the fiber after being dyed in *m*-xylene vapor than in tetrachloroethylene vapor.   Also, these figures show that the sorption of C.I. Basic Orange 21 by the fibers was: Acrilan 36 > Orlon 75 > Acrilan 16.   The order of dyestuff sorption for the Acrilan 36 fiber was consistent with the other data when the effects produced by the *m*-xylene vapor and the tetrachloroethylene vapor were determined. However, the magnitude of dyestuff sorption and the shape of the curve indicate that the data used to plot the *m*-xylene curve are possibly in error.

Figure 8 is a plot of the concentrations of C.I. Basic Red 14 sorbed into the Orlon 75, Acrilan 16, and Acrilan 36 fibers as functions of the dyeing times after exposing one sample in the m-xylene vapor and the second sample in the tetrachloroethylene vapor. From the graphs it was determined that in each case more dyestuff was sorbed by the fiber after being dyed in m-xylene vapor than when dyed in tetrachloroethylene vapor. Also, these figures show that the sorption of C.I. Basic Red 14 by the fibers was: Acrilan 16 > Acrilan 36 > Orlon 75.

Diffusion Coefficients

A system not at equilibrium approaches equilibrium at a rate assumed to be proportional to the departure from equilibrium. Therefore, the
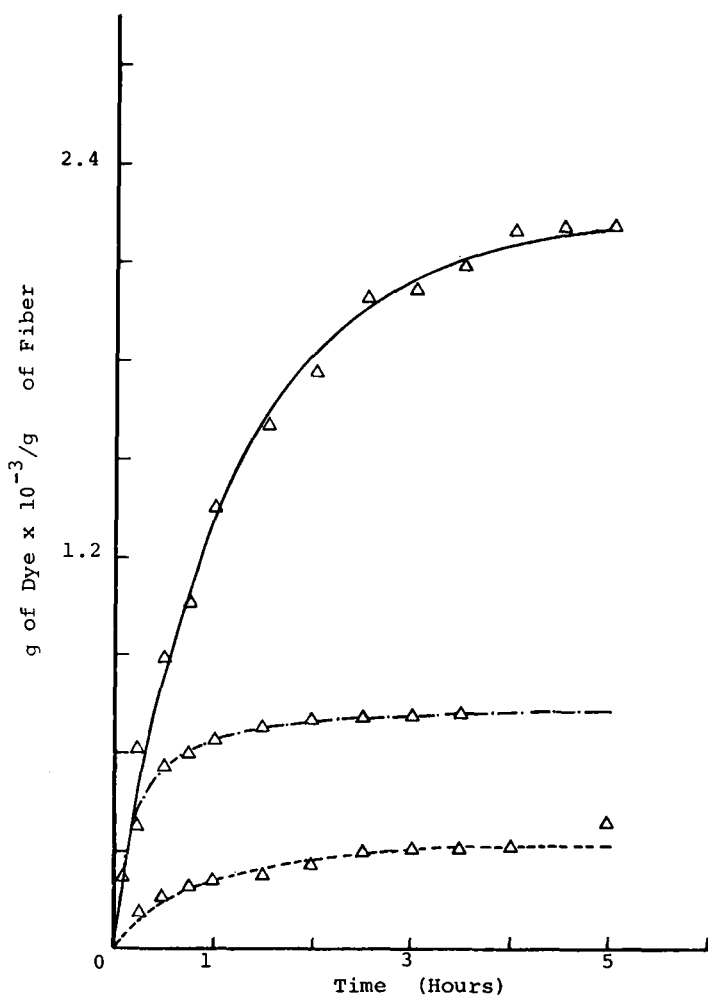

Fig. 3. Aqueous systems, concentrations of C.I. Basic Red 2 sorbed into the fibers. Symbols same as Fig. 2.
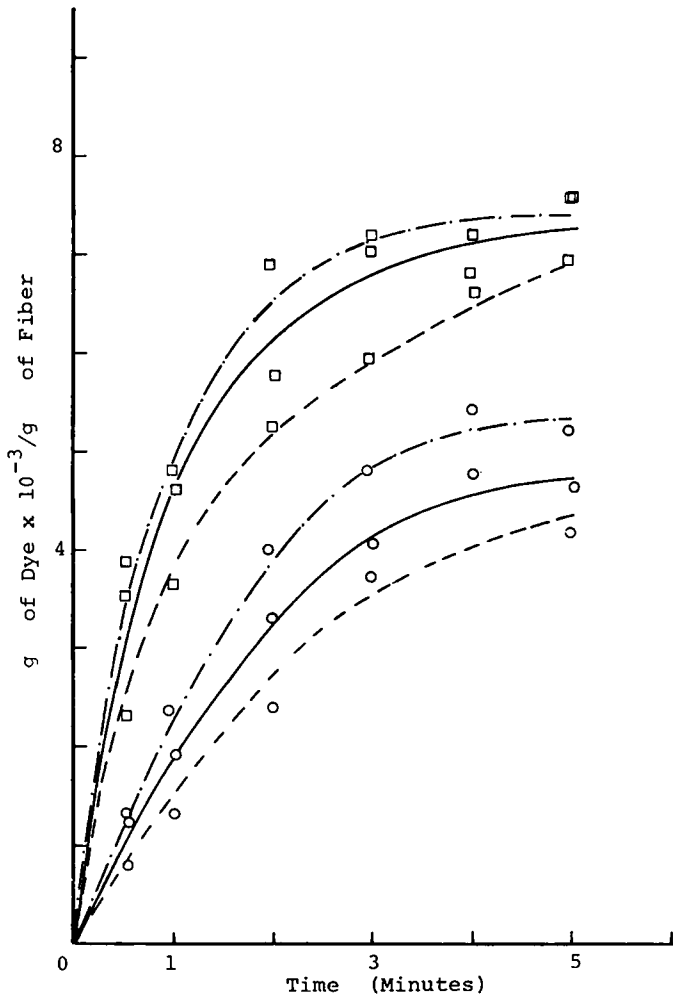
Fig. 4. Series I; concentrations of C.I. Basic Blue 22 sorbed into fibers. Symbols same as Fig. 2.

negative gradient of the chemical potential is the driving force for mass transport, such as diffusion. The rate constant at which a substance diffuses is the diffusion coefficient. For a dyestuff diffusing through a fiber, the diffusion coefficient may depend on the molecular size of the dyestuff, the steric effects within the fiber, the temperature of the system, the charges on both fiber and dyestuff, and the strength and degree of bonding between fiber and dyestuff.

The diffusion coefficients in this work were calculated using Fourier's equation for nonsteady-state thermal conductivity,[55] written in modern notation by Carslaw and Jaeger[56] and for mass transfer by Crank[54,57] and Olofsson.[58] Fourier's equation,

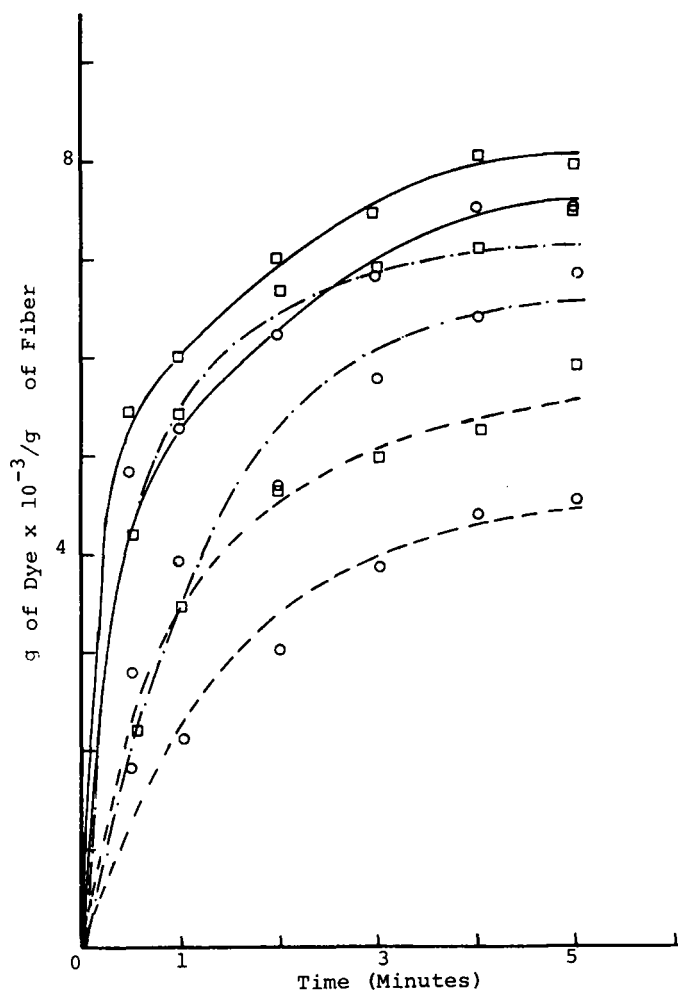$$dC/dt = d/dr(D/r \times \partial C_1/\partial r) \qquad (1)$$

Fig. 5. Series II, concentrations of C.J. Basic Blue 22 sorbed into fibers.   Symbols same as Fig. 2.

assumes the diffusing substance is dissolved in the fiber.   (See List of Symbols used at end of this paper.)   Olofsson modified Fourier's equation by adding a term for sorption.   Olofsson assumes the diffusing substance to be sorbed on sites in the fiber and that desorption from sites is so slight that the sorption process can be considered to be irreversible.

To solve Fourier's equation with and without the site sorption term, the diffusion coefficient must be constant, independent of the radial coordinate, time, and concentration.   Solving the diffusion equations for a homogeneous cylindrical fiber of infinite length assumes that diffusion of dyestuff in the fiber is two-dimensional with diffusion taking place normal to the lengthwise direction of the fiber with no lengthwise diffusion.   Assuming the fiber is homogeneous means that the penetrant concentration varies
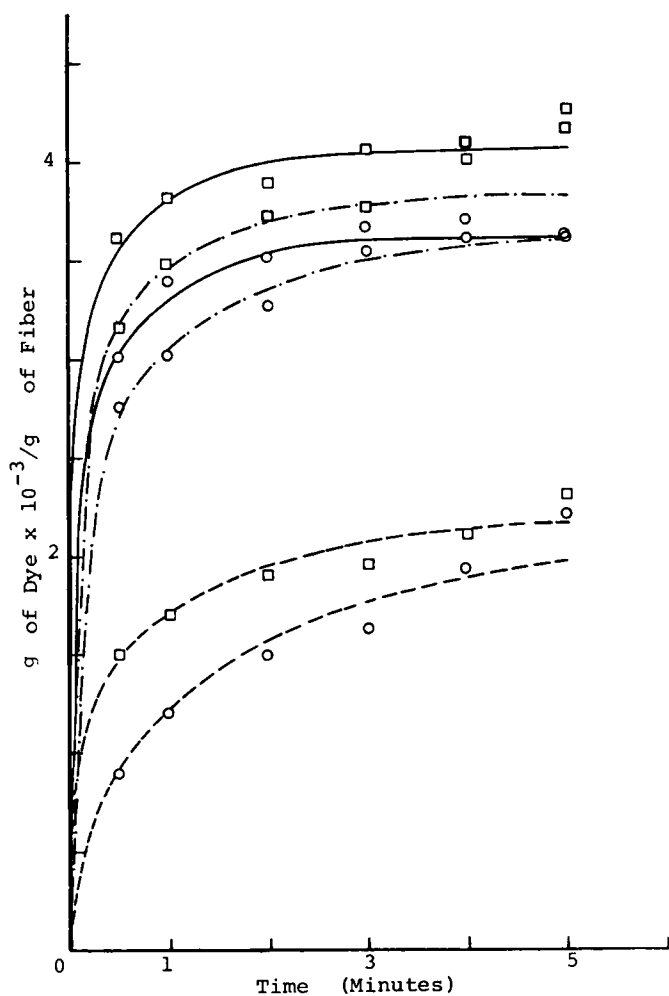
Fig. 6. Series III, concentrations of C.I. Basic Blue 22 sorbed into the fibers. Symbols same as Fig. 2.

smoothly with the radius until the fiber is saturated. A cylindrical fiber shape was assumed in order to solve the diffusion equation. The cross sections of the Acrilan 16 and Acrilan 36 fibers are approximately circular. Therefore, equations for the circular cross sections were used to calculate their diffusion coefficients. The Orlon 75 fiber has a "dog bone" cross section and was imagined to consist of two circular fibers.

Practical dyeing systems have limited dyestuff concentrations which decrease as dyeings take place. Therefore, a well-stirred solution of finite concentration which decreases with time as diffusion proceeds is a good model. Assuming perfect stirring infers that diffusion in the fiber, not in a static liquid layer external to the fiber, determines the rate of diffusion.
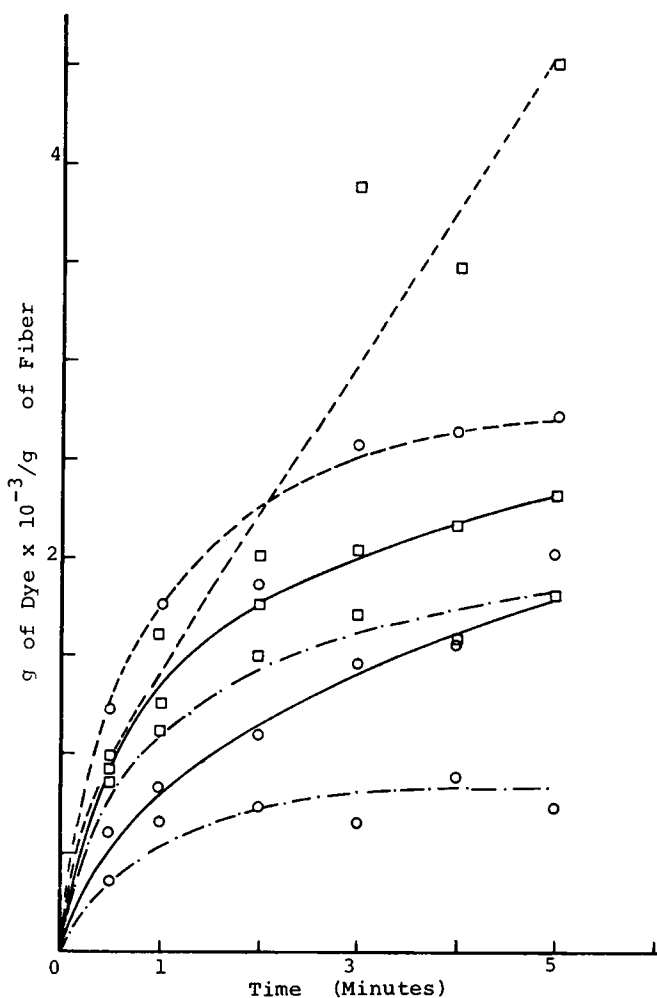
Fig. 7. Series II, concentrations of C.I. Basic Orange 21 sorbed into the fibers.   Symbols
same as Fig. 2.

This condition may not be fulfilled in a solvent system in which the fibers
are padded and dyed in the vapor phase.

The significant difference between the equation which assumes internal
solution and the equation which assumes sorption is the location of the
molecules within the fiber.   Fourier's equation assumes that the dyestuff
remains in an internal solution within the fiber.   The concentration of
dyestuff in the fiber should vary smoothly from the fiber surface to the
center of the fiber.   With this assumption, no well-defined dye boundary
should be observed in the fiber cross section.   Fourier's equation, modified
for sorption by Olofsson, assumes that the dyestuff is irreversibly sorbed
on dye sites within the fiber.   Therefore, a definite dye boundary should
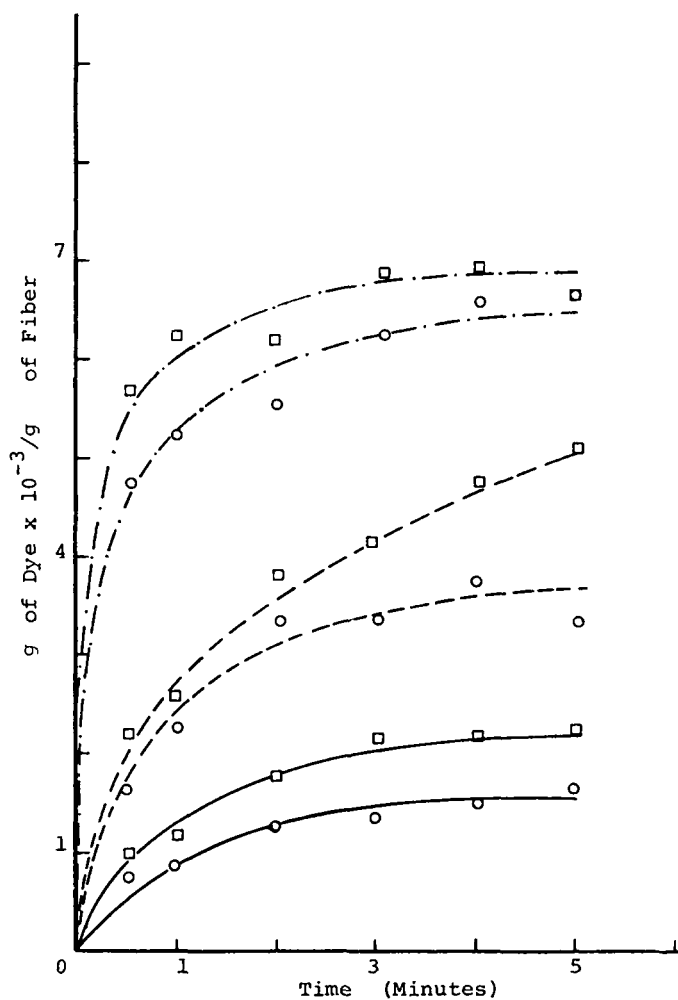be found in the fiber (Fig. 9).

Fib. 8. Series II, concentrations of C.I. Basic Red 14 sorbed into fibers. Symbols, same as Fig. 2.

Fairly well-defined dye boundaries are observed in the fiber cross sections. These are not as sharp as would be expected for an irreversible sorption but certainly are not the smooth variations of concentration, with radius, necessary when assuming dissolution of dyestuffs in the fibers. Apparently these dyeing systems result in an intermediate between the two models.

Equations (2), (3), and (4) are the equations given by Fourier, modified for sorption by Olofsson, for the calculation of diffusion coefficients for a dyestuff in a fiber:

$$\frac{D_1}{r^2} = -\frac{A}{2\pi r^2}\frac{(dC/dt)_{\rho\,=\,1}}{(dC/d\rho)_{\rho\,=\,1}} \tag{2}$$
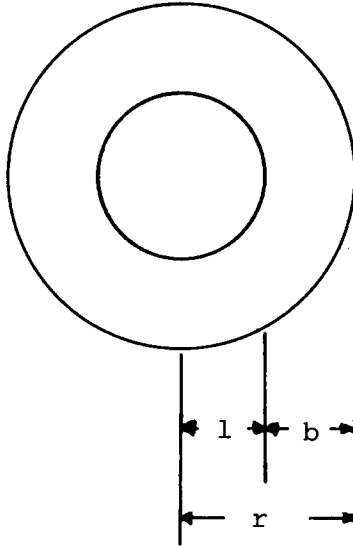
Fig. 9. Depiction of the dye boundary expected assuming irreversible dyestuff sorp-- tion on dye sites: r = radius of the fiber, b = distance the dye boundary advanced toward the center of the fiber and l = undyed radius.

$$\frac{D_2}{r^2} = - S_m \frac{(d\lambda/dt)}{(dC/d\rho)_{\rho\ =\ 1}} \tag{3}$$

$$D_0 = (D_1 + D_2)/2 \tag{4}$$

The term $A/2\pi r^2$ is difficult to estimate for a pad system. The value of the term was taken to be

$$A/2\pi r^2 = [(C_0 \times 100)/(9 \times 10^5)/\text{denier}]/2\pi r^2 \tag{5}$$

where: $C_0 \times 100$ is the amount of dye solution on 1 g of fiber.

This calculation is based on the fact that the dye solution was made using 1% dyestuff and that the gram of fiber picked up C_0 grams of dye- stuff; therefore, the fiber sorbed $C_0 \times 100$ ml of dye solution. Equation (2) requires the area of solution; therefore, the volume of dye solution per gram of fiber was divided by the length of 1 g of fiber, calculated by dividing 9×10^5 by the measured denier of the fiber.

The concentration of dye sites used for the calculation of S_m in the Olofsson equation was assumed to be the number of sulfuric acid groups provided by the fiber manufacturer.

Equation (6a) is the solution of Fourier's equation for a right circular cylinder of infinite length. Diffusion coefficients for dyestuffs in fibers are calculated using eq. (6a):

$$C_t/C_\infty = 1 - \frac{4f(1 + f)}{4 + 4f + f^2q_n^2} e^{\frac{q_n^2 Dt}{r^2}} + \tag{6a}$$

$$0 = \alpha q_n J_0(q_n) + 2J_1(q_n) \tag{6b}$$

where $\alpha = A/\pi r^2 K$, and K = partition factor.

Calculations of the diffusion coefficients based on Fourier's equation are simplified by using a table[59] which assumes internal solution and contains the values of Dt/r^2 for appropriate values of the equilibrium per cent exhaustion and C_t/C_∞. This table was determined by assuming values for Dt/r^2 at various equilibrium exhaustions to calculate the values of C_t/C_∞. The values of D_t/r^2, as functions of C_t/C_∞ at various equilibrium exhaustions, have been plotted in Figure 10. These curves show that when the values of C_t/C_∞ are less than 0.1 and above 0.9, the diffusion coefficients are not accurate because of the drastic changes in the slopes of the curves.
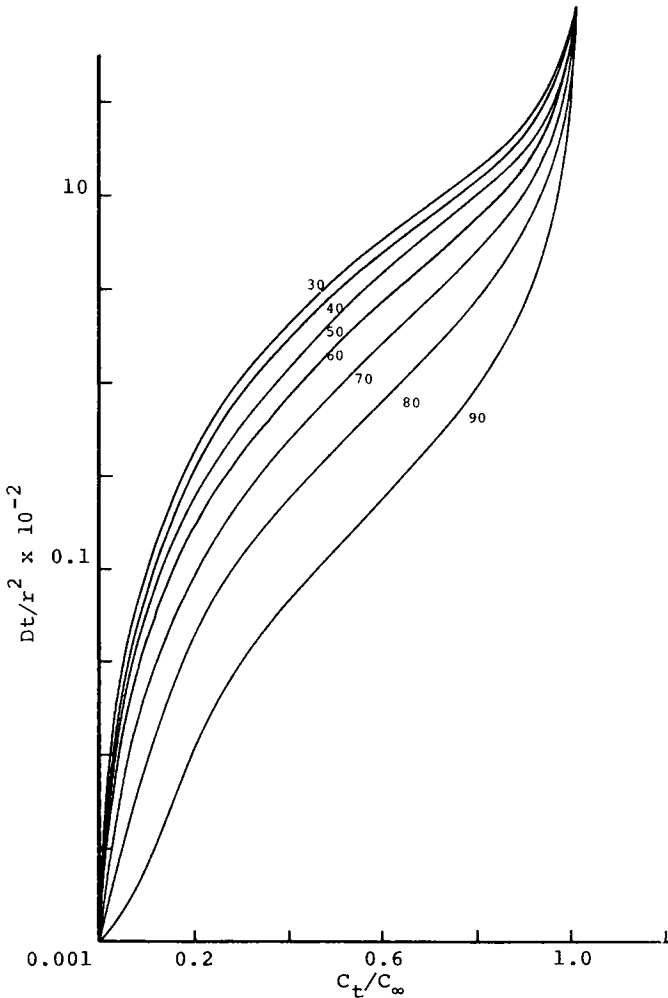

Fig. 10. Plot of Dt/r^2 for values of the equilibrium per cent dye bath exhaustion as a function of C_t/C_∞ for diffusion into an infinite cylinder from a finite dye bath.

In the solvent dye system, the dye solution on the fiber surface altered during the vapor phase dyeing, causing the dyestuff activity in solution to change; thus, the value of C_∞ varied during dyeing. C_∞ was assumed to be the dyestuff concentration sorbed by the fiber when the slope of the rate of dyeing curve was zero.

Discussion of Dye Sorption Curves and the Diffusion Coefficients

The diffusion coefficients calculated from eqs. (4) and (6a) were plotted as functions of the fractional concentration of dyestuff sorbed into the fiber (C_t/C_∞) in order to obtain representative diffusion coefficients. The results are shown in Table VI as a range of diffusion coefficients for a given range of C_t/C_∞ values. The information obtained from a comparison of the data in Table VI should give a better understanding of the solvent system. The comparison of the diffusion coefficients, D (Fourier's equation) and D_0 (Fourier's equation modified for irreversible site sorption by Olofsson), leads to the information given below:

1. With the exception of two dye trials, D_0 was always larger than D.

2. D_0 was generally larger for dyeings in the m-xylene vapor than in the tetrachloroethylene vapor; a similar trend was not found for D.

3. D_0 tended to decrease with increasing time, while D tended to increase with increasing time.

4. D and D_0 were 10 to 100 times larger for solvent system dyeings than those in the aqueous system.

5. D_0 and D increased with increasing THTDO concentration.

6. The orders of magnitude of D_0 and D for the various dyestuffs showed no correlation.

7. The percentage change of D_0, within the given range of C_t/C_∞, was generally less than the percentage change of D within the same range.

The diffusion coefficients, calculated using Fourier's equation modified for irreversible sorption on sites by Olofsson, decreased with increasing time for each dyeing system. This is similar to the results reported by Olofsson for his work[58] on periodate combination with cellulose fibers. The diffusion coefficients calculated by use of Fourier's equation assumes no sorption of dyestuff on dye sites, hence, a homogeneous solution of dyestuff in the fiber generally increasing with increasing time. This variation of the diffusion coefficients with time probably indicates that an equation assuming reversible dyestuff sorption on dye sites might give diffusion coefficients invariant with time (and presumably radius and concentration as well).

From Figures 4–6 and Table VI it was determined that the concentration of C.I. Basic Blue 22 sorbed by the acrylic fiber after being dyed for 5 min decreased, while the diffusion coefficient increased with increasing concentration of THTDO in the pad bath. From these results it was assumed that the THTDO not only plasticizes the acrylic fiber, but also has

a possibility of occupying dye sites within the fiber, and this effect should increase with increasing concentration of THTDO sorbed.

The differences in the concentrations of dyestuff sorbed by the acrylic fibers in the aqueous system, Figure 3, was accounted for by the variation in concentration of dye sites in the fiber, Table III.   The presence of the phenylamine hydrochloride groups, in close proximity to the sulfuric acid dye sites, caused the Acrilan 36 fiber to sorb less dyestuff at equilibrium than would be predicted by considering only the concentration of the sulfuric acid groups in the fiber.   Even though the Orlon 75 fiber was dyed with twice as much dyestuff as the other fibers, the larger sorption of dyestuff caused by the larger concentration of dye sites can be seen for the Orlon 75 fiber.

With regard to the magnitude of dyestuff sorption, the same fiber order occurred in the series II solvent and in the aqueous dyeing system for C.I. Basic Blue 22 and C.I. Basic Red 2, but different orders were found for C.I. Basic Red 14 and C.I. Basic Orange 21.   These order changes indicated that any attempts to correlate dyestuff sorption with dyestuff structure would be difficult and beyond the scope of this work.

From Figures 2 and 4–8, it was shown that the tetrachloroethylene vapor system did not increase dyestuff sorption as greatly as the m-xylene vapor system.   The probable factors influencing the lesser dyestuff sorption were the differences in the boiling points and specific heats of the organic vapors.   The 18°C increase in the boiling point and the 100% increase in the specific heat of m-xylene, as compared to tetrachloroethylene, should produce conditions more favorable for dyestuff sorption because of higher temperature and more heat available in the solvent.

The purpose of the DEA and DBSA in the series III solvent system was to provide a nonionic, organic soluble surfactant in formic acid medium which could be compared to the series I solvent system.   In this manner it was believed that the concentration effects of the cosolvent could be observed and, while the acidic effects were held constant, the emulsifying properties of the surfactant could be estimated.   Dye trials indicated that the concentration effect of the THTDO was the overriding factor, and no discernible contribution was made by either the acid or surfactant.

It was originally assumed that reduced dyestuff sorption was caused by the 50% increase in the concentration of THTDO in series III when compared to series II, rather than by the 1% addition of surfactant.   Research later proved the assumption that an optimum concentration of THTDO exists (approximately 17% by volume) and causes maximum dyestuff sorption.   Increasing the concentration of THTDO in the pad bath caused the per cent of dyestuff sorbed by the fiber to decrease, because the increased THTDO volume dripped off carrying dyestuff with it.   This was attributed to competition between the dyestuff molecules and THTDO molecules for dye sites in the fiber or competition between the dye sites in the fiber and that THTDO molecules for the dyestuff molecules.   Therefore any decrease in dyestuff sorbed by the fiber was attributed to the in-

TABLE VI

Diffusion Coefficients Calculated Using Fourier's Equation (D) and the Diffusion Coefficients Calculated Using Fourier's Equation Modified for Irreversible Dyestuff Sorption by Olofsson (D_0)

System	Fiber	Dyestuff C.I. Basic	Range of C_t/C_∞	Range of $D \times 10^{-10}$	Range of $D_0 \times 10^{-10}$
Aqueous	Orlon 75	Red 2	0.19–0.58	0.00117–0.00583	5.75–4.574
	Acrilan 36		0.27–0.42	0.075–0.097	—
	Acrilan 16		0.58–0.94	0.171–0.211	2.73–1.75
		Meta-Xylene Vapor			
Series II	Orlon 75		0.65–0.93	0.67–1.07	158.0–132.8
	Acrilan 36		0.60–0.90	9.51–11.08	9.0–6.05
	Acrilan 16		0.48–0.77	0.42–0.43	8.0–4.8
Series I	Orlon 75	Blue 22	0.39–0.86	0.019–0.474	12.5–5.49
	Acrilan 16		0.44–0.88	0.14–1.0	4.03–1.845
	Acrilan 36		0.31–0.85	0.37–1.28	13.88–12.63
Series II	Orlon 75		0.66–0.86	0.456–0.454	18.1–14.2
	Acrilan 36		0.22–0.80	0.04–2.01	8.78–8.75
	Acrilan 16		0.59–0.77	0.4–0.67	
Series III	Orlon 75		0.88–0.95	2.13–2.62	—
	Acrilan 36		0.66–0.91	3.63–5.22	—
	Acrilan 16		0.76–0.92	1.25–3.05	
Series II	Orlon 75	Red 14	0.39–0.92	0.76–2.68	7.85–3.275
	Acrilan 36		0.39–0.86	3.13–7.52	5.185–3.86
	Acrilan 16		0.79–0.95	1.27–2.42	24.0–8.675
Series II	Orlon 75	Orange 21	0.37–0.82	0.147–0.357	5.11–2.24
	Acrilan 36		0.62–0.90	1.08–3.25	9.13–3.445
	Acrilan 16		0.36–0.92	1.22–4.95	7.08–3.035

			Tetrachloroethylene Vapor		
Series II	Orlon 75	Red 2	0.66–0.96	1.19–1.4	—
	Acrilan 36		0.56–0.89	8.38–10.66	160.45–126.8
	Acrilan 16		0.53–0.92	1.53–1.87	11.03–3.95
Series I	Orlon 75	Blue 22	0.19–0.69	0.017–0.132	7.0–5.04
	Acrilan 16		0.22–0.89	0.02–0.96	9.2–3.5
	Acrilan 36		0.16–0.93	0.22–2.52	0.795–0.403
Series II	Orlon 75		0.57–0.82	0.332–0.476	9.47–6.75
	Acrilan 36		0.27–0.73	0.70–2.8	12.7–10.1
	Acrilan 16		0.31–0.54	0.16–0.389	14.8–12.3
Series III	Orlon 75	Blue 22	0.88	3.42	—
	Acrilan 36		0.43–0.93	1.31–3.98	—
	Acrilan 16		0.77–0.89	3.3–4.47	—
Series II	Orlon 75	Red 14	0.34–0.92	1.03–3.91	5.65–2.105
	Acrilan 36		0.47–0.92	2.62–6.03	9.835–4.69
	Acrilan 16		0.71–0.91	1.80–2.56	11.095–9.94
Series II	Orlon 75	Orange 21	0.41–0.81	0.197–0.462	4.28–1.915
	Acrilan 36		—	—	—
	Acrilan 16		0.33–0.57	2.51–4.57	4.78–3.81

creased concentration of THTDO and not the minor (1%) concentration of surfactant. Other experiments proved that selected surfactants increased dye sorption. It is inconceivable that DBSA competed for dye sites because DBSA is anionic and thus could not be in competition with anions in the fiber. On the other hand, if the DBSA–DEA remained in combination, then a nonionic condition was present. In either case, the dye situation must be one of complete neutrality or of similar charges repelling each other. Any correlations made between the dye systems for one dyestuff are expected to hold true for all dyestuffs.

Infrared Spectral Analysis

The purpose of obtaining the infrared spectra was to determine the presence of THTDO in the acrylic fibers after processing in the organic solvent systems. Infrared spectra were obtained for the following:

1. Acrilan 16, Acrilan 36, and Orlon 75 fibers, untreated.
2. Acrilan 16, Acrilan 36, and Orlon 75 fibers, padded using a series I solvent solution, not containing dyestuff, and processed as though dyed by exposing one fabric sample to the m-xylene vapor and another sample to the tetrachloroethylene vapor.
3. Acrilan 16, Acrilan 36, and Orlon 75 fibers, padded using a series II solvent solution not containing dyestuff and processed as though dyed by exposing one sample of the fabric to the m-xylene vapor and the second sample to the tetrachloroethylene vapor.
4. Acrilan 16 fibers padded using series II solvent solutions containing 1% C.I. Basic Blue 22 and C.I. Basic Red 14 and processed as though dyed by exposing one sample of the fabric to the m-xylene vapor and the second sample to the tetrachloroethylene vapor.
5. Acrilan 16, Acrilan 36, and Orlon 75 fibers padded using a series III solvent solution not containing dyestuff and processed as though dyed by exposing one sample of the fabric to the m-xylene vapor and the second sample to the tetrachloroethylene vapor.
6. Pure tetrahydrothiophene 1,1-dioxide (THTDO).
7. Pure 2-phenoxy-1-ethanol (EPH).

Each fiber treated in the organic solvent systems was dyed in the appropriate organic vapor for 5 min and was then washed in three solution of boiling acetone.

Qualitative results of the analysis of the infrared spectra of the treated acrylic fibers showed that THTDO was sorbed by Orlon 75 from the three series when exposed to either m-xylene or tetrachloroethylene. On the other hand, Acrilan 16 and Acrilan 36 sorbed THTDO only when exposed to m-xylene vapor, but there was no indication that any was sorbed when suspended in the tetrachloroethylene vapor.

A possible explanation for the fact that the Acrilan 16 and Acrilan 36 fibers contained THTDO after dyeing in the m-xylene vapor may be a physical effect and was probably due to accessibility. The m-xylene

vapor, at a temperature of 139.9°C, provided more energy to the dyeing system than did the tetrachloroethylene vapor, at a temperature of 121.0°C. The m-xylene probably softened the fiber more than did the tetrachloroethylene and thus provided for better penetration of the THTDO into the fiber. The energy provided by the tetrachloroethylene vapor may have been insufficient to allow a detectable concentration of THTDO to penetrate into the fiber.

In dimethylformamide, the Orlon 75 fibers dissolved slightly faster than the Acrilan 16 fibers and much faster than the Acrilan 36 fibers. Therefore, the energy required for the penetration of the THTDO into the Orlon 75 fiber is probably less than for the other fibers, and the energy provided by both vapors could be sufficient to allow detectable concentrations of THTDO to penetrate into the Orlon 75 fiber.

Solvent Dyeing Mechanism

A definite mechanism cannot be proposed from these experimental data; however, a clearer understanding of the solvent systems may be obtained.

Supporting evidence for the free volume theory was given by Rosenbaum.[59] He showed that the diffusion coefficient of a dyestuff in a fiber increased with increasing concentration of dye sites in the fiber. Rosenbaum's data can be explained by the free volume theory but is opposite to that expected by the static pore theory.

An experiment, in this work, was designed to test the validity of the free volume theory. In this experiment, the fabric was padded with an aqueous solution of dyestuff and then exposed to tetrachloroethylene vapor for 5 min. According to the free volume theory, the dyestuff was expected to be attracted to the fiber surface and diffuse into the fiber at temperatures above the glass transition temperature of the fiber. The water was driven off at 100°C and above this temperature the dyestuff was expected to continue to diffuse into the fiber because the fiber was above its dry glass transition temperature. Microscopic observation of the fiber cross section indicated that dyestuff migration had not occurred. It was assumed from this that the water molecules in the aqueous system, and therefore the THTDO in the solvent systems, have much greater importance than was assumed by Rosenbaum.

The results obtained in this work indicate that the solvent dyeing system can be explained using the static pore theory. The reasons for this are given below:

1. There is a definite need for a solvent to transport the dyestuff through the fiber.

2. The different orders of magnitude of dyestuff sorption by the fibers in the various dyeing systems indicate that morphologic changes occur in the polymer during dyeing.

Other results obtained in this work can be explained by both theories. These are: (1) increased diffusion coefficient of the dyestuff in the fiber with

increased THTDO concentration in the pad bath; (2) decreased concentration of dyestuff sorbed by the fiber with increased concentration of THTDO in the pad bath; (3) increased dyestuff sorption by the fiber in the m-xylene vapor when compared to the tetrachloroethylene vapor; and (4) increased rate of dyeing in the solvent systems when compared to the aqueous system.

CONCLUSIONS

1. Greater concentrations of dyestuffs were sorbed into the three different acrylic fibers (Orlon 75, Acrilan 36, and Acrilan 16) after 5 min of dyeing time in the m-xylene vapor system (bp 139.0°C) than in the tetrachloroethylene vapor system (bp 121.0°C).

2. Successive increases of the THTDO concentration in the pad bath formulation initially caused a general increase in the concentration of dyestuff sorbed, which was followed by decreased sorption. A critical cosolvent concentration should exist because, with increasing THTDO concentrations, the order of dyestuff sorbed became more nearly that of available dye-site distribution. Further, the apparent diffusion coefficient of the dyestuff in the fiber was increased with increased THTDO.

3. The addition of dodecylbenzenesulfonic acid and formic acid to the pad bath did not seem to produce an appreciable effect on either the sorption or diffusion of dyestuffs into the fiber. The increased THTDO content apparently obliterates any effect caused by the dodecylbenzenesulfonic acid.

4. The diffusion coefficients calculated by using Fourier's equation modified for irreversible sorption on sites varied less with time than the diffusion coefficients calculated by using Fourier's equation without the sorption term. Therefore, Fourier's equation, assuming site sorption, better describes the dyeing situation.

5. The diffusion coefficients calculated by using both diffusion equations were 10 to 100 times larger for the solvent dyeing systems than for the aqueous dyeing systems.

6. Rates of dyeing in the solvent systems were 30 to 60 times less than the dyeing times in the corresponding aqueous systems.

7. The solvent dyeing system is probably best explained by the static pore theory.

List of Symbols Used in this Work

A area of the dye solution
b dyed fiber radius
C_1 concentration
C_0 concentration of dyestuff in solution at time 0
C_s concentration of dyestuff in solution at time t
C_t concentration of dyestuff in the fiber at time t
C_∞ concentration of dyestuff in the fiber at equilibrium
C C_s/C_0

D diffusion coefficient calculated using Fourier's equation

D_1 diffusion coefficient calculated using Olofsson's equation pertaining to fiber parameters

D_2 diffusion coefficient calculated using Olofsson's equation pertaining to dye sites

D_0 diffusion coefficient calculated using Fourier's equation modified by Olofsson

l undyed fiber radius

r radius of the fiber

S_m concentration of dye sites/concentration of dyestuff in solution at time 0

t dyeing time

b dyed radius

J Bessel function

λ l/r

ρ b/r

$A/2\pi r^2$ area of dye bath/area of fiber

f $(100 - E)/E$

E equilibrium per cent exhaustion of dye bath

q_n successive, positive, nonzero roots of a linear combination of the zeroth and first-order Bessel functions with f as a parameter for the first-order equation

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