

INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.
- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.
- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17"x 23" black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6"x 9" black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.



8710657

Etters, James Nolan

**AN EXPERIMENTAL STUDY OF COLOR YIELD PHENOMENOLOGY IN
THERMAL FIXATION DYEING OF A POLYETHYLENE
TEREPHTHALATE/COTTON FIBER BLEND WITH DISPERSE DYE**

The University of North Carolina at Greensboro

PH.D. 1986

**University
Microfilms
International** 300 N. Zeeb Road, Ann Arbor, MI 48106



AN EXPERIMENTAL STUDY OF COLOR YIELD PHENOMENOLOGY
IN THERMAL FIXATION DYEING OF A POLYETHYLENE
TEREPHTHALATE/COTTON FIBER BLEND
WITH DISPERSE DYE.

by

James Nolan Etters

A Dissertation Submitted to
the Faculty of the Graduate School at
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Greensboro
1986

Approved by


Dissertation Adviser

APPROVAL PAGE

This dissertation has been approved by the following committee of the Faculty of the Graduate School at the University of North Carolina at Greensboro.

Dissertation Adviser Merwin S. Howard

Committee Members Bellie G. Oakland

Arthur Urbank

George Hermans

David G. Bell

3/17/86
Date of Acceptance by Committee

3/17/86
Date of Final Oral Examination

ETTERS, JAMES NOLAN, Ph.D. An Experimental Study of Color Yield Phenomenology in Thermal Fixation Dyeing of a Polyethylene Terephthalate/Cotton Fiber Blend with Disperse Dye. (1986) Directed by: Dr. Melvin D. Hurwitz.

The objective of this research was to develop a mathematical expression for the depth of color obtained on polyester fiber in a 50/50 blend with cotton fiber as a function of both fixed dye content and location of fixed dye in the fabric cross-section. Fixation and reflectance measurements were made on laboratory dyeings in which both dye content and location of dye in the fabric cross-section were carefully controlled. The control was achieved through the use of varying dye and antimigrant concentrations in the pad baths, with all of the other experimental variables held constant.

The experimental methodology which was used resulted in the generation of three primary forms of data: particulate migration, fixation, and reflectance values. Statistical analysis of the data revealed that the contribution to color depth of both uniformly distributed and migrated fixed dye can be quantified- but not derived- independently.

Unification of the two independent effects described above resulted in the construction of a mathematical expression of the form:

$$KN = a_1(C_{fx}) + a_2(M_{fx})$$

where KN is the conventional Kubelka-Munk (K/S) value which is associated with both the uniformly distributed fixed dye concentration in the fabric cross-section (C_{fx}) and the concentration of migrated dye fixed in the fabric surface (M_{fx}). The constants a_1 and a_2 are the reflectance absorptivity coefficients associated with C_{fx} and M_{fx} respectively.

Tests of the mathematical model with C.I. Disperse Blue 165, Red 60, and Brown 1 on a 50/50 polyester/cotton fabric gave high values of R^2 in regression analysis of measured values of K/S vs. measured values of C_{fx} and in regression analysis of estimated values of K/S vs. estimated values of M_{fx} .

Possible uses of the model in attempts to achieve minimum dyeing costs while maintaining satisfactory uniformity of shade are discussed. Also discussed is the possible use of the model in the development of new textile products.

ACKNOWLEDGMENTS

The author gratefully acknowledges the guidance and support of his dissertation committee chairman, Dr. Melvin D. Hurwitz. Appreciation is expressed to the members of the advisory committee, Dr. Harvey B. Herman, Dr. David G. Herr, Dr. Billie G. Oakland, and Dr. Arthur R. Urbanik, for their supportive assistance.

Appreciation is expressed to Dr. Donald L. Wright of Dan River, Inc. for his help in performing analysis of the dyes and chemicals used in the present study, and to Dr. Arthur R. Urbanik of Dan River Inc. for his translating the numerous papers from the German.

The generosity of Dan River, Inc. in providing the author with laboratory space, equipment, chemicals, and fabric is gratefully acknowledged.

TABLE OF CONTENTS

	Page
APPROVAL PAGE	ii
ACKNOWLEDGMENTS	iii
LIST OF APPENDICES	vi
LIST OF TABLES	vii
LIST OF FIGURES	viii
 CHAPTER	
I. INTRODUCTION	1
Objective	7
II. REVIEW OF LITERATURE	8
Background	8
Polyester Dyeing	10
Batch Processes	10
Continous Processes	11
Fixation Mechanisms	13
Vapor Fixation	13
Non-vapor Fixation	16
Kinetics	18
Empirical Equations	18
Diffusion Equations	20
Particulate Migration	24
Causes	24
Solutions to the Problem	27
Light Reflectance	29
Kubelka-Munk Analysis	29
Color Yield	33
III. EXPERIMENTAL METHODOLOGY	36
Materials	36
Fabric	36
Dyes	37
Dimethyl Formamide	37
Sodium Alginate	38
Wetting Agent	38

	Page
III. EXPERIMENTAL METHODOLOGY (Continued)	
Acids	38
Eluents	38
Equipment	39
Pad Mangle	39
Thermal Fixation Oven	39
Colorimeter	39
Spectrophotometer	39
Chromatography Apparatus	39
Preliminary Experiments	40
Thin-Layer Chromatography	40
Activity of Commercial Dye	40
Colorimeter Performance Test	41
DMF Testing	41
Wavelength of Maximum Absorbance	41
Characteristic Spectra	41
Absorptivity Determination	44
Pickup Reproducibility	49
Drainage Effect	49
Particulate Migration Chamber	51
Indirect vs. Direct	
Fixation Measurements	53
Main Experiments	55
Preparation of Pad Baths	55
Application	55
Inducement and Measurement of	
Particulate Migration	56
Thermal Fixation	57
Measurement of Dye Fixation	57
Reflectance Measurements	58
IV. RESULTS AND ANALYSES	59
Particulate Migration	59
Fixation	66
Reflectance	68
Analyses	70
V. CONCLUSIONS	78
Mathematical Expression	78
Examination of Coefficients	79
Possible Uses for Model	80
Areas for Future Research	82
BIBLIOGRAPHY	83

LIST OF APPENDICES

	Page
APPENDIX A. DYE SPECTRA DATA	91
APPENDIX B. TEST OF EFFECT OF MOISTENED PAPER ON SATURATION OF WATCH GLASS CHAMBER	92
APPENDIX C. TEST OF EFFECT OF SATURATED CHAMBER ON PARTICULATE MIGRATION	93
APPENDIX D. TEST OF DIFFERENCES BETWEEN DIRECT AND INDIRECT FIXATION MEASUREMENTS	94
APPENDIX E. REGRESSION ANALYSIS: KC vs C_{fx} FOR BLUE 165	95
APPENDIX F. REGRESSION ANALYSIS: KC vs C_{fx} FOR RED 60	96
APPENDIX G. REGRESSION ANALYSIS: KC vs C_{fx} FOR BROWN 1	97
APPENDIX H. REGRESSION ANALYSIS: KM vs M_{fx} FOR BLUE 165	98
APPENDIX I. REGRESSION ANALYSIS: KM vs M_{fx} FOR RED 60	99
APPENDIX J. REGRESSION ANALYSIS: KM vs M_{fx} FOR BROWN 1	100

LIST OF TABLES

	Page
TABLE	
I. Concentration/Absorbance data for Resolin Blue BBLs pdr. in DMF	46
II. Concentration/Absorbance data for Terasil Red FB pdr. in DMF	47
III. Concentration/Absorbance data for Foron Brown S-3R pdr. in DMF	48
IV. Migration, Fixation, and Reflectance Data Resolin Blue BBLs	60
V. Migration, Fixation, and Reflectance Data Terasil Red FB	61
VI. Migration, Fixation, and Reflectance Data Foron Brown S-3R	62
VII. Percent Migration and Fixation of Applied Particulate Dye Resolin Blue BBLs	63
VIII. Percent Migration and Fixation of Applied Particulate Dye Terasil Red FB	64
IX. Percent Migration and Fixation of Applied Particulate Dye Foron Brown S-3R	65
X. Comparison of Coefficients	79

LIST OF FIGURES

FIGURE		Page
1.	Worldwide Production of Polyester Fiber in Metric Tons	1
2.	Schematic Diagram of the "Thermosol" Process	3
3.	(A)- Fabric Section Removed for Extraction of Dye from Area Covered by Watch glass. (B)- Fabric Section Removed for Extrac- tion of Dye from Area not Subjected to Horizontal Migration	25
4.	Model of Kubelka-Munk Analysis	30
5.	Spectrum and Structure of Disperse Blue 165	42
6.	Spectrum and Structure of Disperse Red 60	43
7.	Spectrum and Structure of Disperse Brown 1	43
8.	Experimental Arrangement of Particulate Migration Test Chamber	51
9.	Absorptivity Coefficient of Uniformly Distributed Blue 165	72
10.	Absorptivity Coefficient of Uniformly Distributed Red 60	72
11.	Absorptivity Coefficient of Uniformly Distributed Brown 1.	73
12.	Absorptivity Coefficient of Migrated Blue 165	76
13.	Absorptivity Coefficient of Migrated Red 60	76

LIST OF FIGURES (Continued)

FIGURE

14. Absorptivity Coefficient of Migrated Brown 1	77
---	----

CHAPTER I
INTRODUCTION

Worldwide production of synthetic fibers increased from 4.81 million metric tons in 1970 to 12.03 million metric tons in 1984 ("Chemiefaser-Weltproduktion," 1985). During the same period, the percent of the total synthetic fiber production due to polyethylene terephthalate fiber increased from thirty-four to forty-eight percent ("Chemiefaser-Weltproduktion," 1985).

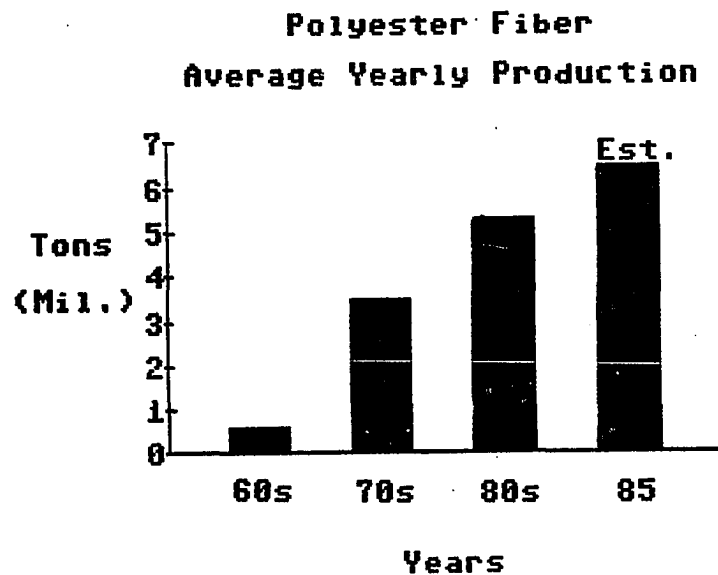


Figure 1. Worldwide production of polyester fiber in metric tons (Caldo, 1985).

As indicated in Figure 1., worldwide consumption of polyethylene terephthalate (polyester) fiber is expected to increase to nearly 6.5 million metric tons, of which North Americans will consume the greatest share (Somm & Buser, 1984). Indeed, since its original development by Whinfield and Dickson, polyester fiber has had a remarkable growth (Moncrieff, 1957).

Much of the growth of polyester fiber has been directly associated with the popularity of permanent press finishes which were introduced in the middle 1960's. Since these finishes, which greatly reduce ironing chores, are applied to fabrics made from blends of polyester and cotton, it is no coincidence that there has been a strong correlation between the growth of such finishes and the growth of polyester fiber. Since 1960, when only about one million linear yards of polyester/cotton fabric were produced in the United States, there has been an increase in annual production to about 2500-3000 million linear yards (Gibson, 1979). It can be argued, however, that such growth in permanent press finished polyester/cotton fabric would not have been possible if an economical, continuous dyeing process for use on such blends had not been readily available.

The "Thermosol" process— the continuous dyeing process for polyester fiber or polyester/cotton blends developed by Joseph Gibson in 1947— now is used for dyeing approximately one billion pounds of polyester/cotton blend fabric in the United States annually (Gibson, 1979). Such a high level of production would be difficult to achieve economically by batch or discontinuous dyeing processes, which normally are used for small poundage of yarn or small yardage of fabric. On the other hand, as much as 100 yards of fabric per minute can be dyed on a single "Thermosol" range, and there are now approximately 200 such ranges worldwide— with perhaps half of these ranges located in the U.S.A. (Gibson, 1979).

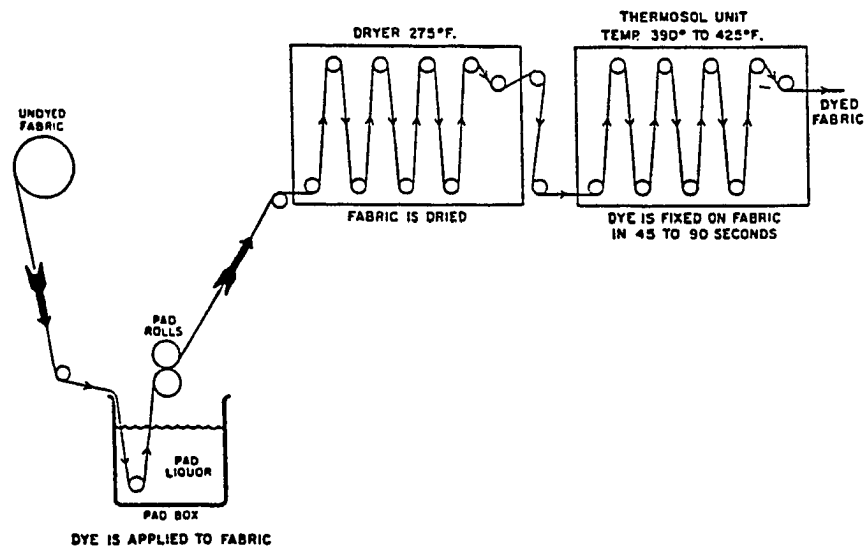


Figure 2. Schematic diagram of the "Thermosol" process. (Gibson, 1979, p. 242)

A schematic diagram (after Gibson, 1979) of the "Thermosol" process, as the process actually is configured and used by the textile industry, is given in Figure 2. As shown in Figure 2., the "Thermosol" process appears to be technologically simple, consisting of:

1. impregnating the fabric with a dispersion of dye,
2. drying the impregnated fabric,
3. heating the dried fabric to about 410°F (210°C) for about 60 seconds, and
4. washing and drying the dyed fabric (not shown).

Simplicity is not, however, the only reason the "Thermosol" process has become widely used. According to Gibson (1979), there are many other reasons for the popularity of the process:

1. Since the process is continuous, long yardage can be dyed much more economically than is possible by the use of batch processes.
2. Dyestuff is used more efficiently.
3. No chemical carrier is needed to render the fiber receptive to dye as is the case in batch dyeing.
4. Open width processing of the fabric eliminates creases and rope marks.
5. Heat setting does not influence the dyeability of the fabric.
6. Energy consumption during dyeing is low.

The leading methods for dyeing apparel and home fabrics in the U.S.A. include the "Thermosol," pad steam, beck, jet, beam, and package processes. But, of all of these various methods, the "Thermosol" process has achieved preeminence and is likely to maintain this state for some time (Hochberg, cited in Gibson, 1979). Indeed, both the scientific and the technological interest which have been sparked by the "Thermosol" process are manifest in the numerous publications cited in Chapter II of this work. Both detailed technological and comprehensive theoretical studies have been made in efforts to improve the useage of the process and in attempts to understand the mechanisms of dye fixation. However, in all of these published studies, there has been no comprehensive investigation of color yield phenomenology associated with the thermal fixation process. In spite of the lack of relevant, published findings, it is widely understood in the industry that color yield- the depth of shade that is obtained on a given substrate with a given amount of applied particulate disperse dye- tends to be a function of both the overall fixed dye content of the substrate and the location of fixed dye in the cross-section of the substrate.

Recognizing the importance of the need for research in the area of color yield phenomenology involving continuously dyed fabric, the Committee on Technical

Subjects of the American Association of Textile Chemists and Colorists (1985) suggested in 1978 that the area was one that should be strongly considered for exploration.

According to the Committee:

The depth of color obtained on textile materials which are dyed by continuous processes tends to be influenced strongly by not only the amount but also the location of fixed dye in the fabric cross-section. Location of fixed dye is influenced strongly by both particulate and molecular migration of dye during continuous dyeing. Studies correlating color yield obtained with a given amount of fixed dye for various levels of particulate or molecular migration can have both economic and technological implications.

However, there appears to have been no response to the AATCC committee's 1978 plea for work in the specific area of color yield phenomenology. This lack of work in the area is regrettable in view of the economic implications such work can have for the American textile industry.

If the American textile industry is to remain viable in the face of increasing competition from imports, it is essential that the domestic textile industry learn as much as possible about the technologically important processes that it uses. In the case of continuous dyeing of polyester fiber in blends with cotton, it is more necessary now than ever before that strict control of the process be achieved to produce better economy and to stimulate the creation of new products. If the present study can convincingly show, for the first time, that it is indeed possible to model color yield phenomenology by the use of a

few parameters specific to fabric and dye, computer analysis of continuous dyeing systems by the use of a developed model may lead to the creation of that very economy and those new products which the industry needs in its fight to remain competitive.

Objective:

The objective of the present research is: To develop a mathematical model which expresses depth of color obtained on polyester fiber in blends with cotton fiber as a function of both fixed dye content and location of fixed dye in the fabric cross-section.

CHAPTER II

REVIEW OF LITERATURE

Background:

The pioneering work of Carothers led to the development by Whinfield and Dickson of a useful polyester fiber. But long before Dupont purchased the patent rights to the new fiber and began manufacturing "Dacron" in Kinston, N. C. in 1953 (Moncrieff, 1957), an experiment of profound technological significance was conducted by Valentin Kartaschoff in a small laboratory in Switzerland (Kartaschoff, 1925). The purpose of Kartaschoff's 1925 experiment was to attempt to generate data which might shed light on the mystery of the mechanism of dyeing cellulose acetate, a forerunner of polyester fiber.

In the early twenties a vigorous debate raged among various members of the technological/scientific community with regard to the "true" mechanism of dye uptake by the hydrophobic cellulose "silk" acetate fiber (Rattee & Breuer, 1974). According to one school, the sparingly soluble disperse dye dissolved into the aqueous dyeing vehicle to form a saturated solution. Dye then was adsorbed from the saturated solution onto the surface of

the fiber, followed by diffusion into the interior of the fiber. This first theory was referred to as the "aqueous solution theory." The second theory was the "solid solution theory" which was supported by Kartaschoff. According to the solid solution theory, dye particles were adsorbed directly onto the surface of the fiber, followed by dissolution into the "substance of the fiber itself." No dissolution of dye into a dyeing medium was necessary; the dye particles simply were attracted to the fiber surface where they dissolved directly into the fiber (Rattee & Breuer, 1974).

Kartaschoff reasoned that if the solid solution theory were correct, dyeing should occur if fibers merely were brought into contact with dry, powdered dye and kept in contact for a sufficient period of time. As noted by Kuth (1975), the dye used by Kartaschoff was dianisidine. Kartaschoff described his experiment as follows:

Finally we introduced an acetate silk skein into the dianisidine base which was finely ground in a ball mill; all this was left at 60C, regulated by an electric thermostat. After 15 days we took out the skein, which was dyed a deep brown.

The results of the experiment clearly suggested to Kartaschoff that it was not necessary for dye to dissolve into an aqueous medium from which adsorption onto a fiber surface then occurred. The solid solution mechanism of

dyeing was "confirmed," and for a time, Kartaschoff's view became widely accepted. But as Rattee and Breuer (1974) point out, it is unfortunate that Kartaschoff's view became so very widespread, for Kartaschoff completely missed the most important point of his own experiment: The dye used by him tended to vaporize at 60C to create a solution of dye vapor in air. The conclusion of Kartaschoff was not completely correct. Solid solution was not the only possible dyeing mechanism. As the work of Majury (1956) has now revealed, Kartaschoff's dyeing probably occurred from a saturated solution of dye- not in water- but in air.

Without realizing it, Kartaschoff had conducted the first vapor phase dyeing experiment ever to be recorded in the literature. Indeed, Kartaschoff perhaps would be surprised to know how many millions of metric tons of fiber are dyed today by the very mechanism which he completely overlooked.

Polyester Dyeing:

Batch Processes- It was found very quickly by early researchers that "Dacron" was not an easily dyed fiber. The disperse dyes, which were easily adsorbed at the boil by acetate and nylon fibers, only faintly tinted polyester

fibers. Special dyeing methods had to be developed (Moncrieff, 1957). For exhaust dyeing processes it was found that temperatures above the boil were necessary for good fixation to be achieved. Indeed, temperatures of 130°C became quite commonly used in dyeings carried out in pressurized vessels. For exhaust dyeing processes conducted at the boil or below, it was necessary to include "carriers" in the dye bath to promote dye uptake by the fiber. These carriers were organic compounds such as o-phenylphenol, diphenyl, and salicylic acid, which functioned by a process of loosening the fiber structure so that dye would penetrate the fiber at the atmospheric dyeing temperatures employed (Ingamells et al., 1973).

Although both high-temperature dyeing and carrier dyeing became very important processes for the coloration of polyester fibers, the two batch processes were not well suited for the dyeing of large amounts of fabric in a short period of time. A more rapid, more efficient, continuous dyeing process was needed.

Continuous Process- Joseph W. Gibson was a young, inexperienced researcher in the area of dyeing technology when he was assigned by DuPont in the late 1940's to the task of developing new and better methods of dyeing Orlon and Dacron (Gibson, 1979). He seems to have been unaware

of Kartaschoff's previous work in the area of dyeing mechanisms, but appears to have shared Kartaschoff's point of view. Gibson, like Kartaschoff before him, was not convinced that it was necessary for an aqueous medium to be present to carry dye to the surface of the fiber. He had an idea that it might be possible for dyeing to occur by the use of dry heat to bring about direct dissolution of dye into the fiber (Gibson, 1979). Even today it is not clear how much of the process developed by Gibson was due to inspiration and how much was due to serendipity (M. J. Schuler, personal communication, October, 1983), but on December 10, 1947, in the Technical Laboratory in Deepwater, N. J., Gibson performed a dyeing experiment which changed forever the technology of polyester dyeing. Gibson placed Orlon and Dacron fabrics, which had been impregnated with disperse dye, between two conventional flat irons for 5 seconds at 200C. When the fabrics then were washed, only the portion of each fabric which had been heated was found to be dyed. The "Thermosol" process was born (Gibson, 1953).

The fact that Gibson, like Kartaschoff before him, incompletely understood the dyeing mechanism is reflected in the very name, "Thermosol." The name implies that thermal energy brings about a direct dissolution of particulate dye into the fiber. As pointed out in the

first Dupont publication of the process ("The 'Thermosol' Process," 1949), "The name 'Thermosol' is a temporary designation for the 'heat soluble' process, and will soon be superseded by a more descriptive term." It has now been strongly suggested by the work of Bent et al. (1969) that only vapor transfer is operative in the "Thermosol" process. According to these researchers, the process is one of localized dyeing from a solution of dye vapor in air. Direct dissolution of particulate dye into the fiber surface by some unstated solid solution mechanism need not occur. But, as will be shown below, not all scientists agree with the view of Bent et al.

Fixation Mechanisms:

Vapor Fixation- As long ago as 1955, Majury (1956) clearly showed that cellulose acetate film, and nylon or polyester fibers could be dyed with vapors of non-ionic (disperse) dyes. In the experimental arrangement used by Majury, the polymeric substrate was separated from the particulate dye within an evacuated and sealed glass tube; the apparatus was heated, and uptake of dye by the various substrates over time at various temperatures was determined by extraction.

Further support for the vapor fixation mechanism has been provided by Bent et al (1969), who conducted what is now regarded by some as a classic experiment. These researchers impregnated a cotton fabric with particulate disperse dye and then dried the fabric. A sandwich assembly was constructed, consisting of a layer of the impregnated and dried cotton fabric and several layers of polyester fabric into which square holes had been cut in a pattern to provide open pathways. The pathways were arranged in a way to provide air gaps of increasing fabric thickness between the cotton fabric and each succeeding layer of polyester. The assembly was placed between metal plates and baked to bring about fixation of dye on the polyester. After the assembly was baked, the amount of dye found in each layer of polyester then was measured. Bent et al. found a linear relationship between the amount of dye fixed on the polyester and the distance from the cotton fabric as measured in number of air gap thicknesses. As expected, it was found that the greater the air gap between the cotton fabric and the polyester fabric, the smaller the amount of fixed dye. Also, when the amount of dye fixed as a linear function of air gap distance was extrapolated to zero air gap, i.e. direct contact between the polyester fabric and the impregnated cotton fabric, it was found that there was good agreement between extrapolated and measured values of dye fixation. This finding suggested to Bent et

al. that only vapor fixation was the operative mechanism. If contact or solid solution fixation were operative, more dye than the extrapolated amount should have been found-- but it was not.

Gerber (1973) has challenged the conclusions of Bent et al. on the grounds that there was never a zero air gap distance in their experiment. Gerber points out that even when the cotton and polyester fabrics were in close contact, the contact was not perfect by any means. Only an unknown fraction of the polyester fabric was in actual contact with particulate dye. It is Gerber's view that the experiment of Bent et al. merely emphasizes the importance of vapor transfer in the "Thermosol" process; the experiment does not prove that solid solution does not occur.

Kuster et al. (1978 & 1979) conclude from the results of very carefully conducted experimental studies, which involved the computation of dyeing enthalpies by two different methods, that only vapor fixation is operative in "Thermosol" dyeing. Again, Gerber (1979) challenges the conclusion, noting that enthalpies are determined from equilibrium measurements, and nothing can be concluded about the pathways to equilibrium from the equilibrium measurements themselves.

Non-vapor Fixation- Gerber and Somm (1971) point out that many disperse dyes melt at temperatures below the usual "Thermosol" temperatures of 200-210C, and are "absorbed by the polyester fiber with the greatest probability from the liquid phase." On the other hand, McDowell (1972), an advocate of the vapor transfer mechanism, maintains that little is known about the wettability of polyester by molten dye. McDowell further maintains that it seems highly improbable that a monomolecular film of molten dye is formed over every fiber during the thermofixation step.

There appears to be much uncertainty with regard to how much solid solution or even "molten solution" mechanisms contribute to disperse dye fixation in the "Thermosol" process. Indeed, no published evidence in support of the solid or molten solution mechanisms is available. On the other hand, no evidence exists to disprove such non-vapor fixation mechanisms. There is, however, another non-vapor mechanism to consider: The case when a non-aqueous medium is present in the fixation system.

As long ago as 1966, von der Eltz (1966) discussed specific agents which may be included in the pad bath to promote fixation of dye during "Thermosoling." According

to von der Eltz, such agents include: "hydroxyethylated fats or fatty alcohols, polyglycol ethers, and hydroxyethylated mono- and polyamides..." A fundamental property of such agents is a limiting dissolving effect on the dye by the agent at the fiber surface (Beckmann, 1966). In the view of Kern et al. (1968), during the thermal fixation step these agents "take effect penetratively, carrying the dissolved dye over the surface of the fiber and through the fiber bundle." Such a phenomenon can be considered a form of localized solvent dyeing from a saturated solution of dye in agent (Northern Piedmont Section, AATCC, 1972). Such a view is supported by the findings of Kuth (1975) that dye is distributed between agent and fiber according to Nernst's Law and that the vapor pressure of dye dissolved in agent is lower than that of dye alone.

An important continuous dyeing use of the agents described above is found in the low-temperature "Thermosol" dyeing of textured polyester fiber (Leube & Richter, 1973). Since the inclusion of such agents in the pad permits the lowering of the usual 210°C dyeing temperature to about 180°C, the texture of the polyester is not so badly damaged as it would be at the conventional higher temperature.

Kinetics:

Empirical Equations- It was shown by the Northern Piedmont Section of AATCC (1972) and by Urbanik and Etters (1972) that a simple exponential equation of the form:

$$F_t = F_m[1 - \exp(-kt)] \quad (1)$$

where F_t is the amount of dye fixed on the polyester at a given time t , F_m is the maximum or "equilibrium" fixation, and k is an empirically determined rate constant of thermofixation, can satisfactorily describe the uptake of disperse dye by polyester fiber during the latter stages of dyeing. Furthermore, when the square root of time is used in Equation 1, the uptake of dye can be described even more accurately over a greater range of the fixation time (Etters & Urbanik, 1977a). Such an equation has the form:

$$F_t = F_m[1 - \exp(-kt^{1/2})] \quad (2)$$

Etters and Urbanik (1977a) have shown that the rate constant of Equation 2 is influenced by the uniformity of distribution of particulate dye in the cross section of the impregnated and dried fabric. (The more uniform the distribution, the higher is the numerical value of the rate constant). Abdel-Fattah et al. (1981) ostensibly have confirmed the findings of Etters and Urbanik in an essential duplication of their original experiment. It is now recognized that the exponent of time in Equation 2 need not be 1/2 (Etters & Urbanik, 1977b). The equation may be

more generally written as:

$$F_t = F_m[1 - \exp(-kt^n)] \quad (3)$$

where n is a constant having a value between 0 and 1.

Cegarra and Puente (1976) prefer an empirical equation of the form:

$$F_t = F_m[1 - \exp(-kt)^n]^{1/2} \quad (4)$$

which now has been shown (Etters & Urbanik, 1977b; Urbanik, 1978, and Etters, 1980) to represent only one form of the general equation:

$$F_t = F_m[1 - \exp(-kt^n)]^x \quad (5)$$

In fact, Etters (1980; 1981) has shown that Equation 5 can reproduce the functional relationship between fractional dye uptake and dimensionless time, as usually expressed by the diffusion equations of Hill (1928), Wilson (1948), or Crank (1976). Maasdorp (1983) has used Equation 5 in studies involving sorption of chromium by wool.

Both the kinetics and the thermodynamics of "Thermosol" dyeing also have been explored in a series of papers by Detscheva et al. (1981a, 1981b, 1981c, 1981d, 1981e, 1981f, and 1981g; 1982a and 1982b). Much of the work of these researchers deals mainly with the confirmation of the findings of previous studies of other researchers.

Diffusion Equations- Diffusion controlled sorption or desorption of chemicals by solids having various geometrical shapes is influenced by the thickness of the diffusional boundary layer at the solid surface. The boundary layer thickness in turn is influenced by the rate of flow of the medium carrying the diffusant to or from the surface of the solid. With increasingly high rates of flow or agitation, the boundary layer tends to approach zero thickness, and sorption (or desorption) is controlled more and more by diffusion in the solid phase. On the other hand, as the flow of the medium approaches zero (or stagnation), the boundary layer thickness becomes quite large, and sorption processes tend to be controlled by diffusion in the medium surrounding the solid (Levich, 1962; McGregor, 1974; Rattee & Breuer, 1974; Iyer, 1974; Peters, 1975, and Jones, 1975).

Boundary layer thickness is, however, only one physico-chemical component of a dimensionless parameter, L , which determines the rate of mass transfer of diffusant between solid and transfer medium (McGregor et al., 1965a, 1965b, 1970, and 1974). The parameter L is defined by:

$$L = [D_m / (D_s K)] [x/b] \quad (6)$$

where D_m and D_s are the diffusion coefficients of the diffusant in the medium and the solid respectively; K is the distribution coefficient of the diffusant between the

medium and the solid surface; x is the solid radius in the case of a sphere or a cylinder, or the half-thickness in the case of a film, and b is the thickness of the diffusional boundary layer. The higher the value of L , the more rapidly will mass transfer occur, and the lower the value of L , the more slowly will mass transfer occur. It is clear, then, that L and b are inversely related. In the case of textile systems, where the patterns of flow are likely to be non-uniform and quite complex, any value of L is possible between the limits of infinity and zero.

McDowell (1972, 1980) has applied the boundary layer concept to the uptake of dye by polyester fiber in the "Thermosol" process, and maintains that the turbulence of the air surrounding the fiber strongly influences the rate at which dye is taken up by the fiber. Description of dye uptake by the use of formal diffusion theory may then be justified, according to McDowell.

As noted by Crank (1976) and by Carslaw and Jaeger (1978), formal solutions to the diffusion equation involving cylindrical mass transfer for certain specified boundary conditions have been available for many years. These equations assume the following functional form for the boundary layer case:

$$M_t/M_\infty = f(Dt/r^2, L) \quad (7)$$

where M_t is the amount of diffusant taken up by the fiber at a given time t , and M_∞ is the amount of diffusant in the fiber at infinite time or equilibrium; D is the constant, concentration-independent diffusion coefficient of the diffusant in the fiber; r is the fiber radius, and L is a boundary layer parameter, as previously shown in Equation 6. The earliest formal solutions to the diffusion equation for boundary layer mass transfer were those of Newman (1931). So warmly welcomed were the equations of Professor Newman that he was given a grant by the Chemical Foundation to support his preparation of a short series of tables showing the values of M_t/M_∞ to be expected for various values of dimensionless time, Dt/r^2 , for specified values of L . Although the tables of Newman are rather incomplete and lacking in a high level of accuracy, these tables represent a significant mathematical accomplishment of Newman's day.

Crank's boundary layer equations (1976), though mathematically equivalent to those of Newman, are notationally less encumbered. His cylinder equation is:

$$M_t/M_\infty = 1 - \sum_{n=1}^i \frac{4L^2 [\exp(-(B_n)^2(Dt/r^2))]}{(B_n)^2 [(B_n)^2 + L^2]} \quad (8)$$

where "i" indicates infinity, and the B_n 's are the roots of the transcendental equation:

$$BJ_1(B) - LJ_0(B) = 0 \quad (9)$$

in which J_0 and J_1 are Bessel functions.

It is not surprising that tables previously constructed without the aid of computers were neither complete nor highly accurate. With lower and lower values of Dt/r^2 and higher and higher values of L , more and more roots found from iterative solutions of the transcendental Bessel equation are necessary for high accuracy to be achieved. However, a new series of computer-generated tables of numerical solutions involving the boundary layer diffusion equations for a cylinder recently has been made available (Etters & Hurwitz, 1986a). The tables consist of iteratively determined numerical values of Dt/r^2 for uniformly spaced values of M_t/M_i over a range of L values from infinity to 0.01. It is believed that the values given are accurate to at least four significant figures. As pointed out by the authors: "By using the tables, one now may make rather sophisticated analyses without having to resort to using the original boundary layer diffusion equation." Such analyses may include computation of diffusion coefficients, half-times of dyeing, or even the apparent thickness of the boundary layer itself. When such quantities are used within a more detailed kinetic model, such as that of transitional kinetics (McGregor & Etters, 1979), a better understanding of the interrelationship of those factors which influence dye uptake in model systems is possible.

Particulate Migration:

Causes- After a properly prepared, absorbent fabric is impregnated with a dispersion of dye, it is found that the particles of dye are uniformly distributed within the capillary network formed by the spaces between fibers and yarns of the fabric cross-section. This fact has been proven by Billie et al. (1973), who used a technique of freeze-drying to immobilize the particles of dye within the impregnated fabric. When these authors examined cross-sections of the freeze-dried fabric, they found a uniform distribution of dye particles. It is unfortunate, from a technological point of view, that the uniform distribution of particulate dye is not maintained during intermediate drying of the fabric. When an impregnated textile material is subjected to a drying process, water vapor is removed from the fabric's surfaces of evaporation. To replace evaporated water, more water flows or wicks through the capillary network from the fabric interior to the fabric surface. The flowing water carries along particles of dye which are dispersed within the aqueous medium, and this movement of dye is referred to as "particulate migration." Since particulate migration tends to be non-uniform, dye can be deposited in a uneven manner throughout the fabric. Such an uneven deposition can have

a negative influence on the quality of the final dyeing. Side-to-center and back-to-face shadings, blotchy appearance, and poor penetration of dye are well known faults caused by particulate migration (Northern Piedmont Section, AATCC, 1975).

Recognizing the importance of the migration phenomenon to the textile industry, a committee of AATCC developed a simple test for estimating the tendency of dye to migrate within a given fabric ("Dyestuff Migration: Evaluation of," 1974). An experimental arrangement of the test is given below in Figure 3:

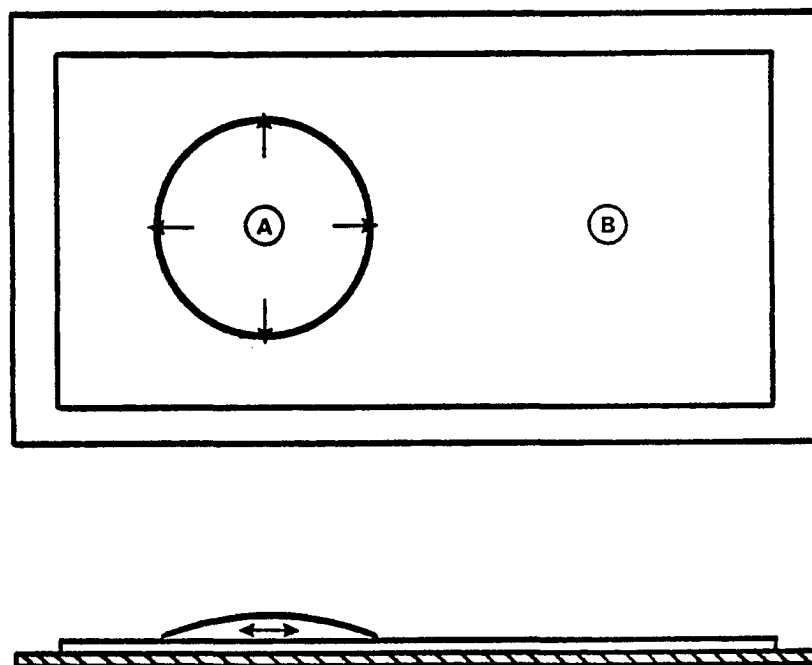


Figure 3. (A)- Fabric section removed for extraction of dye from area covered by watchglass. (B)- Fabric section removed for extraction of dye from area not subjected to horizontal migration.

The particulate migration test is carried out in the following manner: A strip of fabric is impregnated with a dye dispersion and immediately placed onto a non-porous flat surface such as a glass plate. A watch glass is placed onto the fabric, and the fabric is allowed to dry at room temperature. During drying, water evaporates from the fabric area not covered by the watch glass, and water within the watch glass chamber wicks under the influence of capillary forces to an area which extends from the edge of the chamber to perhaps 1 cm beyond. Particulate dye which was carried along by the wicking water is deposited in this area. Particulate dye that has not migrated then is extracted from a sample of the area covered by the watch glass (A). A sample also is taken from the area not covered by the watch glass (B) that is far enough removed from the watch glass to contain the original concentration of applied dye. Determination of particulate migration is made from a comparison of the concentrations of dye in the two areas. Particulate migration, M_p , is computed as the fraction of dye originally under the watchglass that has migrated from beneath the watchglass during the test:

$$M_p = 1 - [(\text{Conc. A})/(\text{Conc. B})] \quad (10)$$

Based in part on a continuation of the work of Gerber (1972), Urbanik and Etters (1973) and Etters (1973) have demonstrated that an equation of the form:

$$M_p = 1 - [(kds)/(q_t - q_b)] \quad (11)$$

satisfactorily expresses the relationships among the various parameters which influence the amount of particulate migration to be expected for a given system. In the equation, k is a proportionality constant specific to fabric and dye; d is the average particle size of the dye (diameter), expressed in cm ; s is the surface area of the fiber in cm^2/g ; q_t is the aqueous pickup of the fabric, expressed in cm^3/g , and q_b is that amount of aqueous pickup that consists of bound, immobile water, also expressed in cm^3/g .

Solutions to the Problem- According to Equation 11, particulate migration will decrease with increasing k , d , s , or q_b but increase with increasing q_t . It is suggested by Equation 11 what must be done to control particulate migration. As summarized by von der Eltz (1972), migration is best minimized by: keeping the pickup as low as possible, batching the fabric before drying, using dye of low dispersing agent content, employing wetting agents judiciously, and including commercial antimigrants in the pad bath. Each of the recommendations of von der Eltz is in agreement with that which is to be expected from Equation 11. For example, low pickup means low q_t ; batching means an increased q_b ; low concentrations of dispersing or wetting agents mean a larger d and a lower

Q_e respectively; and the presence of commercial antimigrants means an increased d . Indeed, of all of the methods suggested by von der Eltz, the inclusion of commercial antimigrants in the pad bath is the method most often used by industry today (Northern Piedmont Section, AATCC, 1975).

Commercial antimigrants consist mainly of polymeric electrolytes such as sodium alginate, sodium polyacrylate, carboxymethyl cellulose (CMC), natural gums, and starches. The inclusion of these agents in a pad bath brings about a controlled agglomeration of particulate dye. Since the resulting agglomerates have a much larger average geometrical size, the particles no longer can move so freely through the fabric capillary network (Northern Piedmont Section, AATCC, 1975). It has been shown repeatedly that the level of particulate migration to be expected for a given dye/fabric system is a function of the concentration of antimigrant. When all other factors are held constant, migration decreases as the concentration of antimigrant increases, and when the concentration of polymeric electrolyte is high enough, migration does not occur at all (Northern Piedmont Section, AATCC, 1972; Ethers, 1972; Ethers, 1973; Northern Piedmont Section, AATCC, 1975).

One consequence of the use of polymeric electrolytes to control migration is the effect on the resulting color yield obtained with the applied disperse dye. As particulate migration is increasingly controlled, the distribution of fixed dye tends to be increasingly uniform in the cross-section of the fabric; less dye is found in the fibers at the fabric surface than is found when particulate migration is not well controlled; consequently less color strength or depth is obtained for a given amount of fixed dye. "From this standpoint, the [particulate] migration phenomenon acts in cooperation with the dyer (Gerber, 1972)." The dyer obtains more color depth for unit concentration of fixed dye as the fraction of dye located in the fibers at the yarn or fabric surface increases.

Light Reflectance:

Kubelka-Munk Analysis- Many mathematical schemes have been developed which permit the conversion of light reflectance of a given wavelength from a textile substrate to an additive linear function of dye concentration in the substrate. A review of the various equations used in colorant formulation has suggested that the equation of Love, Oglesby, and Gailey (1965) has considerable usefulness for color matching by the use of the computer.

Nevertheless, the equation of Kubelka and Munk (1931) still remains the most widely used of all of the additive reflectance functions so far formulated (Nobbs, 1985).

The theory developed by Kubelka and Munk is an elegant one: Consider an ideally homogeneous colorant layer of thickness X , having infinite length and width. This colorant layer is resting on a background which has a reflectance R_0 , as illustrated (after Judd and Wyszecki, 1963) in Figure 4.

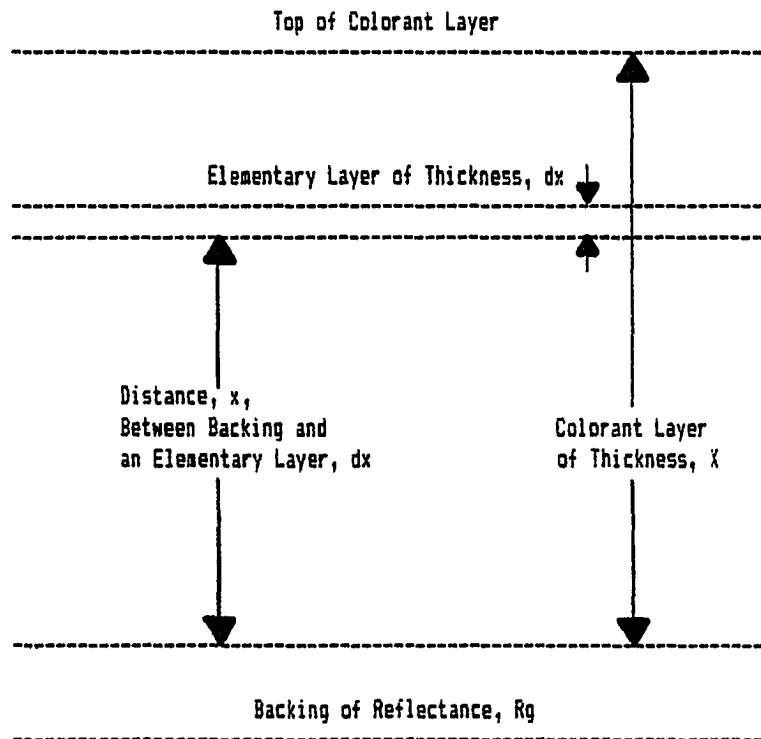


Figure 4. Model of Kubelka-Munk Analysis.

In the case of a colorant layer for which diffuse illumination and viewing without polarization are achievable, analysis can be restricted to the changes which occur in two simultaneous light fluxes; one flux proceeds downward (i), and the other proceeds upward (j). The colorant thickness X consists of an infinite number of elemental layers having a thickness dx. As the light flux (i) proceeds through an elemental layer dx, the flux is decreased both by sorption K and by scattering S, where K and S are respectively the coefficients of sorption and scattering. The amount lost by sorption is $(K_1 dx)$, and the amount lost by scattering is $(S_1 dx)$. The same relationship holds for the flux (j), i.e., $(K_2 dx)$ and $(S_2 dx)$, but since the scattered flux (i) must be added to the flux (j), the overall change of the flux (j) is:

$$dj = -(S + K)_j dx + S_1 dx \quad (12)$$

and similarly for the overall change of the flux (i):

$$-di = -(S + K)_i dx + S_2 dx \quad (13)$$

The Kubelka-Munk solution to the two differential equations given above has resulted in:

$$R = (Q_1 - Q_2)/Q_3 \quad (14)$$

where:

$$Q_1 = (R_0 - R_1)/R_1 \quad (15)$$

$$Q_2 = R_1 (R_0 - 1/R_1) \exp(SX(1/R_1 - R_1)) \quad (16)$$

$$Q_3 = R_0 - R_1 - (R_0 - 1/R_1) \exp(SX(1/R_1 - R_1)) \quad (17)$$

For a colorant layer viewed over a background of

reflectance R_0 , Equation 14 gives the reflectance R of the colorant layer of thickness X , having sorption and scattering coefficients K and S respectively and an opaque reflectance R_1 . For a colorant layer of infinite thickness, the ratio of the sorption and scattering coefficients is given by:

$$K/S = [(1 - R_1)^2]/2R_1 \quad (18)$$

which is the well-known additive function often used in computer colorant formulation.

In view of the fact that textile fabrics hardly fulfill the requirements of ideal colorant layers (Etters & Hurwitz, 1986b), it is remarkable that the Kubelka-Munk additive function appears to work so well with such substrates. Of course, empirical corrections must be made to account for the so-called surface reflectance R_s , i.e., the reflectance of light from a substrate containing an "infinite" amount of dye (Stearns, 1969; Kuehni, 1975). When surface reflectance is taken into account, Equation 18 becomes:

$$K/S = [(1 - R_1 - R_s)^2]/2(R_1 - R_s) \quad (19)$$

It should be recognized, however, that the surface reflectance factor may be used in a purely empirical manner to obtain the most satisfactory linearization of K/S versus concentration, without necessarily implying that R_s has true physical meaning.

Since reflectance measurements made on dyed textile substrates contain a contribution to K/S which originates with the undyed substrate itself, this quantity must be subtracted in order to determine the true relationship between K/S and concentration of dye in the substrate. For example, the additive function due to dye only, $(K/S)_d$, is given by:

$$(K/S)_d = (K/S)_t - (K/S)_u \quad (20)$$

where $(K/S)_t$ is that for the dyed substrate, and $(K/S)_u$ is that for the undyed substrate. $(K/S)_d$ usually is expressed as a function of concentration C by:

$$(K/S)_d = aC \quad (21)$$

where the constant "a" is analogous to the absorptivity coefficient in transmittance measurements of solutions of dye.

Color Yield- Although Gerber (1972) has expressed formally what every continuous dyer knows, i.e., the greater the particulate migration, the more color strength or "depth of color" to be obtained for a unit concentration of fixed dye, neither Gerber nor anyone else appears to have quantified the phenomenon.

Cate (1969) has proposed that a "color efficiency" value, CE, can be calculated from:

$$CE = [((1 - R)^2)/2R]/[\log(1/T)] \quad (22)$$

where the numerator of Equation 22 is equivalent to the uncorrected K/S value previously discussed, and the denominator is a quantity referred to as absorbance. Since absorbance is based on transmission measurements, T, and is known to be a linear function of dye concentration- as is K/S- CE is equivalent to "a" of Equation 21. CE and "a" are ratios of the two linear functions of dye concentration, K/S and absorbance, for a given dye/substrate system. Absorbance is based on transmission measurements made on a standard solution of dye prepared from dye extracted from a unit mass of substrate, and K/S is based on reflectance measurements made on the same substrate. As CE or "a" increases, the color efficiency or color yield increases.

Gorondy (1978) has suggested that a "Color Utilization Index" (CU Index) may provide useful information with regard to "the effectiveness with which a dye is utilized on a fabric, independent of the amount of dye padded and the weight of the fabric." The CU Index is defined as:

$$\text{CU Index} = (F_1)(F_2) \quad (23)$$

where

$$F_1 = [(K/S) / (\text{Dye Wt.} / \text{Fabric Area})] \quad (24)$$

$$F_2 = [(K/S) / (\text{Dye Wt.} / \text{Fabric Wt.})] \quad (25)$$

According to Gorondy, "The higher the CU Index, the more effectively is the dye utilized."

Kissa (1984) proposes that since K/S often may be expressed as a power function of concentration, tinctorial efficacy, E_c , may best be expressed as:

$$E_c = [A/(c^{1-n})] \quad (26)$$

where the coefficients A and n are determined from plots of K/S versus concentration, c, on logarithmic scales, n being the line slope, and A corresponding to the K/S value at $c=1$.

In none of the discussions of color efficiency found in the literature is an attempt made to quantify the effect of dye distribution in the cross-section of fabric on color yield. The primary purpose of the present work is to develop a mathematical model which permits one to segregate the separate influence of uniformly distributed dye and migrated dye on the measured color depth. It is hoped that such a model can be useful in further studies of the "Thermosol" process and can contribute to both economical use of dye and the development of new product ideas.

CHAPTER III

EXPERIMENTAL METHODOLOGY

In order to develop a mathematical model which expresses color depth as a function of dye content and location of dye in the cross-section of the fabric, it was necessary to carry out fixation and reflectance measurements made on laboratory dyeings in which both dye content and location of dye in the fabric cross-section were carefully controlled. This control was achieved through the use of varying dye and antimigrant concentrations in the pad baths, with all of the other experimental variables held constant.

Materials:

Fabric- All migration and dyeing experiments were made using a commercial 290 g/m² intimately blended 50/50 "Dacron" polyester (1.2 denier, 3.81 cm)/cotton woven fabric. The fabric was commercially prepared for dyeing by the industrially standard processes of heat-setting at 420F (216C), peroxide bleaching, and mercerizing.

Dyes- The criteria by which disperse dyes were selected were: (a) The dyes had to be commercially available and actually used in industrial "Thermosol" processes. (b) The dyes had to have structural formulas which were not proprietary. (c) The dyes had to be homogeneous compounds having very few, if any, impurities as determined, for example, by thin-layer chromatography, using chloroform, acetone, and ethyl acetate as separate eluents. (d) The dyes had to be of different colors. Only a limited number of dyes were found to meet all of the above criteria, the following dyes being especially suitable: Disperse Blue 165, Red 60, and Brown 1.

The three dyes were obtained in commercial powder form. Disperse Blue 165 was obtained from Mobay Chemical Corporation as Resolin Blue BBL5; Disperse Red 60 was obtained from Ciba-Geigy Corporation as Terasil Red FB, and Disperse Brown 1 was obtained from Sandoz Chemicals Corporation as Foron Brown S-3R.

Dimethyl Formamide- DMF solvent (technical grade) was obtained from Ashland Chemical Company and was found by Karl Fischer analysis to contain less than 1% water.

Sodium Alginate- A commercial sodium alginate antimigrant solution (Seyco Antimigrant C-45), consisting of 16% solids, was obtained from the AZS Corporation.

Wetting Agent- The wetting agent was obtained from the Chemical Products Division of Dan River Inc. and consisted of a 25% aqueous solution of a modified sodium alkylnaphthalene sulfonate.

Acids- Glacial acetic and concentrated sulfuric acids (technical grades) were obtained from Fisher Scientific Company.

Eluents- The solvents acetone, ethyl acetate, and chloroform that were used in thin-layer chromatography also were obtained in technical grade from Fisher.

Equipment:

Pad Mangle- A simply designed, custom-constructed laboratory pad mangle, consisting of a lower rubber roller and an upper steel roller, was used.

Thermal Fixation Oven- A commercially established, semi-contact Ross Air Systems thermal fixation oven, having a rapid circulation of air was used.

Colorimeter- A Bausch and Lomb Spectronic 20 colorimeter was used for all absorbance measurements involving solutions of dye in DMF.

Spectrophotometer- A Match-Scan spectrophotometer (Diano Corporation) was used for reflectance measurements of the dyed polyester.

Chromatography Apparatus- Kodak chromagram developing apparatus (model 13259) and sheets were used for screening disperse dyes to determine whether or not the dyes were free from impurities. The dyes were developed on flexible polyester sheets, having a silica gel 60 surface with a fluorescence indicator.

Preliminary Experiments:

Thin-Layer Chromatography- Thin-layer chromatograms of approximately 300 disperse dyes were examined in the preliminary screening to find dyes free from colored impurities. The three selected dyes- Disperse Blue 165, Disperse Red 60, and Disperse Brown 1- were further subjected to thin-layer chromatography with chloroform, ethyl acetate, and acetone eluents. All dyes produced single spots on the developing sheets with ethyl acetate and acetone, but with chloroform two trace components in addition to the major component were found with Blue 165. The other two dyes produced only one spot with chloroform. It was concluded that all dyes were essentially free from colored impurities.

Activity of Commercial Dye- Soxhlet extraction of the commercial powder with chloroform, followed by weighing of the extract, revealed that the commercial form contained approximately 24% active dye in the case of Resolin Blue BBLS. The same technique revealed that Terasil Red FB and Foron Brown S-3R contained about 27% and 35% active dye respectively. All dyes contained about 5% moisture, with the remaining composition of each dye consisting of dispersing agents and diluents.

Colorimeter Performance Test- A stock solution, consisting of 22.0 g/l cobalt chloride dissolved in a 1.0% solution of hydrochloric acid in distilled water, was found to have an absorbance maximum at the expected value of 510 nm in a performance test of the colorimeter. It was concluded that the instrument probably did not introduce systematic error in the determination of the wavelength of maximum absorbance of the dyes examined in this study.

DMF Testing- All preliminary experiments revealed no obvious difference between spectrophotometric curves of dye dissolved in redistilled DMF and those of dye dissolved in the DMF as received. The DMF was used without further purification.

Wavelength of Maximum Absorbance- Light transmission measurements were made at 2.5 nm intervals on dilute solutions of each dye in DMF. For Blue 165 the wavelength of maximum absorbance was determined to be 612.5 nm. In the case of Red 60 and Brown 1 the wavelengths were determined to be 520 and 455 nm respectively.

Characteristic Spectra- After the apparent wavelength of maximum absorbance for each dye in DMF had been determined, the concentration of each dye in DMF was adjusted to give approximately 36.8% transmittance at the

wavelength of maximum absorbance. As reported by Ayers (1949), it has been shown that relative analysis error is at a minimum at 36.8% transmittance for the instrument used in the present study. The transmittance of each so prepared dye solution then was recorded over an appropriate range of wavelengths to produce characteristic spectra. These data are given in Appendix A.

Both the characteristic spectrophotometric curve of Disperse Blue 165 in dimethyl formamide (DMF) and the structural formula of the dye according to Dawson (1983) are given in Figure 5.

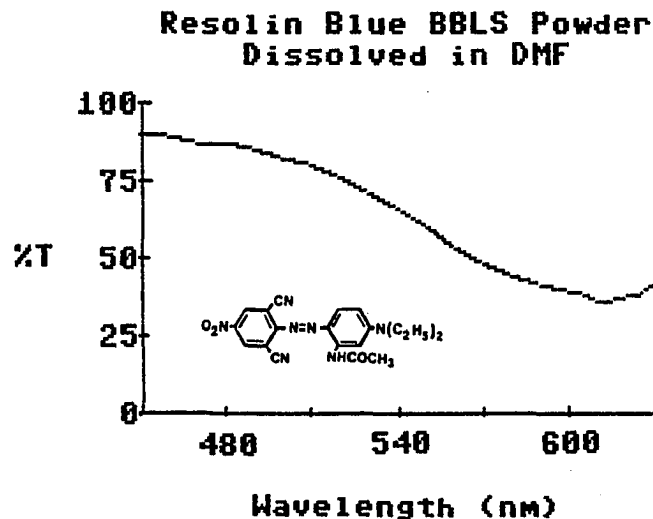


Figure 5. Spectrum and structure of Disperse Blue 165.

Similar information is provided for Disperse Red 60 and

Disperse Brown 1 in Figures 6 and 7 given below.

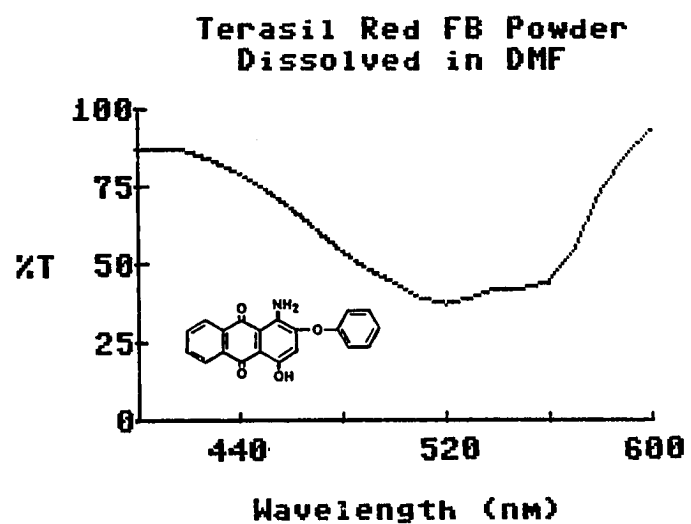


Figure 6. Spectrum and structure of Disperse Red 60.

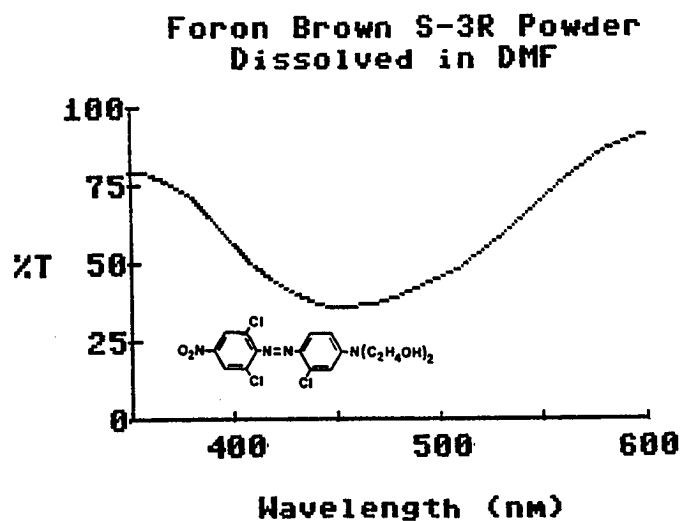


Figure 7. Spectrum and structure of Disperse Brown 1.

Absorptivity Determination- For computations involving both particulate migration and fixation of dye on polyester it was necessary that the quantitative relationship between fractional solution transmittance and concentration of dye in that solution be determined. As discussed in detail by Kuehni (1972) and by Giles (1974), fractional transmittance of light, T , of a given wavelength through a cell containing a solution of dye is given by the Beer-Lambert law:

$$T = \exp(-klC) \quad (27)$$

where k is the absorptivity coefficient; " l " is the cell thickness, and " C " is the concentration of dye. If $\ln(1/T)$ is plotted versus " C ," a straight line of slope kl is obtained. It is current practice for a cell thickness of 1 cm to be used; also, standard practice calls for the use of logs to base 10 rather than natural logs in the computation of absorbance. When plots of absorbance, A , ($\log(1/T)$) versus concentration result in a straight line with zero or nearly zero intercept " I ," it can be assumed that the dye conforms to the Beer-Lambert law. The line slope, a , found from regression analysis of such plots is the practical absorptivity and may be used, along with the intercept value, I , to calculate concentration of dye from a knowledge of fractional transmission according to:

$$C = (A - I)/a \quad (28)$$

In the present study concentration/absorbance data were determined in the following manner: About five grams of each dye sample was weighed to four decimal places on an analytical balance. The dye then was dispersed in 400 ml of distilled water at 100F (39C), transferred to a 500 ml volumetric flask, and allowed to cool to room temperature (75F; 24C). Distilled water at room temperature then was added to the flask to bring the total volume to 500 ml. Five ml of the dye dispersion then was transferred to a 500 ml volumetric flask by the use of a 5 ml pipette and the flask was filled to the mark with DMF, a solvent noted by Kissa (1975) to be a particularly effective solvent for disperse dyes.

Concentration/absorbance data then were gathered for each dye by the usual technique of successively diluting a solution of known concentration with DMF and taking colorimetric readings after each dilution. In order to minimize relative analysis error, only those concentrations which produced transmittance values within the range of 20 to 60% were used (Ayres, 1949).

Tables I-III show the absorbance/concentration values for each dye. Statistical analyses of these data show that all dyes conform to the Beer-Lambert law under these conditions.

Table I
Resolin Blue BBLs pdr. in DMF
(Wavelength = 612.5 nm)

Concentration (g/l)	Absorbance (1/cm)
.0052	.223
.0056	.238
.0060	.260
.0064	.277
.0069	.302
.0076	.328
.0083	.364
.0093	.407
.0104	.450
.0119	.502
.0128	.535
.0139	.580
.0152	.625
.0167	.693

Coefficient of Determination: .999
Coefficient of Correlation: .999
Standard Error of Estimate: .006
Intercept: 00.020
Slope: 40.399

Table II

Terasil Red FB pdr. in DMF
(Wavelength = 520 nm)

Concentration (g/l)	Absorbance (1/cm)
.0161	.223
.0172	.240
.0185	.260
.0200	.277
.0217	.302
.0238	.335
.0263	.367
.0294	.409
.0333	.457
.0357	.482
.0385	.520
.0417	.561
.0152	.625
.0455	.611

Coefficient of Determination: .999
Coefficient of Correlation: .999
Standard Error of Estimate: .004
Intercept: 00.017
Slope: 13.110

Table III

Foron Brown S-3R pdr. in DMF
(Wavelength = 455 nm)

Concentration (g/l)	Absorbance (1/cm)
.0091	.250
.0103	.281
.0110	.301
.0118	.323
.0128	.348
.0140	.381
.0154	.418
.0167	.444
.0182	.482
.0200	.538
.0222	.585
.0250	.658

Coefficient of Determination: .999
Coefficient of Correlation: .999
Standard Error of Estimate: .003
Intercept: 00.021
Slope: 25.540

Pickup Reproducibility- Percent pickup is the number of grams of pad bath retained by 100 g of fabric after the impregnated fabric has passed through the squeeze rolls of the mangle. It was found that a reproducible pad bath pickup by the fabric of about 64% was achieved. A 95% confidence interval of (63.7% +/- 0.25%) was constructed.

Drainage Effect- Since a major portion of the main experiment consisted of drying strips of impregnated fabric by suspending the strips from a line, it was necessary to determine whether or not dye was distributed uniformly along the fabric length at the conclusion of drying. In preliminary experiments it was determined that drainage of dye down the vertically suspended fabric during drying was not a problem. Fabric samples were punched out of the dried fabric with an arch punch at 13 cm intervals over the length of the fabric, and dye content of the removed disks was determined. It was found that the concentration of dye was uniform over the length of the fabric except for the very bottom few centimeters which contained between 3% and 5% more dye than the rest of the fabric. The very bottom few centimeters of fabric were not used in actual experiments.

Particulate Migration Chamber- At least two potential problems exist with the experimental arrangement of the AATCC particulate migration test previously shown in Figure 3. First, the migration chamber consists of a single watch glass resting on an impregnated fabric which itself is resting on a glass plate. Since the fabric under the watch glass is in direct contact with the glass plate, it is possible that the capillary network of the fabric is modified both by the contact and by the pressure of the fabric itself on the glass plate; these factors may influence the level of migration to be obtained during the test. Second, often it is observed that condensed water is found on the inside of the watch glass and on the glass plate under the fabric area covered by the watch glass at the conclusion of the migration test. Since such water of condensation is not available to move particles of dye during the migration phase, the measured level of particulate migration may be slightly reduced. It was with these two potential problems in mind that the experimental arrangement for the migration chambers was modified as shown below in Figure 8.

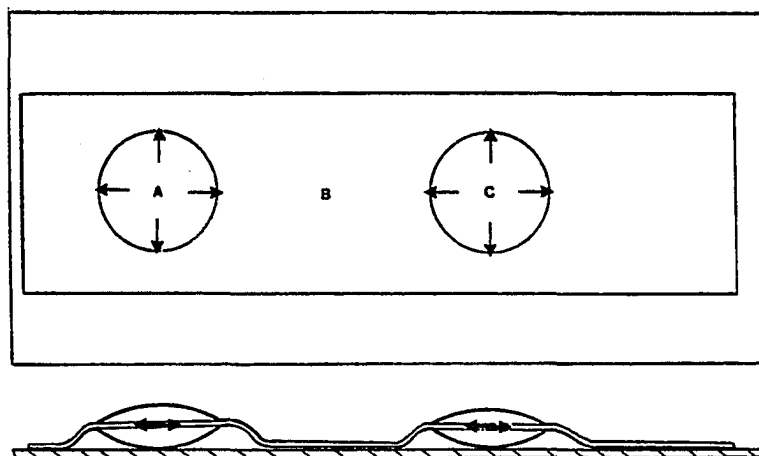


Figure 8. Experimental arrangement of particulate migration test chambers.

In Figure 8 each migration test chamber consists of two 10 cm watch glasses in an arrangement which prevents direct contact between fabric and another surface within the chamber. Preliminary tests revealed that about 0.08 g of condensed water was found in each chamber at the conclusion of migration tests. Since the weight of the fabric within the watch glass area is about 2.31 g, the water of condensation amounts to about 3.5% pickup. In order that the effect of the water of condensation be minimized, 8 cm filter paper which had been moistened with 1.2 ml of distilled water was fixed to the inside of each watch glass. It was found that the amount of water added to the filter paper was not so high as to drain away from the paper and run down the sides of the watch glass onto the fabric during the migration test.

Twelve migration tests were made- six with no filter paper and six with moistened filter paper within the watch glass chambers. The hypothesis was tested in each of the two cases that there was no difference in weight of the watch glass chamber before and after the migration test (due to water of condensation). As given in Appendix B, the t-test p-value found for the migration tests run without filter paper is 0.00036, while the corresponding p-value for the migration tests run with moistened filter paper is 0.38. These results suggest that the hypothesis of zero weight difference before and after the migration test should be rejected for the tests made with no filter paper, but not be rejected for the case when moistened filter paper is used, i.e., the moistened filter paper results in a watch glass chamber that is saturated with water vapor.

One would expect that particulate migration would be slightly higher when a vapor saturated watch glass chamber is used since more water would be available to move particles of dye. In order to test the research hypothesis that there is a difference versus the null hypothesis that there is no difference in the measured values of particulate migration obtained with and without a saturated chamber, eighteen migration tests were run. In nine of the tests no filter paper was used and in the other nine tests

the watch glass chambers contained moistened filter paper. As revealed in Appendix C, the t-test p-value is 0.045, which is evidence against the null hypothesis. There appears to be a real difference in resulting migration values; particulate migration values are slightly higher when the chamber is saturated with water vapor. It is suggested by these data that the experimental arrangement of Figure 8 is more conducive to equilibrium conditions throughout the experiment than are other arrangements which do not result in chambers saturated with water vapor at the beginning of the migration test.

Indirect vs. Direct Fixation Measurements- Indirect measurement of the amount of dye fixed in polyester after a thermal fixation step consists of extracting unfixed dye from the fabric with DMF at room temperature and estimating the amount of dye fixed by difference with the amount of dye applied. Since DMF at room temperature does not extract dye from the interior of the polyester fiber, the measurement discussed above is indirect. In order to check the accuracy of the indirect fixation method, indirect fixation values were compared to direct fixation values determined by extraction of dye from polyester at about 120C with DMF acidified to apparent pH 4.0 with p-toluenesulfonic acid (Kissa, 1975). Five random concentration levels for each dye were selected, and the

hypothesis that $[(\text{Direct fixation}/\text{Indirect fixation}) - 1]$ was equal to zero was tested for each dye. The resulting t-test p-values for Disperse Blue 165, Brown 1, and Red 60 are shown in Appendix D to be 0.061, 0.40, and 0.0003 respectively. The analysis suggests that significant small differences exist between fixation as determined by direct and indirect measurement for Disperse Blue 165 and Red 60 but not for Brown 1.

Main Experiments:

Preparation of Pad Baths- Twenty-four pad baths were prepared with each of the three dyes. Four concentrations of dye and six concentrations of commercial antimigrant were used. The concentrations of dye were 5, 10, 20, and 40 g/l, and the concentrations of antimigrant were 0, 2.5, 5.0, 10.0, 15.0, and 20.0 g/l. Each pad bath, amounting to 250 ml, was prepared in the following manner: Dye was dispersed in 100 ml of distilled water at 100F (38C), and antimigrant was dissolved in another 100 ml of distilled water at the same temperature. Both portions were mixed together and brought to 250 ml with additional distilled water. Three g/l of wetting agent was added, and the pad bath pH was adjusted to 6.00-6.25 by the dropwise addition of 10% glacial acetic acid, as needed. Each bath was allowed to cool to room temperature (75F; 24C) and then was strained through a fine mesh stainless steel screen to remove any very large particles.

Application- Polyester/cotton fabric strips about two meters long and 15.25 cm wide were used. Each strip was padded at room temperature to a pickup of approximately 64%. After passing through the pad bath and between the squeeze rolls, each strip was hung vertically on a line, and an approximately 75 cm length immediately was cut from

the suspended strip and placed on the particulate migration assembly, as described in Figure 8. The strip of fabric which remained suspended from the line was allowed to dry "symmetrically" at room temperature in the absence of strong air currents.

Inducement and Measurement of Particulate Migration-
Pad baths were formulated as previously described, containing each dye at four different concentrations with six levels of antimigrant for each concentration of dye. Twenty-four different pad baths were thus formulated for each of the three dyes. Each padding was placed on the assembly as illustrated in Figure 8 and allowed to dry for 2.5 hr. The watch glasses were removed, and the slight amount of residual moisture remaining on the fabric area that was in the two chambers during the test was allowed to evaporate. Fabric disks were punched out of areas "A" and "B" of Figure 8 with a two centimeter arch punch and placed into separate 100 ml bottles containing 50 ml of DMF at room temperature. The bottles were then sealed and gently shaken several times over a 4 hour period to promote more rapid dissolution of dye from the disks. When visual inspection of the disks indicated that all dye had been extracted, transmission measurements were made, and particulate migration was calculated by use of Equations 28 and 10, based on the regression analysis results of the concentration/absorbance measurements described above.

Thermal Fixation- Both the fabric strip which had been subjected to the migration test and a portion of the complementary fabric strip that had been dried symmetrically while suspended from a line were sewn together and passed through a Ross Air Systems continuous thermal fixation oven having a rapid circulation of air. Thermal fixation time was held constant at 120 seconds for all dyeings, and fabric thermal fixation temperature was maintained within the range of 400-410F (204-210C) as determined by the use of Thermopaper (Paper Thermometer Company) attached to the fabric. It is well understood that time is required to heat the fabric to a high fraction of the final thermal fixation temperature (Hes, 1984), and it is estimated that heat-up time for the system studied was about 15 seconds.

Measurement of Dye Fixation- After completion of the thermal fixation step, additional disks were punched from area "A" of Figure 8 and from the fabric which had been dried on the line. The disks were placed into separate bottles of DMF at room temperature; dye was extracted, and transmission measurements were made, as before. From the weight of the polyester in the disks and the concentration of dye found in solution by the use of Equation 28, the concentration of dye fixed in the polyester was calculated as grams of commercial dye per 100

g of polyester. Where necessary, the concentration of dye estimated by the indirect method to be fixed in the polyester was adjusted by multiplying by the appropriate mean ratio of [Direct fixation/Indirect Fixation], as given in Appendix C, to account for the small differences found by the two methods of measurement.

Reflectance Measurements- After particulate migration and fixation measurements had been made, the two fabric strips were washed with 80/20 DMF/water (volume ratio) to remove all unfixed dye and auxiliaries. The strips then were water rinsed, squeezed to remove most of the water, and entered into a bath of 70% sulfuric acid at an initial temperature of 100F to dissolve away the cotton fiber. The fabric strips were allowed to remain in the acid bath (while the bath cooled to room temperature) for about 12 hours, after which the remaining polyester skeletons were water rinsed, neutralized with soda ash, and finally rinsed in water and dried at room temperature. The polyester skeleton which was in chamber "C" of Figure 8 carefully was cut out of the fabric strip, and reflectance measurements were made on both sides (top and bottom) of the circular cutting after the fabric had been folded to four thicknesses to achieve opacity, in accordance with recommended technique (Connelly, 1983). Reflectance measurements were made in a similar way on the strip which had been dried symmetrically on the line.

CHAPTER IV

RESULTS AND ANALYSES

The experimental methodology used in the present study resulted in the generation of three primary forms of data: particulate migration, fixation, and reflectance values. These data are summarized in Tables IV-IX. A suitable analysis of these data provides the basis from which the sought for mathematical expression of depth of color can be derived.

Particulate Migration:

As shown in Tables IV-IX, the values of particulate migration decrease with increasing concentration of antimigrant in the pad bath. Such behavior is expected and is shown to hold for all concentrations of dye used. The results of the particulate migration experiments confirm that the use of the polymeric electrolyte sodium alginate (C-45) is effective for the control of particulate migration. It is revealed in the tables that the range of migration values obtained with a given range of antimigrant concentrations is different for each dye used.

Table IV
Migration, Fixation, and Reflectance Data
Resolin Blue BBLs

C	C-45	M_p	C_{fx}	U_{fx}	R_{ft}	R_{fb}	R_{fu}
05.0	00.0	.509	0.244	0.372	.0650	.0532	.0333
05.0	02.5	.450	0.307	0.535	.0594	.0484	.0290
05.0	05.0	.277	0.417	0.575	.0444	.0380	.0327
05.0	10.0	.110	0.511	0.580	.0398	.0369	.0329
05.0	15.0	.074	0.516	0.563	.0394	.0381	.0358
05.0	20.0	.036	0.540	0.564	.0409	.0401	.0372
10.0	00.0	.582	0.414	0.720	.0495	.0345	.0235
10.0	02.5	.513	0.556	1.048	.0392	.0298	.0213
10.0	05.0	.288	0.822	1.135	.0336	.0275	.0231
10.0	10.0	.035	1.068	1.104	.0268	.0246	.0235
10.0	15.0	.046	1.049	1.101	.0250	.0246	.0237
10.0	20.0	.026	1.074	1.106	.0248	.0238	.0241
20.0	00.0	.545	0.894	1.353	.0421	.0281	.0215
20.0	02.5	.453	1.097	1.724	.0347	.0246	.0204
20.0	05.0	.296	1.433	1.883	.0267	.0229	.0200
20.0	10.0	.158	1.665	1.863	.0206	.0210	.0212
20.0	15.0	.092	1.732	1.794	.0210	.0206	.0208
20.0	20.0	.082	1.792	1.875	.0210	.0206	.0208
40.0	00.0	.515	1.645	2.170	.0283	.0207	.0208
40.0	02.5	.509	1.664	2.954	.0252	.0196	.0187
40.0	05.0	.333	2.426	3.530	.0214	.0187	.0191
40.0	10.0	.189	2.893	3.595	.0194	.0188	.0192
40.0	15.0	.101	3.257	3.714	.0186	.0174	.0192
40.0	20.0	.104	3.201	3.732	.0191	.0183	.0197

C and C-45 are dye and antimigrant pad bath concentrations in g/l.

M_p is the fractional particulate migration.

C_{fx} is the concentration in g/100g of dye fixed on the polyester in area "A" of Figure 8.

U_{fx} is the concentration in g/100g of dye fixed on the polyester in the uniformly dried fabric.

R_{ft} and R_{fb} are fractional reflectance values respectively of the top and bottom of the polyester skeleton of fabric from area "C" of Fig. 8.

R_{fu} is the fractional reflectance of the polyester skeleton of the uniformly dried fabric.

Table V
Migration, Fixation, and Reflectance Data
Terasil Red FB

C	C-45	M_p	C_{fx}	U_{fx}	R_{ft}	R_{fb}	R_{fu}
05.0	00.0	.438	0.307	0.538	.1844	.1301	.0865
05.0	02.5	.309	0.385	0.552	.1487	.1229	.0879
05.0	05.0	.130	0.484	0.549	.1249	.1120	.0983
05.0	10.0	.034	0.533	0.551	.1039	.1065	.0952
05.0	15.0	.000	0.567	0.547	.1018	.0998	.0919
05.0	20.0	.000	0.529	0.534	.1051	.1039	.0985
10.0	00.0	.447	0.612	1.085	.1297	.0791	.0477
10.0	02.5	.321	0.780	1.139	.0915	.0676	.0560
10.0	05.0	.155	0.955	1.123	.0754	.0634	.0546
10.0	10.0	.045	1.078	1.123	.0611	.0576	.0561
10.0	15.0	.023	1.086	1.107	.0563	.0574	.0554
10.0	20.0	.023	1.086	1.106	.0571	.0575	.0552
20.0	00.0	.403	1.259	2.059	.0594	.0424	.0278
20.0	02.5	.260	1.597	2.125	.0556	.0380	.0315
20.0	05.0	.163	1.864	2.198	.0431	.0358	.0335
20.0	10.0	.067	2.044	2.172	.0358	.0349	.0339
20.0	15.0	.000	2.141	2.140	.0348	.0333	.0335
20.0	20.0	.031	2.124	2.178	.0349	.0333	.0345
40.0	00.0	.327	3.258	4.665	.0354	.0216	.0220
40.0	02.5	.221	3.778	4.741	.0307	.0216	.0227
40.0	05.0	.126	4.156	4.656	.0265	.0211	.0236
40.0	10.0	.074	4.496	4.772	.0237	.0212	.0228
40.0	15.0	.068	3.289	3.484	.0256	.0243	.0253
40.0	20.0	.012	3.378	3.369	.0254	.0245	.0252

C and C-45 are dye and antimigrant pad bath concentrations in g/l.

M_p is the fractional particulate migration.

C_{fx} is the concentration in g/100g of dye fixed on the polyester in area "A" of Figure 8.

U_{fx} is the concentration in g/100g of dye fixed on the polyester in the uniformly dried fabric.

R_{ft} and R_{fb} are fractional reflectance values respectively of the top and bottom of the polyester skeleton of fabric from area "C" of Fig.8.

R_{fu} is the fractional reflectance of the polyester skeleton of the uniformly dried fabric.

Table VI
Migration, Fixation, and Reflectance Data
Foron Brown S-3R

C	C-45	M_p	C_{fx}	U_{fx}	R_{ft}	R_{fb}	R_{fu}
05.0	00.0	.387	0.330	0.522	.1270	.0933	.0522
05.0	02.5	.217	0.459	0.588	.0975	.0760	.0549
05.0	05.0	.102	0.530	0.593	.0788	.0705	.0620
05.0	10.0	.020	0.568	0.584	.0703	.0689	.0642
05.0	15.0	.000	0.563	0.574	.0731	.0699	.0690
05.0	20.0	.000	0.568	0.572	.0706	.0681	.0714
10.0	00.0	.406	0.641	0.994	.0765	.0568	.0301
10.0	02.5	.200	0.906	1.126	.0619	.0482	.0369
10.0	05.0	.054	1.046	1.114	.0489	.0446	.0404
10.0	10.0	.000	1.124	1.140	.0442	.0393	.0417
10.0	15.0	.017	1.131	1.170	.0406	.0402	.0406
10.0	20.0	.000	1.153	1.116	.0401	.0397	.0400
20.0	00.0	.430	1.125	1.692	.0411	.0292	.0234
20.0	02.5	.315	1.508	2.156	.0369	.0290	.0248
20.0	05.0	.133	1.908	2.193	.0302	.0270	.0272
20.0	10.0	.045	2.168	2.282	.0276	.0259	.0277
20.0	15.0	.023	2.220	2.285	.0292	.0267	.0280
20.0	20.0	.000	2.230	2.161	.0272	.0267	.0286
40.0	00.0	.384	2.351	3.068	.0363	.0234	.0219
40.0	02.5	.301	2.950	3.859	.0292	.0221	.0225
40.0	05.0	.133	3.600	3.893	.0262	.0218	.0223
40.0	10.0	.071	3.918	4.045	.0241	.0219	.0223
40.0	15.0	.017	4.005	3.920	.0223	.0203	.0223
40.0	20.0	.062	3.831	3.993	.0235	.0219	.0235

C and C-45 are dye and antimigrant pad bath concentrations in g/l.

M_p is the fractional particulate migration.

C_{fx} is the concentration in g/100g of dye fixed on the polyester in area "A" of Figure 8.

U_{fx} is the concentration in g/100g of dye fixed on the polyester in the uniformly dried fabric.

R_{ft} and R_{fb} are fractional reflectance values respectively of the top and bottom of the polyester skeleton of fabric from area "C" of Fig. 8.

R_{fu} is the fractional reflectance of the polyester skeleton of the uniformly dried fabric.

Table VII
 Percent Migration and Fixation of
 Applied Particulate Dye
 Resolin Blue BBL5

C	C-45	PM _p	PC _{fix}	PU _{fix}
05.0	00.0	50.9	83.8	62.7
05.0	02.5	45.0	86.5	82.9
05.0	05.0	27.7	87.3	87.0
05.0	10.0	11.0	86.9	87.8
05.0	15.0	07.4	86.9	87.8
05.0	20.0	03.6	86.8	87.4
10.0	00.0	58.2	82.8	60.2
10.0	02.5	51.3	86.7	79.7
10.0	05.0	28.8	87.0	85.5
10.0	10.0	03.5	86.7	86.5
10.0	15.0	04.6	86.4	86.5
10.0	20.0	02.6	86.4	86.7
20.0	00.0	54.5	77.0	53.0
20.0	02.5	45.3	80.2	69.0
20.0	05.0	29.6	81.2	75.1
20.0	10.0	15.8	78.2	73.6
20.0	15.0	09.2	77.2	72.6
20.0	20.0	08.2	77.2	74.1
40.0	00.0	51.5	73.0	46.7
40.0	02.5	50.9	68.4	59.6
40.0	05.0	33.3	70.5	68.4
40.0	10.0	18.9	70.0	70.5
40.0	15.0	10.1	69.4	71.2
40.0	20.0	10.4	68.4	71.5

C and C-45 are dye and antimigrant pad bath concentrations in g/l.
 PM_p is the percent particulate migration.
 PC_{fix} is the percent fixation of immobilized particulate dye in area "A" of Figure 8.
 PU_{fix} is the percent fixation of particulate dye from the uniformly dried fabric.

Table VIII
 Percent Migration and Fixation of
 Applied Particulate Dye
 Terasil Red FB

C	C-45	PM _p	PC _{fx}	PU _{fx}
05.0	00.0	43.8	88.5	87.2
05.0	02.5	30.9	88.8	88.0
05.0	05.0	13.0	89.2	88.0
05.0	10.0	03.4	88.7	88.6
05.0	15.0	00.0	89.1	88.4
05.0	20.0	00.0	88.3	88.3
10.0	00.0	44.7	90.1	88.5
10.0	02.5	32.1	89.7	89.0
10.0	05.0	15.5	89.5	89.0
10.0	10.0	04.5	89.7	89.2
10.0	15.0	02.3	89.6	89.2
10.0	20.0	02.3	89.8	89.4
20.0	00.0	40.3	89.8	87.6
20.0	02.5	26.0	89.8	88.4
20.0	05.0	16.3	89.7	88.6
20.0	10.0	06.7	89.3	88.5
20.0	15.0	00.0	89.3	88.8
20.0	20.0	03.1	89.4	88.8
40.0	00.0	32.7	89.9	86.6
40.0	02.5	22.1	89.1	87.1
40.0	05.0	12.6	89.2	87.4
40.0	10.0	07.4	89.2	87.7
40.0	15.0	06.8	89.7	88.6
40.0	20.0	01.2	89.8	88.5

C and C-45 are dye and antimigrant pad bath concentrations in g/l.
 PM_p is the percent particulate migration.
 PC_{fx} is the percent fixation of immobilized particulate dye in area "A" of Figure 8.
 PU_{fx} is the percent fixation of particulate dye from the uniformly dried fabric.

Table IX
 Percent Migration and Fixation of
 Applied Particulate Dye
 Foron Brown S-3R

C	C-45	PM _p	PC _{fx}	PU _{fx}
05.0	00.0	38.7	88.9	86.2
05.0	02.5	21.7	90.3	90.6
05.0	05.0	10.2	90.1	90.6
05.0	10.0	02.0	89.8	90.5
05.0	15.0	00.0	89.3	90.3
05.0	20.0	00.0	89.3	91.0
10.0	00.0	40.6	90.4	83.3
10.0	02.5	20.0	90.8	90.3
10.0	05.0	05.4	90.3	90.9
10.0	10.0	00.0	89.6	90.9
10.0	15.0	01.7	89.4	90.9
10.0	20.0	00.0	89.3	90.3
20.0	00.0	43.0	86.4	74.1
20.0	02.5	31.5	88.3	86.5
20.0	05.0	13.3	89.0	88.7
20.0	10.0	04.5	88.5	88.9
20.0	15.0	02.3	88.3	88.8
20.0	20.0	00.0	87.9	87.7
40.0	00.0	38.4	83.4	67.0
40.0	02.5	30.1	85.6	78.2
40.0	05.0	13.3	86.7	81.3
40.0	10.0	07.1	85.3	81.7
40.0	15.0	01.7	83.7	80.5
40.0	20.0	06.2	82.8	81.0

C and C-45 are dye and antimigrant pad bath concentrations in g/l.

PM_p is the percent particulate migration.

PC_{fx} is the percent fixation of immobilized particulate dye in area "A" of Figure 8.

PU_{fx} is the percent fixation of particulate dye from the uniformly dried fabric.

Fixation:

With decreasing particulate migration, increasing amounts of immobilized particulate dye are found on the fabric area in watch glass chambers "A" and "C" of Figure 8. During thermofixation this immobilized, unmigrated dye is available to be fixed on the polyester fiber. The concentrations of immobilized fixed dye, expressed in grams of dye per one hundred grams of polyester (g/100g), are given in Tables IV-VI in the column labeled " C_{fx} ." In the column labeled " U_{fx} " are given the concentrations (g/100g) of dye fixed on the polyester fiber in the corresponding fabric strips which had been uniformly dried on a line. In Tables VII-IX are given the corresponding percent fixation values in the columns labeled " FC_{fx} " and " PU_{fx} ."

It is revealed in Tables VII-IX that PU_{fx} of Disperse Blue 165 exhibits the greatest sensitivity to particulate migration of the three dyes studied, with that of Red 60 exhibiting the least sensitivity. For the highest values of PM_p , PU_{fx} for Blue 165 and Brown 1 tend to be lowest—even when the absolute concentration of fixed dye is taken into account. There are at least three possible explanations for the observed decrease in fixation with increasing particulate migration. As particulate dye migrates to the surface of the uniformly dried fabric, the

distance between the total absorptive surface of the polyester and the dye increases. Also the dye which has migrated tends to form aggregates, decreasing the particulate surface area. With decreasing particulate surface area available to liberate dye vapor and with increasing distance for the vapor to travel to reach the polyester surface, decreasing fixation occurs (Etters & Urbanik, 1977a). Also it is shown by the work of Beckmann (1966) that high concentrations of dispersing agent tend to reduce fixation. When particulate migration is high, both dye and dispersing agent migrate to the fabric surface. The presence of high dispersing agent concentration in the fabric surface may then cause a reduction of dye fixation.

The quantity U_{fx} consists of both immobilized and migrated fixed dye, and it is shown in Tables VII-IX that PU_{fx} approaches PC_{fx} as migration is increasingly controlled. If it is assumed that the concentration of immobilized fixed dye in the polyester of the uniformly dried fabric is equivalent to the concentration of immobilized dye found in watch glass chambers "A" and "C" (i.e., C_{fx}), the concentration of fixed dye due to dye which has moved, M_{fx} , can be estimated by:

$$M_{fx} = U_{fx} - C_{fx} \quad (29)$$

Since migrated fixed dye, M_{fx} , is located in the polyester fibers predominately in the fabric surface, computation of

the true concentration of dye in these fibers requires knowledge of the fraction of the total cross-sectional fabric mass that these fibers constitute. In the absence of such knowledge and because of the thin fabric cross-section, Equation 29 may be used to express the concentration of migrated fixed dye in terms of fixed dye weight in grams per one hundred grams of total polyester fiber in the fabric cross-section without specifying a concentration gradient through the cross-section.

Reflectance:

Preliminary reflectance measurements were made on polyester skeletons from fabrics dyed with each of the three dyes. The measurements were made over the wavelength range of 400-700 nm at twenty nm intervals to determine the approximate wavelength of minimum reflectance or maximum absorbance. It was found that the maximum absorbance value for Disperse Blue 165 occurred at 620 nm, and the values for Red 60 and Brown 1 occurred at 520 and 480 nm respectively.

Reflectance values of a polyester skeleton from a fabric which had been subjected to all processing steps in the absence of dye, i.e., mock-dyed, were determined at the wavelengths given above. The value found at 620 nm was

0.7717, and the values found at 520 and 480 nm were 0.7321 and 0.7273 respectively.

Even though the fixed dye found on the polyester fabric taken from chamber "A" or "C" of Figure 8 can be considered immobilized or unmigrated dye, differences were detected between reflectance measurements made on the top (R_{ft}) and bottom (R_{fb}) of the polyester skeleton of the fabric taken from chamber "C." As revealed in Tables IV-VI, the differences were greatest for higher values of M_p , with the bottom of the fabric having the lower of the two reflectance values. It is suggested by these data that during the course of the particulate migration process there was some top-to-bottom settling of the dye liquor through the fabric cross-section under the influence of gravity- being more evident in the absence of antimigrant, probably because of differences in dye particle size. In computations to estimate the relationship between "immobilized dye" and K/S , it was necessary to use an average K/S value, determined from both R_{ft} and R_{fb} .

The term "KC" is used to designate the mean $(K/S)_d$ value, found from R_{ft} , R_{fb} , and the reflectance of the mock-dyed fabric given above, by the use of Equations 19 and 20. As is general practice, only the reflectance values at the wavelengths of maximum absorbance were used

in the computations of K/S . It is well understood that the theoretical relationship between K/S and uniformly fixed dye is linear, and experimental data which do not produce a linear relationship can be made to do so by the use of a suitable surface reflectance factor (Kuehni, 1975). In order to obtain the strongest linear relationship between KC and C_{rx} , the surface reflectance values used in Equation 19 were selected according to certain criteria. These criteria were: (1) The coefficient of determination (R^2) found in plots of KC vs. C_{rx} had to be high. (2) The t statistic for a zero intercept in plots of KC vs. C_{rx} had to be low. The surface reflectance values which best met the above criteria were determined by successive regression analyses, using statistical software available through the UNCG computer system (SAS Institute Inc.). The optimum surface reflectance value found at 620 nm (Blue 165) was 0.0145, and the values found at 520 nm (Red 60) and 480 nm (Brown 1) were 0.0090 and 0.0150 respectively.

Analyses:

In Appendix E is given the General Linear Models Procedure (GLM) output from SAS of the regression analysis of the dependent variable KC vs. the independent variable C_{rx} for Disperse Blue 165. Outliers, determined from preliminary analysis, were not included in the analyses

given in the appendices. Outliers were defined as those data points that produced values of KC/C_{rx} greater than 2.5 standard deviations from the mean of KC/C_{rx} . Such data were associated mainly with extremely high concentrations of dye and correspondingly low reflectance values, i.e., saturated systems. In Appendices F and G are given the results of similar SAS outputs for Disperse Red 60 and Disperse Brown 1. Analysis reveals high values of R^2 and low values of the t statistic for all three dyes.

The line slopes found from the regression analyses are equivalent to "a" of Equation 21 and can be considered practical reflectance absorptivity coefficients analogous to those found for solution transmittance measurements. As given in Appendices E, F, and G, the values of the line slopes found for Disperse Blue 165, Disperse Red 60, and Disperse Brown 1 are 38.44, 8.19, and 17.08 respectively. These practical absorptivity coefficients can be used to express the relationship between fabric dye content and reflectance of light from the fabric for a dye/fabric system in which these dyes are distributed uniformly throughout the fabric cross-section.

The slope of the lines in Figures 9-11 illustrates the relationship between KC and the concentration of uniformly distributed dye found for each of the dyes.

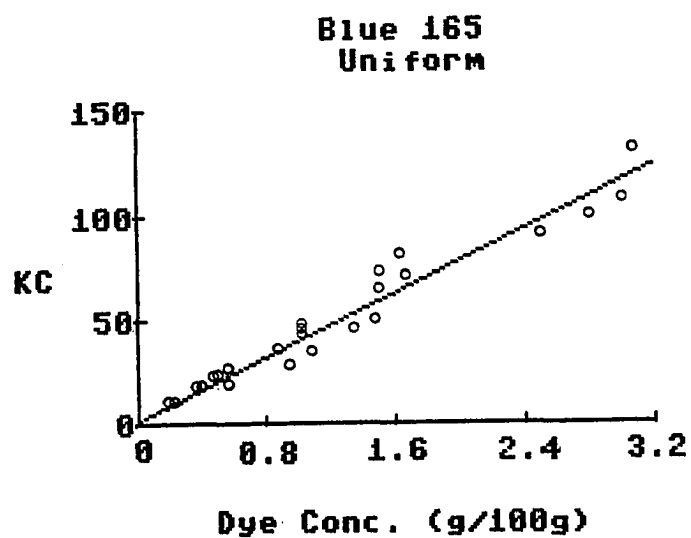


Figure 9. Absorptivity coefficient of uniformly distributed dye.

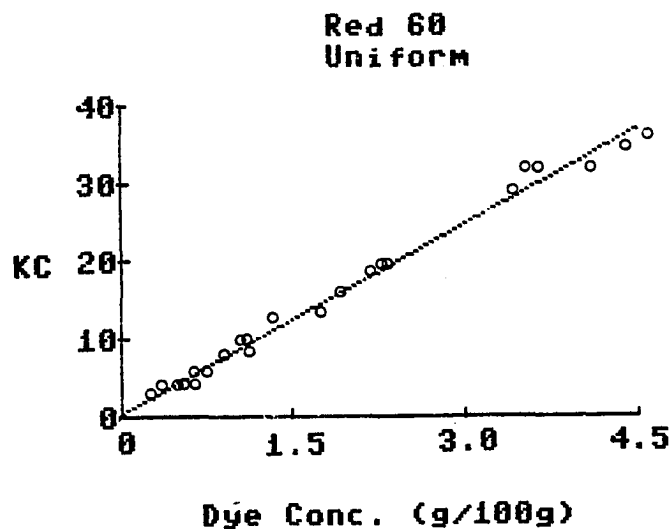


Figure 10. Absorptivity coefficient of uniformly distributed dye.

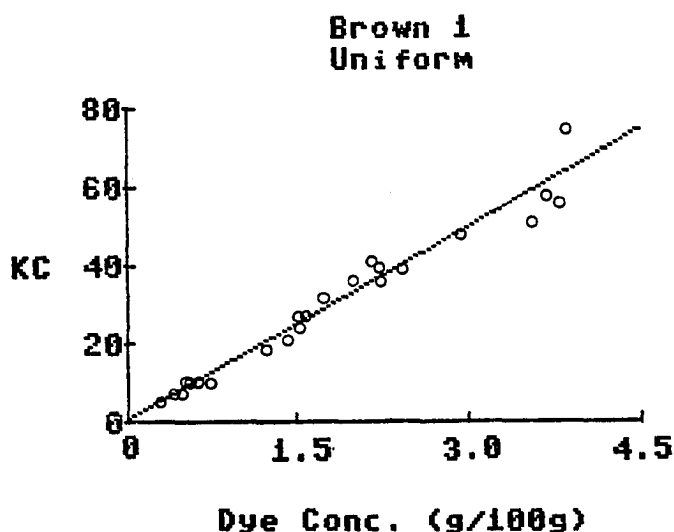


Figure 11. Absorptivity coefficient of uniformly distributed dye.

The values of R_{fu} given in Tables IV-VI represent reflectance values of the polyester skeletons taken from the uniformly dried fabric. These reflectance values, the reflectance values of the mock-dyed fabric, and the previously determined surface reflectance values were used to calculate "KN" in a manner similar to that previously used to calculate KC. The quantity KN is equivalent to $(K/S)_d$ found by the use of Equations 19 and 20. If it is assumed that KN consists of contributions from both migrated and immobilized dye, the $(K/S)_d$ due to the migrated dye can be designated "KM" and estimated by use of the following equation:

$$KM = KN - KC \quad (30)$$

For zero or very low values of particulate migration Equation 30 cannot be used to estimate KM since the reflectance values upon which KN and KC are calculated tend to be equivalent, and zero or even negative values of KM can be obtained. Negative KM values are associated with the small variability of similar, overlapping reflectance values and the lack of instrumental precision in measuring very small reflectance differences. Zero or negative values of KM which resulted from the use of Equation 30 in the present investigation were not used in further analysis.

The analyses performed for the derived quantities KM and M_{rx} were completely analogous to those performed for the quantities KC and C_{rx} based on direct measurements. In Appendix H is given the General Linear Models Procedure (GLM) output from SAS of the regression analysis of the dependent variable KM vs. the independent variable M_{rx} for Disperse Blue 165. Outliers, determined from preliminary analysis, once again were not included in the analyses given in the appendices. Outliers again were defined as those data points that produced values of KM/M_{rx} greater than 2.5 standard deviations from the mean of KM/M_{rx} . Such data again were associated mainly with extremely high concentrations of dye and correspondingly low reflectance

values, i.e., saturated systems. In Appendices I and J are given the results of similar SAS outputs for Disperse Red 60 and Disperse Brown 1. Analysis again reveals high values of R^2 and low values of the t statistic for all three dyes. Once again the line slopes found from the regression analyses are equivalent to "a" of Equation 21 and can be considered practical reflectance absorptivity coefficients analogous to those found for solution transmittance measurements. As given in Appendices H, I, and J, the values of the line slopes found for Disperse Blue 165, Disperse Red 60, and Disperse Brown 1 are 83.07, 15.41, and 41.41 respectively. These practical absorptivity coefficients can be used to express the relationship between fabric dye content and reflectance of light from the fabric for a dye/fabric system in which these dyes are not distributed uniformly throughout the fabric cross-section, i.e., for a dye/fabric system in which migrated dye is fixed predominately in the fibers of the fabric surface.

The slope of the lines in Figures 12-14 illustrates the relationship between KM and the concentration of migrated fixed dye for each of the three dyes used in the present study.

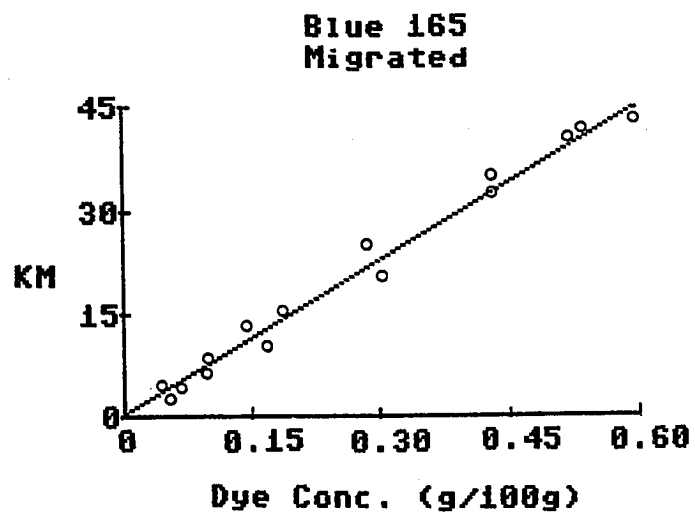


Figure 12. Absorptivity coefficient of migrated dye.

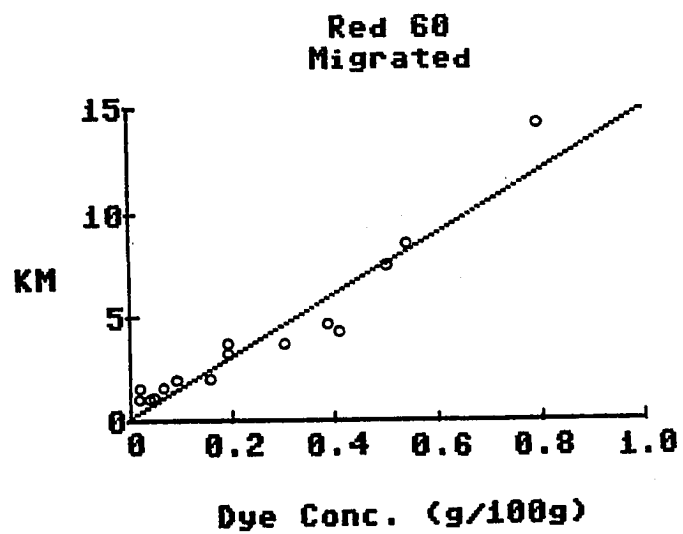


Figure 13. Absorptivity coefficient of migrated dye.

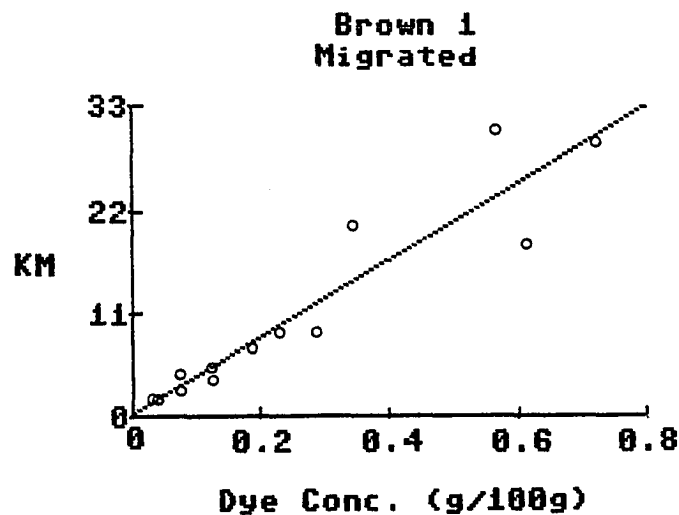


Figure 14. Absorptivity coefficient of migrated dye.

Analyses of the experimental results have revealed that the contribution of both uniformly distributed and migrated fixed dye to the reflectance of light from a dyed textile substrate can be quantified separately. In the following chapter use will be made of the developed relationships to construct a mathematical expression which unifies the two independent effects discussed above.

CHAPTER V
CONCLUSIONS

Analysis of results given in the previous chapter has suggested a means by which a mathematical expression may be developed to satisfy the objective of the present research. The goal of this final chapter is to develop and propose possible uses for the mathematical expression and to suggest areas for future research.

Mathematical Expression:

Rearrangement of Equation 30 shows that KN, the value of $(K/S)_d$ associated with both uniformly distributed and migrated fixed dye, can be expressed as:

$$KN = KC + KM \quad (31)$$

where KC and KM are the values of $(K/S)_d$ associated with uniformly distributed fixed dye, C_{fx} , and migrated fixed dye, M_{fx} , respectively. When the more conventional notation a_1 and a_2 are adopted for the reflectance absorptivity coefficients for uniformly distributed and migrated fixed dye respectively, KC can be expressed as:

$$KC = a_1 (C_{fx}) \quad (32)$$

and KM can be expressed as:

$$KM = a_2 (M_{fx}) \quad (33)$$

It follows that Equation 31 can be expressed in terms of Equations 32 and 33 by:

$$KN = a_1(C_{fx}) + a_2(M_{fx}) \quad (34)$$

Equation 34 therefore is proposed to express the relationship between color depth and both the amount and the location of fixed dye in the fabric cross-section. Although it is well known that KC can be expressed satisfactorily by the use of Equation 32, it is believed that the finding that KM also can be expressed by use of an identical equation form (Equation 33) is original. Futhermore, it is believed that Equation 34 constitutes the simplest possible form that also retains physical meaning.

Examination of Coefficients:

The coefficients of Equation 34 obtained in the current study are summarized below in Table X.

Table X
Comparison of Coefficients

Dye	a_1	a_2	a_2/a_1
Blue 165	38.44	83.07	2.16
Red 60	8.19	15.41	1.88
Brown 1	17.08	41.41	2.42

As given in Table X, the coefficient a_2 is larger than the coefficient a_1 for all dyes. The physical significance of

this is that the influence of migrated dye on color yield is greater than that of uniformly distributed dye- a well known, but previously unquantified fact. For Blue 165 it is revealed that the "strength" of migrated dye is 2.16 times that for uniformly distributed dye. For Red 60 and Brown 1 the ratios are shown to be 1.88 and 2.42 respectively. As far as it is known, the data of Table X represent the first quantification of the relative contribution of migrated and uniformly distributed dye on color depth.

Possible Uses for Model:

Equation 34 can be used in estimating dyeing costs in continuous commercial systems for various levels of migration. It is known in industry that if migration is too severe, the beneficial effect on color yield will be offset by quality problems related to uneven dyeings. On the other hand, if migration is over-controlled, dyeings will tend to be more even, but more dye will have to be used to achieve the desired shade depth, and the final dyeing may appear to be rather grainy or lacking in smoothness. It is possible that a judicious use of Equation 34 could permit the refinement of industrial processes to achieve the necessary evenness of shade but with the minimum amount of dye necessary to produce the

shade. For example, if it were found that for a given fabric a ratio of M_{fx} to C_{fx} of 1 to 4 is necessary to achieve the desired appearance, it should be possible from a knowledge of the coefficients associated with certain dyes to develop the most economical dye formula consistent with the M_{fx}/C_{fx} ratio desired.

Another possible use of Equation 34 is in the characterization or classification of disperse dyes. It is possible that the use of the model could permit a combination of dyes in a specific formula to produce a homogeneous color depth response to migration. If it were possible to select and use only those dyes in a given formula which had similar coefficients a_1 and a_2 of Equation 34, the dyes would react to migration similarly and produce only on-tone depth variations.

New textile products might be possible through the use of Equation 34 in selecting dyes which react extremely differently to migration. For example, dyes deliberately might be selected on the basis of dissimilar coefficients a_1 and a_2 for use together in a dye formulation. The final dyeing of such a heterogeneous combination might consist of almost a sandwich of color which revealed subtle changes of tone with surface distortion of the fabric during laundering or wear.

Areas for Future Research:

A study of the influence of experimental replication on the variability of the coefficients of Equation 34 could be of value.

It has been shown that the coefficients of Equation 34 tend to be different for different dyes on the same substrate. A study of the influence of textile substrate (particularly substrate thickness) on the coefficients would be a useful addition to the present research.

Whether or not the coefficients of Equation 34 are sensitive to dyeing conditions such as temperature and time is an area worthy of investigation.

A determination of the general validity of Equation 34 to systems other than those consisting of polyester fibers and disperse dyes, e.g., cotton fiber and vat dyes, would also be useful.

BIBLIOGRAPHY

- Abdel-Fattah, S. H., Abdou, L. A., Bendak, A. & El-Aref, A. T. Kinetic characterization of the role of anti-migrants in the Thermosol dyeing. Teintex, 1981, 1, 3-16.
- Ayres, G. H. Evaluation of accuracy in photometric analysis. Analytical Chemistry, 1949, 21, 652-657.
- Beckmann, W. Principles of dry heat fixation of dispersion dyestuffs on polyester - (Thermosol Process). Canadian Textile Journal, 1966, 83, 43-48.
- Bent, C. J., Flynn, T. D., & Sumner, H. H. A new insight into the thermofix dyeing of polyester-cellulose blends. I- Investigation of mechanism of transfer of disperse dyes. Journal of the Society of Dyers and Colourists, 1969, 85, 606-617.
- Bille, H., Kruger, R., & Schmidt, G. Have pigment dyes a real chance in dyeing? Canadian Textile Journal, 1973, 90, 51-59.
- Caldo, C. Synthetic fibers: an uncertain future? American Dyestuff Reporter, 1985, 74(3), 16-48.
- Carslaw, H. S. & Jaeger, J. C. Conduction of heat in solids. Oxford: Clarendon Press, 1978.
- Cate, A. L. Evaluating disperse dyes for heat fixation. Textile Chemist and Colorist, 1969, 1, 484-487.
- Cegarra, J. & Puente, P. Kinetics of dyeing polyester fiber by the Thermosol process. Annales Scientifiques Textiles Belges, 1976, 24, 5-23.
- Chemiefaser-weltproduktion auf rekordniveau. Chemiefasern-Textilindustrie, 1985, 35/87(3), 152.
- Committee on Technical Subjects. 1985 technical subjects. Research Triangle Park, NC: American Association of Textile Chemists and Colorists, 1985, 13.
- Connelly, R. L. Preparation and mounting textile samples for color measurement. In G. Celikiz & R. G. Kuehni (Eds.), Color technology in the textile industry. Research Triangle Park, NC: American Association of Textile Chemists and Colorists, 1983.

- Crank, J. The mathematics of diffusion. Oxford: Clarendon Press, 1975.
- Dawson, J. F. The structure and properties of disperse dyes in polyester coloration. Journal of the Society of Dyers and Colourists, 1983, 99, 183-191.
- Detscheva, R., Iltscheva, R. & Waltscheva, E. Kinetics and thermodynamics of continuous dyeing of polyester fibers with disperse dyes. Part 1: the importance of polyester materials. Textilveredlung, 1981, 16, 21-24.
- Detscheva, R., Iltscheva, R. & Waltscheva, E. Kinetics and thermodynamics of continuous dyeing of polyester fibers with disperse dyes. Part 2: influence of dyeing auxiliaries. Textilveredlung, 1981, 16, 24-29.
- Detscheva, R., Iltscheva, R. & Waltscheva, E. Kinetics and thermodynamics of continuous dyeing of polyester fibers with disperse dyes. Part 3: the thermodynamics of Thermosol dyeing. Textilveredlung, 1981, 16, 484-488.
- Detscheva, R., Iltscheva, R. & Waltscheva, E. Kinetics and thermodynamics of continuous dyeing of polyester fibers with disperse dyes. Part 4: influence of accelerators on the thermodynamics of the Thermosol process. Textilveredlung, 1982, 17, 128-133.
- Detscheva, R., Iltscheva, R. & Waltscheva, E. Kinetics and thermodynamics of continuous dyeing of polyester fibers with disperse dyes. Part 5: relationship between the kinetic and thermodynamic characteristics in the Thermosol dyeing of polyester fibers with disperse dyes. Textilveredlung, 1982, 17, 166-168.
- Detscheva, R. & Milkova, A. Kinetics and thermodynamics of the transfer of disperse dye from the print paste film to the polyester substrate. Part I: influence exerted by the type of thickening used in print pastes containing caprolactam. Melliand Textilberichte, 1981, 62, 734-737.
- Detscheva, R., Milkova, A. & Georgieva, A. Kinetics and thermodynamics of the transfer of disperse dye from the print paste film to the polyester substrate. Part II: influence exerted by the type of thickening agent on the thermodynamic values of the transfer. Melliand Textilberichte, 1981, 62, 887-890.

- Detscheva, R., Welewa, P. & Milkowa, A.B. Kinetics and thermodynamics of the fixation of anthraquinone dyes in printing on polyester, Part I. Report I: influence of caprolactam on fixation kinetics. Melliand Textilberichte, 1981, 62, 355-357.
- Detscheva, R., Welewa, P. & Milkowa, A. B. Kinetics and thermodynamics of the fixation of anthraquinone dyes in printing on polyester. Report II: influence of caprolactam on the thermodynamics of the disperse anthraquinone dye. Melliand Textilberichte, 1981, 62, 401-402.
- Dyestuff migration: evaluation of. Technical Manual. Research Triangle Park, NC: American Association of Textile Chemists and Colorists, 1984, p79.
- Etters, J. N. Technical migration of disperse dye in the Thermosol process. Textile Chemist and Colorist, 1972, 4, 160-164.
- Etters, J. N. Thermosol dyeing: the rational use of auxiliaries. Textilveredlung, 1973, 8, 187-190.
- Etters, J. N. Diffusion equations made easy. Textile Chemist and Colorist, 1980, 12, 140-145.
- Etters, J. N. The diffusional boundary layer: some implications for the dyeing technologist. Journal of the Society of Dyers and Colourists, 1981, 97, 170-179.
- Etters, J. N. & Hurwitz, M. D. (in press). Tables of numerical solutions involving the boundary layer diffusion equations. Textile Research Journal, (1986a).
- Etters, J. N. & Hurwitz, M. D. (in press). Predicting opaque reflectance of translucent fabric: effect of background reflectance. Textile Chemist and Colorist, (1986b).
- Etters, J. N. & Urbanik, A. 'Particulate activation' of disperse dye in the Thermosol process. Textile Chemist and Colorist, 1977a, 9, 102-108.
- Etters, J. N. & Urbanik, A. Etters and Urbanik reply. Textile Chemist and Colorist, 1977b, 9, 247-248.
- Gerber, H. Discussion of the problem of dyestuff migration during intermediate drying. Melliand Textilberichte, 1972, 53, 335-339.

- Gerber, H. On the mechanism of fixation of disperse dyes in the Thermosol process and in transfer printing. Textilveredlung, 1973, 8, 449-456.
- Gerber, H. On setting disperse dyes in the Thermosol process. Melliand Textilberichte, 1979, 60, 349.
- Gerber, H. & Somm, F. New knowledge regarding the thermosol process. Textilveredlung, 1971, 6, 372-382.
- Giles, C. H. A laboratory course in dyeing. Bradford: The Society of Dyers and Colourists, 1974.
- Gibson, J. W. Thermosol process. U.S. Patents 2663612 and 2663613. Dec. 22, 1953.
- Gibson, J. W. The Thermosol story. Textile Chemist and Colorist, 1979, 11, 241-245.
- Gorondy, E. J. Vapor fixation of disperse dyes in polyester. Textile Chemist and Colorist, 1978, 10, 105-121.
- Hes, L. Calculation of the heat-up time of a dry textile sheet by consideration of the temperature gradient in the cross section. Textilveredlung, 1984, 19, 175-178.
- Hill, A. V. Diffusion of oxygen and lactic acid through tissues. Proceedings of the Royal Society, 1928, 104B, 39-96.
- Ingamells, W., Peters, R. H. & Thornton, S. R. The mechanism of carrier dyeing. Journal of Applied Polymer Science, 1973, 17, 3733-3746.
- Iyer, S. R. S. In K. Venkataraman (Ed.), The chemistry of synthetic dyes, volume vii. New York: Academic Press, 1974.
- Jones, F. In C. L. Bird & W. S. Boston (Eds.), The theory of coloration of textiles. Bradford: Dyers Company Publications Trust, 1975.
- Judd, D. B. & Wyszecki, G. Color in business, science, and industry. New York: John Wiley and Sons, Inc., 1963.
- Kartaschoff, V. The phenomenon of dyeing silk cellulose acetate. Helvetica Chemica Acta, 1925, 8, 928-942.

- Kern, R., Kissling, B. & Herlaunt, M. Disperse dyes in the Thermosol process- their behavior in the dyeing of self & combination shades on polyester blend fabrics. Textilveredlung, 1968, 3, 595-606.
- Kissa, E. Quantitative determination of dyes in textile fibers. Textile Research Journal, 1975, 45, 290-295.
- Kissa, E. Tinctorial efficacy of dyes in polyester fibers. Textile Research Journal, 1984, 54, 497-504.
- Kubelka, P. & Munk, F. A contribution to the optics of colored coatings. Zeitschrift fur Technische Physik, 1931, 12, 593-597.
- Kuehni, R. G. Computer colorant formulation. Lexington: Lexington Books, 1975.
- Kuehni, R. G. A General procedure for the determination of relative dye strength by spectrophotometric transmittance measurement. In G. Celikiz & R. G. Kuehni (Eds.), Color technology in the textile industry. Research Triangle Park, NC: American Association of Textile Chemists, 1983.
- Kuster, B., Schnaith, E., Schollmeyer, E., & Herlinger, H. Diffusion and aggregation of disperse dyes in the absence of water. Part I: on the fixation of disperse dyes in the Thermosol process. Melliand Textilberichte, 1978, 59, 571-576.
- Kuster, B., Schnaith, E., Schollmeyer, E., & Herlinger, H. Diffusion and aggregation of disperse dyes in the absence of water. Part II: on the diffusion behavior of disperse dyes in polyester fiber in the Thermosol process. Melliand Textilberichte, 1979, 60, 66-68.
- Kuth, R. The continuous fixation of disperse dye on polyester fabric. Textil Praxis International, 1975, 30, 461-468.
- Leube, H. & Richter, P. The continuous dyeing of woven and knitted texturized polyester fabrics. Textile Chemist and Colorist, 1973, 5, 43-47.
- Levich, V. G. Physicochemical hydrodynamics. Englewood Cliffs: Prentice-Hall, 1962.
- Love, R. B., Oglesby, S. & Gailey, I. The relation between dye concentration and reflectance- amendments to the Kubelka-Munk equation. Journal of the Society of Dyers and Colourists, 1965, 81, 609-614.

- Maasdorp, A. P. B. The application of the Etters diffusion equation to the rates of absorption of chromium by dyed and undyed wool. SAWTRI Technical Report, No. 538, 1983, 1-19.
- Majury, T. G. The dyeing of cellulose acetate with non-ionic dyes. III- dyeing from the vapor phase. Journal of the Society of Dyers and Colourists, 1956, 72, 41-49.
- McDowell, W. Constants for controlling polyester dyeing processes. Melliand Textilberichte, 1972, 53, 1265-1270.
- McDowell, W. Dyeing of polyester- from the viewpoint of the dye. Melliand Textilberichte, 1980, 61, 946-951.
- McGregor, R. The effect of flow rate on rate of dyeing, Part II: The mechanism of fluid flow through textiles and its significance in dyeing. Journal of the Society of Dyers and Colourists, 1965, 81, 429-438.
- McGregor, R. Diffusion and sorption in fibers and films. New York: Academic Press, 1974.
- McGregor, R. & Etters, J. N. Transitional kinetics in disperse dyeing. Textile Chemist and Colorist, 1979, 11, 202-206.
- McGregor, R. & Peters, R. H. The effect of flow rate on rate of dyeing, Part I: the diffusion boundary layer in dyeing. Journal of the Society of Dyers and Colourists, 1965, 81, 393-400.
- McGregor, R., Nounou, A. E., & Peters, R. H. The effect of rate of flow on the sorption of dye by a nylon fabric from aqueous solutions. Journal of the Society of Dyers and Colourists, 1974, 90, 246-254.
- McGregor, R., Peters, R. H., & Varol, K. The physico-chemical hydrodynamics of dyeing, Part I: an experimental study of the convective diffusion of a dye to an absorbing surface; Part II: the sorption of disperse dyes by films of methoxymethylnylon 6.6. Journal of the Society of Dyers and Colourists, 1970, 86, 437-445.
- Moncrieff, R. W. Man-made fibers. New York: John Wiley & Sons, Inc., 1957.

- Newman, A. B. The drying of porous solids: diffusion and surface emission equations. Transactions of the American Institute of Chemical Engineers, 1931, 27, 203-220.
- Nobbs, J. H. Kubelka-Munk theory and the prediction of reflectance. Review of Progress in Coloration, 1985, 15, 66-75.
- Northern Piedmont Section, AATCC. The effect of auxiliaries on the thermal fixation of disperse dye. Textile Chemist and Colorist, 1972, 4, 260-267.
- Northern Piedmont Section, AATCC. Processes involved in particulate dye migration. Textile Chemist and Colorist, 1975, 7, 192-201.
- Peters, R. H. Textile chemistry, Vol. III. New York: Elsevier, 1975.
- Rattee, I. D. & Breuer, M. M. The physical chemistry of dye adsorption. New York: Academic Press, 1974.
- Somm, F. & Buser, R. Thermosol dyeing today and tomorrow. Textilveredlung, 1984, 19, 131-137.
- Stearns, E. I. The practice of absorption spectrophotometry. New York: John Wiley and Sons, Inc., 1969.
- The 'Thermosol' process for the coloration of fiber v, Orlon acrylic fiber and nylon. The Technical Bulletin, (DuPont), 1949, 5, 82-103.
- Urbanik, A. A generalized form of the Cegarra-Puente equation- relationships of empirical dyeing rate equations to diffusion parameters. Textilveredlung, 1978, 13, 278-279.
- Urbanik, A. & Etters, J. N. Rate and activation energy of dyeing in the thermofixation process. Textilveredlung, 1972, 7, 440-444.
- Urbanik, A. & Etters, J. N. Particulate migration during drying of fabric padded with dyestuff dispersions. Textile Research Journal, 1973, 43, 657-661.
- von der Eltz, H.-U. The Thermosol dyeing process for polyester fibers and their blends. Melliand Textilberichte, 1966, 47, 1170-1147, 1284-1291.

von der Eltz, H.-U. Can the migration of dyes be prevented in intermediate drying? Textil Praxis International, 1972, 27, 662-664.

Wilson, A. H. A diffusion problem in which the amount of diffusing substance is finite. Philosophical Magazine, 1948, 39, 48-58.

APPENDIX A
DYE SPECTRA DATA

Wavelength nm	Percent Transmittance		
	Blue 165	Red 60	Brown 1
340	-	67.9	79.1
350	-	72.9	79.0
360	-	76.9	78.0
370	-	80.9	75.5
380	-	84.5	71.4
390	-	86.1	64.8
400	-	87.2	56.5
410	-	87.1	49.5
420	-	86.0	44.5
430	-	83.6	40.3
440	-	79.9	37.7
450	90.0	74.6	36.3
455	-	-	36.1
460	89.6	68.2	36.4
470	87.8	61.0	37.9
480	87.2	54.0	39.9
490	85.0	48.9	42.5
500	82.0	44.7	45.5
510	80.1	39.4	48.8
520	76.3	37.2	53.2
530	71.9	39.4	58.6
540	66.5	42.0	64.3
550	60.0	42.0	-
560	53.9	44.8	76.0
570	48.6	55.9	-
580	44.1	73.8	86.1
590	41.6	85.6	-
600	39.4	93.2	91.7
605	38.7	-	-
610	36.8	-	-
615	36.8	-	-
620	37.2	-	-
625	38.5	-	-
630	41.4	-	-

APPENDIX B

TEST OF EFFECT OF MOISTENED PAPER ON
SATURATION OF WATCH GLASS CHAMBER

Pap = 0 for no paper

Pap = 1 for paper

Univariate Analysis
Variable = Wt. Difference

Pap = 0

N	6.000	Sum Wgts	6.000
Mean	0.079	Sum	0.474
Std Dev	0.023	Variance	0.00052
Skewness	-0.816	Kurtosis	-0.427
USS	0.040	CSS	0.00257
CV	28.721	Std Mean	0.00926
T:Mean=0	8.529	Prob> T	0.00036
Sgn Rank	10.500	Prob> S	0.036
Num ^= 0	6.000		
W:Normal	0.913	Prob< W	0.461

Univariate Analysis
Variable = Wt. Difference

Pap = 1

N	6.000	Sum Wgts	6.000
Mean	-0.003	Sum	-0.019
Std Dev	0.008	Variance	0.00006
Skewness	0.296	Kurtosis	-0.552
USS	0.000	CSS	0.00032
CV	-252.230	Std Mean	0.00328
T:Mean=0	-0.971	Prob> T	0.376
Sgn Rank	-5.500	Prob> S	0.294
Num ^= 0	6.000		
W:Normal	0.964	Prob< W	0.811

APPENDIX C

TEST OF EFFECT OF SATURATED CHAMBER
ON PARTICULATE MIGRATION

Pap = 0 for no paper (unsaturated chamber)
 Pap = 1 for paper (saturated chamber)

TTest Procedure
 Variable = Particulate Migration

Pap	N	Mean	Std Dev	Std Error	Min	Max
0	9	61.38	3.38	1.127	54.80	64.69
1	9	64.69	3.07	1.022	59.25	68.55

Variances	T	DF	Prob > T
Unequal	-2.1746	15.9	0.0452
Equal	-2.1746	16.0	0.0450

For H0: Variances are equal, F' = 1.21 with 8 and
 8 DF. Prob > F' = 0.7896

APPENDIX D

TEST OF DIFFERENCES BETWEEN DIRECT AND
INDIRECT FIXATION MEASUREMENTS

Univariate Analysis
Variable = [(Direct/Indirect) - 1]

Blue 165

N	5.000	Sum Wgts	5.000
Mean	-0.094	Sum	-0.468
Std Dev	0.001	Variance	0.00057
Skewness	1.332	Kurtosis	2.926
USS	0.070	CSS	0.0263
CV	-86.593	Std Mean	0.0362
T:Mean=0	-2.582	Prob> T	0.061
Sgn Rank	-6.500	Prob> S	0.106
Num ^= 0	5.000		
W:Normal	0.854	Prob< W	0.258

Univariate Analysis
Variable = [(Direct/Indirect) - 1]

Red 60

N	5.000	Sum Wgts	5.000
Mean	-0.071	Sum	-0.355
Std Dev	0.014	Variance	0.00019
Skewness	-0.344	Kurtosis	-2.869
USS	0.026	CSS	0.0008
CV	-19.389	Std Mean	0.0062
T:Mean=0	-11.533	Prob> T	0.0003
Sgn Rank	-7.500	Prob> S	0.059
Num ^= 0	5.000		
W:Normal	0.873	Prob< W	0.323

Univariate Analysis
Variable = [(Direct/Indirect) - 1]

Brown 1

N	5.000	Sum Wgts	5.000
Mean	-0.031	Sum	-0.157
Std Dev	0.075	Variance	0.00557
Skewness	-0.698	Kurtosis	1.082
USS	0.027	CSS	0.0223
CV	-237.740	Std Mean	0.0334
T:Mean=0	-0.940	Prob> T	0.400
Sgn Rank	-3.500	Prob> S	0.418
Num ^= 0	5.000		
W:Normal	0.964	Prob< W	0.781

APPENDIX E
REGRESSION ANALYSIS: KC vs C_{rx}
FOR BLUE 165

General Linear Models Procedure
 Dependent Variable = KC

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	27662.421	27662.421	498.16
Error	22	1241.584	56.436	PR > F
Corrected Total	23	28904.005		0.0001

R-Square	C.V.	Root MSE	KC Mean
0.957	15.058	7.512	49.888

Source	DF	Type I SS	F Value	PR > F
C _{rx}	1	27662.421	498.16	0.0001

Source	DF	Type III SS	F Value	PR > F
C _{rx}	1	27662.421	498.16	0.0001

Parameter	Estimate	T For H ₀ : Parameter=0	PR > T	Std Error Estimate
Intercept	-0.116	-0.04	0.967	2.738
C _{rx}	38.444	22.14	0.0001	1.736

APPENDIX F
 REGRESSION ANALYSIS: KC vs C_{rx}
 FOR RED 60

General Linear Models Procedure
 Dependent Variable = KC

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	2649.765	2649.765	2946.46
Error	22	19.785	0.899	PR > F
Corrected Total	23	2669.550		0.0001

R-Square	C.V.	Root MSE	KC Mean
0.993	6.687	0.948	14.182

Source	DF	Type I SS	F Value	PR > F
C _{rx}	1	2649.765	2946.46	0.0001

Source	DF	Type III SS	F Value	PR > F
C _{rx}	1	2649.765	2946.46	0.0001

Parameter	Estimate	T For H0: Parameter=0	PR > T	Std Error Estimate
Intercept	-0.076	-0.23	0.817	0.326
C _{rx}	0.189	54.28	0.0001	0.151

APPENDIX 6

REGRESSION ANALYSIS: KC vs C_{fx}
FOR BROWN 1General Linear Models Procedure
Dependent Variable = KC

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	9622.791	9622.791	988.40
Error	21	204.451	9.736	PR > F
Corrected Total	22	9827.242		0.0001

R-Square	C.V.	Root MSE	KC Mean
0.979	11.293	3.120	27.630

Source	DF	Type I SS	F Value	PR > F
C_{fx}	1	9622.791	988.40	0.0001

Source	DF	Type III SS	F Value	PR > F
C_{fx}	1	9622.791	988.40	0.0001

Parameter	Estimate	T For H0: Parameter=0	PR > T	Std Error Estimate
Intercept	-1.860	-1.63	0.118	1.142
C_{fx}	17.081	31.44	0.0001	0.543

APPENDIX H

REGRESSION ANALYSIS: KM vs M_{rx}
FOR BLUE 165General Linear Models Procedure
Dependent Variable = KM

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	4147.461	4147.461	274.18
Error	13	196.645	15.127	PR > F
Corrected Total	14	4344.105		0.0001

R-Square	C.V.	Root MSE	KM Mean
0.955	17.548	3.889	22.163

Source	DF	Type I SS	F Value	PR > F
M_{rx}	1	4147.461	274.18	0.0001

Source	DF	Type III SS	F Value	PR > F
M_{rx}	1	4147.461	274.18	0.0001

Parameter	Estimate	T For H0: Parameter=0	PR > T	Std Error Estimate
Intercept	0.509	0.31	0.762	1.649
M_{rx}	83.872	16.56	0.0001	5.017

APPENDIX I

REGRESSION ANALYSIS: KM vs M_{rx}
FOR RED 60General Linear Models Procedure
Dependent Variable = KM

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	183.595	183.595	227.96
Error	13	10.470	0.805	PR > F
Corrected Total	14	194.065		0.0001

R-Square	C.V.	Root MSE	KM Mean
0.946	20.418	0.897	3.158

Source	DF	Type I SS	F Value	PR > F
M _{rx}	1	183.595	227.96	0.0001

Source	DF	Type III SS	F Value	PR > F
M _{rx}	1	183.595	227.96	0.0001

Parameter	Estimate	T For H0: Parameter=0	PR > T	Std Error Estimate
Intercept	-0.273	-0.84	0.415	0.325
M _{rx}	15.415	15.10	0.0001	1.021

APPENDIX J
REGRESSION ANALYSIS: KM vs M_{rx}
FOR BROWN 1

General Linear Models Procedure
 Dependent Variable = KM

Source	DF	Sum of Squares	Mean Square	F Value
Model	1	1203.099	1203.099	87.59
Error	11	151.099	13.736	PR > F
Corrected Total	12	1354.198		0.0001

R-Square	C.V.	Root MSE	KM Mean
0.888	33.451	3.706	11.000

Source	DF	Type I SS	F Value	PR > F
M _{rx}	1	1203.099	87.59	0.0001

Source	DF	Type III SS	F Value	PR > F
M _{rx}	1	1203.099	87.59	0.0001

Parameter	Estimate	T For H0: Parameter=0	PR > T	Std Error Estimate
Intercept	0.237	0.15	0.881	1.549
M _{rx}	41.409	9.36	0.0001	4.425