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DYEING POLYPROPYLENE WITH ANTHRAQUINONE DERIVATIVE DISPERSE DYES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Susan J. Mangan

May 1989

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DEDICATION

Thus saith the Lord, Let not the wise man glory in his wisdom, neither let the mighty man glory in his might, let not the rich man glory in his riches: But let him that glorieth glory in this, that he understandeth and knoweth me, that I am the Lord which exercise loving kindness, judgement, and righteousness in the earth: for in these things I delight, saith the Lord.

Jeremiah 9: 23, 24

This thesis is dedicated to Jesus, by whose power it was written. May it glorify Him.

ACKNOWLEDGEMENTS

I would like to thank all four members of my committee for making themselves available to me, and for stretching me towards my full potential. Special heartfelt appreciation goes to Dr. John Crouse, who was untiring in his assistance and encouragement. Thanks also to Dr. Frank Calogero for his patient instruction in the techniques of synthetic organic chemistry.

Others have made contributions to the completion of this project, and I am grateful to all of them: Mr. John Brothers, who helped with a hundred little details; Mr. Dick Williams, who prepared the cross sections for microscopy; and Mr. W. David Costner, who arranged for the fastness testing in his lab at CIBA-GEIGY.

Last, but most importantly, I am deeply indebted to my husband Joe Mangan, whose support has enabled me to reach my goal. Thanks for giving me the freedom and inspiration to be all that God has called me to be.

ABSTRACT

Unmodified polypropylene has heretofore proven almost impossible to dye. The objective of this research was to evaluate a series of prototype compounds for a new class of dyes adapted especially for polyolefins. The effect of lengthening the alkyl chain hydrophobic functionality of the dye was tested. Two distinctly different polypropylene fabric types were used for the dyeings. Dye/substrate interactions were explored in preliminary dyeings.

Data for both sorption and rate of dyeing isotherms were gathered via spectroscopic analysis of exhausted dyebaths. Sorption isotherm studies revealed a Nernst isotherm for the series of dyes evaluated. Dye yield on the fiber was as high as 90% and deep shades were obtained. The dyed fabrics were characterized through colorimetry, fastness testing, and optical microscopy.

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CHAPTER 1

REVIEW OF LITERATURE

1.1 THE FIBER

Polypropylene is a synthetic fiber with many physical properties superior to other synthetic fibers available on the market. It has the lowest specific gravity of any fiber, excellent abrasion resistance (second only to nylon), extremely low moisture regain, and superb environmental resistance (Szlosberg, 1985). The dielectric constant of polypropylene is 2.28. Its crystalline melting point is 167°C, but the polymer melting range begins as low as 130°C. A wide range of glass transition temperatures, from -30°C to 25°C, have been determined experimentally (Ahmed, 1982).

The basic building block of polypropylene is the three carbon monomer, propylene. When properly polymerized, the propylene forms isotactic polypropylene, a stereoregular polymer with a spiral helix nature (Figure 1). The polymer is nonpolar and saturated; therefore, it is incapable of secondary bonding with other molecules. This makes for an extremely hydrophobic fiber and provides the basis of polypropylene's environmental resistance. The compact nature of the monomer and extremely stereoregular nature of the polymer yield a fiber with an excellent strength to weight ratio.

Despite the fact that polypropylene technology has been available since the late 1950's, only in the past decade or so has it been a truly viable alternative to other

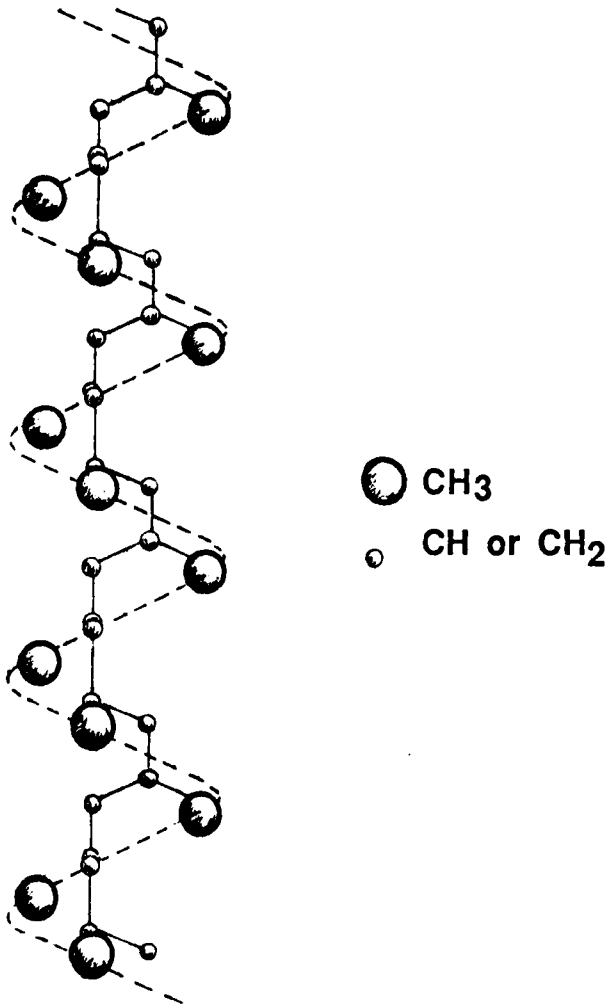


Figure 1. Helical structure of isotactic polypropylene.

fibers (Mansfield, 1982 and Ahmed, 1982). This increasing consumption comes from both creation of entirely new markets, and substitution of polypropylene in existing markets. Polypropylene is an inexpensive fiber to produce, relative to the alternatives. Additionally, the fiber has a lot of positive features and only a few drawbacks. One vital disadvantage of polypropylene as a textile fiber is its inability to be colored by conventional dyeing.

In addition to the low cost of polypropylene fiber, its low density gives it excellent cover per pound. This allows for the production of bulky, yet lightweight, products. More yards of polypropylene fabric can be produced per pound of fiber than could be produced of another fiber, all other factors being equal. This gives polypropylene an additional economic edge over its competitors. Furthermore, polypropylene has low thermal conductivity and excellent wicking properties, making it ideal for many apparel applications, such as activewear, gloves, and thermal underwear. (Kazil, p. 144).

Staining, particularly water borne staining, is not a problem with polypropylene, due to its low absorbency. Low absorbency also reduces processing costs, since drying times are minimal. Additionally, polypropylene fibers tend not to absorb odors, which can be a problem with acrylic fibers (Kazil, p. 144). Polypropylene is soil resistant and chemical resistant. It is also inherently resistant to attack from microorganisms and insects. Properly treated, it has excellent light and ultraviolet resistance as well (Szlosberg, p. 84). All of these features combine to make polypropylene a very versatile textile fiber.

Mansfield (1982) reviewed the use of polypropylene in fiber and textile applications. He states that, in 1981, thirty percent of total production of polypropylene resin in the United States went into fiber and related uses. He goes on to discuss recent developments in polypropylene fiber production and to give an overview

of the prominent U. S. producers of polypropylene fiber. His article concludes with an overview of the major textile end-uses of polypropylene.

Szlosberg (1985) reviews the use of polypropylene in the home furnishings sector. The progress polypropylene has made since being introduced in this area is traced. The strengths and weaknesses of polypropylene and the future outlook for polypropylene in home furnishings are also summarized. Szlosberg notes that in 1983 polypropylene "became the dominant fiber in upholstery". Carpeting still accounts for much of the polypropylene fiber market, however.

Although polypropylene has become an established fiber in the home furnishings sector, it is just beginning to break into the apparel market. Kazil (1986) discusses the movement of polypropylene into the functional clothing market. The properties of polypropylene that make it suited for this end-use are detailed fully. Also covered are processing considerations and some information on current usage of polypropylene in apparel.

Many of the physical and chemical properties which make polypropylene so desirable also make it almost impossible to dye in the conventional manner. Due to its hydrophobicity, lack of functional groups, and highly crystalline, nonpolar nature, most unmodified polypropylene available today is colored by mass pigmentation. While this technique generally produces deep, stable color, it is economical only for large production runs. This limits the available shades and reduces responsiveness to markets (Levine & Weimer, 1970). The rate at which polypropylene is able to penetrate the various textile market segments may reflect its coloration problems. Where fashion seasons are short and color responses must be rapid, polypropylene is less able to compete with fibers that are easily colored by conventional methods.

1.2 THEORY OF DYEING

1.2-1 GENERAL

The Terms and Definitions Committee of the Journal of the Society of Dyers and Colourists (1973 p. 415) defines a dye as "a colorant that has substantivity for a substrate, either inherent or induced by reactants". To be useful, dyes must possess certain properties:

1. They must be highly colored and yield colored goods with fastness.
2. They must be soluble, molecularly dispersible, or capable of being made soluble in the medium in which they are applied.
3. They must be capable of diffusing into the fibers under the conditions of dyeing.
4. The diffused dye must be retained by the fiber.

(Aspland, 1980, p. 41)

Dyeing theory seeks to explain the underlying phenomena that are involved in the successful application of specific colorants to specific textile substrates. Due to the large number of interdependent processes involved, several aspects must be considered.

Rys and Zollinger (1972) give a complete treatment of the science of dyeing. Trotman (1984) presents an introduction to dyeing theory, and a discussion of the various classes of dyes. In a 1980 paper for *Textile Chemist and Colorist*, McGregor summarizes the basics of thermodynamic and kinetic phenomena. In an earlier paper (1967) he discusses the subject in full detail.

The dyeing process can be subdivided into three interdependent stages (Trotman, 1984): The first of these is migration, which involves the assembly of the dye molecules at the fiber/dyebath interface. The second stage is diffusion of the dye molecule into the fiber. Fixation of the dye molecule to the fiber is the third stage. All three stages are essential; each successive stage builds upon the one preceding it.

In seeking a complete understanding of the process occurring during the different stages of dyeing, knowledge of the thermodynamics and the kinetics of the process must be obtained. Briefly, thermodynamics is used to measure a static but generally reversible situation, an end result of the dyeing process known as equilibrium. Kinetics is used to measure the rate of a process, in this case the rate at which dyeing occurs, and hence is irreverisible (Rys & Zollinger, 1972). Thermodynamics is concerned only with the current status of a system, not how that status was attained nor how it might be changed, whereas kinetics is concerned with the rate at which the system is changing. Both types of measurements are necessary to fully explain the system in question. Only when both types of information are known can appropriate dyes be accurately selected and utilized to meet a particular end use.

To investigate the thermodynamics of a particular dye/substrate combination, specific dyeing parameters of temperature, pressure, liquor ratio, and dyebath assistants must be defined. These conditions are then used to dye the selected substrate with a specified dye concentration, determined as a percentage of weight of dye on weight of fiber (owf). When the system reaches equilibrium, that is, when the amount of dye going on to the fiber is equal to the amount of dye returning to the dyebath, dyeing is terminated and the equilibrium exhaustion level is measured. Standard spectrophotometric methods are the most straightforward procedure for determining the exhaustion level, assuming outside factors are controlled (e. g. evaporation, decomposition of the dye, etc.) (McGregor, 1980).

Spectrophotometry is based on the principle of energy absorption by solute molecules within a solution, allowing the concentration of the solute in the solution to be determined. The Beer-Lambert law is used to quantify the amount of energy absorbed by a given solution:

$$A = \log I_o/I = \varepsilon \; l \; c \qquad \text{(Eq. 1)}$$

where A = absorbance or optical density
I_o = intensity of incident light at a certain wavelength
I = intensity of light transmitted through sample at the same wavelength
ε = molar extinction coefficient
l = length of cell in cm , and
c = concentration of sample in moles/liter

(Roberts, et al., p. 307).

A range of solutions of known concentration (standards) are analyzed first, allowing ε to be determined. Unknowns can then be analyzed and their concentrations determined. This technique is most useful for single component systems, and readings should always be made at or near the wavelength of maximum absorbance (λ max). Accurate results depend upon accurate preparation of standards and determination of the linear range in which the law holds. Solutions of known concentration should be randomized with the unknowns to verify that readings are accurate.

Once the equilibrium concentration of the dyebath (c_s^{∞}) has been determined, it can be subtracted from the original concentration of the dyebath (c_s^{i}), then divided by the original concentration and multiplied by 100 to determine percentage exhaustion at equilibrium:

$$\frac{(c_s^i) - (c_s^\infty)}{(c_s^i)} \times 100 = \% \text{ exhaustion} \qquad \text{(Eq. 2)}$$

Based on percentage exhaustion of the dyebath and depth of shade of the dyeing, the amount of dye taken up by the fiber (c_f^∞) can be ascertained:

$$\text{ideal } c_f \text{ (mg. dye available/g. fiber)} \times \% \text{ exh} = c_f^\infty \qquad \text{(Eq. 3)}$$

A curve known as the equilibrium sorption isotherm is obtained by plotting c_f^∞ as a function of c_s^∞. The shape of the sorption isotherm indicates the mechanism by which the dye molecules are fixed within the fiber. Three basic shapes are possible:

1. A Langmuir isotherm (Figure 2-a) reflects increasing levels of sorption up to a certain point, after which no additional dye can be held by the fiber. This type of isotherm is characteristic of wool dyed with acid dyes. There are a finite number of dyesites available, and when these are used there are no more sites for the dye to fix in the fiber.

2. A Freundlich isotherm (Figure 2-b) reflects the law of diminishing returns. This type of isotherm is characteristic of cellulose fibers dyed with direct dyes. Theoretically, there are an infinite number of dyesites available, but most are very difficult for the dye molecules to access. So, as the more accessible sites are

occupied sorption increases, but as only the more hindered sites remain sorption tapers off.

3. A Nernst isotherm (Figure 2-c) reflects sorption at a continuous level, no matter how much dye is initially present in the system. This type of isotherm is truly characteristic only of fibers that have no specific dyesites, such as polypropylene. Within normal limits, the amount of dye sorbed by these fibers is a constant percentage of the original concentration of the dyebath.

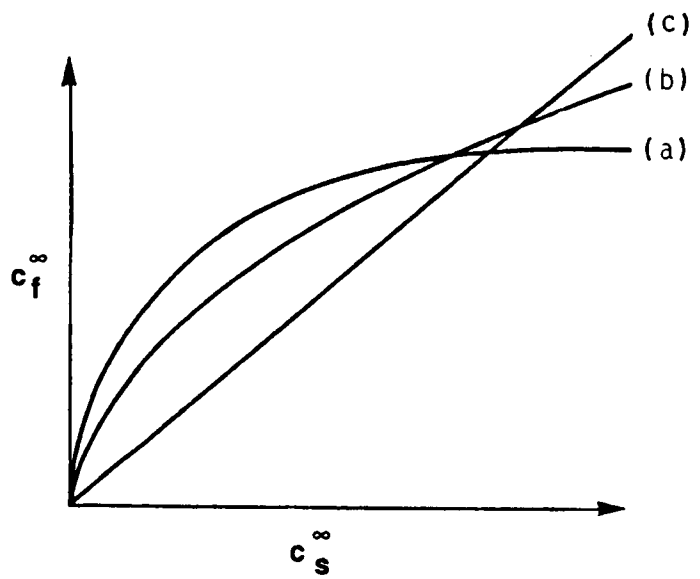


Figure 2. Three basic sorption isotherms. a) Langmuir b) Freundlich c) Nernst.

The individual points on a particular sorption isotherm are significant, since "each point on this curve defines a possible end state of this dyeing process. Each end state corresponds to a definite numerical value of the equilibrium partition coefficient $\tilde{K}$" (McGregor, 1980, p. 307). Therefore, by definition, for a Nernst isotherm $\tilde{K} = K$ since each end point has the same slope at equilibrium.

$$\tilde{K} = \frac{c_f^{\infty}}{c_s^{\infty}} \qquad \text{(Eq. 4)}$$

For the practical dyer, dyes with higher $\tilde{K}$ values have greater affinity for the fiber than those with lower $\tilde{K}$ values. Values of $\tilde{K}$ allow the practical dyer to determine how much dye is necessaary to achieve a desired depth of shade under defined conditions of dyeing. Additionally, in selecting dyes of different colors for use in a binary or tertiary dyebath, the values of $\tilde{K}$ for all dyes in the mixture must be similar. Otherwise, one dye will dye to a much deeper shade than the others, giving end results that vary greatly from those intended.

The rate at which dyeing occurs is also an important criterion when selecting a commercial dye. Not only must a high level of dye uptake be achievable, it must be accomplished within a relatively short period of time. Based on how much time is needed for the system to get half way to its final equilibrium point, times of half dyeing ($t_{1/2}$) are established for a dye. Determination of $t_{1/2}$ involves dyeing at a standard concentration of dye on weight of fiber for varying lengths of time. The exhaustion level is determined for each time, and plotted as a function of dyeing time. The dyeing time is often plotted as log time, since this often yields a more precise point of $t_{1/2}$ than standard plots reveal (Trotman,1984). Knowledge of $t_{1/2}$ allows dyes that

will be taken up by the fiber in approximately the same length of time to be combined. Thus, the final results of a binary or tertiary dyebath can be predicted accurately.

1.2-2 DISPERSE DYES ON HYDROPHOBIC FIBERS

Bird is the foremost authority in the area of dyeing with disperse dyes on hydrophobic fibers. His series of papers spanning from 1954 to 1956 covers all aspects of applying disperse dyes to acetate rayon. The effect of solubility and the use of a dispersing agent were measured, along with sorption isotherms and diffusion coefficients. Additionally, his 1956 paper, "Disperse Dyes on Hydrophobic Fibers", reviews and summarizes the subject. This important paper extends dyeing theory into the application of only sparingly soluble dyes to fibers that are only sparingly absorbent.

Schuler and Remington (1953) also discuss the use of disperse dyes on hydrophobic fibers. Their research covers the sorption of select dyes by PET, and touches on the effect of temperature and use of a dispersing agent on this sorption. Schuler (1980) has also written a survey paper on the subject of disperse dyes for *Textile Chemist and Colorist*. It covers typical applications of disperse dyes and gives suggestions for overcoming common problems encountered in their use.

An extremely useful paper on the role of dispersing agents in dyeing with disperse dyes was written by Jones (1984). The purpose of dispersing agents, their functions within the dyebath, and their interactions with the disperse dye molecule are all detailed fully. Hydrogen bonding and its role in the solubilization of disperse dyes is also covered.

As a class, disperse dyes are known for their very low solubility in water (Schuler, 1980). The use of surface-active or dispersing agents greatly increases the solubilization potential of disperse dyes in water. The action of these dyebath assistants is two-fold: "to minimize the adsorption and build-up of particles on the fibre surface and to increase the amount of dye actually dissolved in the dyebath" (Jones, 1984, p. 66).

The selection of a suitable dispersing agent is critical to successful dyeing with disperse dyes. Each dye interacts with some dispersing agents more beneficially than with others. The correct combination must be found since only that amount of dye which can be induced to dissolve in the aqueous phase is available to be sorbed by the fiber. Additionally, there is a critical minimum concentration level for each dispersing agent in the dyebath, below which little additional solubilization of the dye occurs. Above this critical concentration, the solubility of the dye increases in direct proportion to increases in the concentration of the dispersing agent (Jones, 1984).

Dispersing agents may be one of three types: anionic, cationic, or nonionic. All three types "can be represented by the formula RX, where R is the hydrophobic or oil-soluble component and X is the hydrophilic or water-soluble component of the structure" (Jones, 1984, p. 69). The mechanism of solubilization of disperse dyes is generally held to be one of suspension of the hydrophobic disperse dye molecules in micelles of some type (Bird, 1954). Micelles are formed in one of two different ways, depending upon the type of dispersing agent involved. The action of anionic and cationic dispersing agents strongly resembles that of detergents. The interaction of the charged hydrophilic group X with the surrounding water molecules causes a sheath of water molecules to form around the localized charge. Nonionic dispersing agents have no charged groups, however, and their interaction must entail hydrogen bonding between

the water molecules and electronegative atoms within the hydrophilic group X, resulting in similar micelle formation (Jones, 1984).

Once formed, the micelles serve to suspend the disperse dye as fine particles in the dyebath. There is some disagreement as to how fine the initial dye particles must be for effective micelle formation to occur. Bird & Manchester (1955) state that initial particle size should be as fine as possible, but Schuler & Remington (1954) conclude that initial particle size has no apparent effect. Since the dye must eventually be broken down to a molecular level, it seems probable that a small original particle size would speed solubilization of the dye.

Because of their role in promoting solubility, all effective dispersing agents have at least some retarding effect on the rate of dye uptake by the fiber. Additionally, equilibrium exhaustion will be lowered, since the aqueous phase is made more attractive to the dye molecules by the action of the dispersing agent (Bird, Harris, & Manchester, 1955). Because of these factors, results will only be reproducible at specified surfactant levels.

The actual mechanism of dyeing hydrophobic fibers with disperse dyes is one of "partition of the dye between two immiscible solvents" (Bird & Manchester, 1955, p. 605). The dye appears to be divided between the micelles of dispersing agent, in which it is soluble, and the amorphous areas of the fiber, in which it is also soluble (Schuler & Remington, 1954). This leads to a linear sorption isotherm with constant partition coefficient K (Eq. 4). The value of K for a particular dye/fiber combination is independent of the liquor ratio, but does change with changes in the amount of dispersing agent added to the dyebath (Bird & Manchester, 1955). This is to be expected given the interaction of the dispersing agent with the dye.

In dyeing hydrophobic fibers with disperse dyes, dye molecules tend to aggregate at the surface of the fiber. This phenomenon, known as ring dyeing, can be

detected by examination of cross sections of dyed samples via optical microscopy. The dyebath may appear to be almost completely exhausted, but the majority of the fiber will not have been penetrated by the dye molecules. As dyeing is allowed to continue, the dye molecules continue to diffuse into the fiber until it is evenly distributed, if not saturated. (Bird, 1956). (Saturation of the fiber with dye molecules would require a large amount of dye.)

A much more difficult problem occurs when the dye molecules do not penetrate the fiber structure readily. Exhaustion in this case may appear to be quite high, but the dye is not actually sorbed by the fiber, only adhered to the fiber surface. This type of dyeing may result in very poor attachment of the dye, resulting in poor fastness, especially to rubbing (Bird, Manchester, & Scott, 1956). This problem may be solved by opening up the fiber structure with a swelling agent or carrier. Increasing the energy available to the system through pressure dyeing or the use of ultrasonic energy may also make the fiber structure more accessible to the dye. These methods will then allow true penetration of the dye into the fiber.

1.3 DYEING OF POLYPROPYLENE

Since entering the marketplace, many patents have been issued in attempts to find a way to make polypropylene dyeable. Three general approaches have been taken:

1. Novel methods of dyeing.
2. Modification of the fiber.
3. Development of new dyes.

Creative ideas of all sorts have been explored to allow one or another class of conventional dyes to be used on polypropylene. The use of solvent and carrier dyeing methods has been a popular approach, as has pressure dyeing. Erlich (1965) lists several variations on these themes, such as the use of swelling agents, organic and inorganic dyeing aids, and several fiber pretreatments. He also provides specific examples of patents taken out prior to 1965. It is pointed out that many of these procedures still produce dyed goods with insufficent fastness properties for most end uses. Additionally, although some of these procedures may allow polypropylene to be dyed to acceptable end-use standards, the procedures themselves are often not commercially efficient.

There have also been numerous modifications of polypropylene fiber to make it dyeable. The specific modification is often difficult to determine in evaluating claims of success found in the literature. Copolymerization or chemical modification to provide dyesites for either anionic or cationic dyes has been achieved by various means. Baumann (1963) summarizes at least ten attempts by various researchers to make polypropylene dyeable. Included in this list are grafting of chloromethylstyrene, and mixing with up to 15% of a polyethyleneimine compound. He also comments on the success some of these methods have had. Levine and Weimer (1970) present the results of their research on polypropylene containing a basic additive. The resulting fiber was dyed with six acid dyes. Mukherjee and Gupta (1985) worked on polypropylene graft copolymerized with methacrylic acid. The resulting fiber was dyed with two basic dyes. Shah and Jain (1984) found a way to brominate polypropylene fibers, giving the fibers an affinity for basic dyes. Eight dyes were tested on these fibers.

Unfortunately, the incorporation of even a small amount of polar substance into the polymer tends to decrease the desirable physical properties of the fiber (Baumann, 1963). The incorporation of fine metal particles, particularly nickel, in the polymer to provide mordanting sites has found some commercial use. However achieving adequate levelling has been a serious problem with this approach (Ahmed, 1983).

The development of new dyes seems to be the least prolific area of research into coloration of polypropylene. A line of dyes designed for use in conjunction with nickel-modified polypropylene was introduced by the Chemicals & Dyestuffs Division of Koppers Co. Inc. in the early 1960's, but they are no longer available. Trade named Koprolene dyes, the line included seven basic colors (Baumann, 1963).

Additionally, *Colour Index* (1971) lists a line of dyes tradenamed BAKCAR, produced by DuPont. These dyes were designed for use on unmodified polypropylene, and were especially intended for dyeing carpet backing. Only five dyes were available in the line, but the three primary colors were included. However, the dyes were reportedly not fiber specific, and have been removed from the market.

CHAPTER 2

EXPERIMENTAL

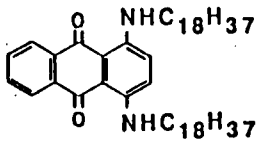
2.1 STATEMENT OF PROBLEM

At this time, unmodified polypropylene is considered undyeable by industry standards. This situation effectively handicaps polypropylene as a fashion fiber. A new class of dyes adapted particularly to the special demands of polypropylene must be developed. This approach should allow polypropylene fibers to be colored so that they retain their desirable physical properties and low cost, yet are available with lead times and shade ranges acceptable to fashion markets. Application with only minor modification of conventional dyeing practice is essential.

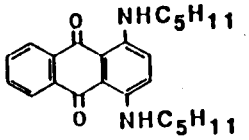
2.2 RESEARCH OBJECTIVE

The objective of this research was to develop a series of prototype dyes for use on polypropylene. Each dye was an anthraquinone derivative with two long chain alkyl group substituents. It was hoped that dyes of this chemical structure would be sufficiently similar to the chemical structure of polypropylene to allow the dye molecules to have an affinity for the fiber. It was also thought that the long alkyl chains would allow for co-crystallization of the dyes in the fiber.

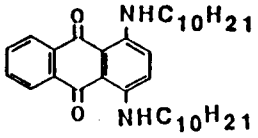
The length of the alkyl chains and the position of substituent group attachment differentiates the five dyes in the series (Figure 3). Varying the position of substituent



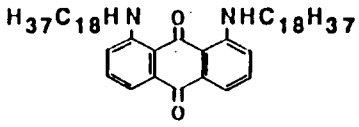
A. 1, 4-[BIS]-OCTADECYLAMINEANTHRAQUINONE
(1,4-C 18)



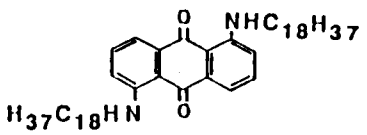
C. 1,4-[BIS]-AMYLAMINE
ANTHRAQUINONE
(1,4-C 5)



B. 1, 4-[BIS]-DECYLAMINE
ANTHRAQUINONE
(1,4-C 10)



D. 1, 8-[BIS]-OCTADECYLAMINE
ANTHRAQUINONE
(1,8-C 18)



E. 1,5-[BIS]-OCTADECYLAMINE
ANTHRAQUINONE
(1,5-C 18)

Figure 3. Five prototype anthraquinone derivative disperse dye molecules.

group attachment should allow dyes of different colors to be produced. Varying the length of the alkyl chains shoud allow their effect on the dye's substantivity for the fiber to be compared.

2.3 HYPOTHESES

1. Incorporating one or more linear long-chain alkyl groups on anthraquinone dye molecules will provide dyes for polypropylene capable of meeting industry standards.
2. Dyes with longer alkyl chains will have higher substantivity for polypropylene than those with shorter alkyl chains.
3. Equilibrium exhaustion levels for these dyes on polypropylene will be sensitive to both the level and type of dispersing agent incorporated in the dyebath.
4. A Nernst sorption isotherm will be exhibited for these prototype dyes on polypropylene substrates.

2.4 RESEARCH APPROACH

Since they were not commercial products, the dyes were synthesized and purified as needed. The first dye prepared, C 18 (Figure 3-A), formed the backbone of the research effort. Its dyeing behavior was fully characterized, then the other dyes were compared to it. It was also used in all the preliminary studies necessary before undertaking the bulk of the research.

To lay the groundwork for the research, three preliminary studies were made: 1. The attempt was made to dye polypropylene with commercially available disperse dyes, and to dye nylon and polyester with the C 18 dye. 2. The ability of the proposed

analytical procedure to assess dyebath concentration was evaluated. 3. A satisfactory set of dyeing conditions were selected.

The dyeing research with the prototype dyes consisted of four studies. First, the prototype dyes themselves were characterized. Relevant observations were compared to data reported in the chemical literature for similar substances.

Second, the effect of alkyl chain length on the substantivity of the dyes for polypropylene was made. Each of the three dyes studied during this phase varied from the other two only in the length of their alkyl chains. Sorption isotherms were plotted for each of the three dyes; partition coefficients were then calculated, providing an index of substantivity under the prescribed dyeing conditions.

The third study involved the complete characterization of the dyeing behavior of the C 18 dye as representative of the series of dyes. Its thermodynamic and kinetic behavior were examined at three temperatures: 80°C, 90°C, and 100°C. Both the extent and rate of exhaustion of the dye were evaluated on two different polypropylene fabric types. The time of half dyeing was calculated at the three temperatures.

The fourth study was the characterization of the dyed fabrics. Once the behavior of the prototype dyes during application was evaluated, assessment of the suitability of these dyes for use on polypropylene was extended to an evaluation of their behavior on the fiber. Colorimetry was used to assess shade differences for samples dyed with each of the three 1,4- dyes. These samples were also tested for light fastness, solvent fastness, and rub fastness. Cross sections of samples dyed with each of the dyes were also examined by optical microscopy to ascertain the extent of penetration of the dyes into the fiber.

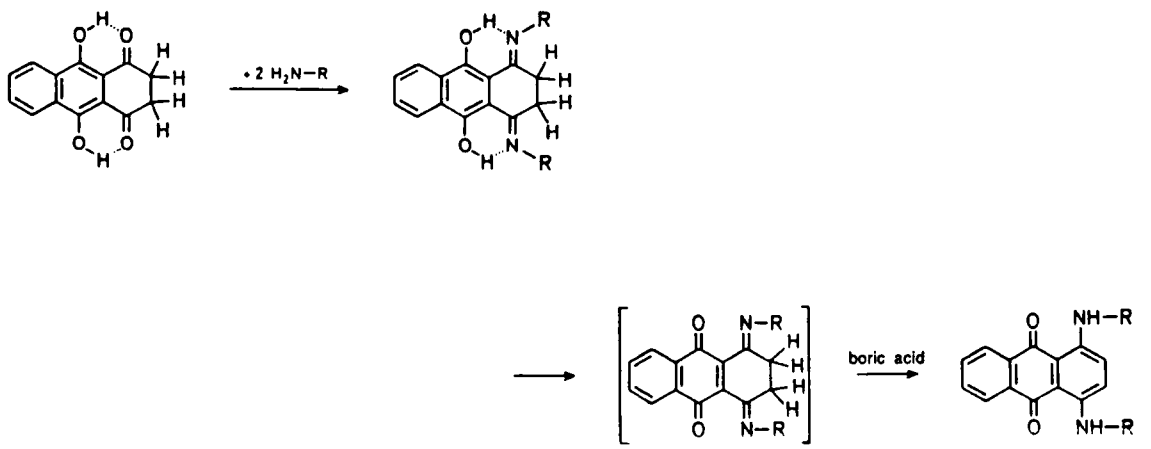
2.5 MATERIALS

2.5-1 THE DYES

As previously illustrated in Figure 3, five different anthraquinone derivative disperse dyes were evaluated during the course of this research. All were synthesized in the same basic manner: A measured amount of the starting anthraquinone material was added to a slight excess of the specific amine needed in the presence of a catalytic amount of base in ethanol. This mixture was refluxed with stirring for twelve hours, followed by the addition of a large excess of boric acid to oxidize the leuko dye compound. The resultant mixture was refluxed for an additional twelve hours.

After filtering off the solvent, the dyes were purified. The purity of the dyes was assessed by means of Thin Layer Chromatography (TLC).

The 1,4- dyes were synthesized according to the general outline provided in *Methoden der Organischen Chemie:*



2.5-1(1) 1,4-[bis]-octadecylamineanthraquinone (C 18)

This dye (Figure 3-A) was prepared following the general outline given above. Specific amounts are given in Table 1. After removing the solvent, the crude dye was washed with approximately 500 mL of hot water, followed by approximately 500 mL of warm acetone.

2.5-1(2) 1,4-[bis]-decylamineanthraquinone (C 10)

This dye (Figure 3-B) was prepared following the general outline given above. Specific amounts are given in Table 2. The dye was purified by first filtering off the solvent. The solid material was recrystallized from water and allowed to dry. The crude dye was then extracted with acetone to remove the desired dye product. After removal of the acetone, the solid was washed with 300 mL of methanol to remove final traces of side products.

2.5-1(3) 1,4-[bis]-amylamineanthraquinone (C 5)

This dye (Figure 3-C) was prepared following the general outline given above. Specific amounts are given in Table 3. After filtration, the crude dye was recrystallized twice from water, then allowed to dry. The solid was washed with methanol to remove side products, then extracted with acetone.

2.5-1(4) 1,8-[bis]-octadecylamineanthraquinone (1,8-C 18)

This dye (Figure 3-D) was prepared following the general outline given above, except that the dihydroxy compound was reduced in-situ by combining it with sodium hydroxide and sodium hydrosulfite in the solvent and refluxing for 15 minutes prior to beginning the amination reaction. Specific amounts are given in Table 4. The dye was purified by first filtering off the solvent. The solid portion was then recrystallized twice from water. After washing with 300 mL of warm acetone, the solid was Soxhlet extracted for three hours with methanol.

Table 1. Synthesis of 1,4-[bis]-octadecylamineanthraquinone.

substance	FWT	amt. used	moles used	supplier	purity
leucoquinizarin	242	12.0 g	0.05	Aldrich	
octadecylamine	269	30.0 g	0.11	Aldrich	90%
sodium hydroxide		2.5 g		Fisher	
ethanol (95%)		500 mL		Fisher	
boric acid	62	26.0 g	0.42	Aldrich	

Table 2. Synthesis of 1,4-[bis]-decylamineanthraquinone.

substance	FWT	specific gravity	amt. used	moles used	supplier	purity
leucoquinizarin	242		3.0 g	0.0125	Aldrich	
decylamine	157	.787	5.5 mL	0.0275	Aldrich	99%
sodium hydroxide			.625 g		Fisher	
ethanol (95%)			125 mL		Fisher	
boric acid	62		1.85 g	0.030	Aldrich	

Table 3. Synthesis of 1,4-[bis]-amylamineanthraquinone.

substance	FWT	specific gravity	amt. used	moles used	supplier	purity
leucoquinizarin	242		3.0 g	0.0125	Aldrich	
amylamine	87	.752	3.19 mL	0.0275	Aldrich	97%
sodium hydroxide			.625 g		Fisher	
ethanol (95%)			125 mL		Fisher	
boric acid	62		1.85 g	0.030	Aldrich	

Table 4. Synthesis of 1,8-[bis]-octadecylamineanthraquinone.

substance	FWT	amt. used	moles used	supplier	purity
1,8-dihydroxy-anthraquinone	240	6.0 g	0.025	Aldrich	96%
sodium hydroxide		1.25 g		Fisher	
sodium hydrosulfite	174	3.0 g	0.017	Amer. Sci.	
ethanol (95%)		250 mL		Fisher	
octadecylamine	269	15.0 g	0.056	Aldrich	90%
boric acid	62	3.7 g	0.048	Aldrich	

2.5-1(5) 1,5-[bis]-octadecylamineanthraquinone (1,5-C 18)

This dye (Figure 3-E, page 18) was prepared following the general outline above, except that an excess of sodium hydroxide was added to the reaction mixture to neutralize the hydrochloric acid that was formed during the amination reaction. Specific amounts are given in Table 5. After the solvent was removed, the crude dye was recrystallized from water twice. The dried solid was washed with 500 mL of warm acetone. The solid material was further purified via Soxhlet extraction with ethanol for six hours.

Table 5. Synthesis of 1,5-[bis]-octadecylamineanthraquinone.

substance	FWT	amt. used	moles used	supplier	purity
1,5-dichloro-anthraquinone	277	6.9 g	0.025	Aldrich	96%
sodium hydroxide		1.25g		Fisher	
sodium hydrosulfite	174	3.0 g	0.017	Amer. Sci.	
ethanol (95%)		250 mL		Fisher	
octadecylamine	269	15.0 g	0.11	Aldrich	90%
sodium hydroxide		4.0 g		Fisher	
boric acid	62	3.7 g	0.048	Aldrich	

2.5-2 THE FABRICS

Two different polypropylene fabric types were used in this research. The first was a highly crystalline, biaxially drawn split-film primary carpet back fabric (CB) manufactured by Patchogue and provided by Shaw Industries. The second was a much less crystalline, randomly oriented melt blown nonwoven fabric (MB) manufactured in The University of Tennessee melt blown processing lab under the direction of Dr. Larry Wadsworth (Wadsworth & Jones, 1986).

2.5-3 OTHER

All dyeing was done on an Ahiba Texomat textile laboratory dyeing machine. Tergitol TMN 10 (91 AQ), a nonionic surfactant manufactured by Union Carbide was used as the dispering agent unless otherwise noted. Dye was weighed on a Mettler analytical balance. A Unicam SP1800 ultraviolet/visible spectrophotomer was used to determine dyebath exhaustion. Solvents used in the spectrophotometric analysis were HPLC grade.

A Hunter Color Lab was used to assess the color difference between the dyed samples. Proton Nuclear Magnetic Resonance (PMR) spectra were obtained for the prototype dyes in the University of Tennessee Chemistry Department on a 200 MHz Nuclear Magnetic Resonance Spectrometer. Differential Scanning Calorimetry (DSC) was obtained in the Polymer Engineering Department on a Perkin-Elmer 7 Series thermal analysis system to determine the thermal behavior of the dyes.

2.6 METHODS

2.6-1 CHARACTERIZATION OF THE DYES

2.6-1(1) Thin Layer Chromatography

The standard system for TLC used a silica gel stationary phase and a 9:1 mixture of chloroform/acetone as the mobile phase. Chromatograms of the starting materials were compared to those of the final product to ensure that the pure product was not starting materials that had been reisolated. In addition to allowing the purity of the final dye product to be assessed, the relative polarity of each dye was evaluated by comparison of the R_f value for each. The R_f value was calculated as the ratio of the movement of the material (a) under study to the movement of the solvent front (b): $\frac{mm_a}{mm_b} = R_f$. For any TLC system, a more polar material will lag further behind the solvent front than a less polar one. Therefore, the material having the highest R_f value was the least polar, and that with the lowest R_f value was the most polar.

2.6-1(2) Solubility Studies

To select a suitable solvent for later analysis of dyebath exhaustion, and to confirm the polarity of the purified dyes, a solubility study was conducted on each dye: Approximately 0.5 mg of the dye were placed in a 10 mL test tube. Two to three mL of the solvent under study were added and the mixture was swirled briefly. The solid/solvent interaction was observed both during addition of the solvent to the solid and after swirling the mixture. Up to a total of 5 mL of solvent were used in an attempt to solubilize the dye. Once the mixture had been swirled, it was poured through a cone of #4 grade filter paper onto a #2 grade filter paper which served as a blotter. The

resulting stain was assessed. Results of both stain assessment and visual observation of the mixture were used to rate the solubility of each dye in each solvent:

i - insoluble: solid floats on solvent

sl - slightly soluble: solid mixes with solvent, but is not visible on blotter after filtration

par - partially soluble: small stain of dye visible on blotter after filtration

s -soluble: solid appears to be partially dissolved into solvent and leaves an easily seen stain on blotter after filtration

v - very soluble: solid appears to be almost completely dissolved in solvent, and leaves a dark stain on blotter after filtration

∞ - soluble in all proportions: solid appears to be rapidly dissolved in a few drops of solvent

2.6-2 PREPARATION OF STOCK SOLUTIONS

The stock solution of dispersing agent was prepared at a concentration of 40 g/L. A few drops of stock dispersing agent were added to the weighed amount of dye to form a thick paste. Additional cool water was then added slowly to a volume of approximately 100 mL. The pasted dye was transferred quantitatively to a suitable size volumetric flask. The flask was brought almost to volume with cool distilled water and allowed to stand at room temperature overnight. Before use, the stock dye was brought to volume, then stirred with a magnetic stir bar for at least fifteen minutes before dispensing in order to provide for the highest possible homogenity of the dispersion.

2.6-3 PREPARATION OF DYEBATHS

Ten mL of the stock solution of dispersing agent was measured into each dye beaker with a burette. This gave a concentration of 1 g/L of dispersing agent in each 400 mL dyebath.

The stock dye solution was measured with either a burette or a volumetric pipette. If a burette was used, only enough stock dye for one or two baths was added to the burette at a time, to minimize settling of the dye at the bottom of the burette. The remaining stock dye solution was stirred magnetically between measurements. After dye had been added to each beaker, the beakers were filled to 400 mL with distilled water and loaded into the lab dyeing machine. Fabric specimens were added, the dye beakers were covered, and dyeing was begun.

2.6-4 ANALYTICAL PROCEDURE

2.6-4(1) Sampling Procedure

After the stated dyeing time had elapsed, the heating element in the Ahiba was turned off and cold water was circulated to cool the dyeing chamber. After the oil surrounding the baths reached 120°F, the dyed specimens were removed and rinsed. After the dyebaths reached 80°F they were sampled. A 50 mL sample of each exhausted dyebath was stored for future reference as needed.

Since none of the dyes formed a true solution in water, the spectrophotometric analysis required that the solid portion of the dyebath sample be dissolved in a suitable solvent. Hexane was used for analysis of the C 18 dye. Acetone was used for the C 10 and C 5 dyes. To make this possible, a measured aliquot (normally 10 mL) of the exhausted

dyebath was placed in a small beaker. The liquid portion was allowed to evaporate and the solid was then dissolved in a measured amount of solvent for analysis. The concentration was determined at λ max using the Beer/Lambert law (Eq. 1, page 7) based upon previously prepared and analyzed standards.

2.6-4(2) Preparation of Standards

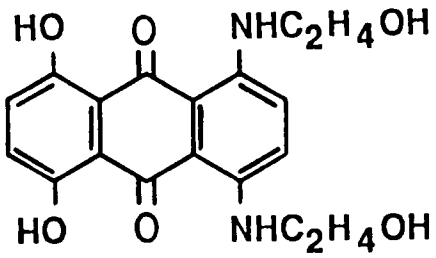
Standards were selected to be within the optimum range of absorbance/ transmittance for the instrument used. The target absorbance range was from 0.10 to 1.2, and solutions within this range were found to obey the Beer/Lambert law. The standards were prepared using a measured amount of stock dye solution. Since more work was done with the C 18 dye, several batches of C 18 stock dye solution were used during the course of the research. Thus, several sets of standards were prepared for this dye. Two sets of standards each were prepared for the C 5 and C 10 dyes, since only one stock dye solution of each was required to perform the necessary dyeings.

2.6-5 CONTROL DYEINGS

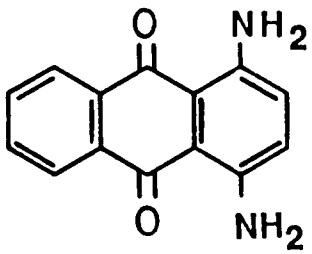
Three control dyeings were done:

1. To assess its ease of dyeing, the melt blown nonwoven fabric was dyed with three conventional disperse dyes. Disperse Blue 7 (Artisal Blue Green, CI #62500), Disperse Red 15 (Atlantic Disperse Pink, CI #60710), and Disperse Orange 3 (Cibacete Orange 2RN, CI #11005) were selected as representative nonionic dyes for this experiment (Figure 4).

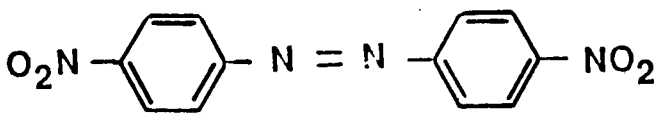
2. Nylon, polyester, and polypropylene fabrics were dyed with the C 18 dye to determine its substantivity for other fibers.



DISPERSE BLUE 7



DISPERSE RED 15



DISPERSE ORANGE 3

Figure 4. Three conventional disperse dyes used in the control dyeing.

Both of the preceding studies were conducted at two percent dye on weight of fiber (2% owf) with five gram fabric samples. Dyebaths were 400 mL, giving an 80:1 liquor ratio. The dyeing was done at 195°F for 60 minutes. The dispersing agent was used at a 1 g/L concentration.

3. Two dye beakers were prepared as for normal dyeing at 2% C 18 dye owf. Dye baths were processed in the usual way, except that no fabric was added. Exhaustion was calculated on these blanks to assure accuracy of the analytical technique.

2.6-6 SELECTION OF DYEING CONDITIONS

Dyeing with nonpolar dyes from aqueous media typically requires the use of a dispersing agent (Bird & Manchester, 1955). Therefore, two preliminary dyeings were done with the C 18 dye to establish the standard dyeing parameters for future work. The first test used five different surfactants at the concentration of 1 g/L of dyebath. These dyeings were maintained at the dyeing temperature for 60 minutes:

1. Tergitol 15-S-9 (nonionic)
2. Tergitol TMN 10 (91 AQ) (noninoic)
3. Zonyl FSA (anionic)
4. Zonyl FSC (cationic)
5. Zonyl FSK (nonionic)

Based on the results of the first test dyeings, the two surfactants giving the most level results were selected for inclusion in a final test of dyebath conditions. The amount of surfactant, specific surfactant, length of dyeing, and use of salt (NaCl) as a dyebath

assistant were each used as an independent variable in one bath, giving five dyeing conditions and a control:

S (control)	1g/L Tergitol 15-S-9	dye 60 minutes
T	1g/L Tergitol 15-S-9	dye 120 minutes
W	2g/L Tergitol 15-S-9	dye 60 minutes
X	0.1g/L Tergitol 15-S-9	dye 60 minutes
Y	1g/L Tergitol 15-S-9 20% owf NaCl added after 30 minutes	dye 60 minutes
Z	1g/L Tergitol TMN 10(91 AQ)	dye 60 minutes

All of these tests were conducted at 2% C 18 dye owf with five gram fabric samples. Dye baths were 400 mL, giving an 80:1 liquor ratio. The dyeing was carried out at 195°F for the specified time period.

2.6-7 SORPTION ISOTHERMS

For the determination of sorption isotherms, five initial dyebath concentrations were used, ranging from 0.1% to 3.0% owf. Dispersing agent was present at the concentration of 1 g/L. As usual, the liquor ratio was 80:1, and the dyeing temperature was 195°F. The length of dyeing was 90 minutes. The C 18 dye was evaluated on five gram samples of both fabrics, allowing differences in dyeing behavior between the two fabrics to be noted. The C 10 and C 5 dyes were evaluated on the carpet back fabric.

2.6-8 RATE STUDIES

Times of half dyeing were determined for the C 18 dye using eight time points, ranging from one minute to 200 minutes. The dye was studied at 80°F, 90°F, and 100°F to observe the effect of temperature on both rate and extent of exhaustion. As usual, an 80:1 liquor ratio was used, with a surfactant concentration of 1 g/L. Five gram samples of both fabrics were used, and initial dye concentration was fixed at 2% C 18 dye owf.

2.6-9 CHARACTERIZATION OF DYED FABRICS

2.6-9(1) Colorimetry

The three series of samples of carpet back fabric from the sorption isotherm studies were analyzed for shade build-up via colorimetry. The CIE system of color measurement was used (Trotman, 1984). After calibration of the Hunter Color Lab, two fabric samples for each depth of dyeing (% owf) were each presented to the colorimeter four times. The mean tristimulus values X, Y, and Z were used to calculate the x and y chromaticity coordinates for each depth of dyeing:

$$\frac{X}{X+Y+Z} = x \quad \text{and} \quad \frac{Y}{X+Y+Z} = y \qquad \text{(Eq. 5)}$$

The coordinate values for each sample in a series were then plotted on the standard chromaticity chart (Figure 5). Drawing a line from equienergy white (x=0.333, y=0.333) through the chromaticity coordinates of each sample to the spectral loci allowed the dominant wavelength (λ_d) of each sample in the series to be identified. The distance from equienergy white to the sample chromaticity coordinates

divided by the distance from equienergy white to the spectral location of the dominant wavelength gives the color saturation value of the sample:

$$\frac{(C_{xy}, W)}{(W, \lambda_d)} = \text{color saturation} \qquad \text{(Eq. 6)}$$

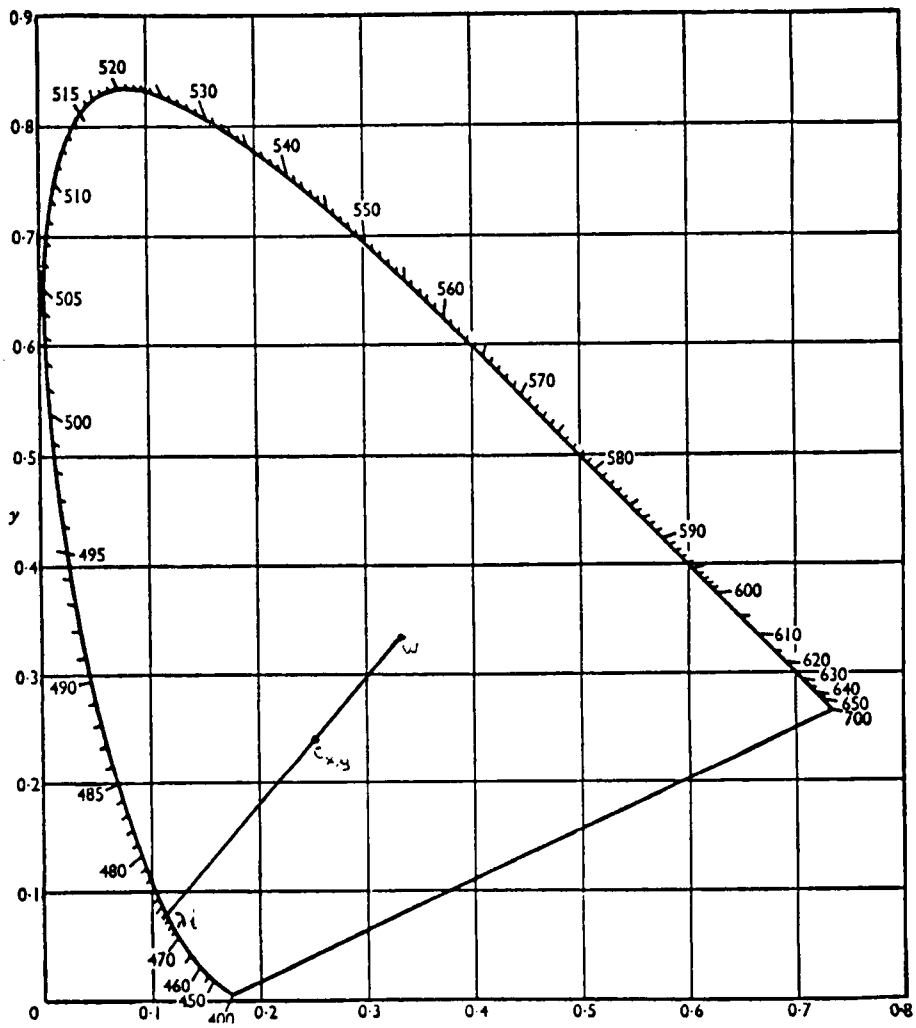


Figure 5. CIE system chromaticity chart.

2.6-9(2) Fastness Testing

Samples of the dyed fabrics, as well as samples of the undyed fabrics, were tested for fastness using standard AATCC testing methods. Carpet back fabric dyed at 2% owf with the C 5 and C 10 dyes, and melt blown nonwoven fabric dyed at 2% owf with the C 18 dye were tested, as well as a sample of the carpet back dyed at 6% owf with the C 18 dye. It was necessary to use 6% owf of the C 18 dye on the carpet back fabric to obtain a depth of shade comparable to that achieved with 2% owf of the C 5 and C 10 dyes.

All of the fastness tests were conducted by the Technical Services Department, Carpet Division, of CIBA-GEIGY. These three tests were conducted:

1. AATCC 16E-1982 Colorfastness to Light: Xenon-Arc Lamp
   Two-step exposure at 10 and 20 AATCC Fading Units
2. AATCC 8-1985 Colorfastness to Crocking: Wet and Dry
3. AATCC 157-1981 Colorfastness to Solvent Spotting:
   Perchloroethylene

2.6-9(3) Microscopy

In addition to fastness testing, cross sections of the dyed fabrics were viewed under a Zeiss compound light microscope to assess penetration of the dye into the fiber.

The dyed yarns were embedded in Spurr low viscosity resin prepared following the recipe for 'firm' resin provided with the resin kit. A small amount of the prepared resin was placed in each mold. Samples of the dyed yarns were placed on top of the resin, and the resin was cured at 65°C for eight hours. Additional prepared resin was added to fill the molds and the whole was cured at 65°C for an additional eight hours.

The cross sections were cut with a microtome equiped with a diamond edge knife.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 THE DYES

Four of the five prototype dyes were successfully synthesized. Experimental yields varied: 52% for the C 18, 51% for the C 10, 34% for the C 5, and 26% for the 1,8-C 18. This variation probably reflects the efficiency of the purification technique more than the efficiency of the synthetic reaction. Those dyes which were most easily purified and/or least soluble in the solvents used for removing impurities were obtained in the highest yields. The C 18, C 10, and C 5 dyes were all isolated as crystalline blue substances. The 1,8-C 18 dye was isolated as greenish yellow crystals.

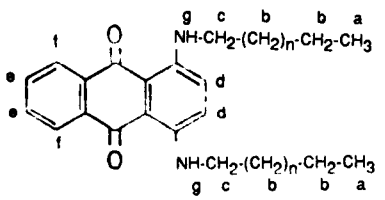
No dye appears to have been isolated following the synthesis with the 1,5-dichloroanthraquinone starting material. The resulting solid appears to be a mixture of salts, relatively insoluble in most organic solvents, except chloroform. When dyebaths were prepared and applied in the usual way, no dyeing of either polypropylene fabric was observed.

As determined by Differential Scanning Calorimetry, all three of the 1,4- dyes appear to be stable up to at least 250°C (Figures B-1 to B-3, Appendix B). This is well above the melting point of polypropylene (167°C), thus precluding the thermal degradation of the dyes during processing of the dyed polypropylene fabrics.

3.1-1 PROTON NUCLEAR MAGNETIC RESONANCE

The PMR spectra (Figures B-4 to B-6, Appendix B) appear to support the proposed structures of the three blue dyes. Other than the peak integration values for the long alkyl chain protons, the PMR for all three dyes appear to be very similar. This confirms that they are indeed a series.

When the PMR data were compared to data recorded in *Sadtler Standard Spectra*, several observations could be made: The spectra for 1-(methylamino)anthraquinone (#4221) and 1,4-dimethylanthraquinone (#12096) show that, as expected, the alkyl protons resonate at the lowest energy level of any of the protons in the molecule. After the alkyl protons, the next energy level for both of these molecules was assigned to the protons on the substituted aromatic ring (about 7.1). Next are the ß protons on the unsubstituted ring (7.6), followed by the α protons on the unsubstituted ring (8.1). Both of these peaks appear to be multiplets, although doublets would be expected. The amine proton on 1-(methylamino)anthraquinone resonates farthest downfield, at 9.6. The similarity of these two spectra to the spectra of the prototype dyes allows the following assignments to be made:



a	0.9	triplet integrates for six
b	1.2 to 1.5	wide multiplet
c	1.8	quartet integrates for four
d	7.2	doublet integrates for two
e	7.7	multiplet integrates for two
f	8.3	multiplet integrates for two
g	10.8	triplet integrates for two
h	2.2	singlet integrates for <1 (contamination)
i	3.4	quartet integrates for four (ethanol)

3.1-2 SPECTROPHOTOMETRY

All three of the blue dyes exhibit dual absorption maxima in two different solvents (Figures B-7 to B-10, Appendix B). The absorption maxima for the C 18 dye are 594 nm and 638 nm. For the C 10 dye they are 592 nm and 634 nm. The C 5 dye exhibits maxima at 592 nm and 636 nm. Unlike the 1,4- dyes, the 1,8-C 18 dye exhibits only one absorption maximum, at 390 nm.

The occurance of dual absorption maxima may be characteristic of 1,4-[bis]-aminoanthraquinones, since it is reported in *Beilstein's Handbuch der Organischen Chemie* (1985) for five 1,4-[bis]-aminoanthraquinones (diamino through butylamino). Varsanyi (1961) discusses this phenomenon on page 12 of his technical introduction to the analysis of UV-Vis absorption spectra. He explains that multiple absorption maxima occur when ". . .the bands of a system converge into groups around individual bands of higher intensity. . . . This phenomenon is especially frequent in case of aromatic hydrocarbons."

3.1-3 THIN LAYER CHROMATOGRAPHY

Since the C 18 dye had the longest alkyl chains, it seems plausible to expect that it would also be the least polar of the dyes in the series. Likewise, C 5 would be expected to be the most polar dye of the group. The calculated R_f values of the three dyes confirm these expectations. The values range from 0.71 for the C 18 dye to 0.67 for the C 5 dye. The C 10 dye, with an R_f value of 0.68, was closer to the C 5 than to the C 18 dye. The 1,8-C 18 dye had an R_f value of 0.69, which was less that that of the 1,4-C 18 dye. Probably the 1,8- series as a whole would exhibit lower values than

the 1,4- series, due to the difference in location of the amine linkages on the anthraquinone ring.

3.1-4 SOLUBILITY STUDIES

Solubility data for the four dyes are presented in Table 6. As might be expected, the C 18 dye was more readily soluble in solvents with low dielectric constants. The C 5 dye was more soluble in those solvents with higher dielectric constants. The C 10 dye fell directly between the other two. This order confirms the relative polarities observed with TLC. The 1,4-C 18 dye and the 1,8-C 18 dye had similar solubilities, indicating similar polarities.

Table 6. Solubility data for all prototype dyes.

solvent	dielectric constant	C 18	C 10	C 5	1,8-C 18
water	78.5	i	i	i	i
methanol	32.6	sl	par	s	sl
ethanol	24.6	sl	par	s	sl
acetone	20.7	par	s	v	par
pyridine	12.3	s	v	∞	par
chloroform	4.8	v	∞	v	v
hexane	1.89	s	v	v	s

i = insoluble
sl = slightly soluble
par = partially soluble
s = soluble
v = very soluble
∞= soluble in all proportions

3.2 CONTROL DYEINGS

When melt blown fabric specimens were dyed with conventional disperse dyes, poor exhaustion levels were observed for all dyebaths. The specimens showed a moderate amount of surface adsorption that was easily rinsed away. The specimens dyed with 2% owf commercially available disperse dyes were only very lightly tinted. They had a depth of shade lighter than that achieved with 0.1% owf of the C 18 dye, as measured by colorimetry (Table 7). This indicates that under the stated conditions, even the more easily dyed of the two polypropylene fabrics studied was not dyeable with conventional dyes, thus validating the usefulness of the prototype dyes.

In the test of the prototype dyes on other fibers, the C 18 dye showed almost no affinity for either nylon or polyester. On nylon the dye showed virtually no exhaustion, whereas on polyester it exhibited limited exhaustion but no fixation of the dye in the fiber. Since one of the problems with previous dyes for unmodified polypropylene has been their lack of specificity for polypropylene, this again reinforces the usefulness of the prototype dyes.

When two normally prepared dyebaths were processed with no fiber added to the bath, recovery of the dye was 97% or better. Variation from theoretical dye concentration was +1.78% and -2.28%, indicating that the dye did not decompose during the dyeing process, nor was it lost during analysis. Recovery of the dye was within experimental error, therefore the proposed processing and analytical methods were adopted with confidence.

Table 7. Color difference of melt blown fabric samples as assesed with the Hunter Color Lab. Equienergy white=0. Spectral loci=1.

dye	color saturation	saturation ratio
0.1% - C 18	0.13	1
2.0% - Blue 7	0.11	0.85
2.0% - Orange 3	0.08	0.62
2.0% - Red 15	0.03	0.23

3.3 SELECTION OF DYEING CONDITIONS

3.3-1 SURFACTANT EFFECTS

In the preliminary study with five different surfactants, exhaustion levels ranged widely, as did levelness of dyed samples. Dyebaths containing any of the Zonyl products exhibited extremely rapid strike, accompanied by very high exhaustion, indicating poor solubilization of the dye. On the other hand, dyebaths with Tergitol 15-S-9 had good diffusion and exhibited better levelling due to much better solubilization of the dye. Tergitol TMN 10 (91 AQ) gave somewhat less level results, but higher exhaustion levels than those seen with Tergitol 15-S-9, indicating that the former dispersing agent probably has less retarding effect on the diffusion of the dye than the latter.

3.3-2 EXPANDED STUDY OF CONDITIONS

3.3-2(1) Surfactant Level Effects

When dyeing conditions were further refined, an interesting difference was noted in the behavior of the two fabrics: Both appear to be sensitive to the level of surfactant (Figure 6). This was especially notable with the carpet back fabric, where exhaustion levels ranged from 25% to zero, depending on the amount of surfactant in the dyebath. The highest exhaustion level on the carpet back specimens was achieved with the least surfactant, whereas somewhat higher exhaustion on the melt blown fabric specimens was achieved at the highest surfactant concentration.

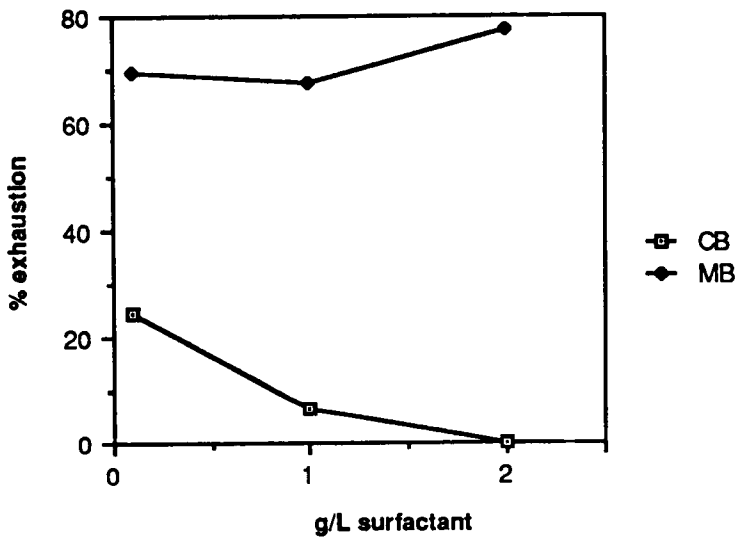


Figure 6. Percent exhaustion of C 18 dye as a function of surfactant level in the dyebath.

These results show that the dispersing agent exhibits a strong retarding effect when used in conjunction with the carpet back fabric. On the other hand, the dispersing agent may actually act as a carrier if present in high enough levels when dyeing the melt blown web. There may be several plausible explanations for these observations. The most significant factors must be estimated, due to the lack of precise information on the processing variables of the two fabrics.

It is certain the melt blown nonwoven presented much more surface area for diffusion of the dye than did the split film carpet back. This extremely large surface area may have allowed the melt blown web to take much better advantage of the solubilizing effect of the dispersing agent. That is, the dye in solution would diffuse rapidly into the fiber of the melt blown web via this large surface area, allowing additional dye particles in the bath to be continually solubilized. On the other hand, the extent of dye adsorption by the carpet back fabric did not deplete the solubilized dye in the bath very rapidly. Instead, the retarding effect produced by a high concentration of dispersing agent took precedence, lowering equilibrium exhaustion levels.

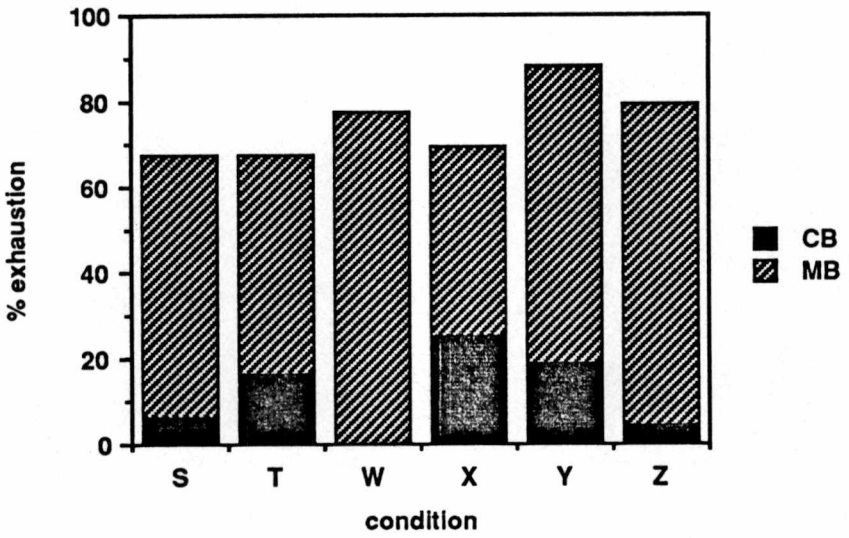
Besides having a much larger surface area, the microstructures of the fibers composing the two fabrics were very different. The melt blown fabric had a much higher ratio of noncrystalline to crystalline area than did the carpet back fabric. Also, the carpet back fabric had been drawn, producing a highly oriented fiber, whereas melt blown fibers are characterized by a lack of orientation (Wadsworth & Jones, 1986). It is likely that the molecules of the dispersing agent were able to penetrate the fiber and function as a carrier with the melt blown fabric, but not with the carpet back fabric. Due to the high orientation and limited noncrystalline area of the fiber composing the carpet back fabric, increasing the level of dispersing agent may have made the dyebath more attractive to the dye, but did not enhance the dye's ability to diffuse into the fiber.

Additionally, there was probably a great deal of difference in the amount and kind of additives contained in the fibers composing the two fabrics. It is obvious that the carpet back fabric contained one or more pigments. (The fabric was a grey color when received from the supplier.) It probably also contained a much higher level of UV stabilizing agents to allow it to perform well in its intended end-use. The performance requirements of the melt blown fabric were very different, and it is unlikely that additives other than antioxidants were used in its manufacture. These chemical differences alone may account for much of the observed difference in the dyeing behavior of the two fabrics. If the dispersing agent interacted chemically in some way with one or another additive in one or both fibers, this could have caused a marked change in equilibrium exhaustion levels.

3.3-2(2) Other Findings

Figure 7 summarizes other findings from this study of dyebath conditions. Addition of salt increased exhaustion levels 31% for the melt blown web and 198% for the carpet back compared to the control dyebaths. This suggests that changing the ionic character of the bath during dyeing may help optimize dyeing conditions by driving the dye onto the fiber. Doubling dyeing time increased exhaustion on the carpet back fabric, but made no difference with the melt blown specimens. This indicated that equilibrium had been reached in 60 minutes with the melt blown nonwoven, but that more time was required for the carpet back fabric to reach equilibrium. Tergitol TMN 10 (91 AQ) gave somewhat better overall exhaustion than Tergitol 15-S-9 and was used exclusively as the dispersing agent in all future research.

It is important to note that optimization of dyeing conditions on one fabric will likely not optimize conditions on the other. Since the exhaustion levels for the melt blown web promised to be higher that those for the carpet back fabric, dyeing conditions were chosen to maximize yield on the melt blown fabric.



CONDITIONS:

S (control)	1g/L Tergitol 15-S-9	dye 60 minutes
T	1g/L Tergitol 15-S-9	dye 120 minutes
W	2g/L Tergitol 15-S-9	dye 60 minutes
X	0.1g/L Tergitol 15-S-9	dye 60 minutes
Y	1g/L Tergitol 15-S-9	dye 60 minutes
	20% owf NaCl added after 30 minutes	
Z	1g/L Tergitol TMN 10(91 AQ)	dye 60 minutes

Figure 7. Effect of dyebath conditions on dye uptake by the fiber.

3.4 SORPTION ISOTHERMS

3.4-1 1,4-[BIS]-OCTADECYLAMINEANTHRAQUINONE

Sorption isotherm dyeings were conducted with the C 18 dye using both fabrics. When the data for all dyeings with this dye were averaged, the mean results for each depth of dyeing were plotted. A Nernst sorption isotherm with high linear correlation was revealed for both fabrics.

The K value for the C 18 dye on the melt blown web was 304 mg/mL. The mean equilibrium exhaustion level of the dye on this fabric was 77.8% with a standard deviation of 11.5% (Figure 8). On the carpet back specimens a K value of 15.3 mg/mL was calculated. The mean equilibrium exhaustion level was 13.4% with a standard deviation of 9.70% (Figure 9).

Since dyeing conditions were selected to optimize exhaustion onto the melt blown fabric, it was not surprising that the data obtained for the two fabrics were very different. Additionally, it may be speculated that the difference in equilibrium dye uptake between the two fabrics was proportional to the differences in the noncrystalline areas of the two fibers from which the fabrics were manufactured.

3.4-2 1,4-[BIS]-DECYLAMINEANTHRAQUINONE

The carpet back fabric was used to evaluate the C 10 dye. Data for all dyeings were averaged and the mean values for each starting concentration were plotted. A

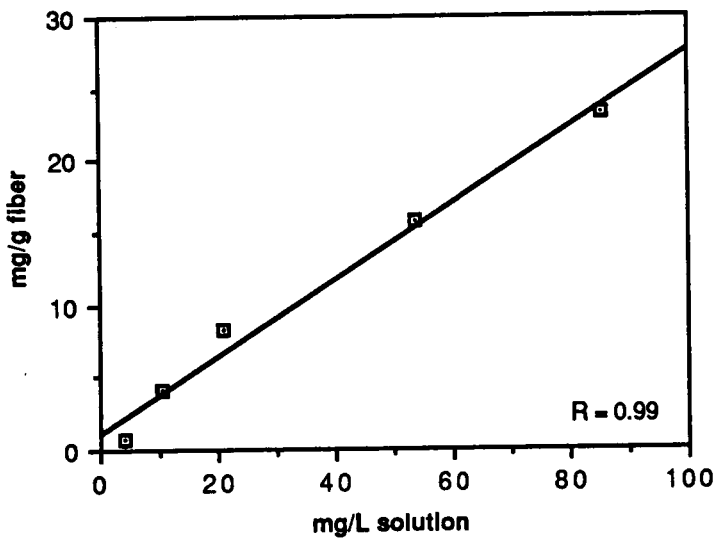


Figure 8. Sorption isotherm for the C 18 dye on the melt blown nonwoven fabric.

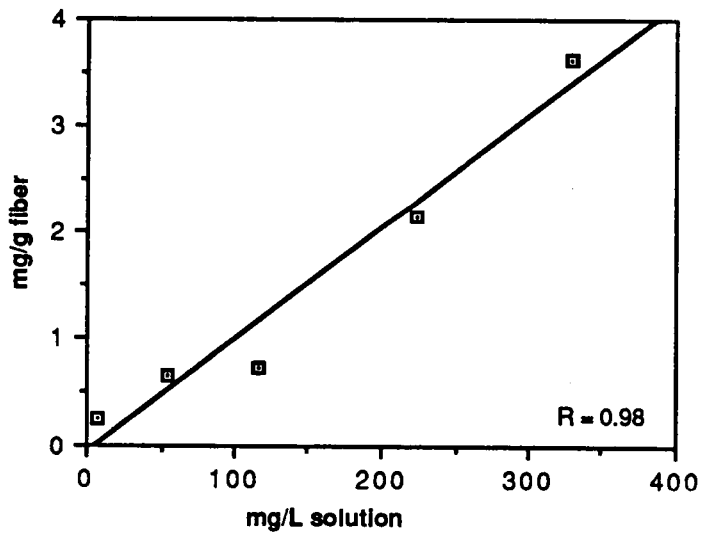


Figure 9. Sorption isotherm for the C 18 dye on the carpet back fabric.

Nernst sorption isotherm was revealed, with a very high linear correlation (Figure 10). The mean equilibrium exhaustion level of the dye onto the fabric was 83.6% with a standard deviation of 1.31%. The K value of this dye was 412 mg/mL.

3.4-3 1,4-[BIS]-AMYLAMINEANTHRAQUINONE

The carpet back fabric was also used to evaluate the C 5 dye. Again, data for all dyeings were averaged and mean values plotted. A Nernst sorption isotherm with high linear correlation was again revealed (Figure 11). The mean equilibrium exhaustion level of the dye onto the fabric was 78.7% with a standard deviation of 3.47%. The value of K for this dye was 293 mg/mL.

3.4-4 DISCUSSION

The standard deviations reflect the amount of scatter present in the data, particularly for the C 18 dye. Due to these high standard deviations, it was necessary to compute mean equilibrium exhaustion levels for each depth of dyeing. This allowed the sorption isotherms to be plotted with good linear correlation between the points on each graph.

In addition to experimental error, the standard deviations may reflect a high degree of variability within the fabrics themselves. The C 18 dyeings were conducted over a broad time range, with other studies conducted between dyeing repetitions. Hence, the fabric samples were cut from different locations on the fabric roll. On the

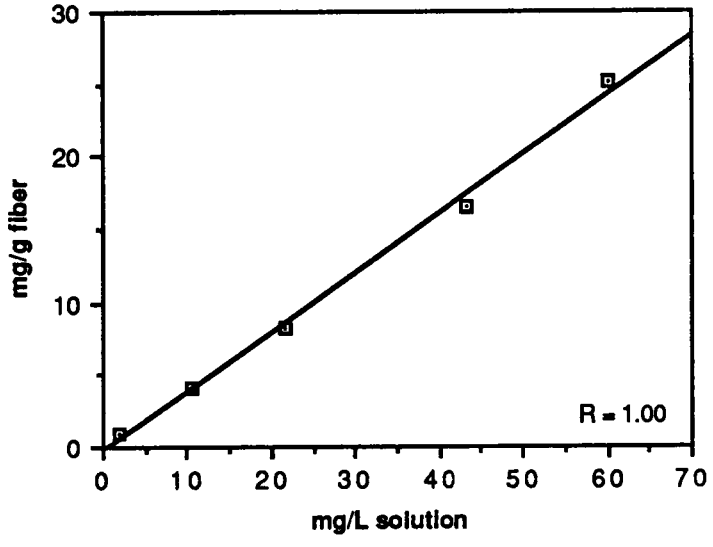


Figure 10. Sorption isotherm for the C 10 dye on the carpet back fabric.

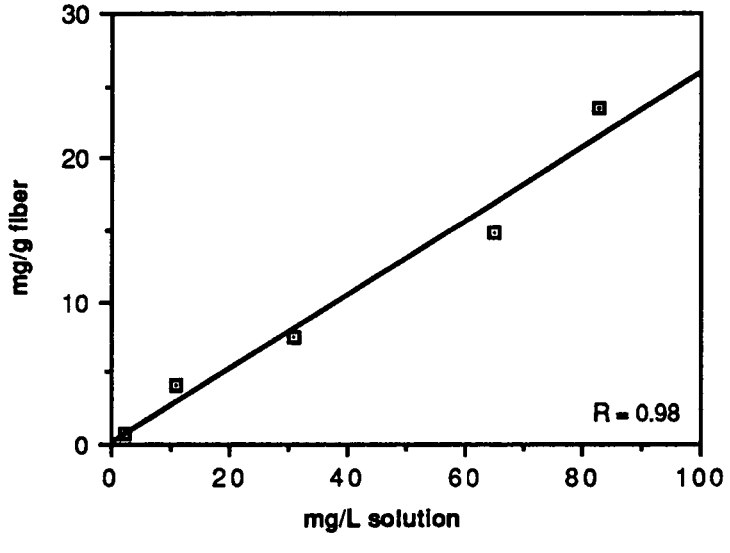


Figure 11. Sorption isotherm for the C 5 dye on the carpet back fabric.

other hand, the C 10 and C 5 dyeing repetitions were run consecutively, allowing all of the fabric samples to be cut from a single yard of fabric. This would greatly reduce the likelihood that fabric variability would be a major factor for these isotherms.

The C 5 and C 10 dyes on the carpet back fabric had equilibrium exhaustion levels far above the equilibrium exhaustion level determined for the C 18 dye on the carpet back fabric. Differences are most likely occuring at all three stages of dyeing. The retarding effect of the dispersing agent in conjunction with the C 18 dye and the carpet back fabric has already been discussed in section 3.3-2(1). The C 10 and C 5 dyes appeared not to exhibit this effect, thus allowing much more rapid migration of the dye to the fiber/dyebath interface. Additionally, the C 5 dye, with its short alkyl chains, likely diffused much more rapidly into the fiber as compared to the C 18 dye. It was surprising to note that the C 10 dye displayed the highest mean equilibrium exhaustion level of the three dyes. Further studies indicated that this level may not be an accurate representation of the amount of dye actually fixed in the fiber, however, but may include dye that was only adsorbed on the surface .

3.5 RATE STUDIES

3.5-1 MELT BLOWN NONWOVEN FABRIC

At a 2% dye owf concentration of the C 18 dye, exhaustion levels at 80°C (Figure 12) and 90°C (Figure 13) at 200 minutes were 75.1% and 81.7% respectively, within six percentage points of each other. However, at 100°C (Figure 14) the exhaustion level had increased to 94.7%, 20 percentage points over that

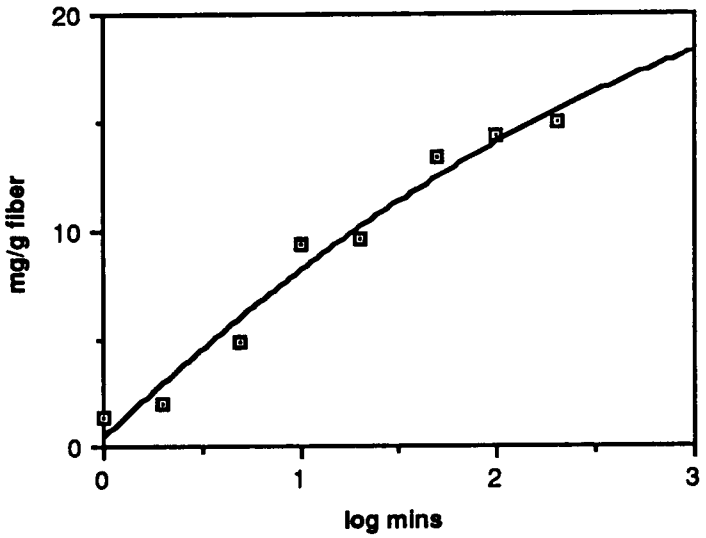


Figure 12. 80°C kinetic isotherm for the C 18 dye on the melt blown nonwoven.

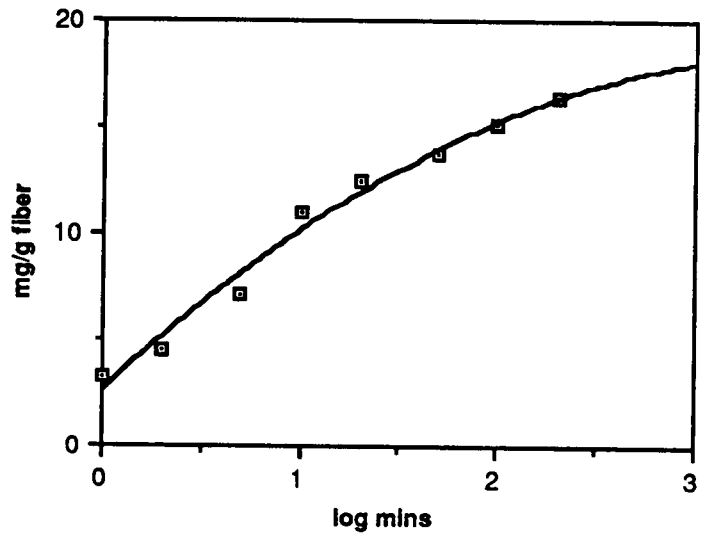


Figure 13. 90°C kinetic isotherm for the C 18 dye on the melt blown nonwoven.

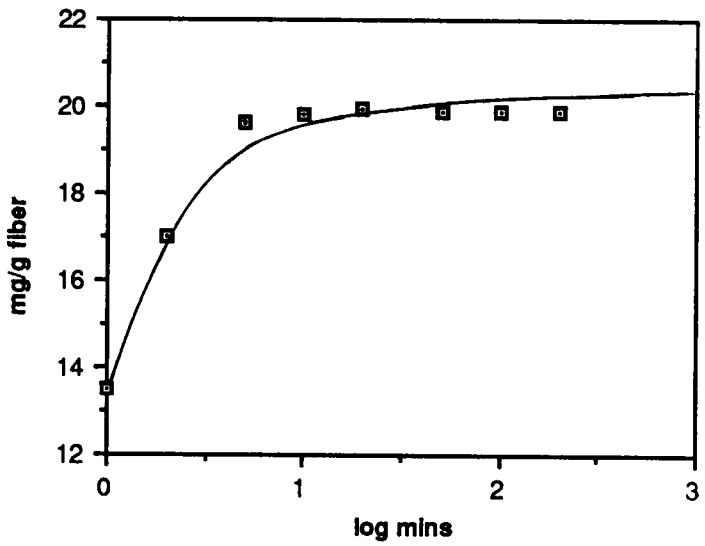


Figure 14. 100°C kinetic isotherm for the C 18 dye on the melt blown nonwoven.

achieved at 80°C. Likewise, $t_{1/2}$ decreased from 8 minutes at 80°C to 6.25 minutes at 90°C, then to under 1 minute at 100°C.

These observations indicate that although the fabric is dyeable at lower temperatures, dyeing is much more rapid and achieves a much higher yield of dye on fiber at 100°C than at 90°C or less. It seems certain that the fiber has undergone a second order transition as the temperature was raised from 90°C to100°C. This transition temperature could possibly be determined by studing the rate of dyeing at several temperatures between 90°C and100°C. Computation of $t_{1/2}$ for each temperature would reveal a temperature at which the time of half dyeing plunged. This would determine the transition temperature more exactly for this polypropylene fiber.

3.5-2 CARPET BACK FABRIC

The rate of dyeing at 80°C with the C 18 dye on the carpet back fabric could not be determined. All exhausted dyebaths for two repetitions had absorbances within a very narrow range. Mean exhaustion level for all baths (1 to 200 minutes) was calculated to be only 1.28%. This indicates that virtually no exhaustion occured, although the dyed fabrics appeared to be colored to somewhat different depths of shade. Likely there was insufficient energy available at this temperature to promote diffusion of the dye into the fiber. The somewhat different depths of coloration observed on the samples dyed at this temperature may have been caused by slight surface adsorption, which would have used up only a negligible amount of dye.

A result similar to that observed at 80°C was also observed with the carpet back fabric dyed at 90°C. The exhaustion at this temperaure did not increase significantly with increasing time and variability made a trend difficult to determine. Exhaustions for two repetitions ranged within plus or minus four percentage points of the mean. In the study of preliminary dyeing conditions at 90.5°C, an increase in dye exhaustion from 6.4% at 60 minutes to 16.5% at 120 minutes was observed for one repetition. It may be that at this temperature range, only a slight increase in temperature makes a large difference in exhaustion level onto the carpet back fabric.

A kinetic isotherm was determined for the C 18 dye on the carpet back fabric at 100°C (Figure 15). Exhaustion levels ranged from 62.6% at one minute to 94.7% at 200 minutes. Time of half dyeing on the carpet back at 100°C was less than two minutes.

These data suggest that the fiber from which the carpet back fabric was manufactured also undergoes a second order transition somewhere between 90°C and 100°C. When the transition temperature was reached, dye uptake by the fiber was

greatly increased. Also, exhaustion at one minute was quite high, indicating very rapid surface strike by the dye at this temperature, probably followed by slightly slower diffusion of the dye into the fiber interior.

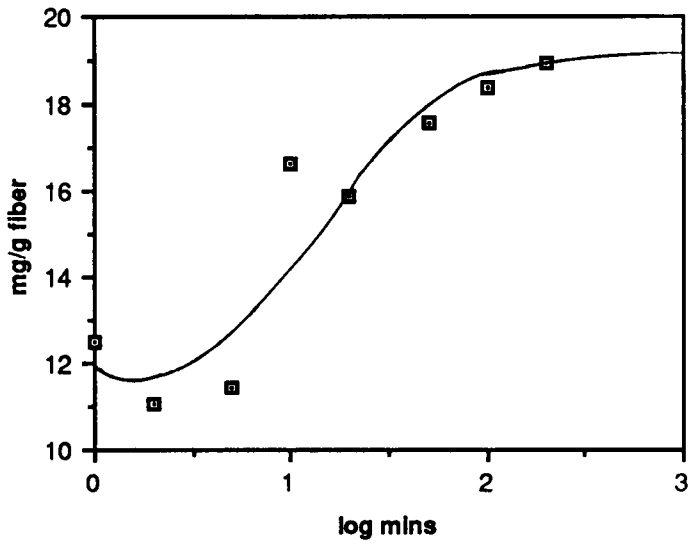


Figure 15. 100°C kinetic isotherm for the C 18 dye on the carpet back fabric.

3.6 CHARACTERIZATION OF DYED FABRICS

3.6-1 COLORIMETRY

Colorimetric analysis of the carpet back fabrics dyed at increasing depths of dye on fiber with the C 18, C 10, and C 5 dyes demonstrated differences in the depth of color over the entire range of initial dyebath concentrations (Table 8). The fabrics dyed with 2% C 18 dye owf had much lower color saturation at all depths of dyeing than

the samples dyed with 2% of the C 10 or C 5 dyes owf. The fabrics dyed with the C 5 and C 10 dyes had very similar color saturation values.

The dominant wavelength of the darkest samples of each series fell within the blue color range: C 18 - 430 nm, C 10 - 472 nm, and C 5 - 476 nm. It may be observed that the dyed fabrics showed a hypsochromic shift in the dominant wavelength of reflectance as the alkyl chain length was decreased. A sample of the carpet back fabric dyed with the 1,8-C 18 dye showed a dominant wavelength of 585 nm, within the yellow range.

Table 8. Color saturation values of dyed carpet back samples as assessed with the Hunter Color Lab. Equienergy white = 0. Spectral loci = 1.

	depth of dyeing				
dye	0.1% owf	0.5% owf	1.0% owf	2.0% owf	3.0% owf
C 18	0.029	0.039	0.050	0.064	0.11
C 10	0.08	0.24	0.28	0.34	0.44
C 5	0.08	0.21	0.31	0.36	0.43

3.6-2 FASTNESS TESTING

The carpet back samples performed better in the light fastness and solvent fastness tests than the melt blown nonwoven samples (Table 9). The much larger surface area and the lower crystallinity of the melt blown web as compared to the split

film carpet back probably accounts for this difference. The greater surface area would expose much more dye either for removal by the solvent or for degradation by the light. It may also be possible that a different type of dye/fiber interaction was occuring with the two different fabric types, causing the dye to be better fixed in the carpet back than in the melt blown fabric. The melt blown nonwoven samples tended to

Table 9. Colorfastness of dyed samples. Rating scale extends from 1 to 5 where 5 indicates no color change and 1 indicates much color change.

dye	fabric	lightfastness 10	lightfastness 20	crocking wet	crocking dry	solvent spotting
C 18	MB	4	2 - 3	not done	not done	1
		4	2 - 3	not done	not done	1
	CB	5	5	4 - 5	4	4
		5	5	4	3 - 4	4
C 10	CB	5	4 - 5	3 - 4	2 - 3	2 - 3
		5	4 - 5	3	2 - 3	2 - 3
C 5	CB	5	4 - 5	4 - 5	4	4 - 5
		5	4 - 5	4 - 5	4 - 5	4 - 5
none	MB	5	5	not done	not done	5
		5	5	not done	not done	5
none	CB	5	5	5	4 - 5	5
		5	5	5	5	5

tear and were deemed by the testing laboratory to be too fragile to be subjected to rub fastness testing.

The carpet back fabric dyed with 6% of the C 18 dye owf had the best lightfastness of all the dyed samples, with both samples showing no change at 20 AATCC Standard Fading Units of exposure. These samples also had good fastness to crocking and solvent spotting. Previous solubility studies indicated that the C 18 dye should be quite soluble in perchloroethylene. That the dye was not removed from the fiber during the solvent spotting test indicated that a high level of fixation had been achieved. The excellent light fastness rating and good rub fastness rating also indicated that the dye had been well fixed within the fiber to avoid degradation or crocking.

The carpet back fabric dyed with 2% C 10 dye owf rated the lowest of the carpet back samples in both rub fastness and fastness to solvent spotting. This probably indicated that despite its high equilibrium exhaustion levels, the dye was either not very well fixed in the fiber, or the fiber was only ring dyed. If much of the dye was only adhered on the fiber surface, both rub fastness and fastness to solvent spotting would be anticipated to be low. The light fastness of the samples dyed with the C 10 dye was very good, an indication that the dye itself was not degraded by light within the time period of the test.

The carpet back fabric dyed with 2% of the C 5 dye owf rated very well on all three of the fastness tests. Its light fastness was only slightly lower than that of the C 18 dye. It had the highest rub fastness and fastness to solvent spotting of any of the carpet back samples. These results, especially the very good resistance to removal of the dye by perchloroethylene, indicate that this dye was also well fixed within the fiber.

3.6-3 MICROSCOPY

Ten micrometer thick cross sections of carpet back split film dyed with 6% of the C 18 dye owf appeared bluish throughout, demonstrating that the dye had penetrated throughout the fiber. This observation indicated that the dye was not merely adsorbed on the fiber surface, and that the fibers were not ring dyed .

Fibers dyed with 2% of the C 10 dye owf appeared approximately the same color as the surrounding embedding medium. The C 10 dye seemed to have migrated into the embedding compound, as the area near the edge of the fiber appeared bluish in some places. This may have been due to surface deposition of dye on the fiber. Fastness test results tend to reinforce this possibility.

The fibers dyed with 2% owf of the C 5 dye appeared faintly blue throughout. There was no indication of dye migration into the embedding compound with this dye, indicating that this dye also had little surface deposition.

The fiber dyed with the 1,8-C 18 dye was yellow. Unfortunately, the embedding medium was also yellowish when cured. This made it difficult to observe whether the dye had penetrated throughout the fiber, since the dyeing could not be well differentiated by color.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

These conclusions are based solely on the work reported herein. Further research may yield additional or conflicting results, due to the complex nature of the dye/fiber interaction. The variabilities exhibited in the application and analysis of these dyes make precise measurement difficult, but efforts have been taken to ensure the accuracy of final results. Even though the data reflect a great deal of scatter, several strong trends were observed.

This research has shown that the prototype dyes are true disperse dyes for polypropylene. The dye exhaustion levels were generally high and deep shades were obtained. In addition, different colors were achieved by altering the position of the aminoalkyl chains in the anthraquinone ring system. Dyeing of polypropylene fabrics with conventional disperse dyes resulted in only lightly tinted fabrics. Moreover, the prototype dyes are specific for polyproplyene. When nylon and polyester were dyed with the C 18 dye there was essentially no affinity for either fiber.

The alkyl chain length does not appear to dictate the level of dye uptake by polypropylene substrates, as had been hypothesized. When mean exhaustion levels onto the carpet back fabric for the three dyes in the series were compared, the C 10 dye had the highest mean exhaustion level, at 83.6%. The C 5 dye was slightly lower, with a mean exhaustion level of 78.7%. The C 18 had a mean exhaustion level of 13.4% onto the carpet back, significantly lower than either of the other two.

Fastness testing and optical microscopy revealed, however, that the equilibrium exhaustion levels are only part of a larger picture. The carpet back fabrics dyed with the C 18 dye had very good fastness properties and high levels of dye penetration. These observations indicate that although the C 18 dye had a very low rate of diffusion, it had a good level of fixation in the fiber. The C 10 dye, on the other hand, had a much higher apparent rate of diffusion, but a much lower level of fixation in the fiber. The C 5 dye had both a good rate of diffusion and a good level of fixation in the fiber.

These findings suggest that there may be different mechanisms of dyeing occuring for the very long alkyl chain dye (C 18) than for the dye with relatively short alkyl chains (C 5). On the other hand, the C 10 dye with medium length chains appears to be dominated by surface adsorption.

The linear partition of the dye between the fiber and the dyebath suggests a mechanism of unlimited saturation for all three dyes tested. This observation fulfills the hypothesis that a Nernst sorption isotherm would be exhibited for the novel dyes on polypropylene substrates. An upper limit likely exists beyond which dye uptake is diminished (Bird and Manchester, 1955), but this was not approached within the range of this research. It would be expected that fabrics with greater amorphous content such as the melt blown nonwoven web would have a much higher upper bound than fabrics with high crystalline content such as the carpet backing.

As was hypothesized, it has also been shown that the quantity and quality of the dyeings with the prototype dyes are highly dependent upon the choice of dyeing auxiliaries. It is crucial that the dispersing agent give a stable dispersion without undue retarding effects. Optimization of this factor holds promise for improved dye levelness and yield on the fiber. Limited experiments also showed that changing the ionic character of the bath improves dye exhaustion significantly. One possible

explanation for this observation might be that the dyebath consists of a collodial suspension of dye particles, which was destroyed by the addition of salt (NaCl). The dye was thus driven out of suspension onto the fiber (Etters, 1988).

Additionally, the sensitivity of the carpet back fabric to the surfactant choice and temperature of dyeing indicated that the fabric/fiber structure was an important factor to be considered in the choice of dyeing conditions. Drawn polypropylene fibers would likely show improvement in dyeing behavior at elevated pressures. It has been shown that the fiber structure was much more accessible at temperatures higher than were used through much of this research.

4.2 RECOMMENDATIONS

The expectations of the first hypothesis that the prototype dyes will be capable of meeting industry standards has not yet been fully met. Further research in three areas will allow the potential of the prototype dyes to be further explored. First, the dyeing technique must be improved. Second, the dyes themselves may need refinement. Third, the fastness performance of the dyed fabrics needs to be more fully tested.

Several areas of dyeing and experimental technique require revision:

1. The low aqueous solubility of the dyes made it difficult to accurately prepare and process dyebaths and samples for analysis. Finding a way to reduce initial particle size would be very helpful, as would finding a surfactant that better solubilized the dye particles. Use of a different surfactant might also give more uniform dyeing results by reducing the rate of dye strike. It seems obvious that a distinct surfactant choice may need to be made for each fabric to be dyed.

2. The high standard deviations obtained for the C 18 sorption isotherm indicate that there may be some difficulty in measurement with this dye. Analysis of the final concentration of C 18 dyebaths might be more accurate if an alternate solvent were used to prepare samples for spectrophotometric analysis. Although it was originally thought that hexane would be a suitable solvent, it is now apparent that the dye is not as soluble in hexane as in slightly more polar solvents, such as chloroform.

3. The length and temperature of dyeing need to be modified. Again, it appeared at the outset that 90.5°C and 90 minutes would be suitable conditions. It now seems that dyeing at the boil would yield much higher exhaustion levels. If dyeing is to be done at 90.5°C, the length of time needed to establish true equilibrium appears to be closer to four hours than to 90 minutes.

4. Crystallinity studies would likely provide useful information on the relation of fiber structure to dyeing behavior.

Besides improving dyeing conditions, further work needs to be done to develop additional dyes. These dyes would have related functionalities to those already prepared. Due to the difference in the polarity of starting materials and that of the desired products, High Pressure Liquid Chromatography analysis might be very useful to rapidly purify these compounds. Also, the current prototype dyes need to be more fully characterized and identified, as will any new compounds.

The final hurdle to industry acceptance will probably be sufficient, suitable color fastness of dyed samples. In addition to the testing already performed, additional lightfastness testing for longer time periods would be desirable. Washfastness testing might be appropriate, as would sublimation testing. Additionally, the dyed fabrics should be stored for a period of time, then retested to determine their stability over time.

In spite of the many recommendations for further study produced by this initial research, much useful information has ben obtained. Based on the knowledge gained in this research, there is promise that a new class of disperse dyes for polyolefins can be developed in the near future.

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APPENDIXES

APPENDIX A

RAW DATA

Table A-1. Selection of dyeing conditions. Initial dyebath concentration = 0.25 mg/mL. Absorption coefficient = 19.65 m L/mg. Potential dye on fiber = 20 mg/g fiber.

sample	absorbance	dilution	A	c_s^{∞} mg/mL	% exh	C_f mg/g
S MB	.64	2.5	1.6	0.081	67.4 %	13.5
CB	.92	5	4.6	0.234	6.3	1.27
T MB	.63	2.5	1.58	0.080	67.8	13.6
CB	.82	5	4.1	0.209	16.5	3.30
W MB	.66	2.5	1.1	0.056	77.6	15.5
CB	1.0	5	5.0	0.255	-1.8	-.356
X MB	.60	2.5	1.5	0.076	69.5	13.9
CB	.74	5	3.7	0.188	24.7	4.94
Y MB	.58	_	.58	0.030	88.2	17.6
CB	.86	5	4.0	0.204	18.6	3.72
Z MB	1.02	_	1.02	0.052	79.2	15.9
CB	.94	5	4.7	0.239	4.3	.865

S (control)	1g/L Tergitol 15-S-9	dye 60 minutes
T	1g/L Tergitol 15-S-9	dye 120 minutes
W	2g/L Tergitol 15-S-9	dye 60 minutes
X	0.1g/L Tergitol 15-S-9	dye 60 minutes
Y	1g/L Tergitol 15-S-9	dye 60 minutes
	20% owf NaCl added after 30 minutes	
Z	1g/L Tergitol TMN 10(91 AQ)	dye 60 minutes

Table A-2. C 18 sorption isotherms on carpet back.

sample		absorbance	dilution	A	abs. coeff.	c_s^i mg/mL	c_s^∞ mg/mL	% exh	mg dye / g fiber	C_f mg/g
0.1	A	.28	_	.28	20.56	0.0125	0.0136	0	1	0
	B	.18	_	.18	20.46		0.0088	29.6		.296
	C	.17	_	.17	19.19		0.0089	29.1		.291
	D	.15	_	.15	19.19		0.0078	37.5		.375
	mean						0.0098	24.1		.241
0.5	A	1.16	_	1.16	20.56	0.0625	0.0564	9.7	5	.485
	B	.50	2.5	1.25	20.46		0.0611	2.3		.115
	C	.95	_	.95	19.19		0.0495	20.8		1.04
	D	.98	_	.98	19.19		0.0511	18.3		.915
	mean						0.0545	12.8		.639
1.0	A	.92	2.5	2.3	20.56	0.125	0.112	10.5	10	1.05
	B	.96	2.5	2.4	20.46		0.117	6.2		.620
	C	.44	5	2.2	19.19		0.115	8.3		.829
	D	.46	5	2.3	19.19		0.120	4.1		.412
	mean						0.116	7.3		.728

Table A-2. Continued.

sample		absorbance	dilution	A	abs. coeff.	c_s^i $\frac{mg}{mL}$	c_s^∞ $\frac{mg}{mL}$	% exh	$\frac{mg\ dye}{g\ fiber}$	C_f $\frac{mg}{g}$
2.0	A	.88	5	4.4	20.51	0.25	0.215	14.2	20	2.84
	B	.90	5	4.5	20.46		0.220	12.0		2.40
	C	.88	5	4.4	19.19		0.229	8.3		1.66
	D	.88	5	4.4	19.19		0.229	8.3		1.66
	mean						0.223	10.7		2.14
3.0	A	1.26	5	6.3	20.51	0.375	0.307	18.0	30	5.43
	B	1.26	5	6.3	20.46		0.308	17.9		5.37
	C	.65	10	6.5	19.19		0.339	9.7		2.90
	D	.70	10	7.0	19.19		0.365	2.7		.818
	mean						0.330	12.1		3.63

Table A-3. C 18 sorption isotherms on melt blown nonwoven.

sample		absorbance	dilution	A	abs. coeff.	c_s^i mg/mL	c_s^∞ mg/mL	% exh	mg dye / g fiber	C_f mg/g
0.1	A	.13	_	.13	20.56	0.0125	0.00632	49.4	1	.494
	B	.04	_	.04	20.46		0.00196	84.4		.844
	mean						0.00414	66.9		.669
0.5	A	.30	_	.30	20.56	0.0625	0.01459	76.6	5	3.83
	B	.13	_	.13	20.46		0.00635	89.8		4.49
	mean						0.01047	83.2		4.16
1.0	A	.42	_	.42	20.56	0.125	0.0204	83.7	10	8.37
	B	.44	_	.44	20.46		0.0215	82.8		8.28
	mean						0.0210	83.3		8.33
2.0	A	.82	2	1.64	20.56	0.25	0.0798	68.0	20	13.6
	B	.22	2.5	.55	20.46		0.0269	89.2		17.8
	mean						0.0534	78.6		15.7
3.0	A	.84	2.5	2.10	20.56	0.375	0.1024	72.7	30	21.8
	B	.56	2.5	1.4	20.45		0.0685	81.8		24.5
	mean						0.0854	77.3		23.2

Table A-4. C 10 sorption isotherms.

sample		absorbance	dilution	A	abs. coeff.	c_s^i mg/mL	c_s^∞ mg/mL	% exh	mg dye / g fiber	C_f mg/g
0.1	A	.02	2	.04	22.40	0.0125	0.00179	85.7	1	.857
	B	.02	2	.04			0.00179	85.7		.857
	mean						0.00179	85.7		.857
0.5	A	.12	2	.24	22.40	0.0625	0.0107	82.9	5	4.15
	B	.115	2	.23			0.0103	83.6		4.18
	mean						0.0105	83.3		4.16
1.0	A	.235	2	.47	22.40	0.125	0.0210	83.2	10	8.32
	B	.25	2	.50			0.0223	82.1		8.21
	mean						0.0217	82.7		8.27
2.0	A	.18	5	.90	22.40	0.25	0.0400	84.0	20	16.8
	B	.21	5	1.05			0.0469	81.3		16.3
	mean						0.0434	82.7		16.5
3.0	A	.27	5	1.35	22.40	0.375	0.0603	83.9	30	25.2
	B	.27	5	1.35			0.0603	83.9		25.2
	mean						0.0603	83.9		25.2

Table A-5. C 5 sorption isotherms.

sample		absorbance	dilution	A	abs. coeff.	c_s^i mg/mL	c_s^∞ mg/mL	% exh	mg dye / g fiber	C_f mg/g
0.1	A	.095	_	.095	39.67	0.0125	0.00239	80.8	1	.808
	B	.10	_	.10			0.00252	79.8		.798
	mean						0.00246	80.3		.803
0.5	A	.44	_	.44	39.67	0.0625	0.0111	82.3	5	4.12
	B	.42	_	.42			0.0106	83.1		4.16
	mean						0.0108	82.7		4.14
1.0	A	.50	2.5	1.25	39.67	0.125	0.0315	74.8	10	7.48
	B	.48	2.5	1.2			0.0302	75.8		7.58
	mean						0.0309	75.3		7.53
2.0	A	.96	2.5	2.4	39.67	0.25	0.0605	75.8	20	15.2
	B	1.1	2.5	2.75			0.0693	72.2		14.4
	mean						0.0649	74.0		14.8
3.0	A	.71	5	3.55	39.67	0.375	0.0895	76.1	30	22.8
	B	.60	5	3.0			0.0756	79.8		23.9
	mean						0.0826	78.0		23.4

Table A-6. 80°C rate of dyeing study. All data are for the C 18 dye on the melt blown fabric. Initial dyebath concentration =0.25 mg/mL. Potential dye on fiber=20 mg/g. Absorption coefficient =19.65 mL/mg.

sample		absorbance	dilution	A	c_s^∞ mg/mL	% exh	C_f mg/g
1min	A	.88	5	4.4	0.224	10.4	2.09
	B	.95	5	4.75	0.242	3.3	.662
2min	A	.82	5	4.1	0.208	16.5	3.31
	B	.945	5	4.73	0.241	3.8	.743
5min	A	.70	5	3.5	0.178	28.8	5.75
	B	.78	5	3.9	0.198	20.6	4.12
10min	A	.54	5	2.7	0.137	45.0	9.01
	B	.50	5	2.5	0.127	49.1	9.82
20min	A	.585	5	2.93	0.149	40.5	8.09
	B	.44	5	2.2	0.112	55.2	11.0
50min	A	.325	5	1.63	0.083	66.9	13.4
	B	.33	5	1.65	0.084	66.4	13.3
100min	A	.305	5	1.53	0.078	69.0	13.8
	B	.25	5	1.25	0.064	74.6	14.9
200min	A	.21	5	1.05	0.053	78.6	15.7
	B	.28	5	1.4	0.071	71.5	14.3

Table A-7. $90^{o}C$ rate of dyeing study. All data are for the C 18 dye on the melt blown fabric. Initial dyebath concentration =0.25 mg/mL. Potential dye on fiber=20 mg/g. Absorption coefficient =19.65 mL/mg.

sample		absorbance	dilution	A	c_s^{∞} mg/mL	% exh	C_f mg/g
1min	A	.86	5	4.3	0.219	12.5	2.49
	B	.78	5	3.9	0.199	20.6	4.12
2min	A	.78	5	3.9	0.199	20.6	4.12
	B	.74	5	3.7	0.188	24.7	4.94
5min	A	.68	5	3.4	0.173	30.8	6.16
	B	.58	5	2.9	0.148	41.0	8.19
10min	A	.90	2.5	2.25	0.115	54.2	10.8
	B	.43	5	2.15	0.109	56.2	11.3
20min	A	.80	2.5	2.0	0.102	59.3	11.9
	B	.68	2.5	1.7	0.087	65.4	13.1
50min	A	.59	2.5	1.48	0.075	70.0	14.0
	B	.63	2.5	1.58	0.080	67.9	13.6
100min	A	.52	2.5	1.3	0.066	73.5	14.7
	B	.43	2.5	1.08	0.055	78.1	15.6
200min	A	.42	2.5	1.15	0.059	76.6	15.3
	B	.26	2.5	.65	0.033	86.8	17.4

Table A-8. $100^{o}C$ rate of dyeing study. Data are for the C 18 dye on both fabrics. Initial dyebath concentration =0.25 mg/mL. Potential dye on fiber=20 mg/g. Absorption coefficient =19.65 mL/mg.

sample	absorbance	dilution	A	c_s^{∞} mg/mL	% exh	C_f mg/g
1min MB	.64	2.5	1.6	0.081	67.4	13.5
CB	.735	2.5	1.84	0.094	62.6	12.5
2min MB	.295	2.5	.74	0.038	85.0	17.0
CB	.875	2.5	2.19	0.111	55.5	11.1
5min MB	.09	_	.09	0.005	98.2	19.6
CB	.842	2.5	2.11	0.107	57.0	11.4
10min MB	.04	_	.04	0.002	99.2	19.8
CB	.33	2.5	.825	0.042	83.2	16.6
20min MB	.02	_	.02	0.001	99.6	19.9
CB	.405	2.5	1.01	0.052	79.4	15.9
50min MB	.028	_	.028	0.001	99.4	19.9
CB	.24	2.5	.60	0.031	87.8	17.6
100minMB	.038	_	.038	0.002	99.2	19.9
CB	.16	2.5	.40	0.020	91.9	18.4
200minMB	.03	_	.03	0.002	99.3	19.9
CB	.105	2.5	.263	0.013	94.7	18.9

APPENDIX B

ANALYTICAL SPECTRA

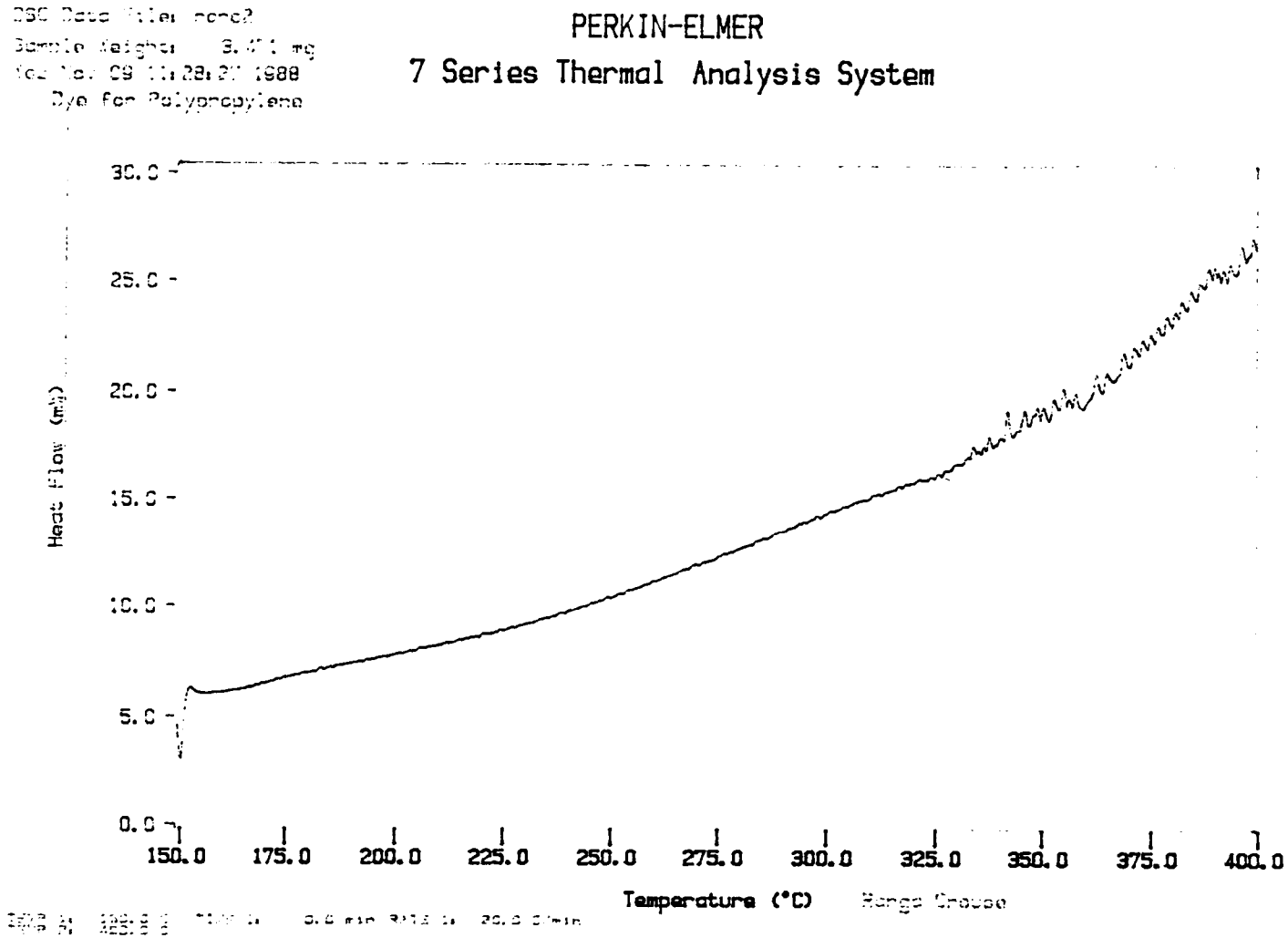


Figure B-1 Differential Scanning Calorimetry scan for the C 18 dye. Heating range is 150°C to 400°C.

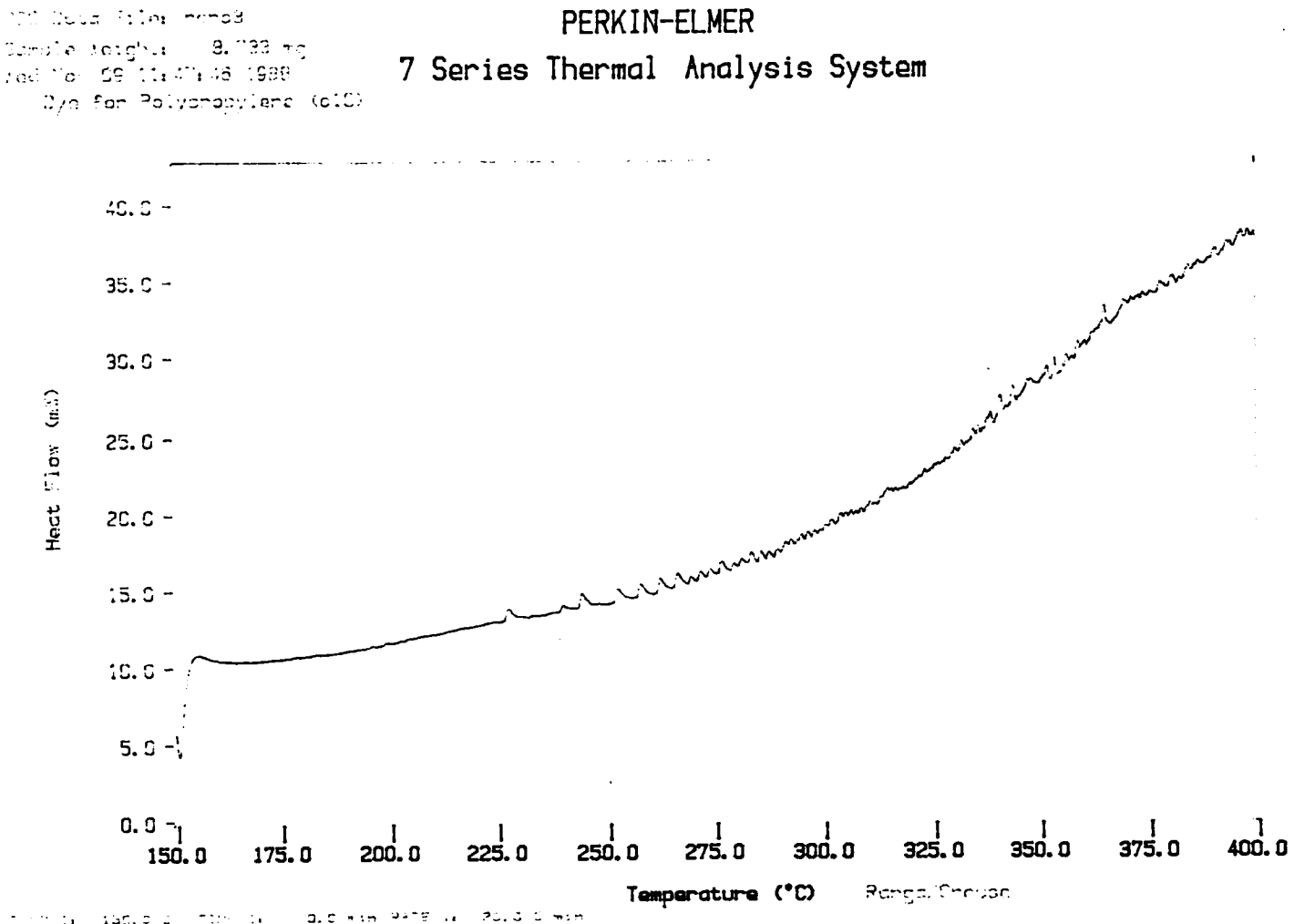


Figure B-2. Differential Scanning Calorimetry scan for the C 10 dye. Heating range is 150°C to 400°C.

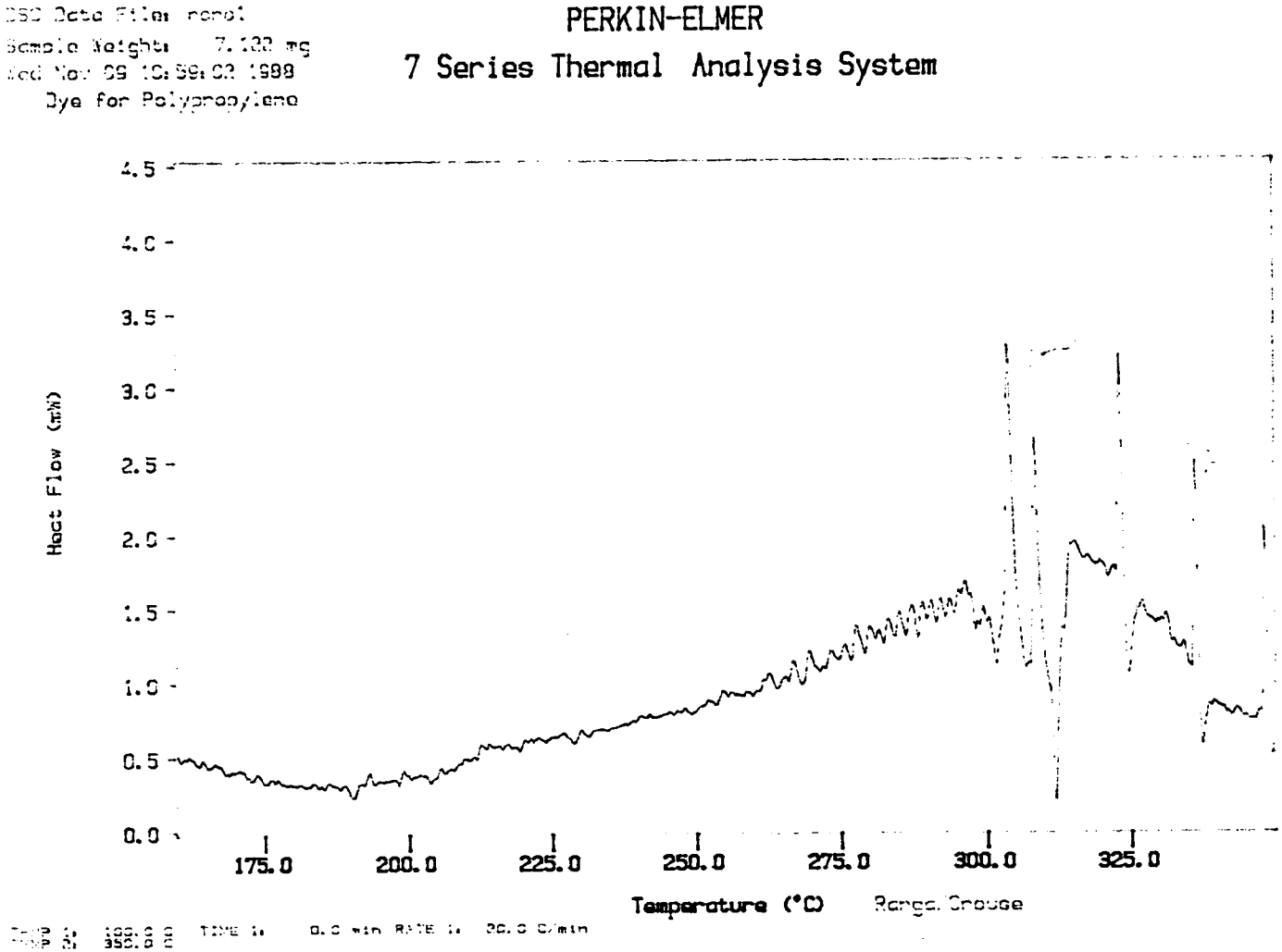


Figure B-3. Differential Scanning Calorimetry scan for the C 5 dye. Heating range is 175°C to 325°C.

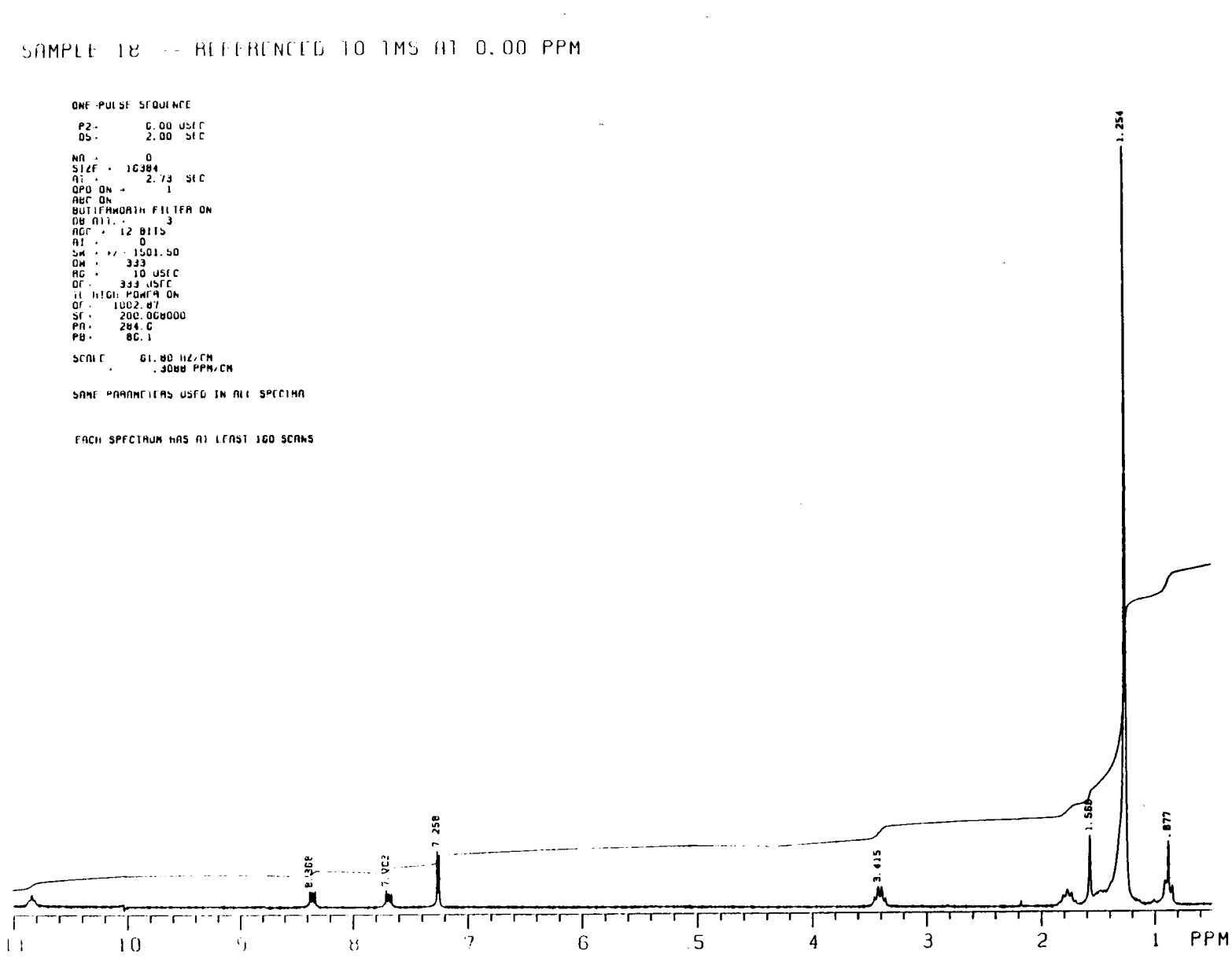


Figure B-4. Proton Nuclear Magnetic Resonance spectra for the C 18 dye.
A: Entire spectra.

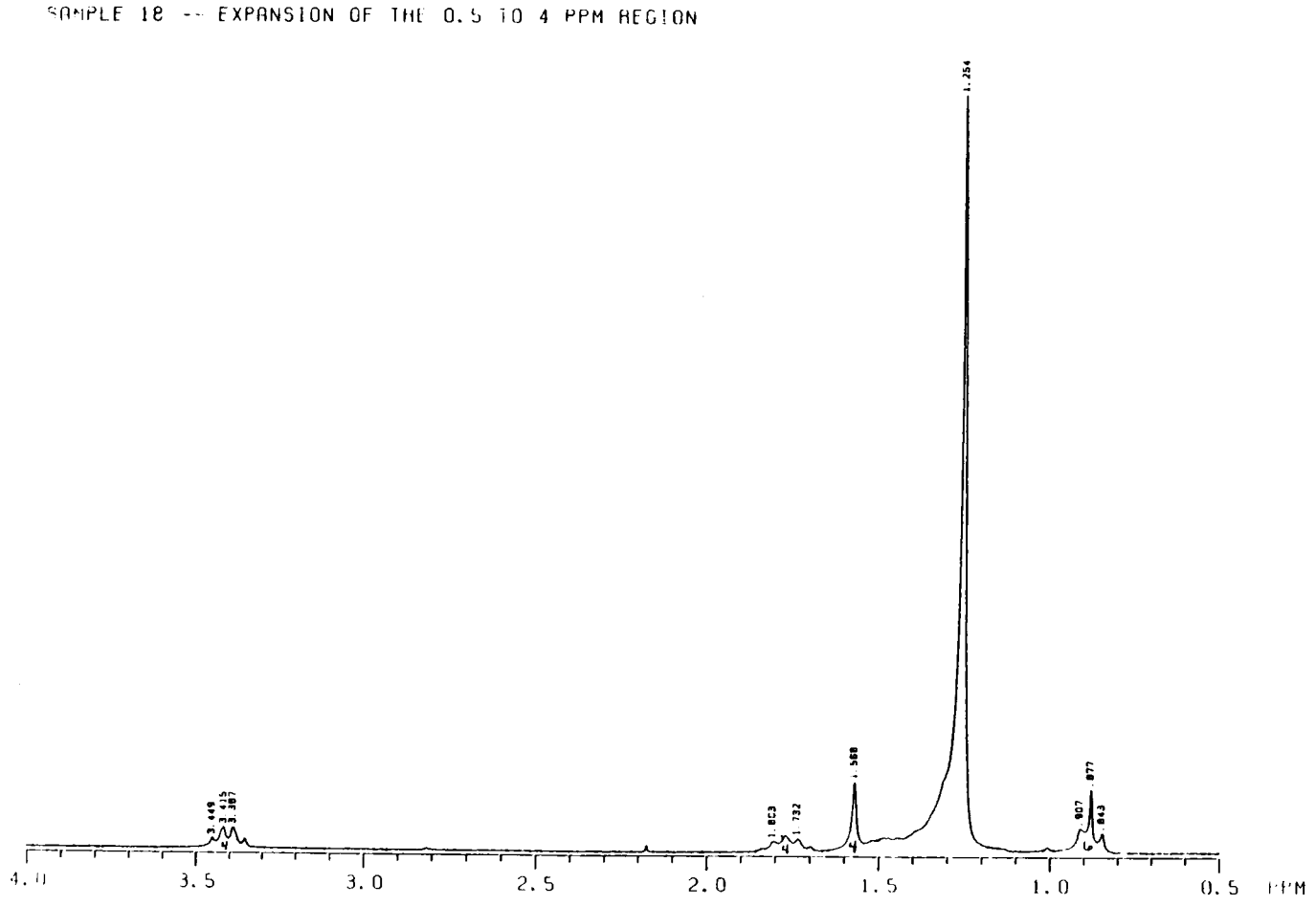


Figure B-4. **B:** Expansion of the 0.5 to 4 ppm region.

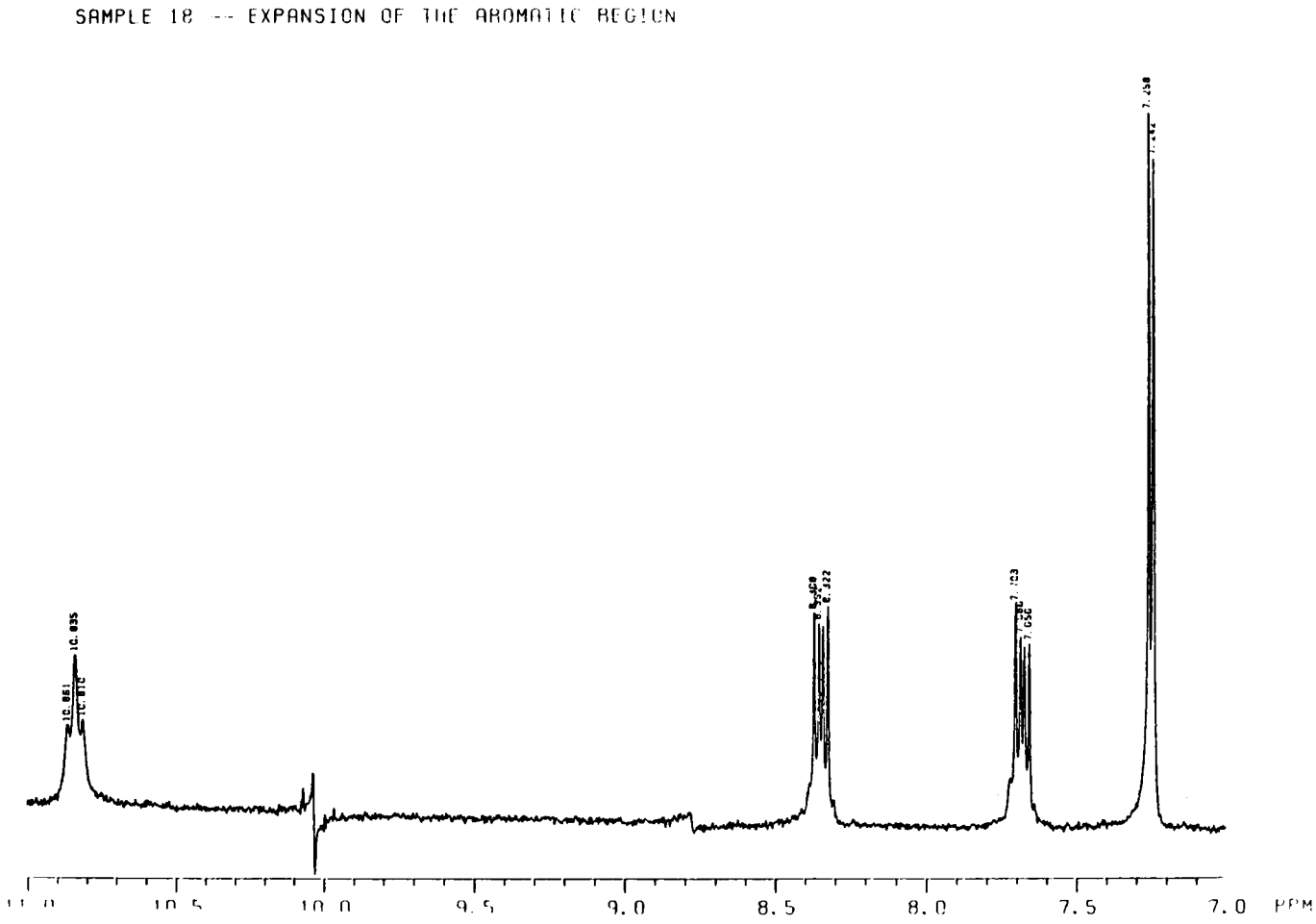


Figure B-4. C: Expansion of the aromatic region.

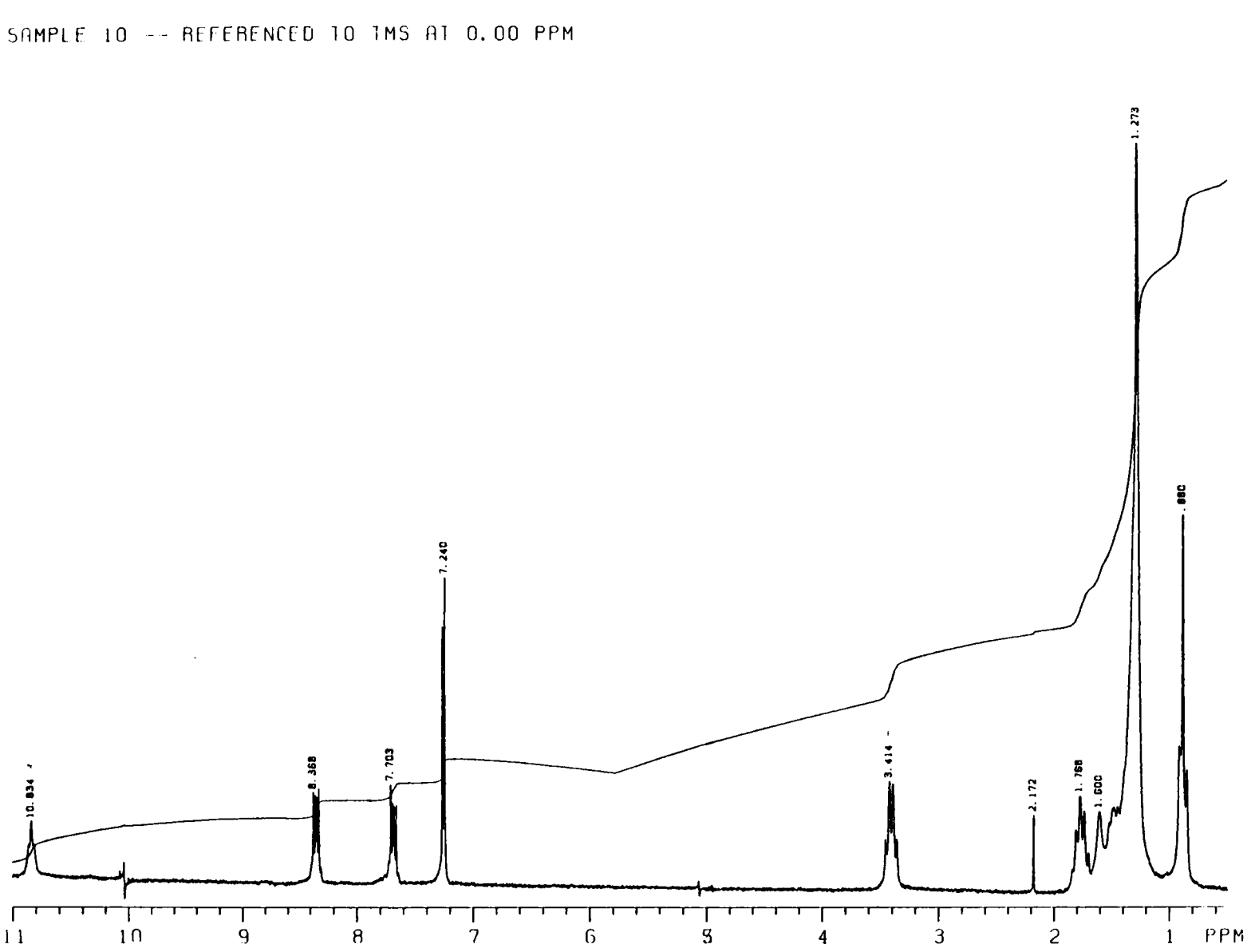


Figure B-5. Proton Nuclear Magnetic Resonance spectra for the C 10 dye.
A: Entire spectra.

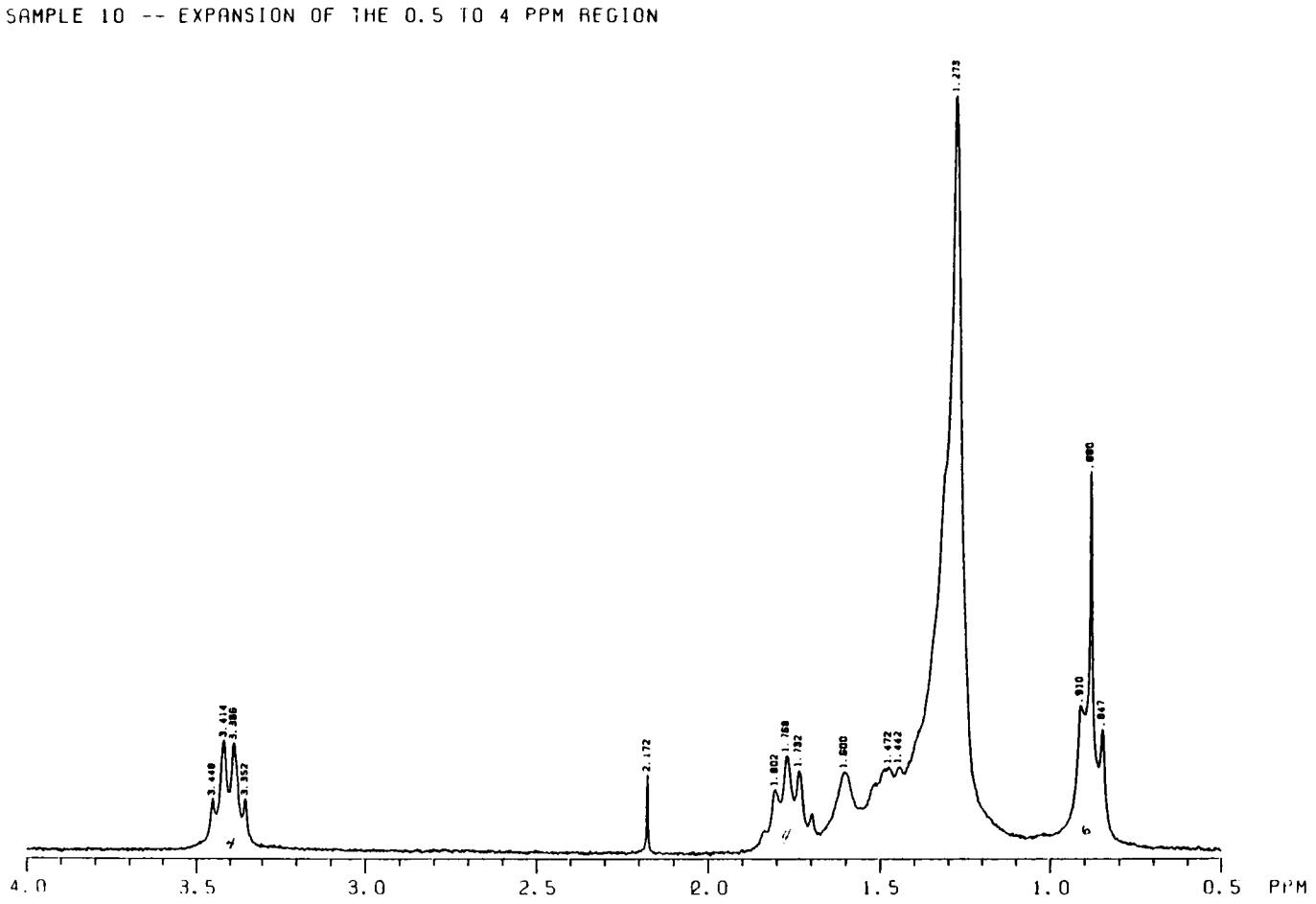


Figure B-5. **B**: Expansion of the 0.5 to 4 ppm region.

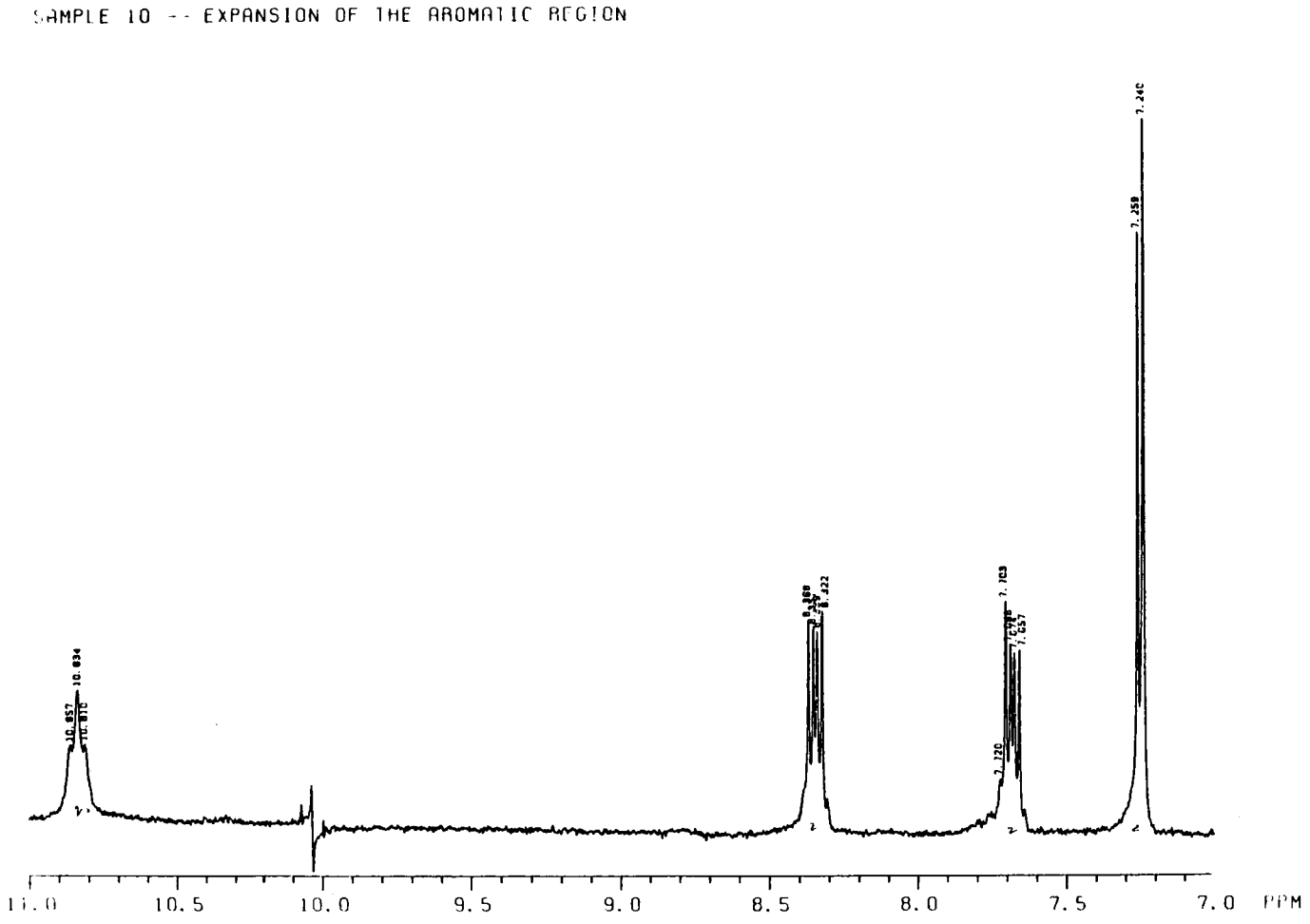


Figure B-5. C: Expansion of the aromatic region.

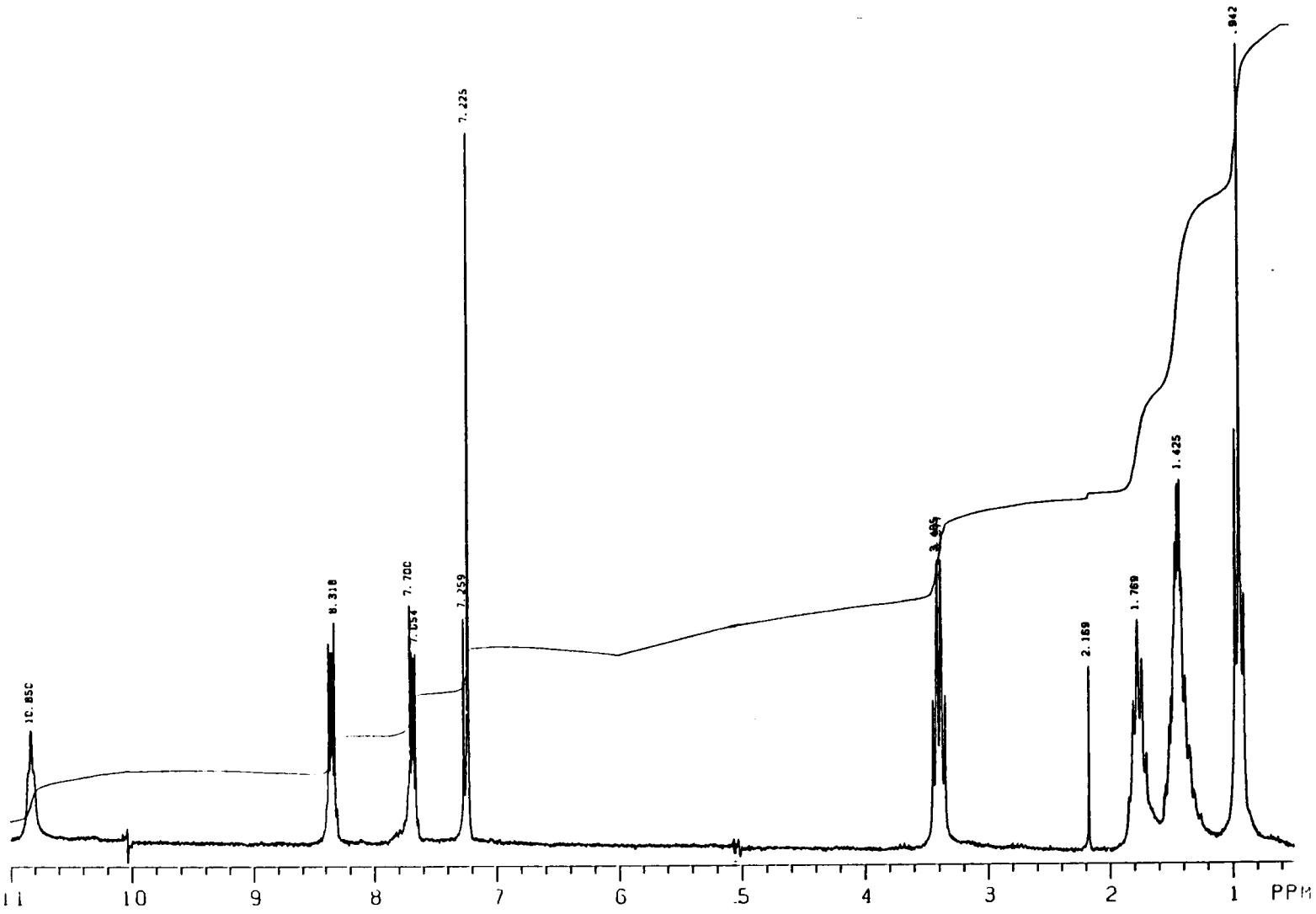


Figure B-6. Proton Nuclear Magnetic Resonance spectra for the C 5 dye.
A: Entire spectra.

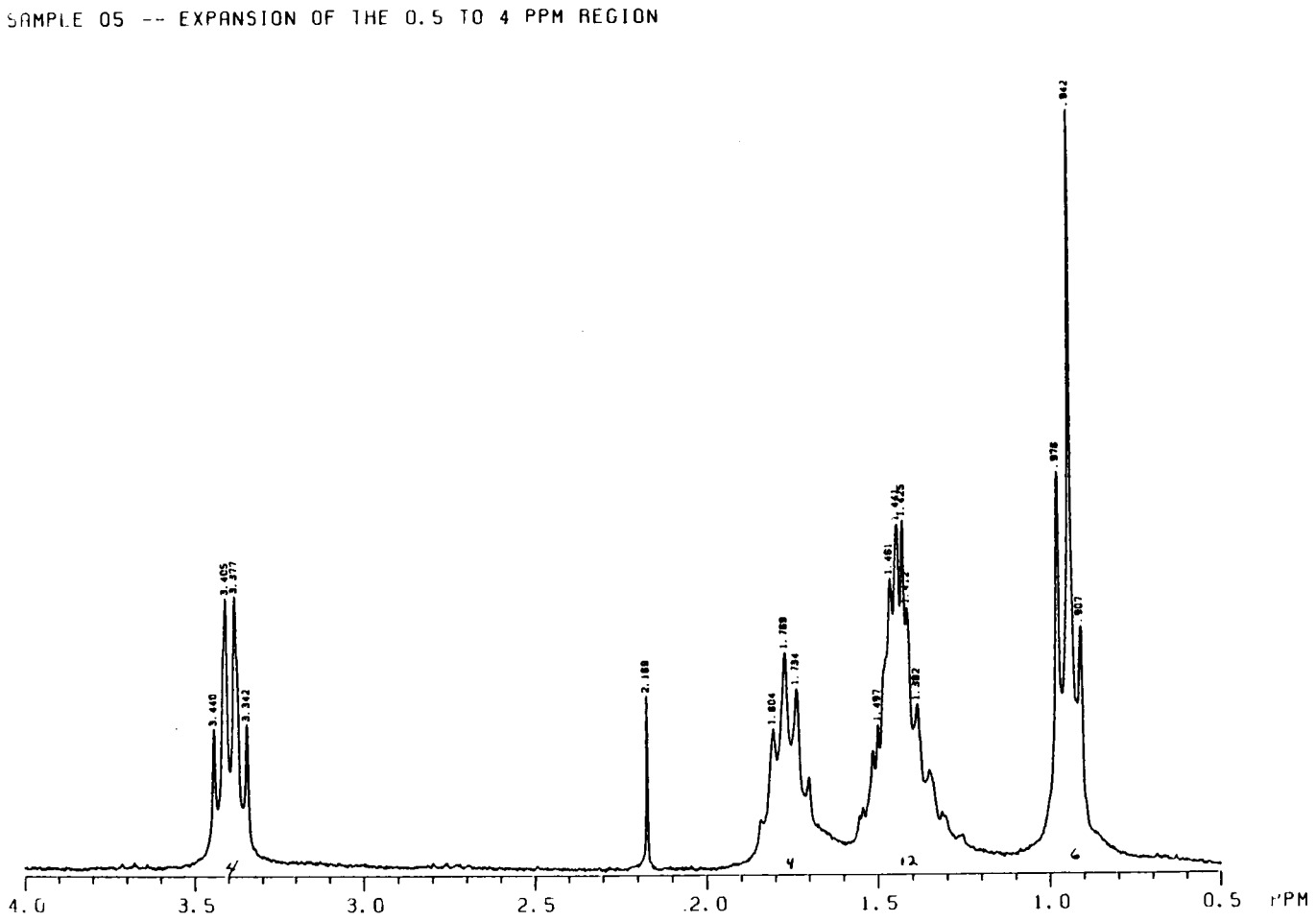


Figure B-6. **B**: Expansion of the 0.5 to 4 ppm region.

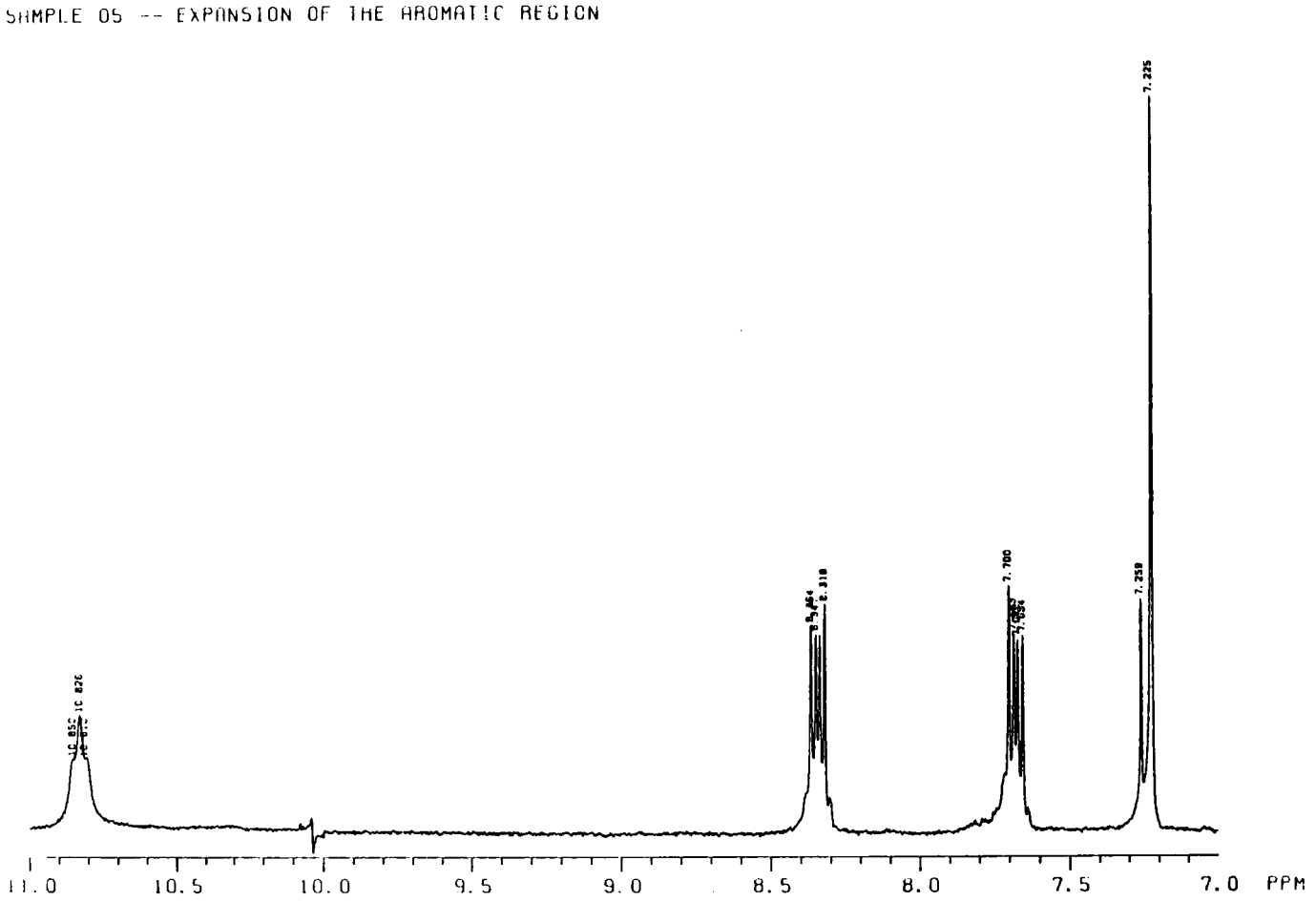


Figure B-6. C: Expansion of the aromatic region.

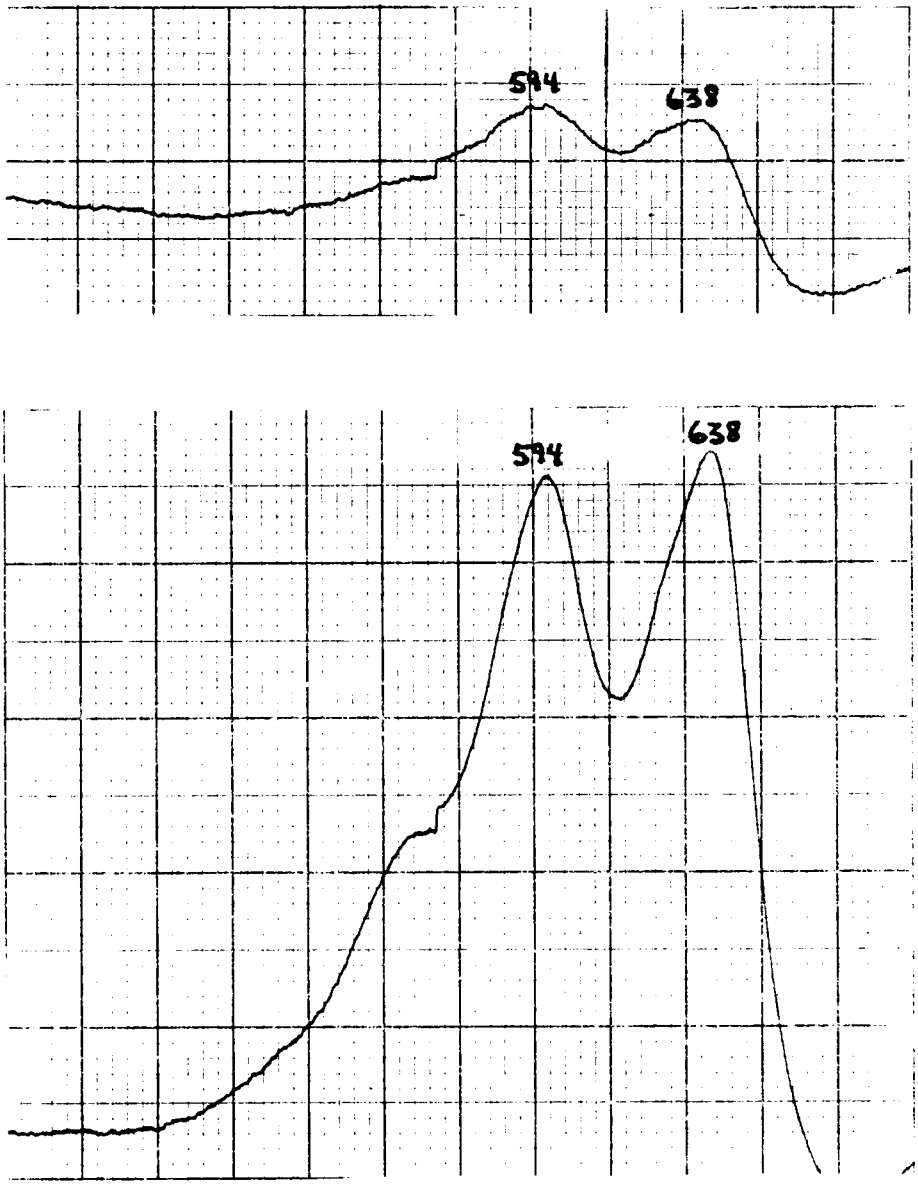


Figure B-7. UV-Vis spectra for the C 18 dye. Top tracing is the dye in ethyl acetate. Lower tracing is the dye in hexane. Range = 450nm to 700nm. Expansion = 20nm/second.

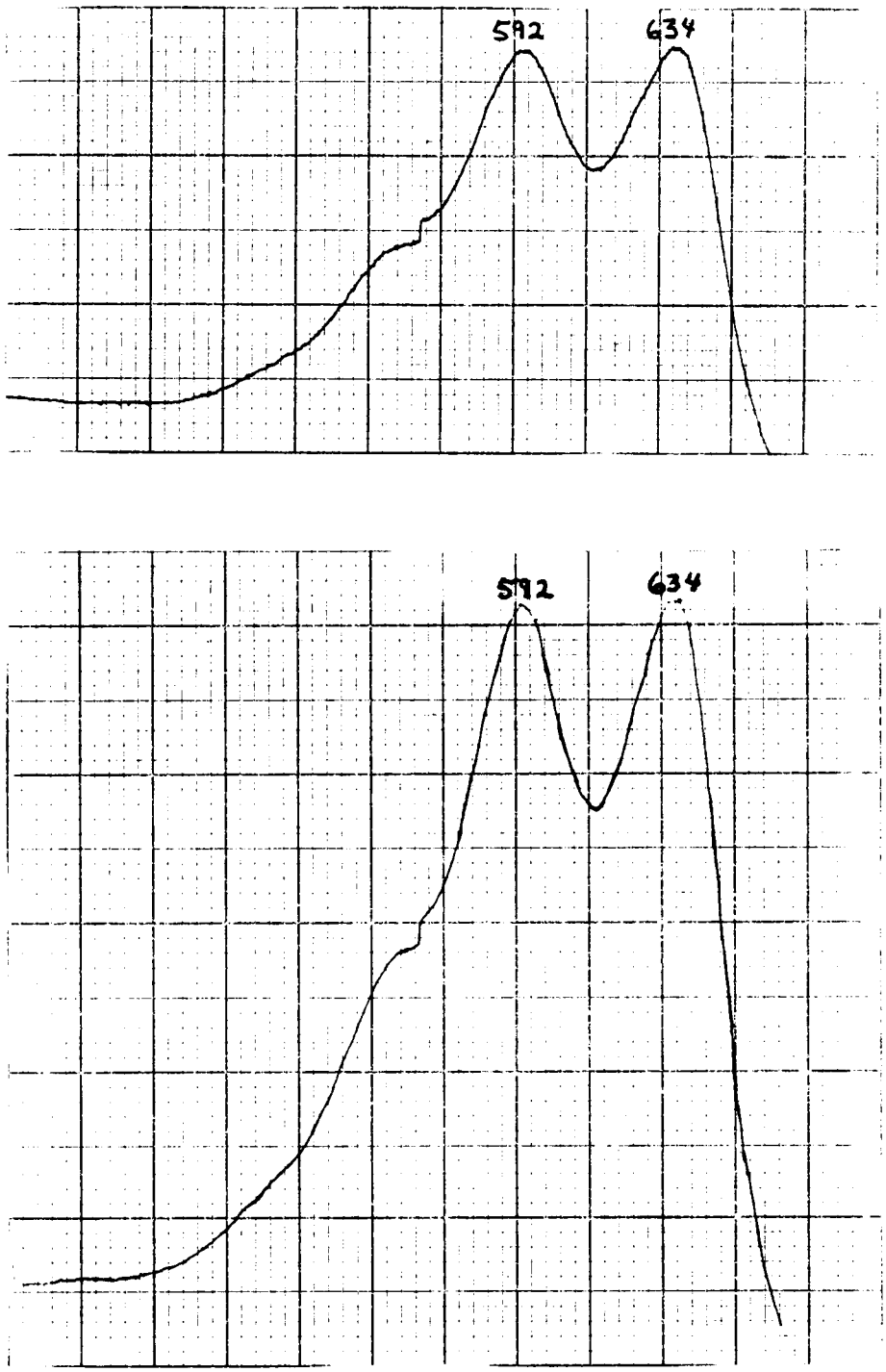


Figure B-8. UV-Vis spectra for the C 10 dye. Top tracing is the dye in ethyl acetate. Lower tracing is the dye in acetone. Range = 450nm to 700nm. Expansion = 20nm/second.

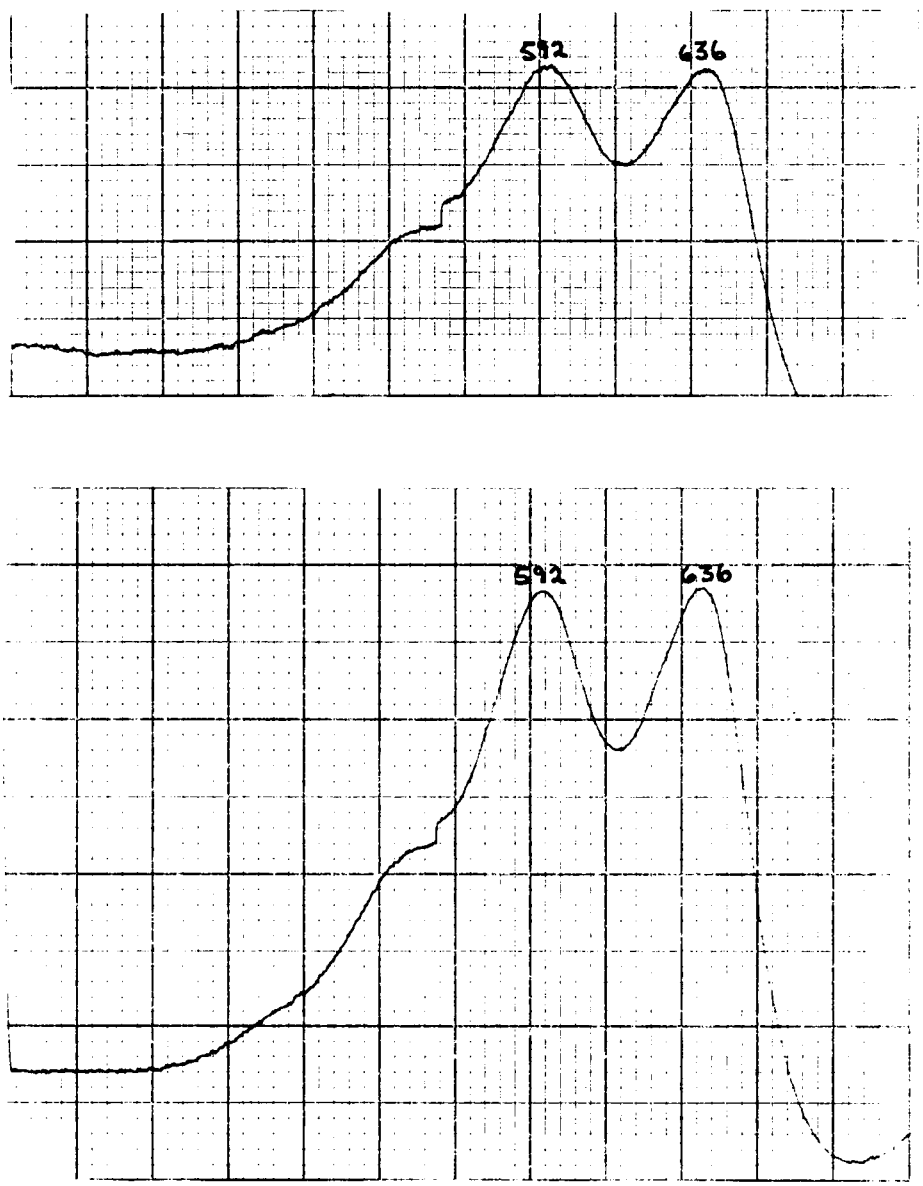


Figure B-9. UV-Vis spectra for the C 5 dye. Top tracing is the dye in ethyl acetate. Lower tracing is the dye in acetone. Range = 450nm to 700nm. Expansion = 20nm/second.

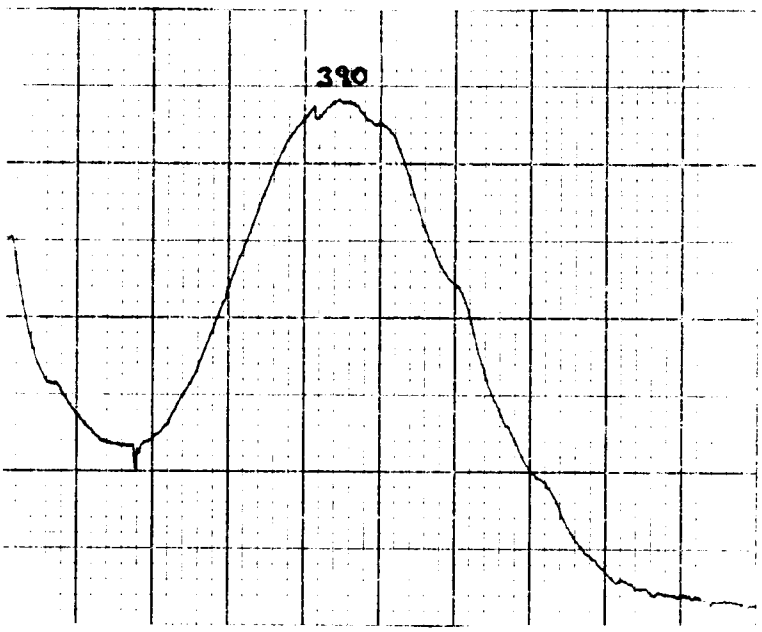


Figure B-10. UV-Vis spectra for the 1,8- dye in hexane. Range = 300nm to 500nm. Expansion = 20 nm/sec.

VITA

Susan J. Humberstone was born in Seattle, Washington. She was raised in Enumclaw, Washington, a rural community nestled at the base of the Cascade Mountains. She attended the Enumclaw Public Schools. As a senior in high school she was a Rotary International exchange student to Darmstadt, West Germany.

Soon after graduation from high school she enlisted in the United States Air Force and served a four year tour of duty as a medical corpsman. While in the Air Force she met and married Joe Mangan. They have two sons, Robert and Douglas.

Susan received an Associate Degree in Mid-Management from Crowder College, Neosho, Missouri in May of 1983. After working as a custom seamstress for two years, she returned to school. She received her Bachelor of Arts degree in General Home Economics in May,1987, from Louisiana Tech University in Ruston, Louisiana. In the fall of 1987 she accepted a teaching assistantship at The University of Tennessee, Knoxville, and began her graduate education. She received an MS in Textiles and Apparel in May, 1989.

Mrs. Mangan is a member of the American Association of Textile Chemists and Colorists, Phi Kappa Phi, and Omicron Nu.