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A STUDY OF THE EQUILIBRIUM SORPTION OF
ACID DYES ON MODIFIED POLYPROPYLENE FIBERS

A THESIS

Presented to

The Faculty of the Graduate Division

by

John Harry Underwood

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A STUDY OF THE EQUILIBRIUM SORPTION OF
ACID DYES ON MODIFIED POLYPROPYLENE FIBERS

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SUMMARY

The commercial production of isotactic polypropylene in textile fiber form provided the textile industry with a light, strong, and abrasive resistant fiber which could, and did, find many uses in carpets, household goods, and apparel fabrics. Unfortunately, the available classes of dyes -- acid, basic, disperse, premetallized, and others -- did little more than stain unmodified polypropylene fibers because of the chemical inertness and hydrophobic nature of the fiber.

Any synthetic fiber, to become a fiber of high fashion, should be easily dyeable, therefore efforts were made to modify the polypropylene to provide dyesites or lessen the hydrophobic nature in the fibers. One such modification was the incorporation of a poly(alkyl vinyl pyridine)-type copolymer in the polypropylene melt. This copolymer is cationogenic -- able to be protonated by acid treatment to form a cationic dyesite.

Fibers modified by the addition of a poly(alkyl vinyl pyridine)-type copolymer were dyed with a series of selected dyes which were purified by recrystallization of the commercial product. The effects of pH change, dye molecular size, ionic charge of the dye, and acid treatments to the fibers were determined by kinetic studies on the sorption of the dyes by the fibers. A dyeometer with continuous flow of dyebath through a spectrophotometer was used to follow the change in concentration, i.e., exhaustion, of the dyebath.

The commercially available fibers modified with a poly(alkyl

vinyl pyridine)-type copolymer are acid dyeable, either as the commercial product, e.g., U.S. Rubber's Polycrest SDR-2, or as the commercial fiber pretreated with an aqueous solution of concentrated acid, e.g., Hercules' Herculon H-2 and U.S. Rubber's Polycrest SDR-1.

CHAPTER I

INTRODUCTION

Commercial Polypropylene Fiber

The discovery of stereospecific polymerization techniques twelve years ago provided new methods for the preparation of crystalline polymers from simple olefins. These polymers were first investigated for use as plastics and films, but further research proved them to be suitable for conversion into textile fibers. These fibers were designated as olefin or polyolefin fibers and were defined by the Federal Trade Commission Rules as: a manufactured fiber in which the fiber-forming substance is any long chain synthetic polymer composed of at least 85% by weight of ethylene, propylene, of other olefin units.

Polypropylene fibers, isotactic polypropylene derived from propylene (Figure 1.), are classified as polyolefins. Polypropylene fibers combine light weight with high strength and good abrasion resistance, but they soften at relatively low temperatures. They are hydrophobic and chemically non-reactive, and, when properly inhibited, have good resistance to sunlight. Because of the low cost of the propylene monomer, these fibers are relatively inexpensive.

Polypropylene fibers have been used where strength, abrasion resistance, and chemical inertness were important, e.g., industrial filters, ropes, and tarpaulins. With the advent of a suitable coloring technique these fibers will also find other uses in carpets, drapery material, and apparel goods.

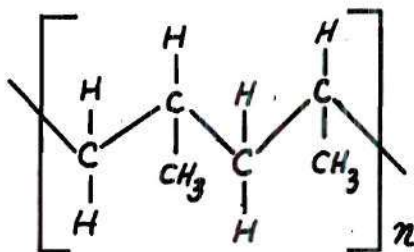


Figure 1. Isotactic Propylene

Statement of Problems

Melting Point

Compared to other synthetic textile fibers such as nylons, polyesters, and acrylics, crystalline polypropylene has a relatively low melting point of 176°C. This is an inherent property which is impossible to correct without drastically altering the basic structure and properties of the polymer. The public has become accustomed to the extra care required for synthetic textile fibers in both apparel and household uses, and thus the low melting point should not be a severe problem even in ironing and machine drying, when extreme care must be used. Commercial processes which dictate prolonged heating operations such as crease resistance finishing and thermosetting could further complicate the problem because of the fiber's low melting point.

Degradation by Sunlight

Polypropylene, as with many other polymer chains, is susceptible to degradation of the polymer chains by ultraviolet radiation from sunlight, etc., by cleavage of the polymer chain at the tertiary hydrogen. This problem has been practically solved by the addition of certain compounds to the polymer melt before extrusion. These compounds are either screening type stabilizers, or reactive type stabilizers (1). Many of

the reactive type stabilizers are organometallic coordination compounds.

The Problem of Dyeability

In order for a synthetic fiber to be acceptable for large volume use in textile applications, such as apparel and household uses, there must be a method for imparting an extremely large range of colors with reasonable ease and expense. There has been much research done in an attempt to dye knitted and woven fabrics and yarns made of polypropylene (2,3).

These attempts to devise a method of dyeing polypropylene have been hindered by the physical and chemical nature of the fiber. Because of the compact nature of the highly crystalline isotactic polypropylene, the diffusion of dyes and dyeing assistants into the fiber occurs slowly, if at all. The non-polar nature of polypropylene does not provide dyesites as are found in natural, man-made, and many synthetic fibers, thus ionic dyes are not deemed usable unless the polypropylene fiber is modified to provide ionic dyesites for these dyes. Also the hydrophobic nature of the polymer makes sorption of hydrophilic dyes extremely difficult.

Most coloring of commercially available polypropylene is done by adding pigments to the polymer before melt-spinning. This method has disadvantages in complicating production in the sense that new production problems are created, finding pigments which are stable at the melt-temperature, and requiring the keeping of an inventory of fibers in multiple colors. This method of coloring also requires the coloring to be imparted by the fiber producer, thus adding expense to the manufacture of customer goods and necessitating color-matching at the fiber

producer's plant. The light, wash, and dry cleaning fastness of pigment colors is outstanding, and thus the manufacturers of many products which require extreme fastness properties, e.g., outdoor carpets, and awnings, find this method of attainment of color very desirable even with the added expense and inconvenience.

There are two general methods in commercial use for modifying polypropylene fibers to give satisfactory coloring and color stability; both methods are being used in small-volume production. One method is the addition of small amounts of metal or organometallic compounds to the polymer melt; these compounds being selected on the basis of their ability to form chelates or coordination complexes with polar organic compounds. Aluminum, chromium, nickel, and zinc are some of the metals which are effective. By using selected disperse dyes containing functional groups which will coordinate with the metal, colors can be obtained with excellent permanence properties (4). The commercialization of this method has been dependent upon the development of new dyes to provide a full range of colors. Such a range is now available from some commercial sources, e.g., National Aniline Division, Allied Chemical Corporation, and polypropylene fibers modified to provide dyeability in this manner are being produced commercially or in developmental quantities by several companies in this country and Japan, e.g., Hercules Powder Corporation.

The other method for modifying polypropylene to make the fibers dyeable is the dispersion of a small amount of another polymer in the polypropylene before melt spinning. The selection of the alloying polymer is based on its ability to adsorb sufficient dye to color the fibers

containing the polymer mixture. Several such copolymers have been developed, and these are divided into two classes: cationic, and anionic. The cationic compounds are typically polyamides, long-chain alkylamines, and nitrogen containing heterocyclic compounds all of which are cationogenic thus dyeable with acid dyes, although some of these compositions require a chemical treatment of the fibers after spinning to form the cationic dyesite. This type of copolymer affords dyeability with anionic dyes of the acid dye class thus giving a very broad and previously tested selection of dyes. Anionic copolymers are typically poly-basic acids, alkyl-benzene sulfonates, and acid anhydrides all of which give dyeability with cationic or basic dyes.

Purpose of the Research

There are several companies in the U.S. which produce polypropylene fibers modified with a cationic copolymer of the poly(alkyl vinyl pyridine)-type. (See Figure 2.) Fibers modified in this way are commercially available as disperse dyeable fibers from Hercules Powder Corporation or U.S. Rubber Company and, acid dyeable fibers from U.S. Rubber Company. The acid dyeable fiber is chemically treated after melt spinning to produce the cationic dyesites. The purpose of this research is to investigate some of the dyeing properties of fibers modified by the use of this copolymer, and to determine the effect of acid treatment of the disperse dyeable fibers on the sorption of acid dyes by these fibers. Also the dyeability of the polypropylene fibers will be compared to such standard fibers as normal and deep-dyeing nylon, and the fastness of the dyes on the different polypropylene fibers will be evaluated.

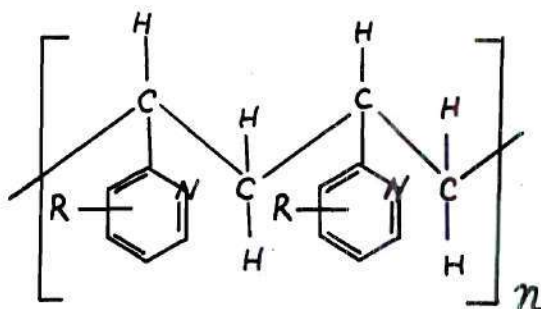


Figure 2. Poly(Alkyl Vinyl Pyridine) Copolymer Used in Polypropylene

Organization and Approach

In order to evaluate the dyeability of any one fiber, certain standard parameters must be determined for each fiber to be studied, and then optimum conditions can be set under which each fiber will perform best. The parameters of initial dye concentration in dyebath, pH and ionic strength of dyebath buffer, and temperature and temperature control of the dyeing operation will be determined for each fiber resulting in data which should determine the proper conditions under which each fiber should be evaluated for dyeability.

After the standard conditions have been set, then the effects of pretreatments, various anionic charges of dye molecules, molecular weight and size of dye molecules, and aftertreatments of dyed fibers can be accurately investigated, evaluated, and rated.

Literature Survey

The subject of polypropylene fibers modified to improve dyeability has been covered very extensively in patents (5,6,7), but very little has appeared in technical publications on this subject.

Ivett (8) gives a summary of the methods of modifying polypropylene to produce dyeability. Farber (9,10) states that not only the lack

of dye receptors, but also the lack of permeability to dyes is responsible for the lack of dyeability of polypropylene. This concept is shown by the grafting of vinylpyridine to a polypropylene fiber making the fiber highly dyeable with acid dyes. When this fiber was melted and spun into fiber form again, it was no longer dyeable. This leads to the theory of "pathways" to dyesite. The remelting of the fiber closed the pathways, thus destroying permeability and dyeability. The formation of these "pathways" is done by incorporating in the polypropylene melt a basic polymer dye receptor and then giving the fiber a treatment after spinning (11). U.S. Rubber produces two fibers through this method, both of which are dyeable -- one with disperse dyes, (SDR-1), and one with acid dyes, (SDR-2). Another fiber, designated PPX, has been reported to show good dyeability with disperse, premetalized, and naphthol dyes; dyeings being considered potentially adequate for most civilian and military textile applications with good fastness properties (12).

Numerous extensive reviews of the "state of the art" have highlighted the need for further substantial improvements in dyeability if dyed polypropylene fiber products are to measure up to the performance and appearance level of competitive products (13,14,15,16,17,18,19,20, 21).

CHAPTER II

APPARATUS AND SPECIMENS

Fiber Specimens

Commercial Fibers

Samples of commercial polypropylene fibers utilizing the cationic (or cationogenic) copolymer were obtained from two United States companies. These fibers were: Type 60 Herculon (H-2), a disperse dyeable fiber manufactured by Hercules Powder Corporation (3900/210, 18.6 d.p.f.); Polycrest SDR-1, a disperse dyeable fiber manufactured by U.S. Rubber Company (4000/156, 25.6 d.p.f.); and Polycrest SDR-2, an acid dyeable fiber manufactured by U.S. Rubber Company (4000/156, 25.6 d.p.f.). These fibers were in filament form. The nylon fibers used in the Praxitest dyeings were supplied by E.I. duPont de Nemours and are: 845 - low dyeing nylon, 846 - normal dyeing nylon, and 847 - deep dyeing nylon. These fibers were all 1300 total denier, 68 filament, 26.5 denier per filament (1300/68, 26.5 d.p.f.) yarns.

Experimental Fibers

Two experimental fibers were prepared by use of a treating method described in (22). The Hercules H-2 fiber and the SDR-1 fiber were both treated by immersion in conc. HCl (38%) for two min. at 49°C. The treated Hercules fiber was given the designation BB-1, and the treated SDR-1 fiber was designated as BB-2. The fibers were acid treated to increase the acid dyeability by protonating the poly (alkyl vinyl pyridine)-type copolymer (Figure 3.) present in small amounts in each fiber.

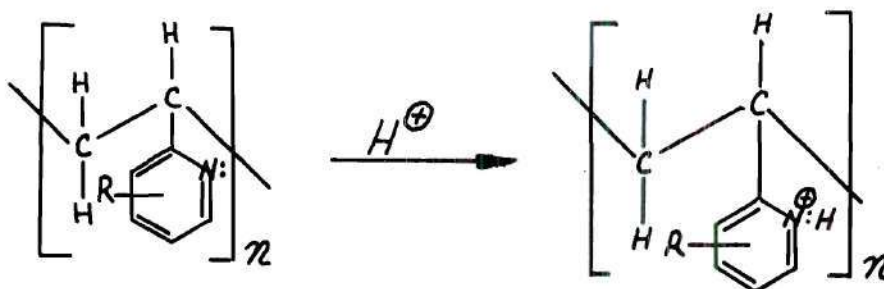


Figure 3. Protonation of Poly(Alkyl Vinyl Pyridine)
By Strong Acid Treatment

Dye Specimens

Acid Dyes

Dyes of the anionic or acid class which are structurally similar, yet quite dissimilar in dyeing properties were chosen for use in this work. The dyes shown in Figure 4 were selected and obtained from commercial sources.

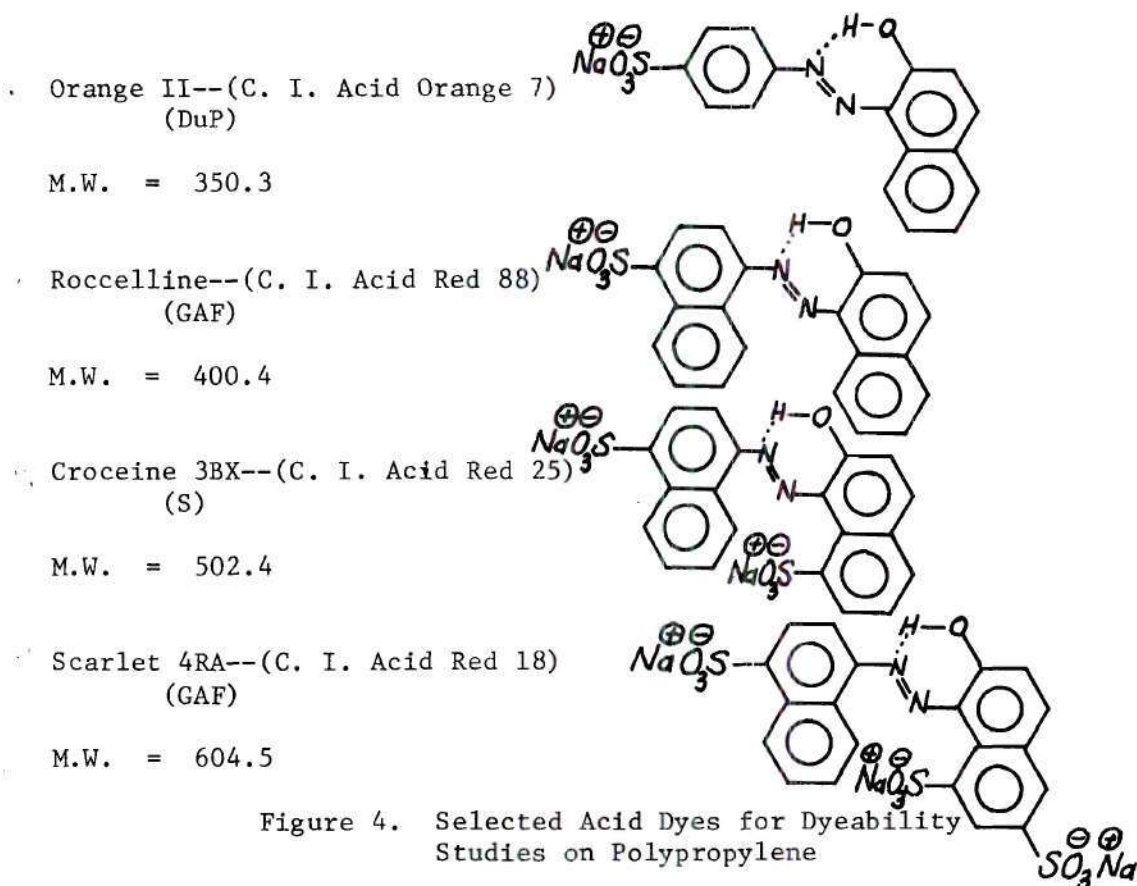


Figure 4. Selected Acid Dyes for Dyeability
Studies on Polypropylene

These four dyes have very similar molecular structure, and they cover the range of acid dyeing behavior, leveling to milling. These dyes are also representative of the three charge types common to acid dyes: D^{1-} , D^{2-} , and D^{3-} . The variation in molecular weight without drastic alteration of the molecular structure (see Figure 4) will allow the study of such fiber structural features as permeability, internal volume, and placement of dyesites.

The commercial forms of the chosen acid dyes were purified by means of recrystallization from saturated aqueous solutions until chromatographic and optical measurements methods showed no colored and/or uncolored impurities. The impurities in commercial dyes are colored isomers and/or unreacted intermediates and/or diluents such as common salt. The degree of efficiency of the purification process was checked by use of thin layer chromatography to separately show the colored isomers having different R_f values. UV studies of these chromatography plates also showed the degree of removal of inorganic uncolored materials. Visible spectrophotometry was used to check the purity of each of the purification steps, i.e., recrystallizations.

Premetallized Acid and Neutral Dyes

Examples of an acid premetallized and a neutral premetallized dye were selected for further study of the fibers, and for comparison of the dyeability of polypropylene fibers with that of nylon fibers having various degrees of dyeability. These dyes were: Chromacyl Blue GG, an acid dyeing premetallized (1:1) dye from DuPont; and Irgalan Grey BL, a neutral dyeing premetallized (2:1) dye from Geigy. These dyes were not purified, but used in the commercial form supplied by the makers.

Dyeing Apparatus

All dyeings with the purified acid dyes were conducted in a glass vessel slightly modified from the dyeometer described in (23). Figures 5, 6, and 7 show the main features and dimensions of the apparatus.

The dyeing apparatus was an all glass instrument with standard taper ground glass joints (e.g., 24/40), as shown in Figures 5, 6, and 7. The head of the dyeometer, Figure 6, fits onto the bottom of the body of the dyeometer, Figure 5, at the 29/42 standard taper joint. The top to the dyeometer is attached at the 55/50 standard taper joint. This top lifts out and the sample holder, Figure 7, is lowered down into the body of the dyeometer. The 18/7 standard taper ball joint on the sample holder fits into the corresponding sized socket joint on the head of the dyeometer. The top of the dyeometer is then replaced, a stirring rod sleeve with a 35/25 ~~3~~ ball joint is fitted into the top of the dyeometer, passing the solid rod of the sample holder through, and a constant speed stirrer motor is attached to the solid glass rod end of the sample holder by means of a length of plastic tubing.

The solution, e.g., dyebath, is continuously pumped through the dyeometer and the measuring device (to be discussed later) by a veristaltic pump. As shown in Figure 7, the dyebath is drawn through the head of the dyeometer, past the bulb of the thermometer, and exits to the constant flow cell of the measuring device by the lower tube (Figure 6). The pump then returns the solution through the upper tube of the head of the dyeometer. The sample holder (Figure 7) is made of a hollow tube attached to a solid rod, and the hollow tube extends through the sample

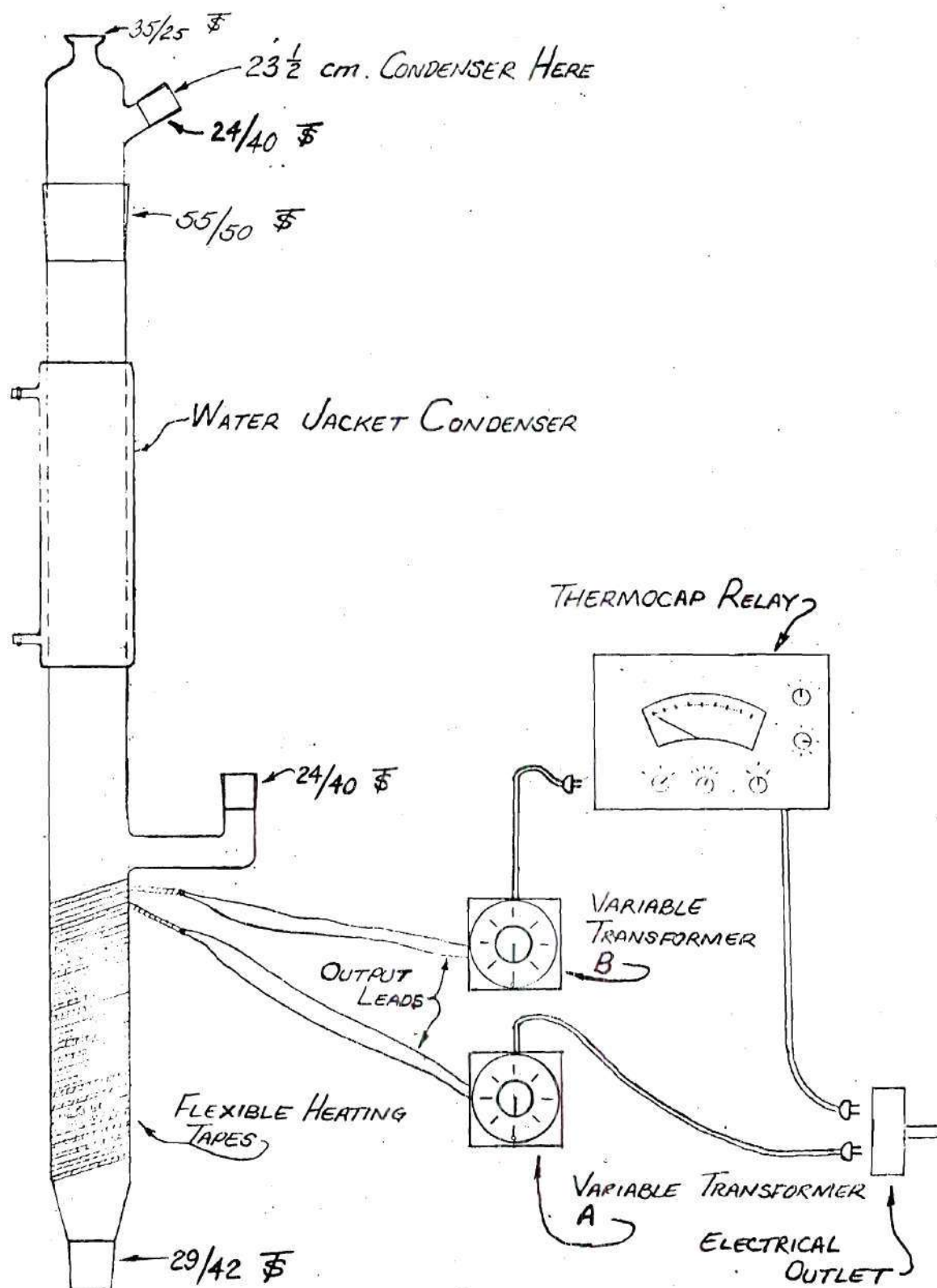


Figure 5. Body of the Dyeometer (1 in. = 10 cm.)

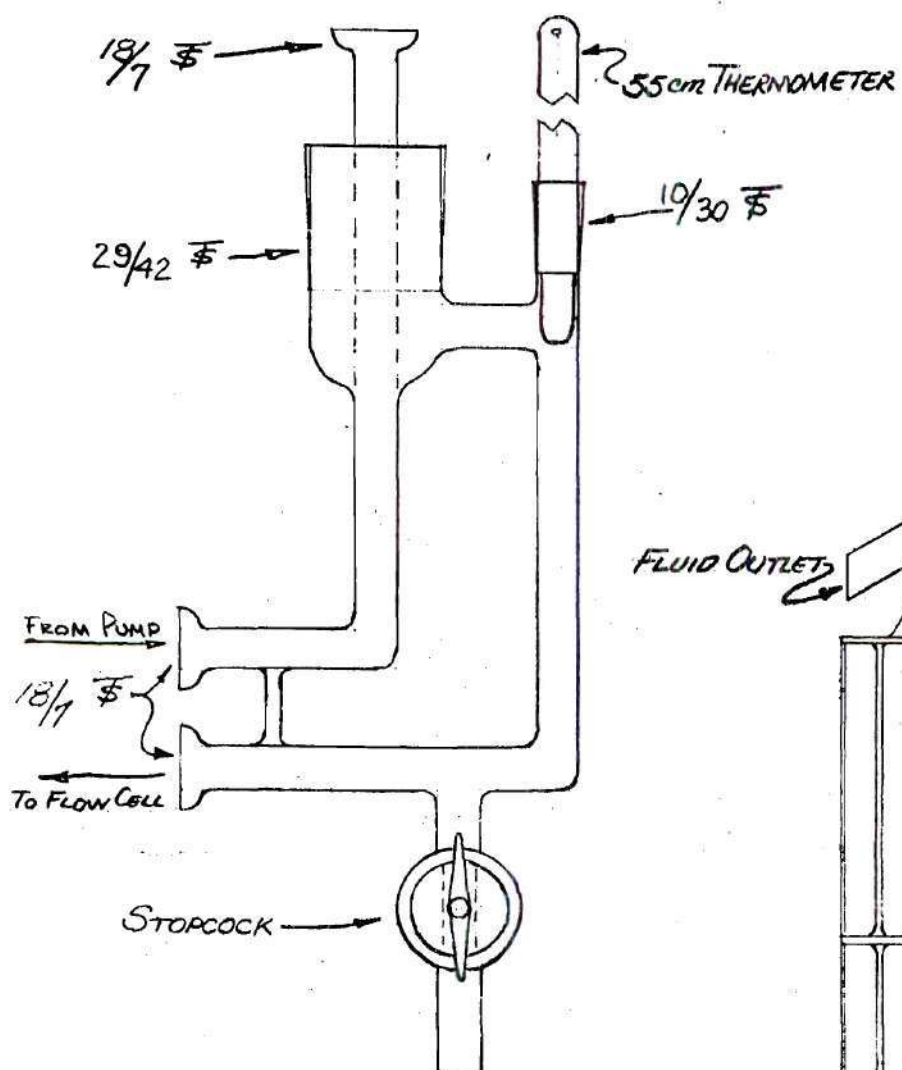


Figure 6. Head of the Dyeometer
(1 in. = 5 cm.)

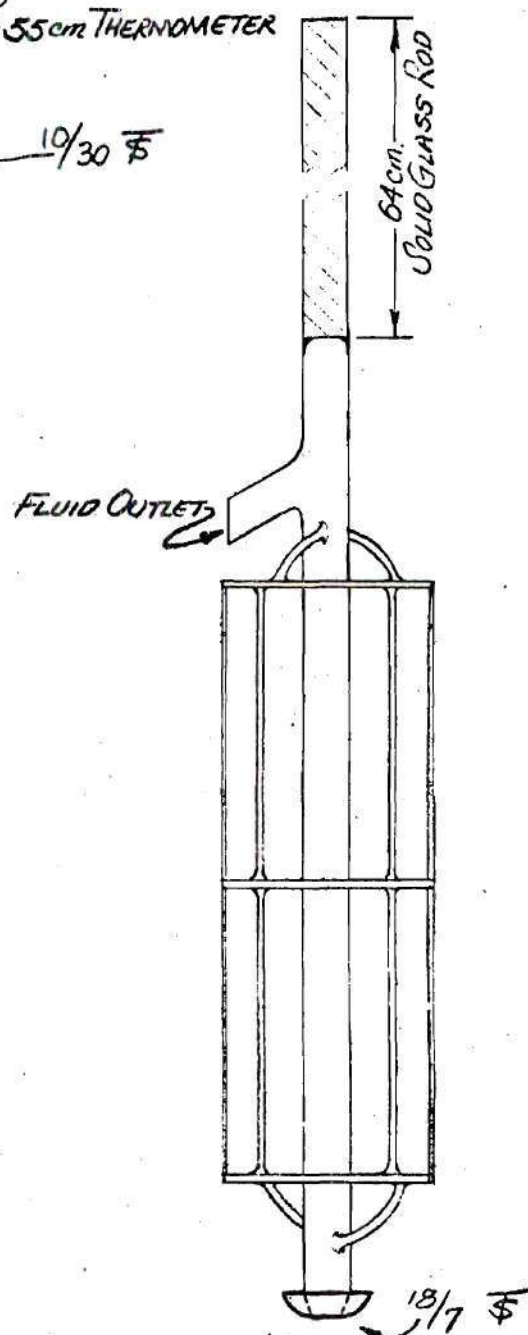


Figure 7. Dyeometer Sample Holder
(1 in. = 5 cm.)

carriage with an outlet approximately one centimeter above the carriage. The returning solution is pumped through this hollow tube and flows out the output above the sample being dyed. In this way there is a constant thorough circulation of the dyebath around the sample.

The dyeometer is filled with desired solutions through an eight cm. right angle arm with 24/40 fitting. The dyeometer, when filled to the level of this arm, will hold approximately 600 ml. At this level the sample holder is immersed far enough to cover the outlet, and thus the sample is totally immersed in the dyebath. Filling of the dyeometer above this level will not give even heating and circulation of the dyebath, and the ease of adding additional reagents to the bath, after the dyeing has begun, is severely hampered.

The heating of the dyebath is accomplished by two systems of flexible heating tapes. The first system is controlled by variable transformer A, see Figure 5. This system is continuously in operation, and is set to keep the temperature of the bath at approximately 94°C. The second system of heating tapes is used to regulate the temperature to $95^{\circ}\text{C} \pm .2^{\circ}$. The regulation is accomplished by plugging the variable transformer B, which controls the second system of tapes, into a Thermocap^R relay. The detecting lead of the relay is attached to the thermometer from the head of the dyeometer (Figure 6) at the 95° level. The transformer B is powered through the relay until the temperature of the bath is indicated by raising the column of mercury in the thermometer to be 95°C at which time the lead of the relay detects the column of mercury, i.e., temperature, and interrupts current flow to the transformer B. When the mercury falls below 95°C, the relay opens, and the second

set of tapes begins heating again. This allows a regulation of temperature of $95^{\circ}\text{C} \pm .2^{\circ}$ when a 55cm, -1 to 101°C , $1/10^{\circ}$ divisions, thermometer is used. All surfaces of the dyeometer which contain the bath are wound with asbestos rope to reduce heat losses.

After dyeing, the sample rod is removed and the bath is drained through the stopcock on the head of the dyeometer (Figure 6).

Measuring Apparatus

Beckman DU Spectrophotometer

Sufficiently dilute solutions which absorb electromagnetic radiation in the visible range of 400 to 700 m μ obey the Lambert-Beer Law which states that the absorbance of the solution is directly proportional to the pathlength of the light through the solution and the concentration of the solution. In equation form:

$$A = a \cdot b \cdot c \quad (1)$$

Where: A = absorbance

a = extinction coefficient (the proportionality constant)

b = pathlength of solution

c = concentration of solution.

From Equation (1) one may readily determine the concentration (c) of a solution, e.g., dyebath, when A is determined by use of a spectrophotometer a is calculated for the dye by use of a solution of known concentration at the wavelength being used, and b is measured or known. A Beckman DU Spectrophotometer was used to determine A for the dyebaths used, thus the exhaustion of the dyebath in the dyeometer was easily calculated.

Continuous Flow Cell

In order to determine the adsorbance of the dyebath using the dyeometer previously described, one of two methods of sampling the solution must be chosen. The first method involves the removal of a small portion of the dyebath through the stopcock, and then filling a sample cell with this portion of the bath and determining the absorbance with a spectrophotometer. This method is undesirable for several reasons, the main ones being that there is a large temperature difference between measured sample and running dyebath, and there is a small decrease in the amount of dye available in the system for sorption by the fiber specimen each time a sample is taken. Although the removal of a portion of the dyebath does not in itself change the absorbance of the solution, as is intuitively obvious, it may have an effect upon the equilibrium between dye in solution and dye on fiber by removing dye through an outside operation, i.e., not through sorption by the fiber specimen being studied. Other factors such as liquor ratio, heating constancy, and circulation of bath are adversely affected by this method.

The other method is to incorporate into the dyeing-measuring apparatus a system of tubes which will transfer the bath from the dyeometer through the tubes to a sample cell in the spectrophotometer and then back into the dyeometer. In this way the absorbance of the solution can be continuously monitored without the removal of any portion of the bath, therefore the amount of dye in the dyeometer is not decreased by removals from outside operations, and the temperature of the measured sample is equal to the dyeing temperature. This method required the designing of a modified sample cell to accommodate the flow of the dyebath.

Figure 8 shows the flow cell as designed by Ulrich Meyer while at the Georgia Institute of Technology.* Figure 9 shows the flow block which is attached to the cell compartment of the Beckman DU Spectrophotometer. This flow block is necessary to minimize the vibration of the flow cell when the bath is circulating through it. Figure 10 shows one possible configuration of the continuous flow apparatus mounted in the cell compartment of a Beckman DU Spectrophotometer.

The dyebath is pumped from the dyeometer through a plastic tube which is attached to the bottom 18/7 standard taper socket by a ball joint fitting of corresponding size, (See Figure 6). This tube is in turn attached to the flow block by a glass tube with two female 14/20 standard taper fittings. The flow cell is connected to the flow block by a length of plastic tubing with proper 14/20 standard taper joints. The continuous flow apparatus must be set up so that the dyebath enters the flow cell through the lower glass tube attached to the square cell (see Figure 8). This is necessary to eliminate the formation of bubbles in the sample cell. From the upper glass tube attached to the circular extension of the sample cell, (see Figure 8) a length of plastic tubing is attached to the other glass tube in the flow block by proper 14/20 standard taper joints. From this tube a plastic tube is attached by means of another glass tube with two female 14/20 standard taper fittings. Then the plastic tube runs through a veristaltic pump, and is connected to the dyeometer by a 18/7 ball joint into the upper socket joint of the same size on the head of the dyeometer. (See Figure 6). The two

*Presently with Stoffel A.G., Mels, Switzerland.

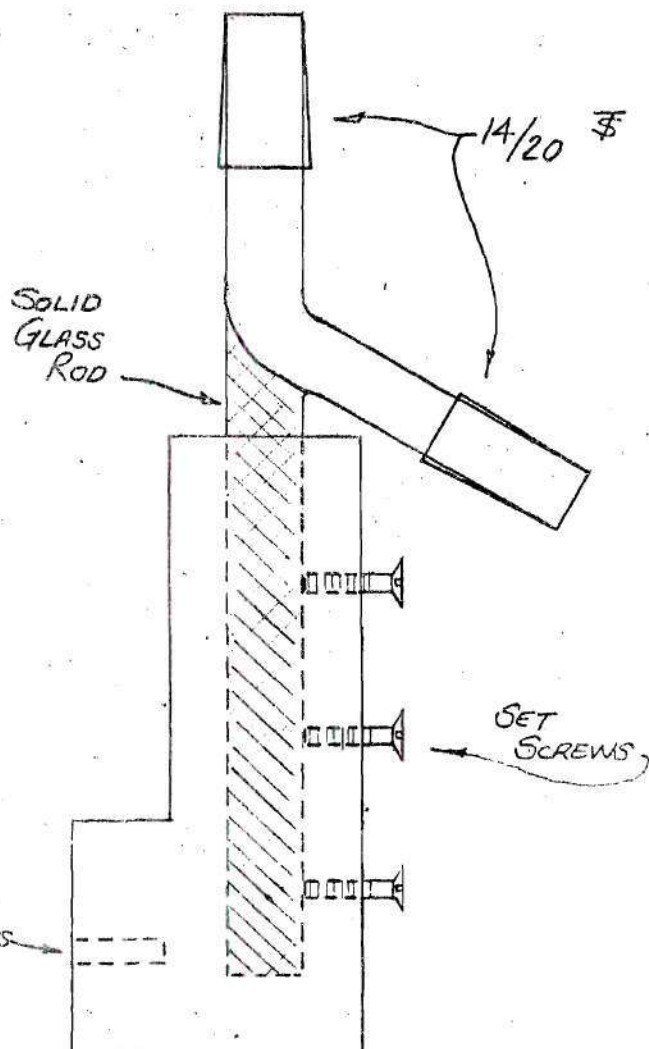
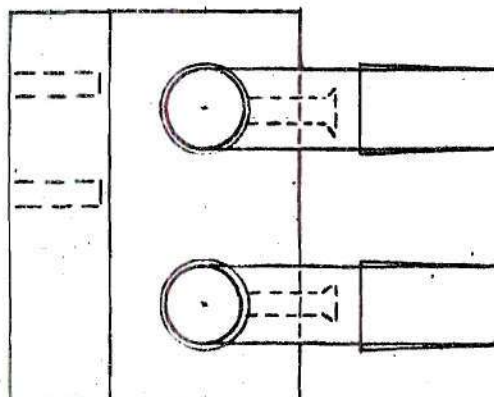
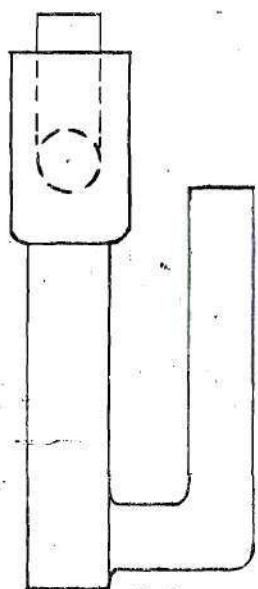
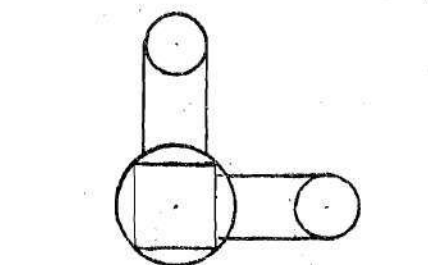


Figure 8. Flow Cell (4 in. = 10 cm.) Figure 9. Flow Block (4 in. = 10 cm.)

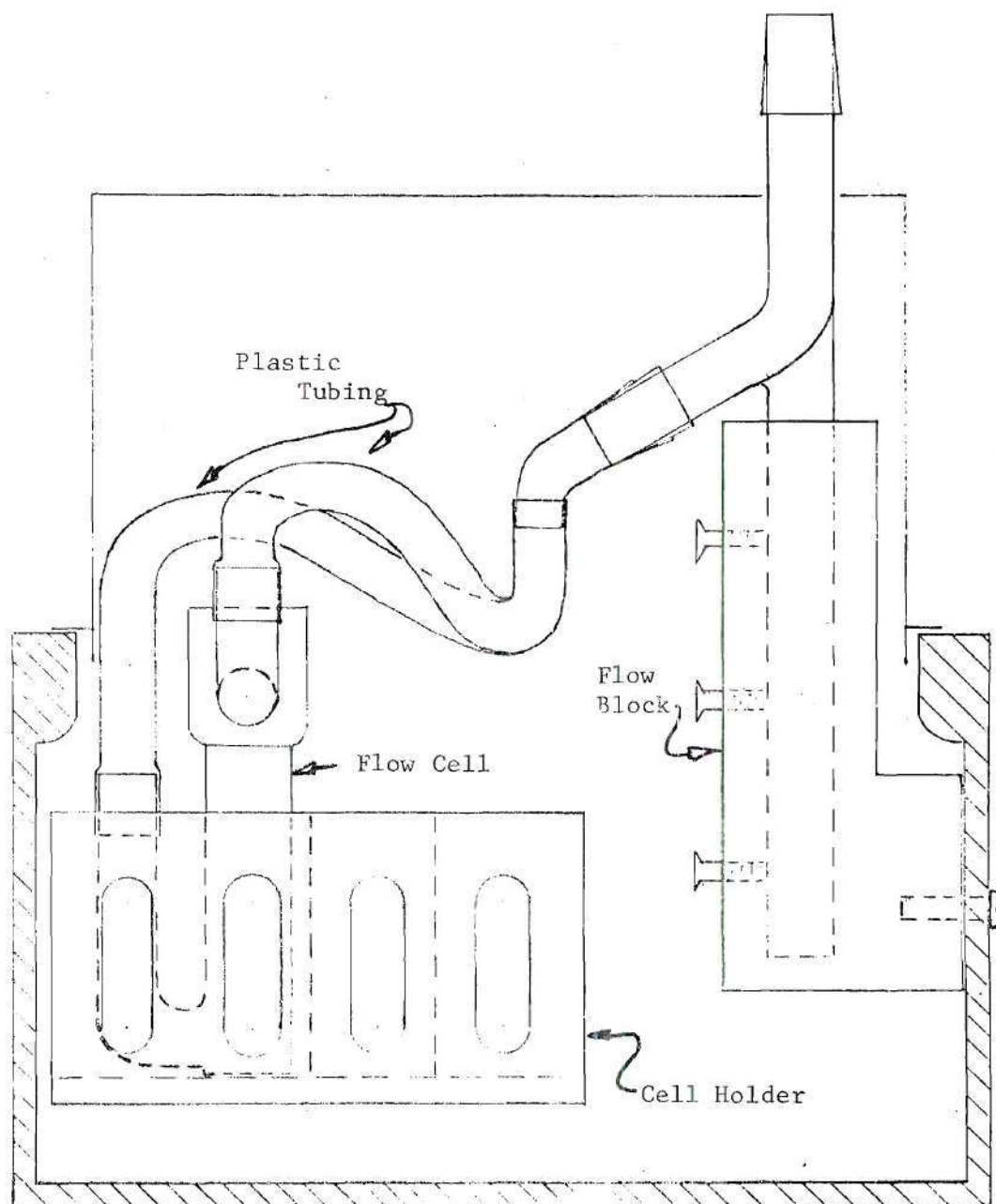


Figure 10. One Possible Flow Apparatus Configuration
(Looking toward Monochromator)

glass tubes with two female 14/20 standard taper fittings are interconnected through a plastic tube attached to nipple outlets in the middle of each tube. (See Figure 12) This connection serves as a "bypass" and increases the flow rate of the bath through the dyeometer. It also lowers vibration in the flow cell caused by the pulse of the pumping motion, keeps the rate of flow in the flow cell low enough to avoid vibration or movement of spacers when spacers are used in the flow cell, and when firmly squeezed raises the flow rate in the cell to purge all bubbles which have formed in the cell.

Figure 11 shows three views of the dyeometer with the flow apparatus attached. The pump is partially hidden behind the cell compartment of the spectrophotometer in each view.

Certain modifications were made to the cell compartment of the Beckman DU Spectrophotometer in order for the flow apparatus to fit. Two holes were drilled in one side of the compartment through which the flow block was rigidly attached to the spectrophotometer, and two holes were cut in the top of the compartment lid to allow the 14/20 male joints of the flow block tubes, Figure 9, to protrude through far enough to be connected with flow block connector, Figure 12. The cell holder is a standard Beckman holder, but one of the internal partitions was cut out so that the flow cell would fit.

All glass tubes and connectors were covered with plastic electrical tape to reduce the possibility of stray light in the cell compartment. The plastic tubes used for connectors were wrapped with asbestos rope to minimize heat losses. All connections made with glass used standard taper ground glass joints as shown in drawings.

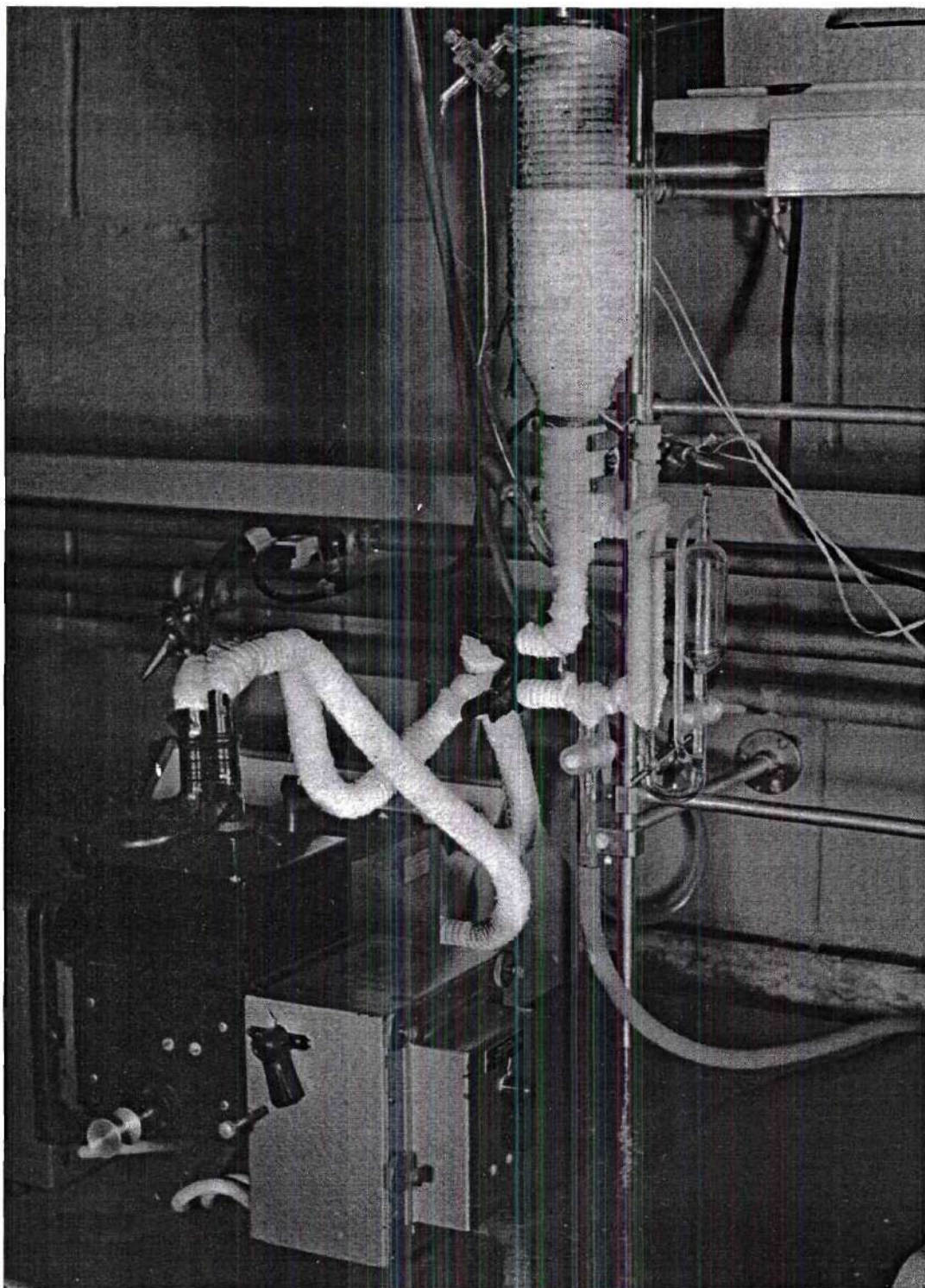


Figure 11. The Dyeometer with Flow Apparatus Attached

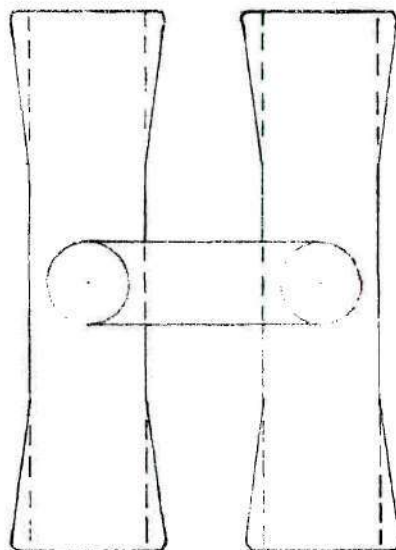
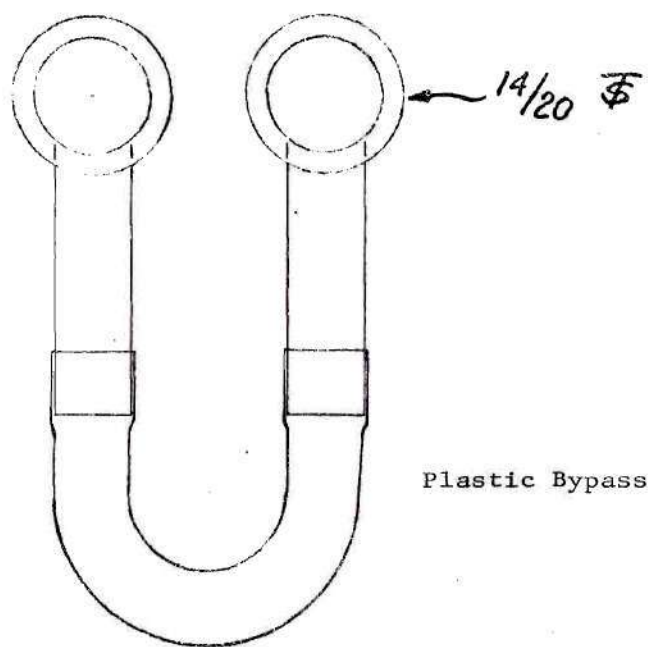


Figure 12. Flow Block Connector (4 in. = 10 cm.)

CHAPTER III

PROCEDURE

Preparation of Fiber Specimens

Commercial Fibers

The preparation of the commercial fibers H-2, SDR-1, SDR-2, and the nylon fibers consisted of weighing out 2.00 grams of the fibers from the package of yarn, and then winding the specimen loosely on the sample holder. No pretreatments were made to remove finishes applied by the fiber producer.

Experimental Fibers

The two experimental fibers, BB-1 and BB-2, were made from commercial fibers Hercules H-2, and U.S. Rubber SDR-1, respectively, by treatment with acid to cause protonation of the copolymer present in the fiber. First, approximately five grams of the commercial fiber to be treated were unwound from the package, formed into a loose skein, and then immersed in 400 ml. of concentrated (38%) HCl for two minutes at the temperature of 49°C, with constant stirring (24). After removal, the fiber was washed for 30 seconds in running tap water, and then washed for two minutes in distilled water. After the washings the fiber was squeezed between paper towels and allowed to dry in the air.

Prior to dyeing, the dry fiber was weighed out into 2.00 gram portions. For the dyeing operation the 2.00 grams of fiber was loosely wound on the sample holder in the same manner as were the commercial specimens. (See Figure 7).

Preparation of Dyes

Purification of Dyes

The dyes shown in Figure 4 were all purified by recrystallization from hot, saturated aqueous solutions of the commercial products. The individual characteristics of the different dyes determined how many recrystallizations were performed to reach the final purity. Orange II was quite simple to recrystallize by slowly lowering the temperature of the saturated solution to room temperature and allowing the solution to stand while recrystallization occurred. The crystals were then filtered off, and the liquid retained for further studies. The recrystallization was performed three more times, always using the recrystallized solid from the preceding step.

Roccelline purification turned out to be a more difficult and time-consuming task. Roccelline has a great tendency to aggregate, and does not recrystallize satisfactorily upon the cooling of a hot, saturated solution of the dye. Thus it was necessary to remove some of the water by means of a rotary evaporator, and then allow the solution to cool and the dye to precipitate. This method gave a gel which was very difficult to filter. Most of the water was drawn off, and then it was possible to filter off the precipitated dye by vacuum filtration methods. Because of this difficulty Roccelline was only purified by one recrystallization from water, but a small amount was recrystallized another time to check the efficiency of the purification process.

Scarlet 4RA and Croceine 3BX were easy to recrystallize, and the same procedure as outlined for Orange II was followed except only three recrystallizations were made for each of the dyes.

Determining the Purity of the Pure Dyes

Samples of each step of the purification process and the solvent from each step were retained and checked by thin-layer chromatography and visible spectrophotometry to determine the efficiency of each of the purification steps.

Thin-layer Chromatography. In order to determine the degree of removal of colored impurities from the chosen dyes, thin-layer chromatography plates were made using Silica Gel G, and two drops of a solution of the solid sample taken at each purification step and also two drops of the solvent of each step were placed on the plate. The chromatogram was then developed with a solution of butanol, absolute ethanol, and water (55%, 22.5%, and 22.5%, respectively) as the eluting agent. Orange II was shown to be free of colored impurities after the first recrystallization; both the solute and the solvent were free. The solution of the purified Roccelline was shown to be free of colored impurities after one step, but the solvent of this dye showed an orange impurity with an R_f value of 0.5 compared to the Roccelline value of 0.3. This impurity disappeared after one more recrystallization.

Croceine 3BX did not show any impurities in the solutions of the purified dyes, but the solvents showed a purple impurity of R_f equal to 0.3 compared to R_f equal to 0.6 for Croceine 3BX. This impurity decreased in concentration until it was only slightly visible after three recrystallizations. Scarlet 4RA did not show any colored impurities in either the dye solutions or the solvents, but the solvent from the first recrystallization step showed a non-colored impurity which fluoresced under UV examination and also smeared the development of the dye left

in the solvent. This impurity was most likely one of the diluents used in the commercial grade of the dye. None of the other dyes showed any fluorescent impurities.

Visible Spectrophotometry. In order to determine the efficiency of the purification process with respect to the removal of non-colored or electrolyte impurities, a method was developed using solutions of equal concentration of the products of each recrystallization. The solutions were made 6×10^{-5} molar and the absorbance was checked at the wavelength having highest absorbance of each solution. In this way the increasing purity was shown as increasing absorbance at this peak wavelength, corresponding to the increase in the amount of pure dye per weight of the sample taken. The absorbance at peak wavelength was plotted against the number of purification steps, (Appendix Figure 17). Orange II, Croceine 3BX, and Scarlet 4RA all had curves which flattened out at the third step, and the curve for Roccelline showed a tendency to flatten out although only one recrystallization was performed. These data defend the theory that, for all practical purposes, the dyes are all pure one-component systems after the purification.

The final pure dyes (the crystals collected after the last recrystallization) were then sampled, and these samples were dried in a drying tube over solid phosphorous pentaoxide, (P_2O_5), under a vacuum of between 0.5 and 1.0 mm Hg, and at a temperature of approximately $80^\circ C$ for three days. A dilute solution was then made of these dry dyes, and the spectrum of each dye was determined using the spectrophotometer. These spectra were then used as a basis for deciding the wavelength at which each dye would be monitored during the dyeing operations.

The spectra of these dyes are shown in Appendix Figures 18, 19, 20 and 21.

Preparation of Stock Dye Solutions

All stock dye solutions were made 10^{-2} molar using the purified dyes dried in the manner outlined in the above section. The solutions were made by weighing out the required quantity of the dye to make a liter of solution at the selected concentration. Care was taken to weigh out the dye rapidly enough so that there was little chance for it to pick up moisture from the air. The stock solutions were then stored in a dark place to minimize fading. Distilled water was used throughout.

Dyeing Operations

Previous work by R.F. Johnson and U. Meyer* showed that a $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ buffer gives the widest range of pH's and best results in a polypropylene-acid dye system. The dependence of dye uptake upon ionic strength of buffer was also found by Johnson and Meyer to be quite small, although an ionic strength of 0.03 gave optimum results. Following these findings, it was decided to use the $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$ buffer system with 0.03 ionic strength in this work.

Buffers

A buffer made of 4.3 grams per liter KH_2PO_4 and 6.3 grams per liter H_3PO_4 (85.6%) has a pH of 2.00 ± 0.05 and an ionic strength of 0.03. Thirty liters of this buffer was made up for use in all dyeings at pH of 2.00. Buffers of 3.00 and 4.00 pH were made by dropwise addition of the acid to a 4.3 g/l solution of the salt until the desired pH

*Confidential research for Phillips Petroleum Company to be published after 1970.

was reached. The pH 5.00 buffer was more difficult, because the pH of the 4.3 g/l salt solution was on the order of 4.5, thus the salt solution required dilution until the pH was above 5.3, and then the pH was adjusted to 5.00 by addition of the acid. The ionic strength of the 3.00, 4.00, and 5.00 buffers was not held constant because the influence of the ionic strength was assumed negligible relative to the effect of pH variance in the design of the experiments.

Preparation of the Dyebath and Fiber Specimen

All fiber specimens were 2.00 grams as described in the section, Apparatus and Specimens. The amount of buffer used in each dyeing operation was held constant at 600ml. The only entities varied in the dyeings were the pH (and indirectly, ionic strength) of the buffer, the initial concentration of dye, and the type of dye. The temperature, circulation rate, and r.p.m. of the sample holder were also held constant.

The dyebath was prepared by measuring out 600ml of the desired pH buffer, adding the correct volume of stock dye solution to give the desired initial concentration of dye, and entering the dyebath into the dyeometer. The bath was then brought up to 95°C, and the absorbance of the solution was monitored until a constant reading was obtained.

Measurement of the Sorption of Dye During Dyeing Operations

After the absorbance of the dyebath solution had become constant, the specimen was introduced into the bath, the constant speed stirring motor attached to the sample holder rod, and the absorbance of the dyebath was read from the spectrophotometer and recorded at 6, 12, 18, 30, 42, 54, 72, 90, 120, 150 minutes, and every 30 minutes thereafter until

a constant reading was obtained indicating equilibrium had been reached between the dye in solution and dye on fiber. Before each reading the "bypass" on the flow block connector was squeezed to clear any bubbles out of the flow cell. Readings were taken at two wavelengths using distilled water as the reference; one wavelength being a peak or shoulder on the spectrum of the dye (Appendix Figures 18, 19, 20, and 21) and one wavelength at which the pure dye absorbed no radiation. The reading at the latter wavelength was algebraically subtracted from the former reading to correct for any absorbing impurity in the dyebath, e.g., finish or additives desorbed from the fiber. In all cases the pathlength of the cell was reduced to 1 mm by insertion of a 9 mm silica spacer into the flow cell before assembling the apparatus. The readings were recorded on a standard form data sheet, an example of which is given in Appendix Table 9.

The concentration of the dye in the dyebath was calculated in terms of milliequivalents of dye per kilogram of fiber, because the amount of dye added to the bath was carefully pipetted from the stock solution, and the weight of the fiber remained constant at 2.00 grams. For example, if 16 ml of the stock dye solution was added to the bath, then the calculations would be:

$$\frac{(1.6 \cdot 10^{-2} \text{ l}) \times (1 \cdot 10^{-2} \text{ moles/l}) \times (\chi^{\text{eq.}}/\text{mole})}{(2.0 \cdot 10^{-3} \text{ kg})} =$$

$$\frac{\chi(1.6 \cdot 10^{-4} \text{ eq.})}{2.0 \cdot 10^{-3} \text{ kg}} = \chi(8.0 \cdot 10^{-2} \text{ eq/kg})$$

$$\chi(8.0 \cdot 10 \text{ meq/kg})$$

$$\chi(80 \text{ meq/kg})$$

χ = 1 for Orange II and Roccelline

χ = 2 for Croceine 3BX

χ = 3 for Scarlet 4RA

To further simplify this calculation the concentration of the dye was plotted against the volume of stock solution used for the three cases. (Appendix Figure 20)

The initial concentration of the dye in the bath was assumed to come only from the portion of the stock dye solution added. Thus the initial reading of absorbance before the specimen fiber was introduced was recorded, and this value was allowed to represent the concentration stoichiometrically determined as shown above. In this way the effect of any condensation left in the dyeometer would not be interpreted analytically as a lower initial concentration of dye. The subsequent readings were then converted to concentrations on the basis of the initial reading, and any decrease in the concentration of dyebath was assumed to have been caused by uptake of dye by the fiber.

When the dyeing had reached equilibrium the sample rod was removed and the specimen unwound and washed with distilled water, after which the specimen was allowed to air dry. The dyebath was then drained from the dyeometer, and the dyeometer was washed. This washing consisted of one wash with strong sodium hydroxide solution, one wash with tap water, one wash with strong HCl solution, another wash with tap water, and a final wash with distilled water. The sample holder was washed with the same reagents, and dried with paper towels. The flow apparatus was then disassembled, washed with 95% ethanol, and allowed to air dry. The sodium hydroxide wash removed all dye sorbed

on the glass parts of the dyeometer and flow apparatus, and the HCl wash removed any finishes and/or additives desorbed from the fiber during the dyeing.

Wash Tests

The washfastness of a dye on a fiber will indicate certain properties of the fiber such as type of dyeing affected, type of dyesites available, and strength of these dyesites with respect to bonding with the dye molecules. By comparing the washfastness of each fiber dyed under identical conditions, it was hoped to be able to relate the results to the properties of fibers given in the preceding sentence.

To evaluate the washfastness of the five fibers, one specimen of each fiber was dyed with Orange II, pH = 2.00, ionic strength (I) = 0.03, 160 meq/kg initial dye concentration, for 240 minutes. The procedure followed was AATCC Washfastness Test IIA, Standard Test Method 61-1962. This procedure was followed exactly except for the test specimens, where there was no procedure stated for yarn specimens. Therefore, a method was developed in which the multifiber test fabric was stapled to the wound yarn specimen, and then the specimen was inserted into a six-inch perforated stainless steel dyeing tube, both ends closed with large cork stoppers, and then placed in the stainless steel test cylinder.

Evaluation of the results of the washfastness test was made using the Geometric Staining Scale for color transference, and the International Geometric Gray Scale for the color change of the test specimens.

Praxitest Dyeings

To determine whether the results obtained with the dyeometer were

comparable to those obtained in a full-scale or pilot plant operation, Praxitest dyeings were made of the three nylon fibers and three of the polypropylene fibers.

The Praxitest is an instrument utilizing a continuous flow of the dyebath through a filter colorimeter. The instrument is attached to a recorder which records both the per cent exhaustion of the dyebath and the temperature with respect to time. This instrument is marketed by Brinkmann Instruments, Westbury, New York, and is more representative of a full-scale or pilot plant scale dyeing apparatus than the dyeometer.

The Praxitest was used to compare the equilibrium uptake of SDR-1, BB-1, and SDR-2 to the equilibrium uptake of the low-dyeing nylon, 845, the normal-dyeing nylon 846, and the deep-dyeing nylon, 847, respectively, using a leveling acid dye, an acid dyeing premetallized dye (1:1), and a neutral dyeing premetallized dye (2:1). The dyeings were made with commercial grade dyes according to manufacturer's specifications, and one gram of fiber was used throughout the dyeings.

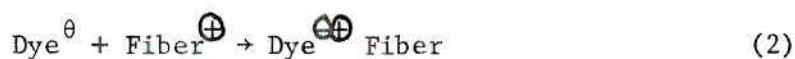
CHAPTER IV

DISCUSSION OF RESULTS

In order to properly evaluate the performance properties of each of the fiber specimens, it was necessary to follow a method of attack which would first determine the optimum dyeing conditions for each of the fibers, therefore the first object was the optimization of these conditions.

Effect of pH on Dye Uptake of the Fibers

The anionic class of dyes, i.e., acid dyes, are all applied from an acid bath. The pH of the bath can be varied from around six, as for super milling acid dyes, to very strong acidic conditions, as for leveling acid dyes, according to the leveling and/or sorption and/or solubility properties of the particular dye in question. But generally the acidity of the bath promotes the equation:



It was decided to use the simplest dye, Orange II, and to vary the pH of the dyebath by use of the different buffer solutions described previously.

Table 1 shows the equilibrium uptake of each of the five fibers at the different values of pH of the dyebath. Plotting the equilibrium uptake of the fibers versus the pH clearly shows the effect of pH on the sorption of dye, (Figure 13). From this graph it is evident that the

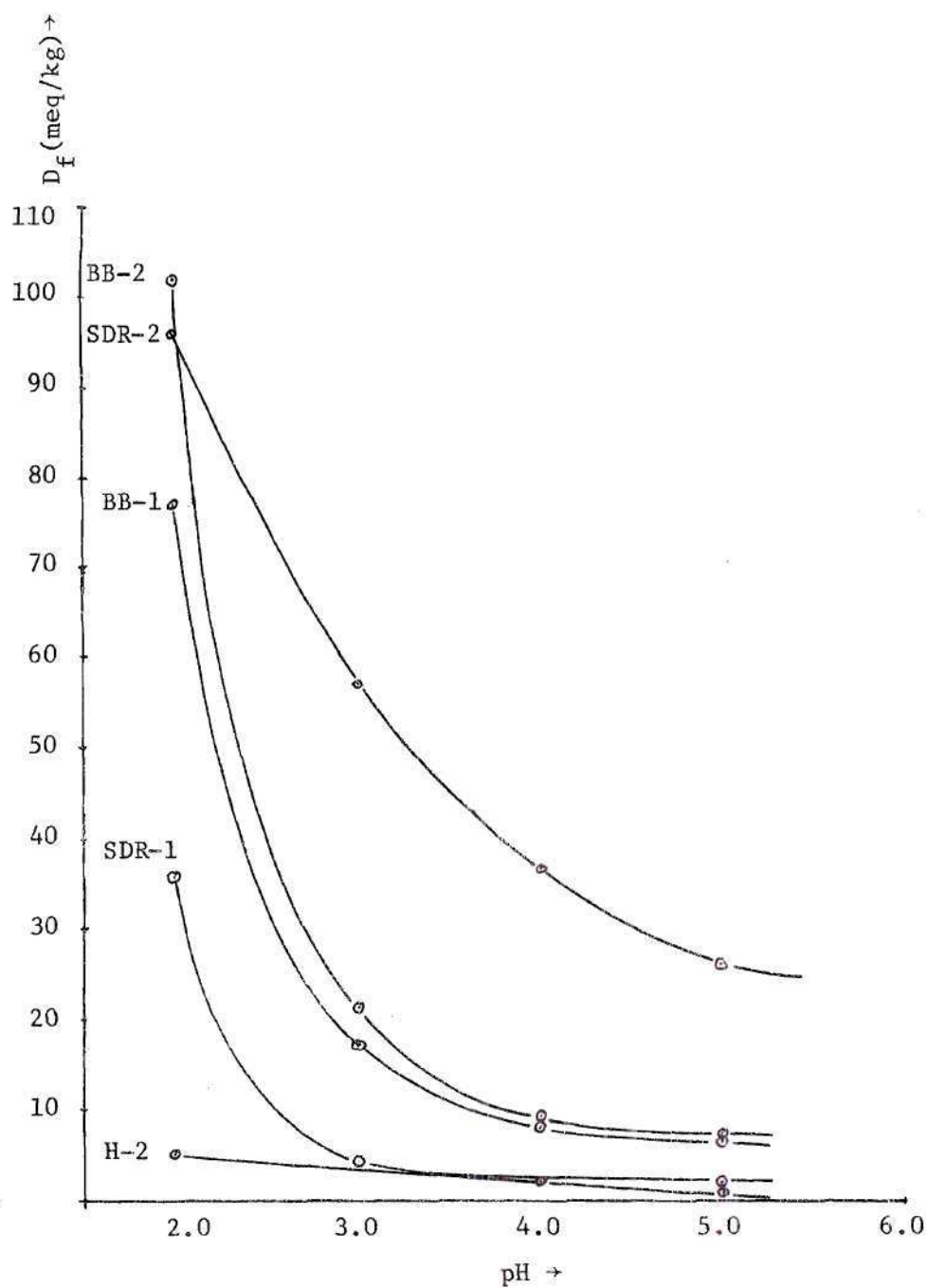


Figure 13. Effect of pH on the Equilibrium Uptake (D_f) of the Fibers SDR-1, SDR-2, H-2, BB-1, and BB-2

Table 1. Equilibrium Uptake of Orange II on the Fibers SDR-1, SDR-2, H-2, BB-1, and BB-2 at pH = 2, 3, 4, and 5

Fiber	pH			
	2	3	4	5
SDR-1	35.5	4.0	-	1.8
SDR-2	95.8	57.0	36.5	26.0
H-2	4.2	-	1.0	0.3
BB-1	76.5	16.8	8.4	7.0
BB-2	102.0	21.5	9.0	7.6

fiber BB-2 has the largest dependence on pH, with BB-1, SDR-2, SDR-1, and H-2 completing the order towards least dependence. Fiber SDR-2 continues to adsorb a substantial amount of dye even at pH above 5.00, whereas the curves for the other fibers tend to level off above pH of 4.00. Fiber H-2 does not show any ability to adsorb dye even at pH of 2.00, and its dyeing is thus not, for all practical purposes, really dependent upon the pH of the bath. Fiber BB-2 begins to adsorb more dye than SDR-2 at pH of 2.1 and this trend is likely to increase as the pH goes lower than 2.00, but pH's of this order were not investigated because the high concentration of the acid necessary to lower the pH to this level could possibly adversely affect the fiber, and also operations at this degree of acidity would be of no practical use in industry. Appendix Figures 23, 24, 25, 26, and 27 show the rate curves for each fiber at the pH's studied. Appendix Table 10 is the summary of all pH experiments.

The optimum pH of 2.0 for all the fibers is indicated from this data. This result is expected for at the lower pH values there is more

protonation of the poly(alkyl vinyl pyridine)-type copolymer thus creating more cationic dyesites (see Figure 3). This result excludes all pH's below the value of 2.00 for the reasons stated. The use of Orange II in this phase of the work was for several reasons, namely, it has the simplest molecular structure, only one sulfonic group to react with the dyesite of the fiber, and there are no other mechanisms such as aggregation of the dye to contend with in the dyeing operation. Other dyes will show different dependence on pH, but the results will be of the same form, if not the same order of magnitude.

Determination of the Number of Dyessites per Unit Weight of Fiber

A simple method of determining the number of dyessites per a given weight of a fiber is to vary the initial concentration of the dye in the dyebath until the amount of dye adsorbed by the fiber reaches a constant value even though the initial concentration of the dye is increased. Table 2 shows the initial concentration of the dye (D_{si}), the concentration of the dye in solution at equilibrium as determined by optical measurements (D_s), and the dye on the fiber (D_f) calculated by $D_f = (D_{si} - D_s)$. When D_f is plotted versus D_s (Figure 14) and the curves extrapolated to D_s equal to 300 meq/kg, the curves all level out giving a constant value for D_f . This result is taken to be the maximum amount of dye that can be adsorbed by the fiber under the conditions of pH 2.00 buffer with Orange II. Again Orange II was chosen for the same reasons as stated in the above section.

From Figure 14, Table 3 was calculated for each dye to summarize the results of this phase of the work. From this table it is evident that SDR-2 has the most dyessites at 170 per kg. of fiber. (All the

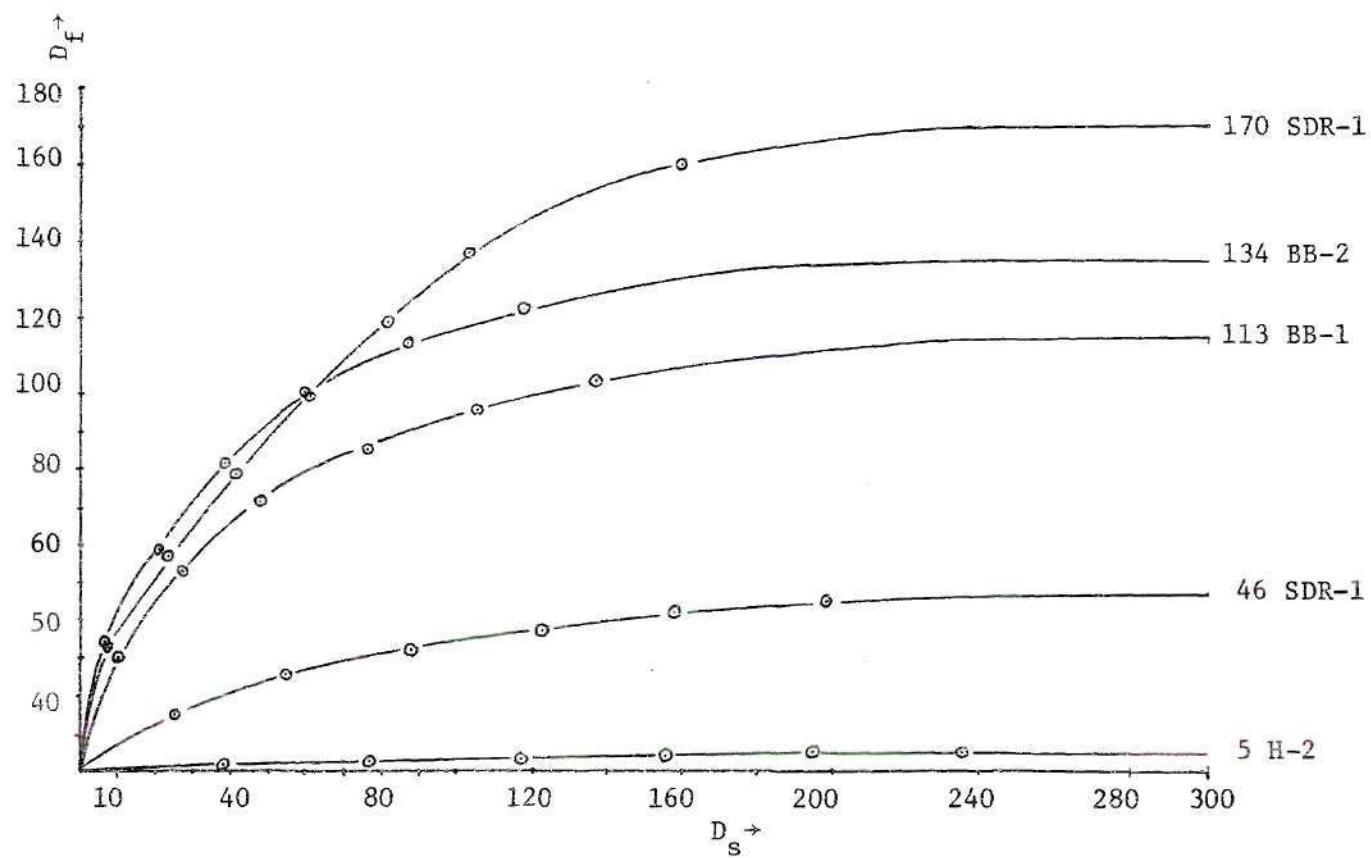


Figure 14. Equilibrium Uptake (D_f) of the Fibers versus Dye in Solution at Equilibrium (D_s) for Different Initial Concentrations of Dye bath (D_{si})

Table 2. Equilibrium Uptake of the Fibers (D_f) with Varied Initial Concentration (D_{si}) of Orange II (D_s = dye in solution)

SDR-1			SDR-2			H-2		
D_{si}	D_s	D_f	D_{si}	D_s	D_f	D_{si}	D_s	D_f
40	25	15	40	7	33	40	38	2
80	55	25	80	23	57	80	77	3
120	88	32	120	41	79	120	117	3
160	123	37	160	61	99	160	156	4
200	159	41	200	81	119	200	195	5
240	195	45	240	103	137	240	235	5
			320	160	160			

BB-1			BB-2		
D_{si}	D_s	D_f	D_{si}	D_s	D_f
40	10	30	40	6	34
80	27	53	80	21	59
120	48	72	120	38	82
160	76	84	160	60	100
200	105	95	200	87	113
240	137	103	240	118	122

Table 3. Dyesites per Kilogram of Fiber

Fiber	Dyesites/kg Fiber
SDR-1	46
SDR-2	170
H-2	5
BB-1	113
BB-2	134

results are given as number of dyesites per kg. of fiber.) Completing the order are: BB-2, BB-1, SDR-1, and H-2. Figure 14 also indicates that BB-2 shows a higher per cent of exhaustion at lower D_{si} than SDR-2; this may indicate that the dyesites in BB-2 form a more stable bond with the dye molecule and/or be more accessible than the dyesites in SDR-2, although they are fewer in number.

Equilibrium Dyeings with Selected Dyes

The use of dyes which differ in molecular structure only slightly, but which have a different number of available sulfonic groups to react with the cationic dyesite in the fiber, will provide evidence for formulating conclusions about the type, availability, dispersion, and mechanism of reaction of the dyesites on the fiber.

Orange II is the simplest dye with only one sulfonic group to react (Figure 4); Roccelline differs from Orange II only in that it is a derivative of naphthionic acid instead of a derivative of sulfanilic acid as is Orange II. Croceine 3BX and Scarlet 4RA differ from Roccelline only in the number of sulfonic groups on the molecule. Croceine 3BX has sulfonic groups in the 4 and 8' positions; Scarlet 4RA has sulfonic groups in the 4, 6', and 8' positions. This gives two dyes of the same ionic charge (1^{θ}), but with different molecular structure, and three dyes with the same molecular structure, but with 10, 20, and 30 ionic charges.

Table 4 shows the equilibrium uptake (D_f) of each of the dyes where the initial concentration (D_{si}) was held constant at 160 milli-equivalents/kg. on the five fiber specimens. The per cent exhaustion is also given. Plotting the D_f versus the type of dye gives a visual

Table 4. Equilibrium Uptake and Per Cent Exhaustion
of the Selected Dyes on the Fibers

	Or II		Rocci		Scar		Croc	
	D _f	%E	D _f	%E	D _f	%E	D _f	%E
SDR-1	36	.4	25	15.6	12	7.5	10	6.3
SDR-2	96	59.8	121	75.6	130	81.2	104	65.0
H-2	4	2.6	5	3.1	5	3.1	3	1.9
B -1	77	47.8	78	48.7	84	52.4	60	37.5
BB-2	102	63.7	130	81.2	126	78.8	81	50.6

interpretation of the table (Figure 15). In Figure 15 these results are shown in milliequivalents of dye per kilogram of fiber.

The tendency of Roccelline to aggregate is shown markedly on all fibers except SDR-1 and BB-1. Fiber SDR-1 adsorbs less Roccelline than Orange II, which indicates that the larger dye molecule was not able to penetrate to the dyesites in the fiber. The aggregation effect on BB-1 was very small, but the uptake of Roccelline was greater than Orange II, yet this uptake may have included the aggregation effect, thus masking any effect of the larger molecule such as seen on SDR-1 with Roccelline.

Croceine 3BX was adsorbed the least of all the dyes in all but one case, SDR-2. This result tends to imply that one dye molecule is reacting with more than one dyesite, thus forming two bonds between the dye molecule and the fiber. Not all the dye is reacting in this way, for the total uptake of the dye is too great to allow all the dyes to be double-bonded to the fiber.

On the other hand, Scarlet 4RA, is adsorbed to a greater extent than Orange II in all cases except SDR-1, and more than Roccelline in

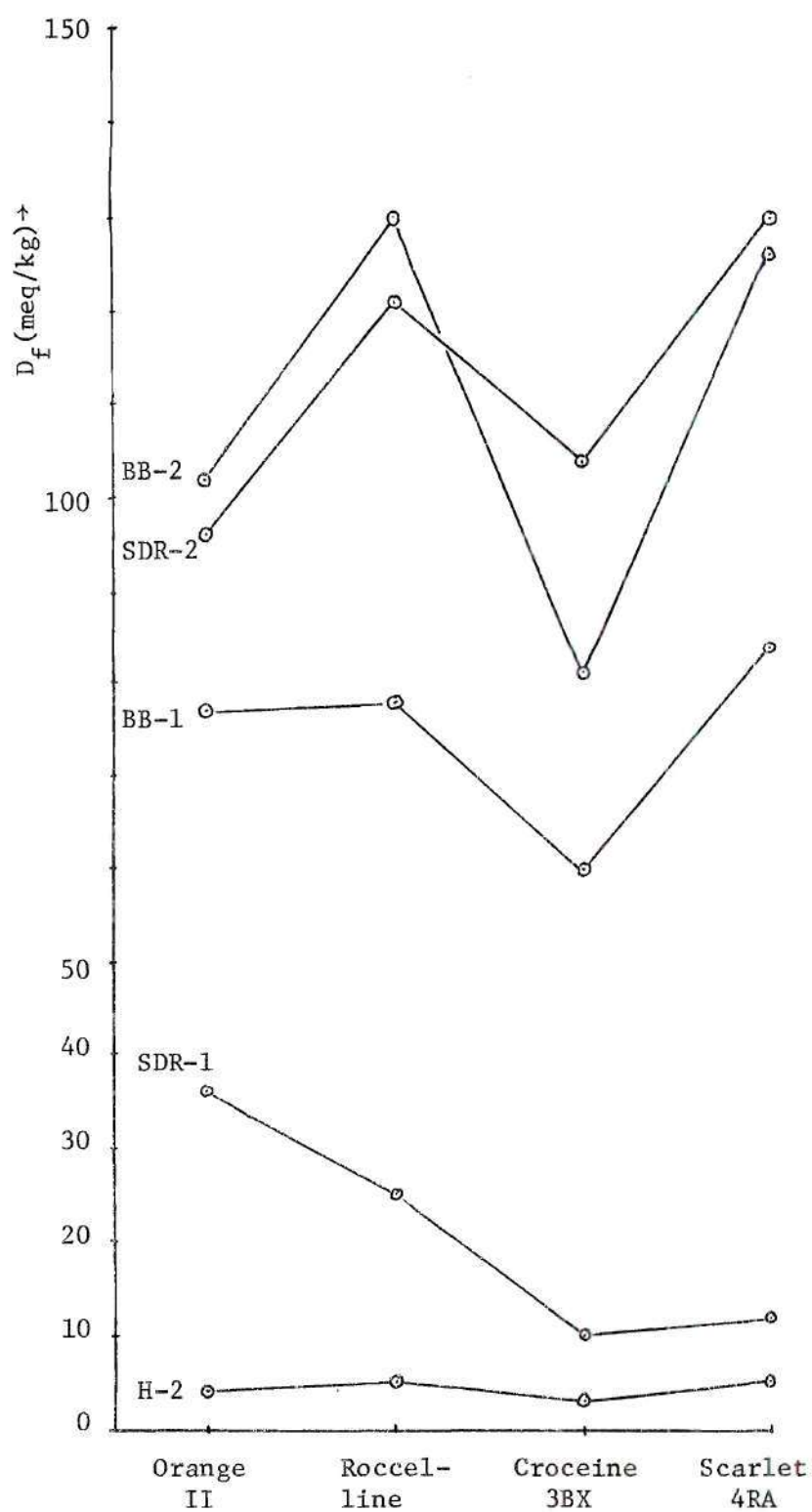


Figure 15. Equilibrium Uptake (D_f) in meq/kg of the Selected Dyes on Each Fiber

three cases. This implies that the Scarlet 4RA dye molecule with three sulfonic groups is reacting with the fiber dyesites in a 1:1 ratio only. There is no reason to justify this type of behavior from Scarlet 4RA, because one would expect this type of dye to react in some other ratio of dye to fiber, i.e., up to three bonds per dye molecule. There could be several reasons for this unusual behavior: rigidity of the molecule hindering multiple reactions, weakness of the second and third sulfonic groups in bonding, steric hindrance of the sulfonic groups not encountered with Croceine 3BX, and position of the dyesites on the fiber adverse to multiple bonding mechanisms.

When the dye uptake of the different dyes on the fibers is converted into millimoles per kilogram of fiber, then the differences between the dyes of different ionic charge can be seen readily. Table 5 shows the uptake of each dye calculated in both meq./kg. and moles/kg., and the rank of the uptake with respect to the other dyes on the same fiber in both cases. On this basis the uptake of Croceine 3BX and Scarlet 4RA is never higher than that of Orange II or Rocceline. Theoretically, half as much Croceine 3BX, and one-third as much Scarlet 4RA, should be adsorbed as Rocceline if the multiple bonding mechanism is followed for each of these dyes. Because of the aggregation properties of Rocceline, this comparison cannot be accurately drawn. Ignoring the effect of structure on the uptake, it is possible to compare the actual (U_A) of Croceine 3BX and Scarlet 4RA to the theoretical uptake (U_T) of these two dyes based on the uptake of Orange II, which is done in Table 6. The theoretical uptake of the two dyes Croceine 3BX and Scarlet 4RA should be approximately the millimoles of Orange II sorbed by the fiber

Table 5. Equilibrium Uptake (D_f) of the Selected Dyes on the Fibers Calculated in Milliequivalents and Millimoles per Kilogram of Fiber (meq/kg and mmole/kg)

Fiber	Dye	D_f in		D_f in		Remarks
		meq/kg	Rank	mmoles/kg	Rank	
SDR-1	OR II	36	High	36	High	No Aggregation
	ROCCI	25	2nd	25	2nd	
	SCAR	12	3rd	4	Low	
	CROC	10	Low	5	3rd	
SDR-2	SCAR	130	High	43	Low	Aggregation
	ROCCI	121	2nd	121	High	
	CROC	104	3rd	52	3rd	
	OR II	96	Low	96	2nd	
H-2	ROCCI	5	High	5	High	Very little Aggregation
	SCAR	5		1.6	3rd	
	OR II	4	2nd	4	2nd	
	CROC	3	Low	1.5	Low	
BB-1	SCAR	84	High	28	Low	Very little Aggregation
	ROCCI	78	2nd	78	High	
	OR II	77	3rd	77	2nd	
	CROC	60	Low	30	3rd	
BB-2	ROCCI	130	High	130	High	High Aggregation
	SCAR	126	2nd	42	3rd	
	OR II	102	3rd	102	2nd	
	CROC	81	Low	41	Low	

Table 6. Comparison of the Theoretical Uptake (U_T) of Croceine 3BX and Scarlet 4RA with Actual Uptake (U_A) on the Fibers (Uptakes in mmole/kg)

Fiber Dye	SDR-1		SDR-2		H-2		BB-1		BB-2	
	U_T	U_A	U_T	U_A	U_T	U_A	U_T	U_A	U_T	U_A
Croceine 3BX	18	5	48	52	2.0	1.5	39	30	51	41
Scarlet 4RA	12	4	32	43	1.3	1.6	26	28	34	42

in question divided by the ionic charge of the dye, i.e., Croceine 3BX or Scarlet 4RA. Thus, if Orange II was sorbed on BB-2 to the extent of 102 mmoles/kg., then Croceine should sorb 51 mmoles/kg., and Scarlet 4RA 34 mmoles/kg. This uptake is theoretically possible under the assumption that each of the sulfonic groups on the dye molecule reacts with a different dyesite on the fibers. As can be seen from Table 6, the actual uptake of Croceine is less than the theoretical uptake except for the SDR-2 fiber, which showed unusual uptake, whereas the actual uptake of Scarlet 4RA is greater than the theoretical uptake on all fibers except SDR-1. This table verifies the implication that the Croceine molecules are reacting with the fiber to form more than one bond between dye molecule and fiber, but Scarlet 4RA is not reacting in this manner, although this table cannot be assumed to have a large degree of accuracy. The uptake of Croceine also indicates that the size of the molecule does have some influence on the sorption that cannot be ignored; this is why the actual uptake is lower than the theoretical uptake, and not slightly higher as would be expected for a dye which is partially reacting with a multiple bond formation mechanism, and partially with a single bond formation mechanism. Figure 16 shows the uptake of each dye as mmoles/kg. for each fiber.

The rate of dye uptake differs with each dye studied. Roccelline shows a slower rate of uptake, but the aggregation property of the dye causes the rate curve to increase slightly after the rate has decreased to almost equilibrium conditions. Because of this, equilibrium is reached after a greater length of time than with the other dyes. The rates of uptake of the other three dyes are nearly equal with Scarlet

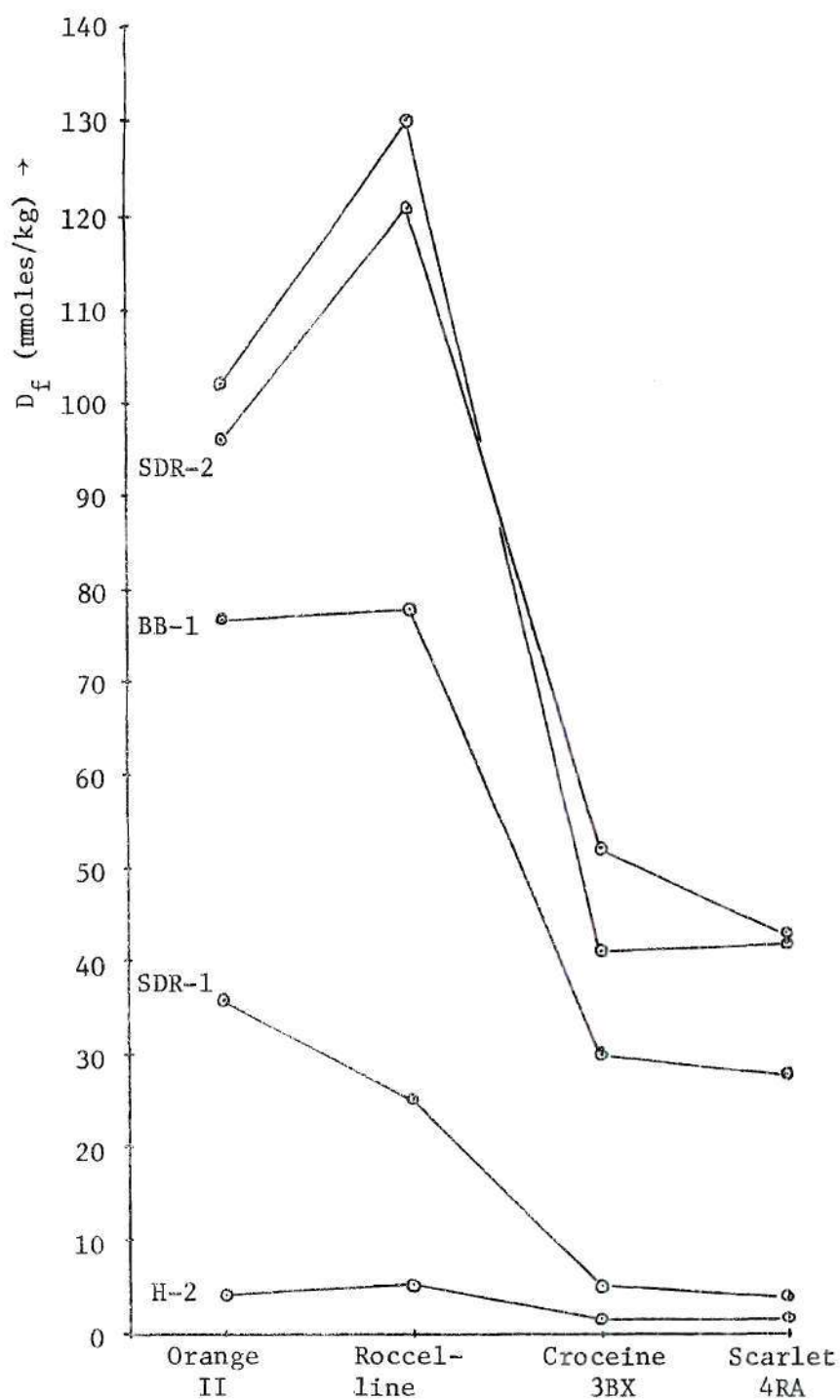


Figure 16. Equilibrium Uptake (D_f) in mmol/kg of the Selected Dyes on the Fibers

4RA having the highest rate of the three. See Appendix Figures 28, 29, 30, 31, and 32.

Washfastness Results

Fiber specimens dyed with 160 meq/kg Orange II, pH of 2.00, ionic strength of 0.03, for 240 minutes were submitted to the AATCC Washfastness Test IIA. The results of this experiment are shown in Table 7. Fibers SDR-2 and BB-2 are shown to have the same degree of washfastness with little color change compared to the other fibers, and with a corresponding staining of the nylon 66 and wool of the multi-fiber test specimen. Fiber H-2 does not show any degree of washfastness, probably due to the lack of dyesites on the fiber, thus surface or ring dyeing is easily removed by washing. The chemical treatment of H-2 to produce the fiber BB-1 not only improves the dyeability of the fiber, but also greatly improves the washfastness of the dyed fiber. Fiber BB-1 showed good washfastness, being lower only than SDR-2 and BB-2. Fiber SDR-1 did not show very good washfastness because the lack of dyesites of the fiber, and the subsequent surface dyeing behavior.

Table 7. Results of Washfastness Test

Fiber	Color Change	Staining	
		Wool	Nylon 66
SDR-1	3	3	2 - <u>3</u>
SDR-2	3 - <u>4</u>	2	2
H-2	1 - <u>2</u>	<u>1</u> - 2	1
BB-1	<u>3</u> - 4	2 - <u>3</u>	2 - 3
BB-2	<u>3</u> - 4	2 - 3	2

(Underlined numbers indicate the closer value of the two given)

Praxitest Dyeings

Using the Praxitest instrument dyeings were performed on the fibers with a leveling acid dye, Orange II, a 1:1 premetallized dye, Chromacyl Blue GG, and a 2:1 premetallized dye, Irgalan Grey BL. The fibers SDR-1, SDR-2, and BB-1 were compared to nylon 66 samples which were low-, deep-, and normal-dyeing as explained in the section on Procedure. The initial concentration of the dye was set so that the per cent exhaustion of the deep-dyeing nylon would be between 85% and 100%. All dyes were used as commercially available, and the stock solutions were made up as grams per liter. The initial concentrations of the dyebath were in per cent dye on weight of fiber.

Table 8 is a tabulation of the results of these dyeings. The polypropylene fibers are listed directly above the nylon fiber which has the corresponding dyeing properties. The dyeings with Orange II (leveling acid dye) show good correlation between the pairs of fibers, but the results with the premetallized dyes show that even the low-dyeing nylon (845) adsorbs almost as much (Chromacyl Blue GG - 1:1) or more (Irgalan Grey BL - 2:1) dye than the corresponding polypropylene fiber, SDR-1. Figure 33 (Appendix) shows two examples of the Praxitest recorder charts -- one showing 82% exhaustion and the other showing 41% exhaustion, both at 95°C.

Table 8. Results of Praxitest Dyeings

Fiber	Dye	% Exhaustion of Orange II (3% owf) (leveling acid)	% Exhaustion of Cromacyl Blue GG (3% owf) (1:1 pre- metalized)	% Exhaustion of Irgalen Grey BL (6% owf) (2:1 pre- metalized)
SDR-2		82	34	12
847		95	81	100
(deep dyeing)				
BB-1		41	13	10
846		62	51	83
(normal)				
SDR-1		10	12	8
845		13	27	71
(low)				

CHAPTER V

CONCLUSIONS

1. The commercial grade of U.S. Rubber Polycrest Fiber SDR-2 is acid dyeable with acid dyes, both leveling and milling, in equipment and by application techniques commonly used in industrial operations; the dyed fiber shows good washfastness with this type of dyes. Fiber SDR-2 is also dyeable with 1:1 premetallized dyes and 2:1 premetallized dyes and 2:1 premetallized dyes with no unusual dyeing conditions necessary.

2. Treatments with strong aqueous solutions of HCl prior to dyeing will render Hercules Herculon Fiber H-2 and U.S. Rubber Polycrest Fiber SDR-1, and thus any other fiber modified with poly(vinyl pyridine) copolymer, dyeable with acid and premetallized dyes, both having good equilibrium uptake and rate of uptake.

3. Treatment of SDR-1 with concentrated HCl produces a fiber which is comparable to SDR-2 in many respects, but which does not have the same number of dyesites per kilogram of fiber, and the dyesites produced do not exhibit the same properties, i.e., strength of dye-fiber bonds (washfastness), and rate of sorption of dye, as the commercial SDR-2.

4. By comparing the dyeings with Orange II to those with Roccel-line it is evident that the size of the dye molecule affects the uptake of the dye by the fiber only if the fiber is designed for small dye

molecules, e.g., disperse dyes, as is the case with fibers SDR-1 and H-2. Aggregation properties of the dye may cover any effects of dye molecular size on the uptake of the dye on the fiber studied.

5. The mechanism of dye-fiber bond formation cannot be deduced by simple study of the dyes. That is, dyes containing more than one sulfonic group capable of forming ionic bonds will not necessarily react to form more than one dye-fiber bond. In order to predict the mechanism through which dyes with more than one sulfonic group will react with the dyesites provided in the fiber, more study must be made to determine the effects of hindrance of sulfonic groups and bond strengths.

6. All the fibers studied here (excluding H-2, which cannot be considered to be acid dyeable because of the lack of dyesites, and because of the poor washfastness of the "dyed", i.e., stained fiber, show a great dependence of equilibrium uptake and rate of dyeing upon the pH of the dyebath when using leveling acid dyes such as Orange II, the explanation of this effect being that at the lowest of all possible pH values, with the lower limit of the pH set by practical reasons as explained in the section Discussion of Results, the nitrogen in the poly (alkyl vinyl pyridine)-type copolymer is more likely to be protonated thus making more cationic dyesites available for reaction with the dye.

7. The use of a delustrant in fiber H-2 and thus in fiber BB-1 gave the dyed BB-1 a seemingly deeper shade than either SDR-2 and BB-2 even though the BB-1 had adsorbed less dye in the dyeing operation. This is an optical effect familiar to most people in the dyeing profession; delustrants increase scattering and reduce transmittance with resulting increases in reflectance.

8. The fibers SDR-1 and BB-1 do not show any tendency to allow and/or promote the aggregation of dye, whereas the other fibers show a marked tendency to favor the aggregation of dye as with Roccelline.

CHAPTER VI

RECOMMENDATIONS

Proof of the dyeability of the commercial fibers SDR-1 and SDR-2 and the experimental fibers BB-1 and BB-2 has been established. Further investigation into the mechanism of dyeing of these fibers is recommended for a more thorough evaluation of dyeability and to set up a model for future theoretical expressions of the dyeability.

For studies concerning the type and strength of the dyesites available, a careful screening of dyes of the acid type is in order to select several dyes which perform similarly with respect to the aggregation problem or property. When this selection of dyes is completed, then it will be possible to design an experimental procedure which will show the effect of molecule type and/or size on the dyeing properties of the fibers studied. In this way one will have only the effect of differing molecular type and/or size to contend with in the evaluation of the experimental results. This will greatly simplify the process and enhance the accuracy of conclusions drawn.

Selection of dyes of the same molecular structure, but differing in the position of the sulfonic groups, and not the number of sulfonic groups, will enable the researcher to determine the effect of hindrance of the sulfonic groups on the dye uptake and mechanism of dyeing. For example, a dye of the Croceine 3BX type could be taken as a member of a group of identical dyes which have two sulfonic groups as Croceine 3BX does, but the position of the second sulfonic group, the 8' group,

could be varied to lessen or increase the amount of steric hindrance experienced by this group in reacting with the cationic dyesite in the fiber.

The above described selection of dyes could also be used to determine which dyes could be expected to form multiple bonds between dye and fiber. Dyes of more than two ionic charges could be substituted for the Croceine type to determine the strength of the ionic bonds formed by the different sulfonic groups between dye and fiber.

More accurate analytical methods should be devised to determine the number of dyesites provided by each kilogram of fiber studied. The method this author used was accurate enough for the necessities of the program, but if more precision in experimental work is desired, then a better method must be found. One simple answer would be a statistical determination of the number of dyesites made from many dyeings by the same techniques as reported here. In this way any variation in procedure or experimental errors would have less effect upon the results. Another approach to this problem would be the analytical determination of the nitrogen present in the fibers. In this way one could ascertain the total number of potential cationic dyesites that could be produced by protonation of the poly(alkyl vinyl pyridine)-type copolymer.

Dyes of classes other than leveling acid dyes should be used to determine the effect of varying the pH of the buffer dyebath solution on the rate of dyeing and the equilibrium uptake of the dye on the fiber studied. Milling, super milling, 1:1 premetallized and 2:1 premetallized dye classes could be represented by one example of each and the entire spectrum of the acid dye class in general industrial use would have been

covered. This type of research would be of great interest to dye manufacturers, fiber producers, and the commercial dyeing industry.

The washfastness tests were not primarily to evaluate end use performance, but to determine all that was possible about the dyeing mechanism and/or dyesites of each fiber. In order to evaluate dyed polypropylene fiber with respect to fastness, wash, light, crock, and dry cleaning, the fibers should be made into a construction which is comparable to the end use product and then a series of dyes tested for all fastness properties which will be required in the commercial product. Evaluation of light fastness is quite necessary in the outdoor carpets for which a growing market is indicated. Fastness to dry cleaning is necessary for apparel fabrics.

The dyeability of the disperse dyeable fibers SDR-1 and H-2 can be investigated through the use of highly soluble disperse dyes in dilute solutions either in the dyeometer or the Praxitest instrument. The effect of carriers or wetting agents upon the dyeability of these fibers has been studied, but a more comprehensive study is needed.

Chemical treatments and the effects of these treatments upon the dyeability of the fibers produced, e.g., BB-1 and BB-2, other than the treatment with concentrated HCl, is a promising field for research. In the same line, modification of the fiber surface through chemical reactions and copolymer grafting of unmodified polypropylene fibers is another phase which would yield matter for research. Fibers commercially available modified with copolymers or agents other than the poly(vinyl pyridine)-type could also be studied in the same method as this author followed.

The dyeometer used in this work is an extremely accurate research instrument and capable of being most efficiently used in a wide range of research work making use of color changes during an operation or a reaction. Further modifications to the dyeometer flow apparatus is not necessary, but the incorporation of a recording spectrophotometer which could monitor the change in absorption of the system at one wavelength would be of great advantage in accuracy of measurement.

Additional research could be made in the area of fiber structure. By taking one dye and one dyeing condition, the effects of varying such fiber parameters as amount and dispersion of copolymer, crystallinity, density, drawing ratio, type of copolymer, etc., could be studied in depth. This work would require sophisticated polymerization and melt spinning equipment, and extensive testing facilities.

APPENDIX

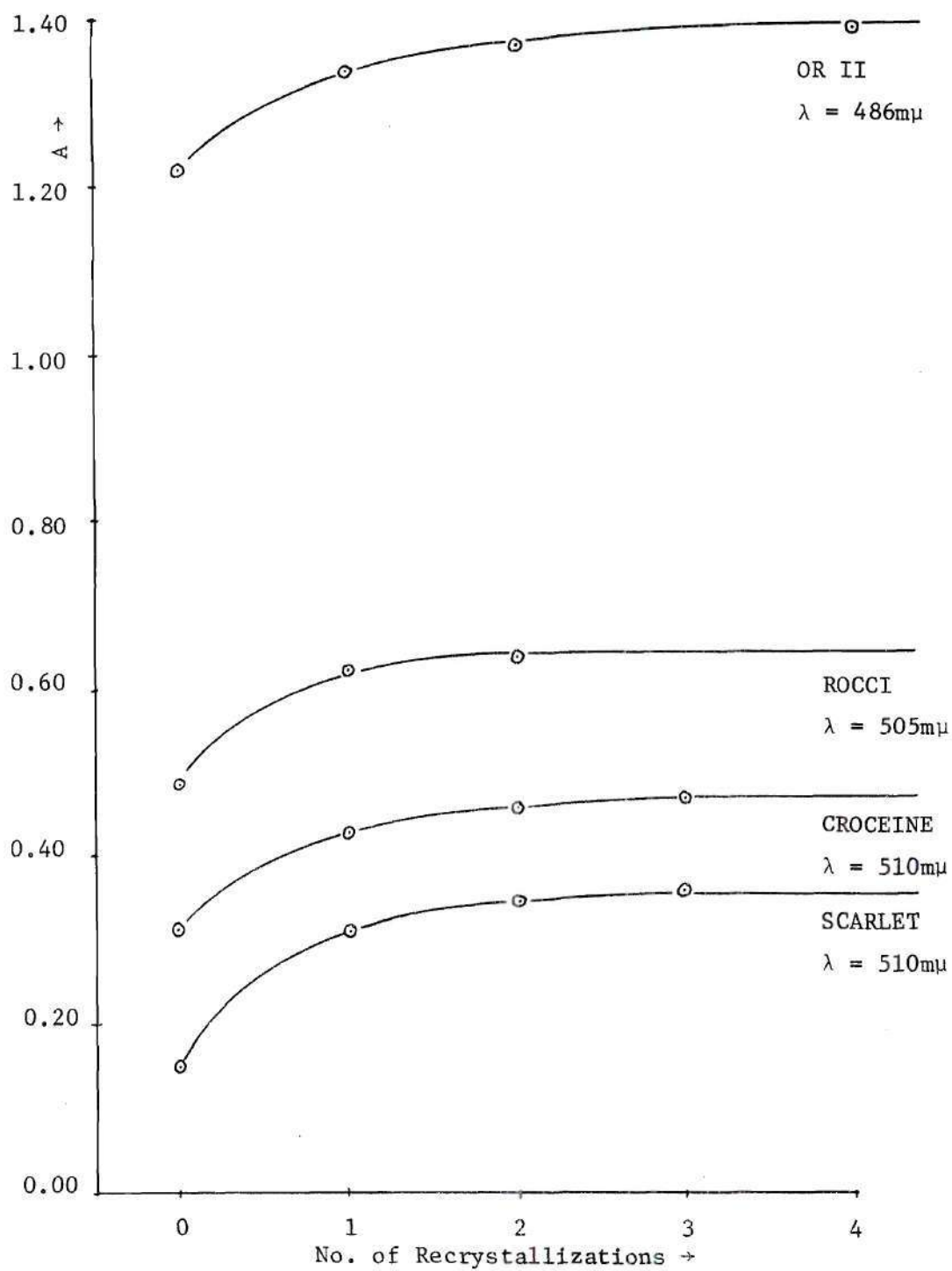


Figure 17. Effect of Recrystallization on the Absorbance of the Selected Dyes

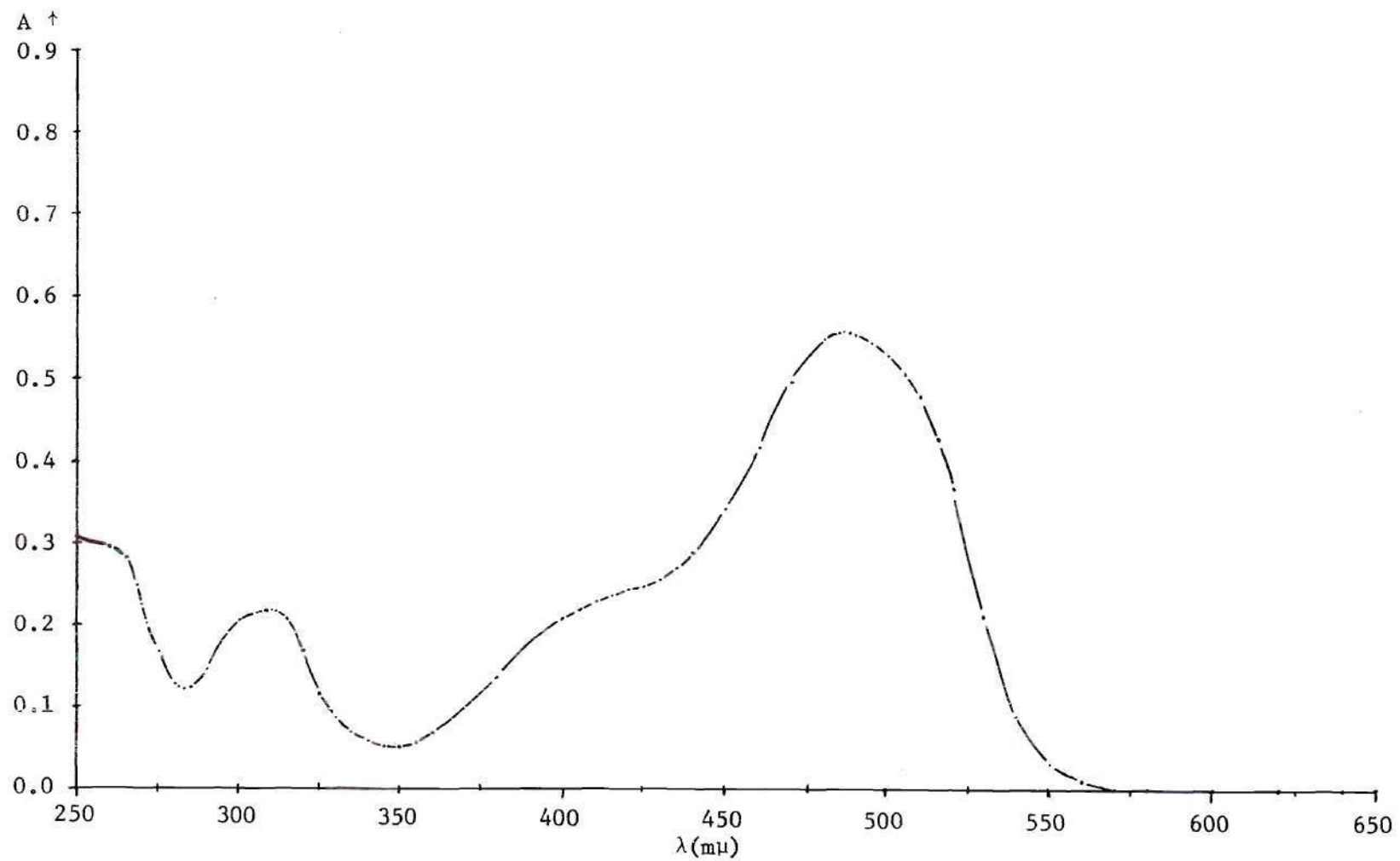


Figure 18. Spectrum of Pure Orange II

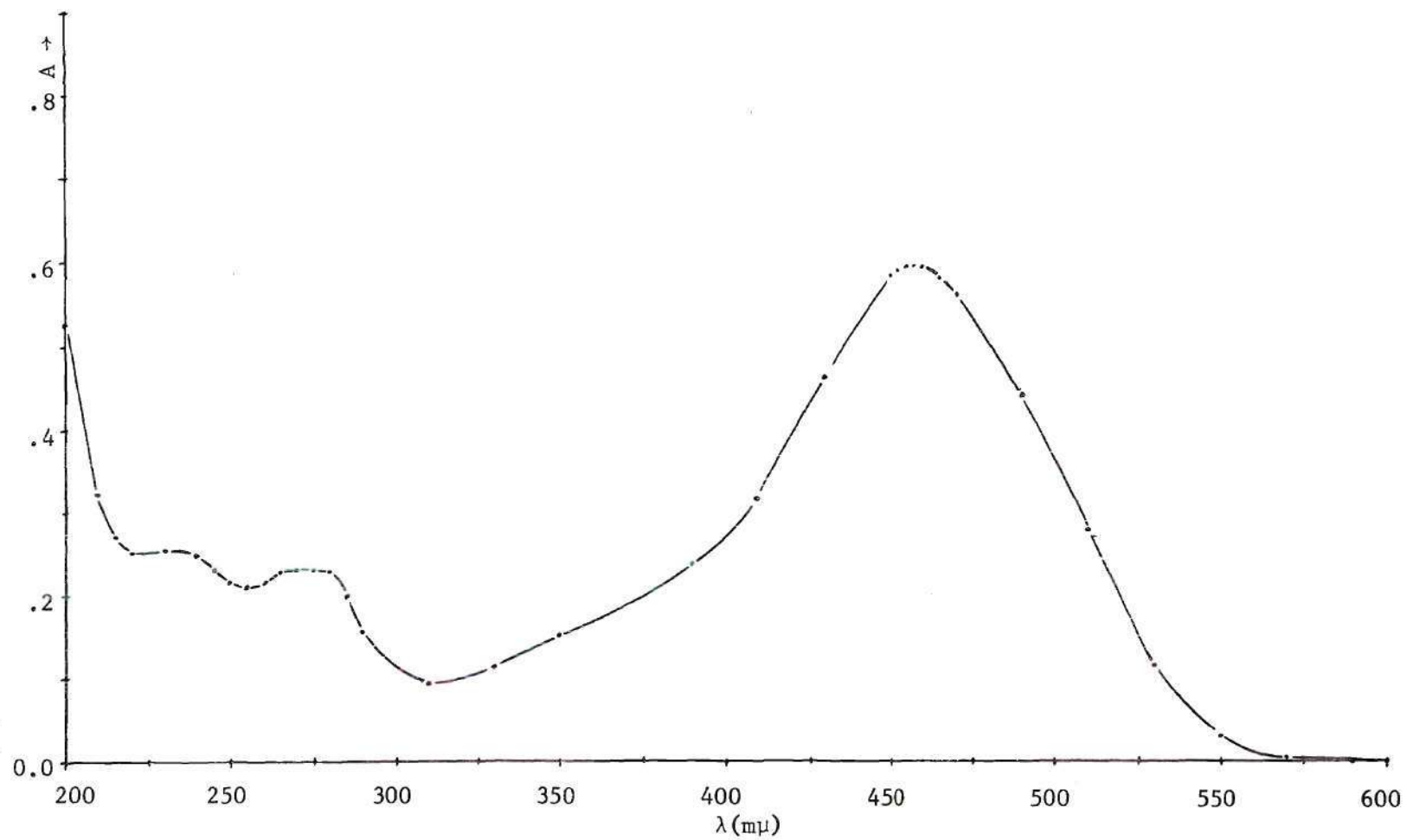


Figure 19. Spectrum of Pure Roccelline

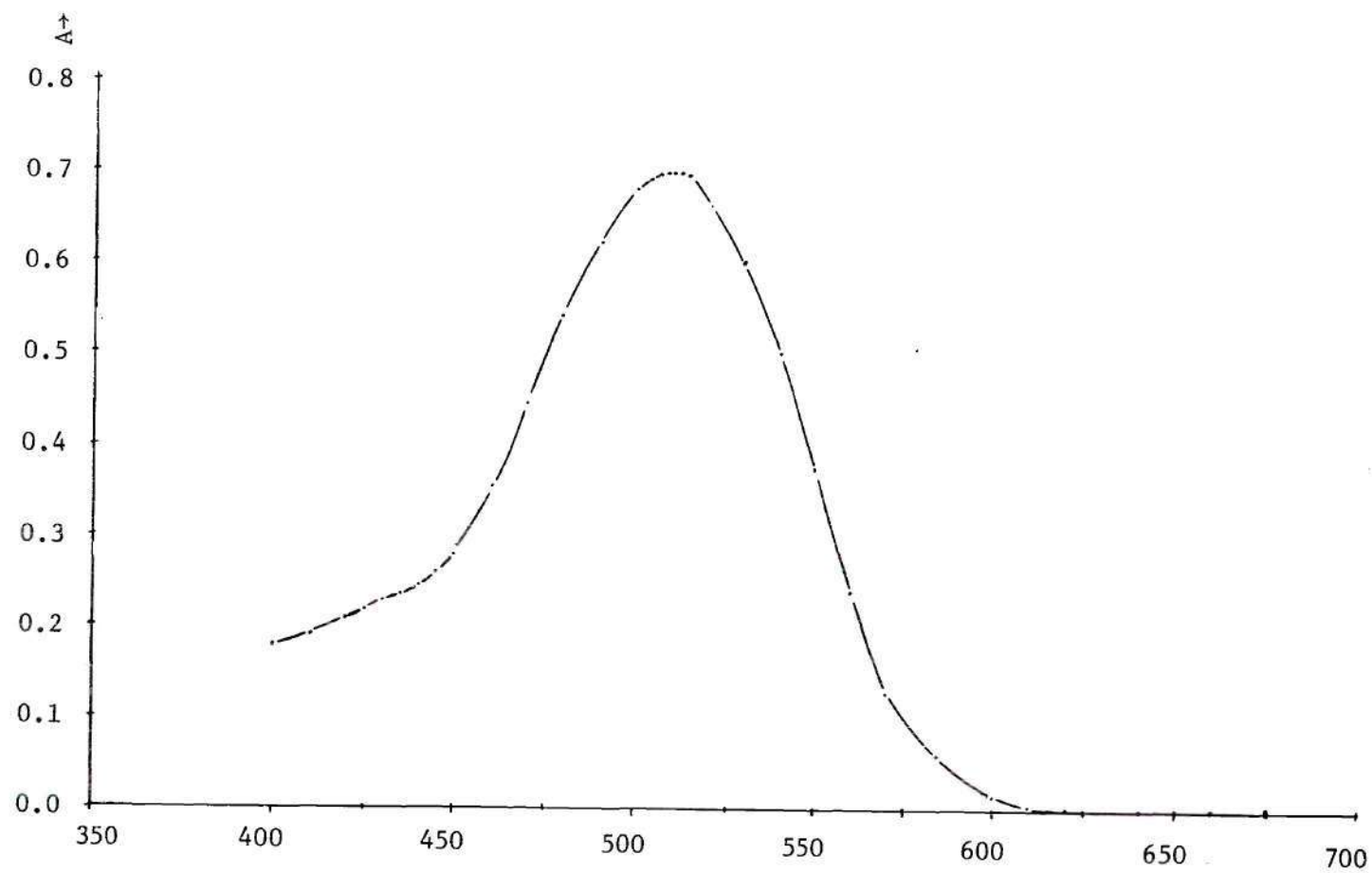


Figure 20. Spectrum of Pure Croceine 3BX

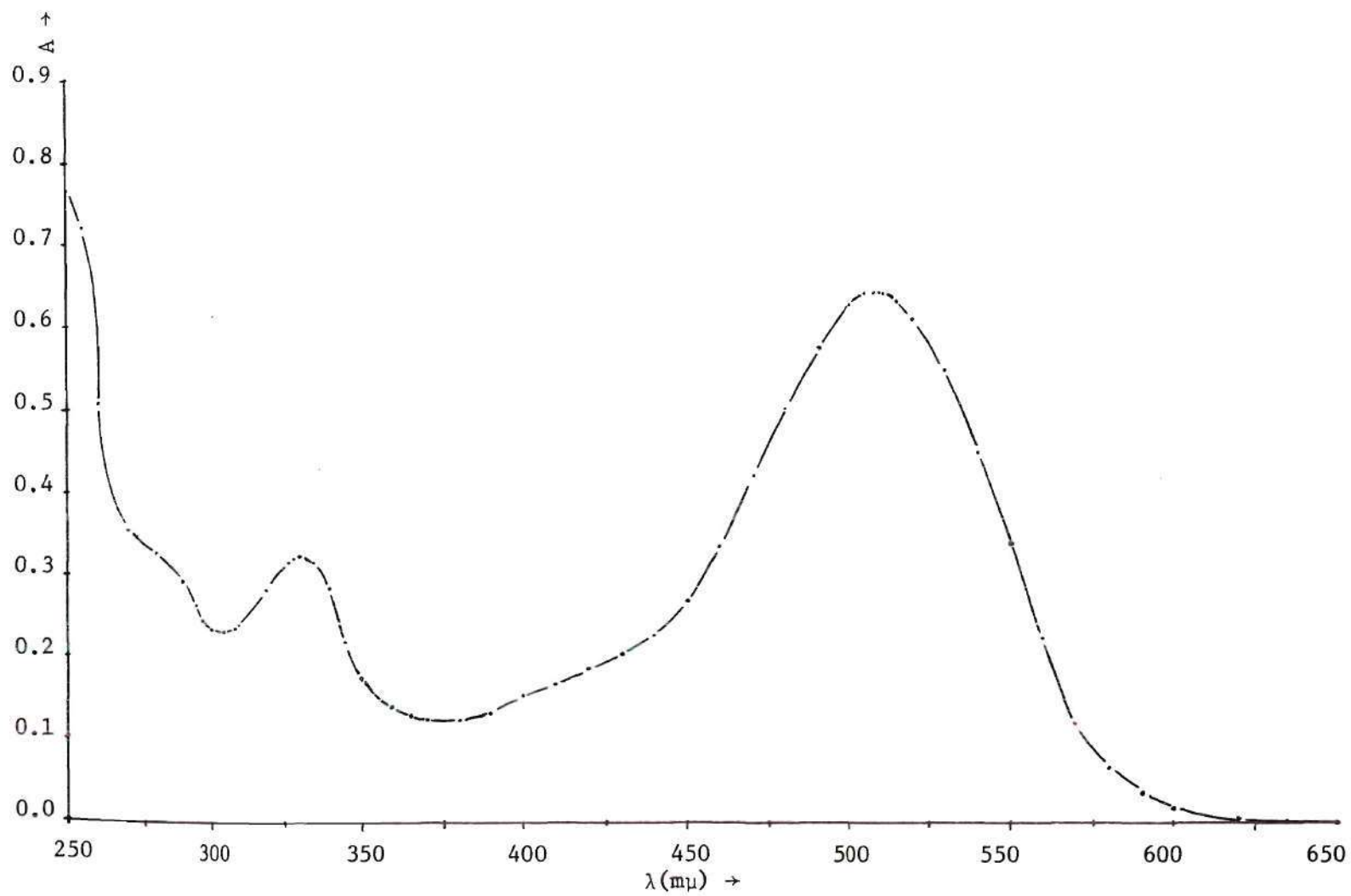


Figure 21. Spectrum of Pure Scarlet 4RA

Table 10. Summary Table of Results from pH Dependence Experiments

Time	pH = 2.00 D_f	pH = 3.04 D_f	pH = 4.04 D_f	pH = 5.04 D_f	Fiber
6	4	2.0		1.5	SDR-1
12	5.5	3.0		1.8	
18	5.5	3.5		1.8	
30	6.5	3.5		1.8	
42	8.5	4.0		1.8	
54	11.5	4.0		1.8	
72	15.0	4.0		1.8	
90	18.5	4.0		1.8	
120	23.0	4.0		1.8	
180	28.5	4.0		1.8	
180	32.0	4.0		1.8	
Equil	37.0	4.0		1.8	
Time	pH = 2.00 D_f	pH = 3.04 D_f	pH = 4.04 D_f	pH = 5.00 D_f	
6	30.5	30.0	16.0	6.5	SDR-2
12	40.0	39.0	22.0	10.5	
18	49.0	44.0	25.0	14.5	
30	69.0	50.0	29.0	19.0	
42	82.5	53.0	32.0	22.0	
54	90.0	54.0	33.5	23.5	
72	94.5	56.0	35.0	25.0	
90	96.0	57.0	36.0	26.0	
120	96.0	57.0	36.5	26.0	
Equil	96.0	57.0	36.5	26.0	
Time	pH = 2.00 D_f	pH = 3.04 D_f	pH = 4.04 D_f	pH = 5.00 D_f	
6	4.2		1.0	0.3	H-2
12	4.2		1.0	0.3	
18	4.2		1.0	0.3	
30	4.2		1.0	0.3	
Equil	4.2		1.0	0.3	
Time	pH = 2.00 D_f	pH = 3.04 D_f	pH = 4.04 D_f	pH = 5.00 D_f	
6	38.0	14.0	7.5	4.0	BB-1
12	50.0	15.0	8.0	5.0	
18	57.0	16.0	8.5	6.0	
30	65.5	16.0	8.5	7.0	

Table 10. Summary Table of Results from pH
Dependence Experiments
(Continued)

	pH = 2.00	pH = 3.04	pH = 4.04	pH = 5.00	
Time	D _f	D _f	D _f	D _f	Fiber
42	70.0	16.0	8.5	7.0	BB-1
54	73.0	16.5	8.5	7.0	
72	74.5	16.5	8.5	7.0	
90	76.0	17.0	8.5	7.0	
120	76.5	17.0	8.5	7.0	
150	76.5	17.0	8.5	7.0	
Equil	76.5	17.0	8.5	7.0	
	pH = 2.00	pH = 3.04	pH = 4.04	pH = 5.00	
Time	D _f	D _f	D _f	D _f	
6	73.0	15.0	8.0	6.0	BB-2
12	81.5	17.5	9.0	7.5	
18	86.0	19.0	9.0	7.5	
30	94.5	20.0	9.0	7.5	
42	98.0	20.5	9.0	7.5	
54	99.5	20.5	9.0	7.5	
72	100.0	21.5	9.0	7.5	
90	101.0	21.5	9.0	7.5	
120	102.0	21.5	9.0	7.5	
150	102.0	21.5	9.0	7.5	
Equil	102.0	21.5	9.0	7.5	

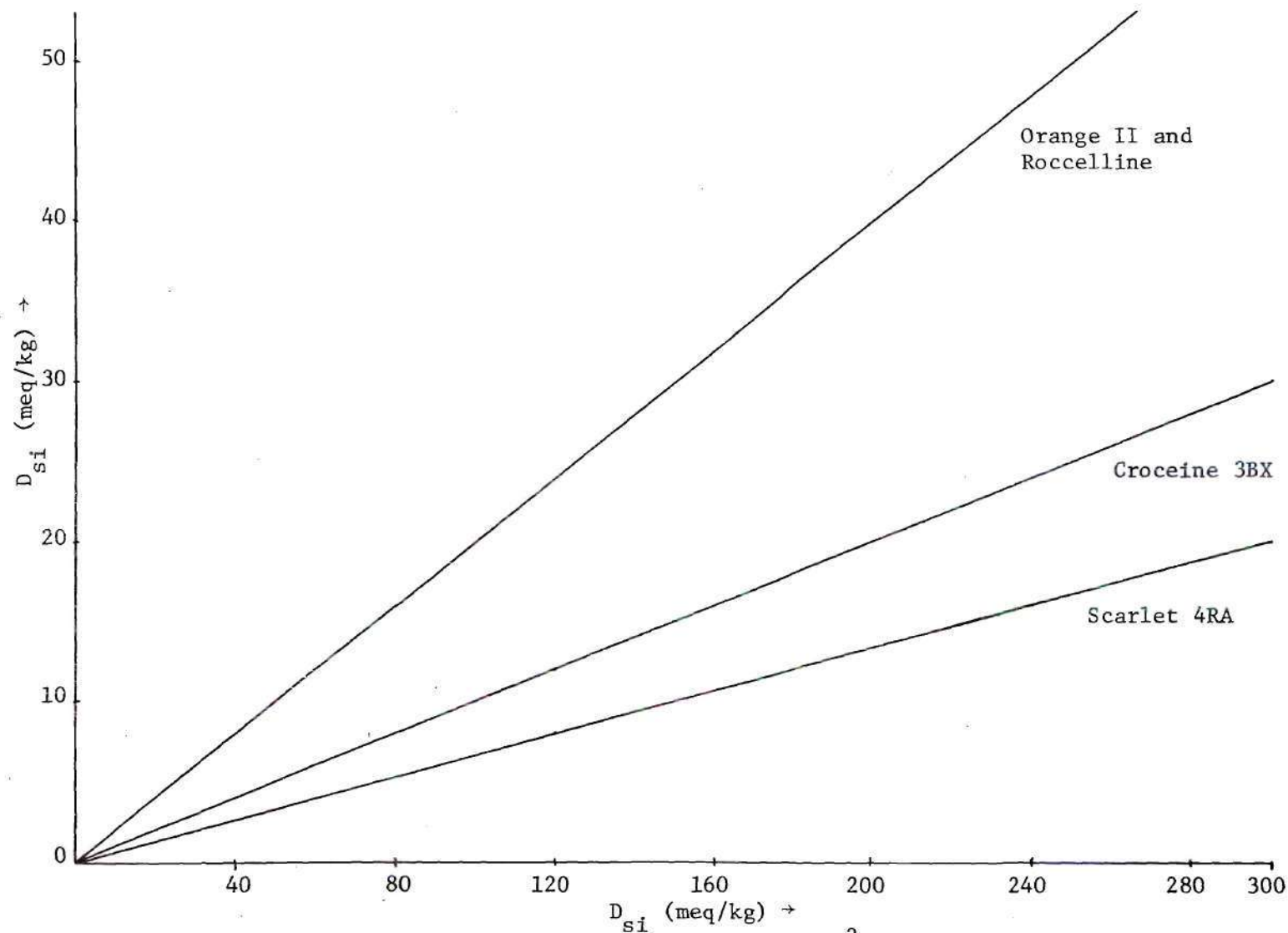


Figure 22. Volume of Stock Dye Solutions (10^{-2} molar) versus Initial Concentration (D_{si}) of Dye in the Bath in meq/kg

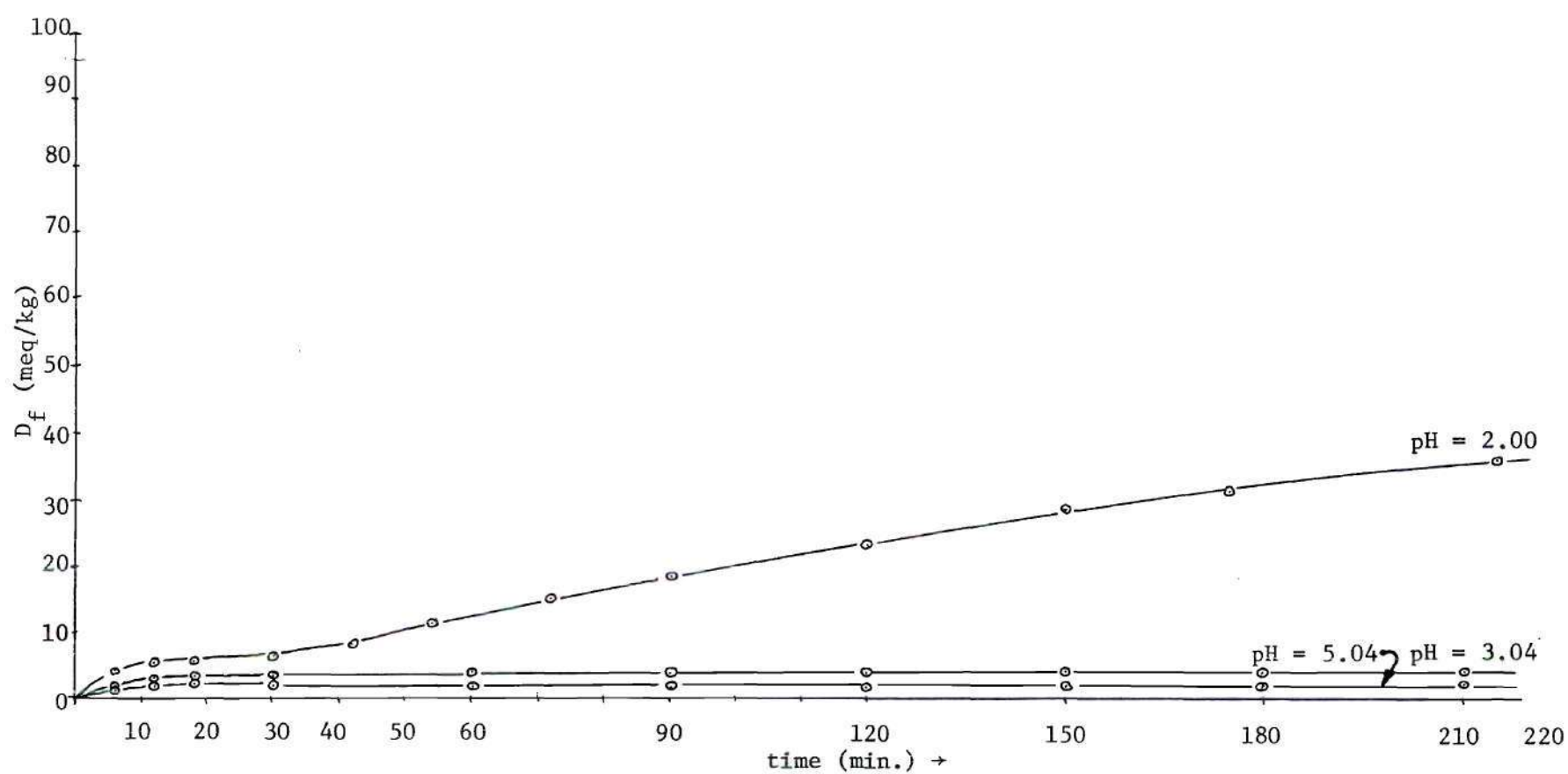


Figure 23. Effect of pH on Rate of Dyeing of Fiber SDR-1
(D_f = dye on fiber)

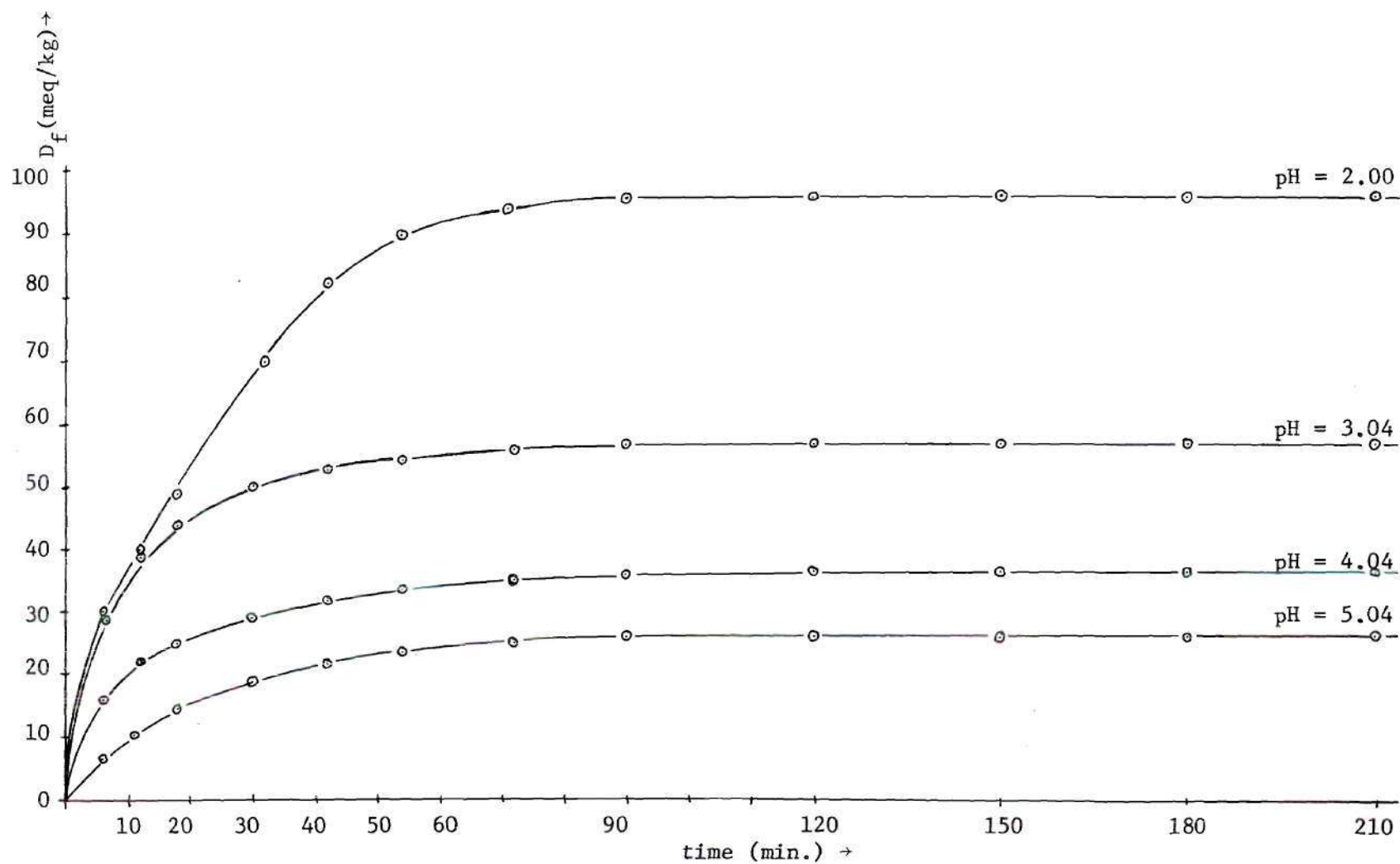


Figure 24. Effect of pH on Rate of Dyeing of Fiber SDR-2
(D_f = dye on fiber)

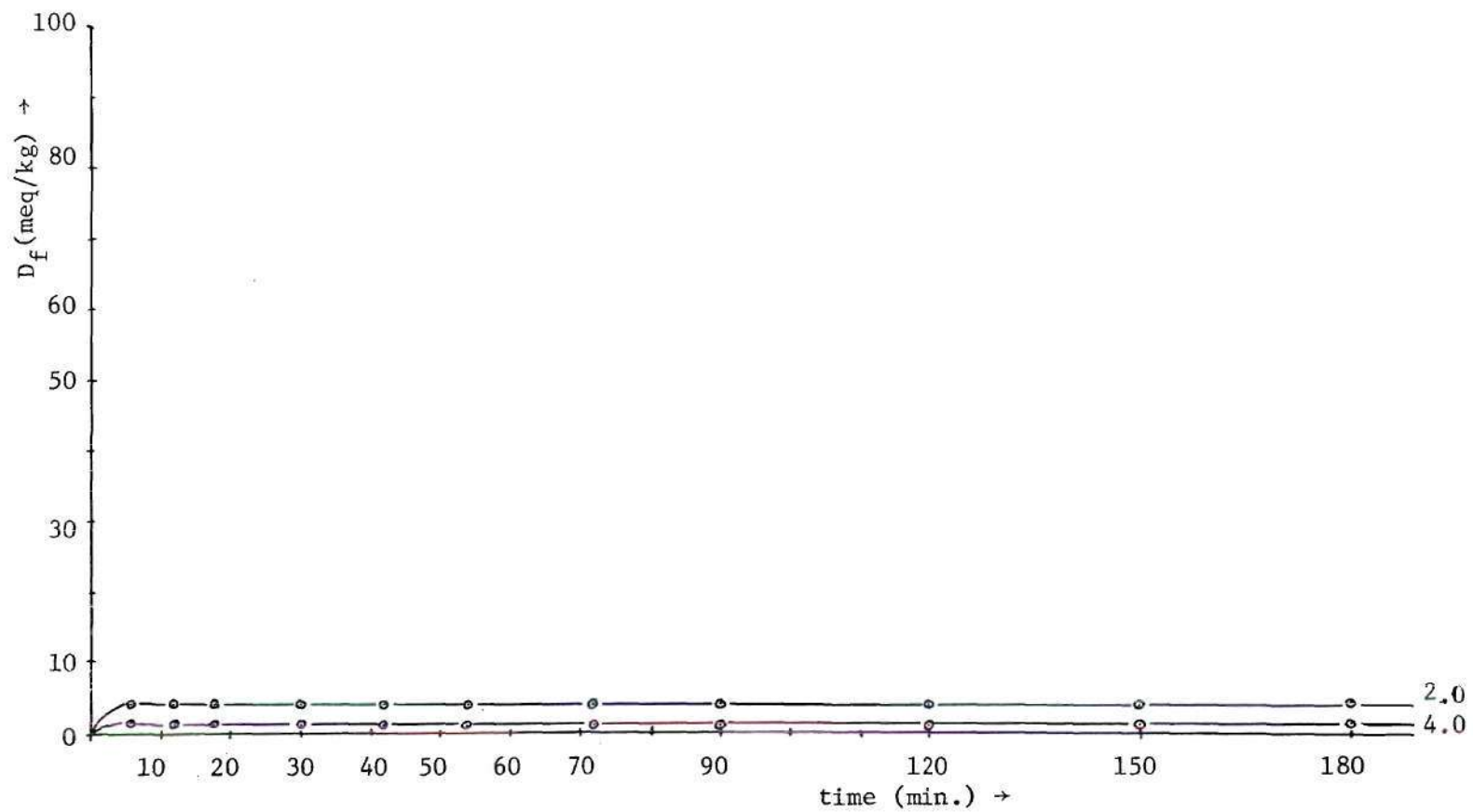


Figure 25. Effect of pH on Rate of Dyeing of Fiber H-2
 $(D_f = \text{dye on fiber})$

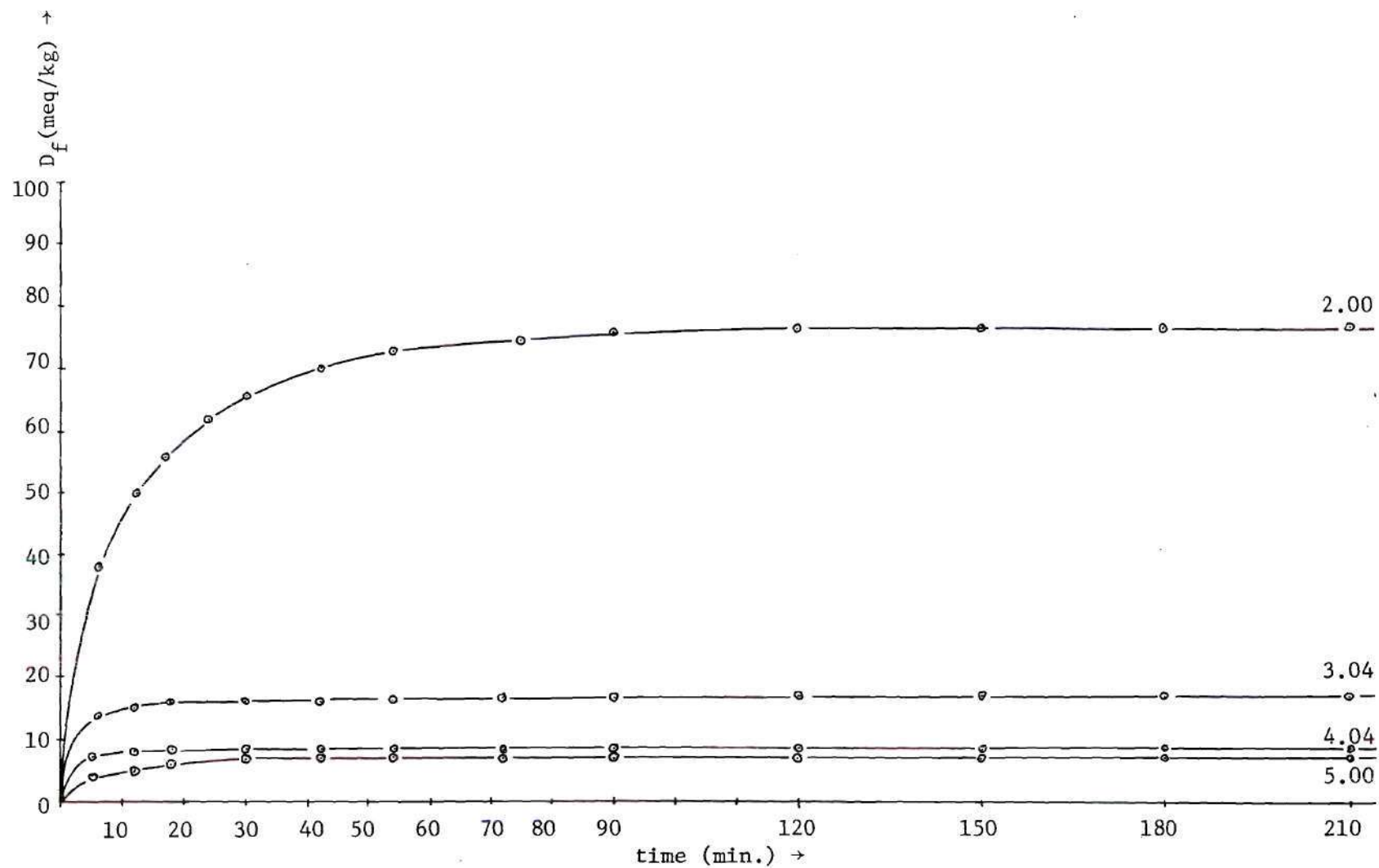


Figure 26. Effect of pH on Rate of Dyeing of Fiber BB-1
(D_f = dye on fiber)

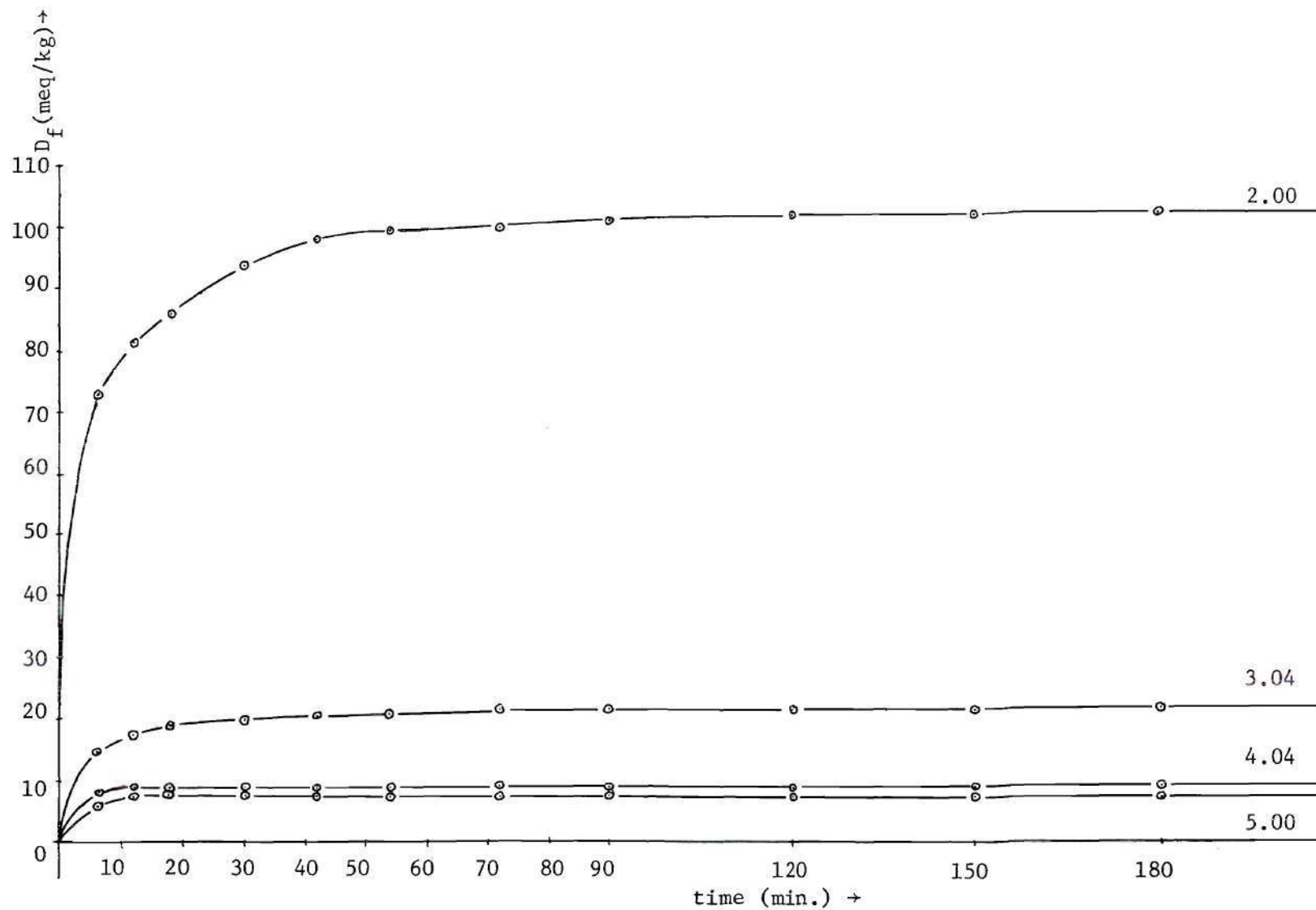


Figure 27. Effect of pH on Rate of Dyeing of Fiber BB-2
(D_f = dye on fiber)

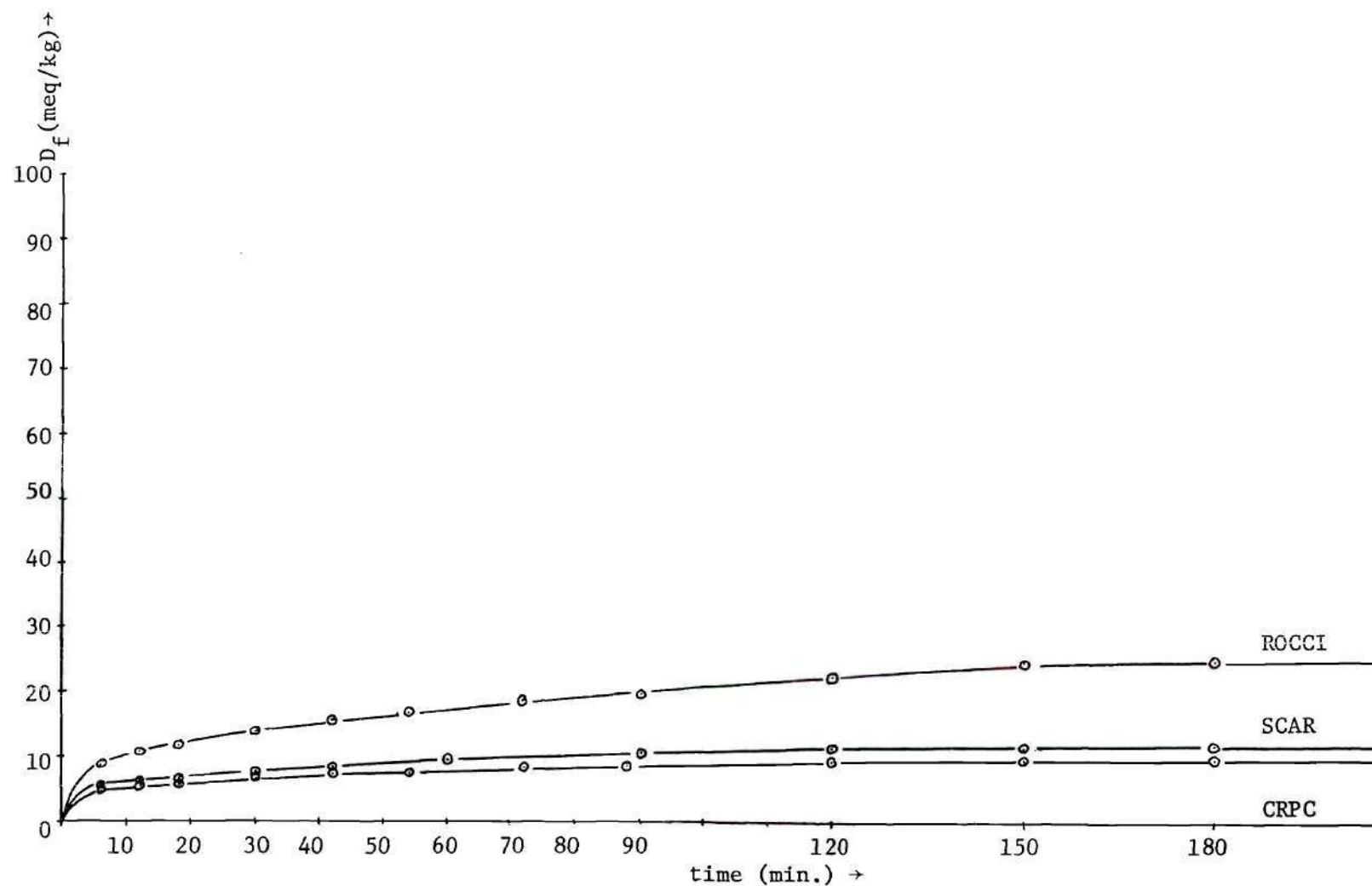


Figure 28. Rates of Dyeing with Roccelline, Croceine 3BX, and Scarlet 4RA on Fiber SDR-1 (ph = 2.00, I = 0.03, T = 95°C, D_f = dye on fiber)

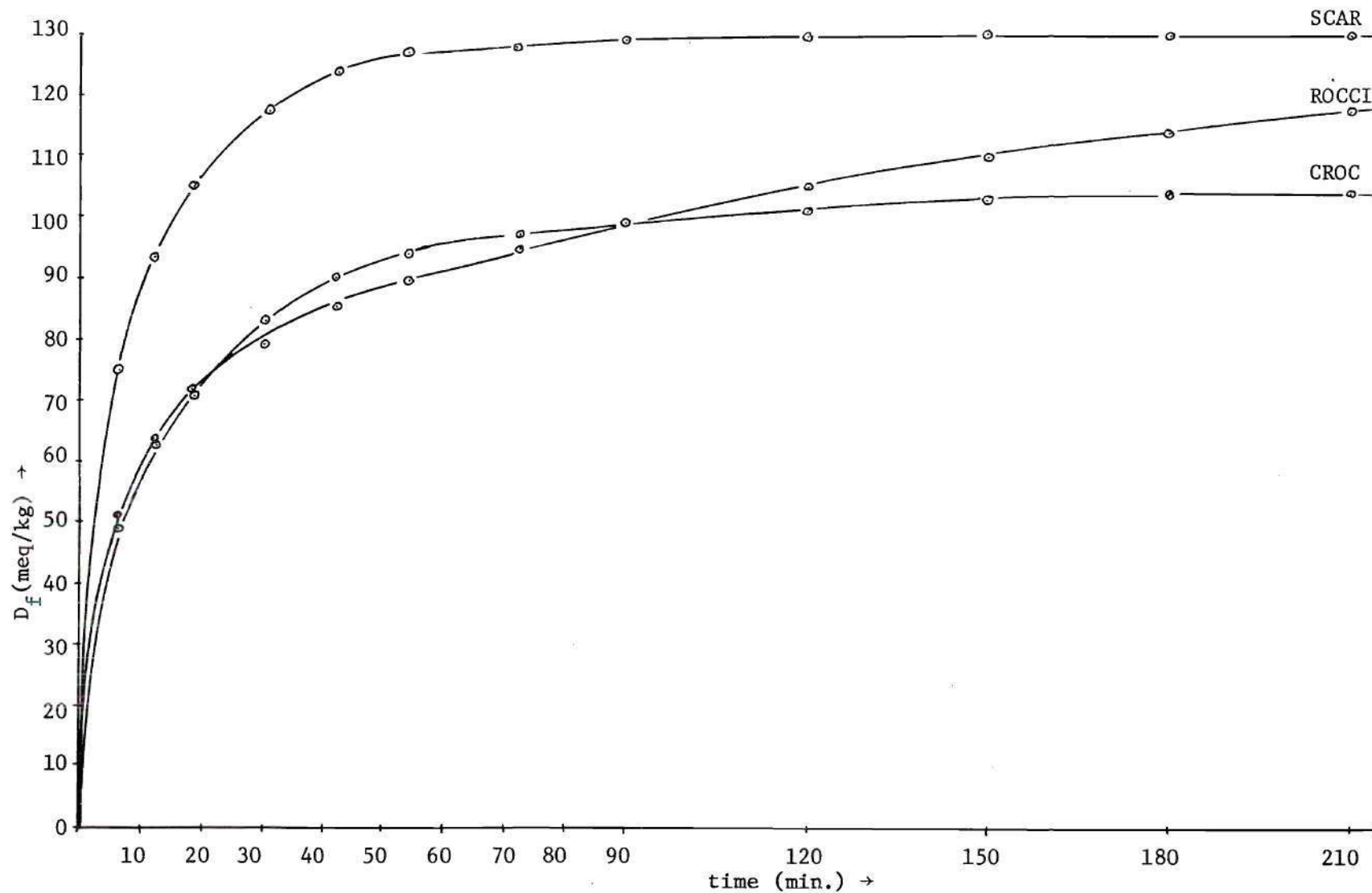


Figure 29. Rates of Dyeing with Roccelline, Croceine 3BX, and Scarlet 4RA on Fiber SDR-2 ($\text{pH} = 2.00$, $I = 0.03$, $T = 95^\circ\text{C}$, D_f = dye on fiber)

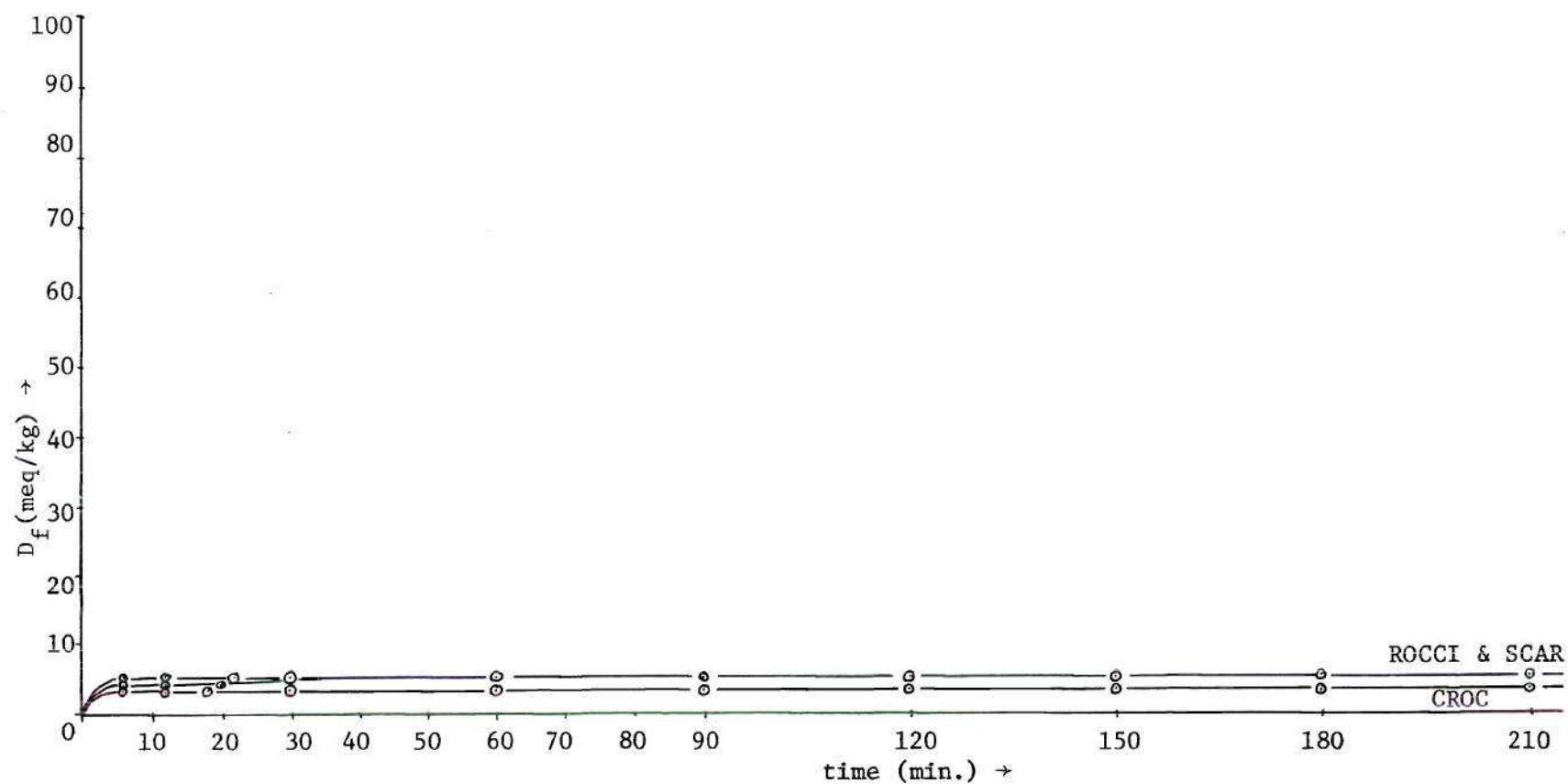


Figure 30. Rates of Dyeing with Roccelline, Croceine 3BX, and Scarlet 4RA on Fiber H-2 ($\text{pH} = 2.00$, $I = 0.03$, $T = 95^\circ\text{C}$, D_f = dye on fiber)

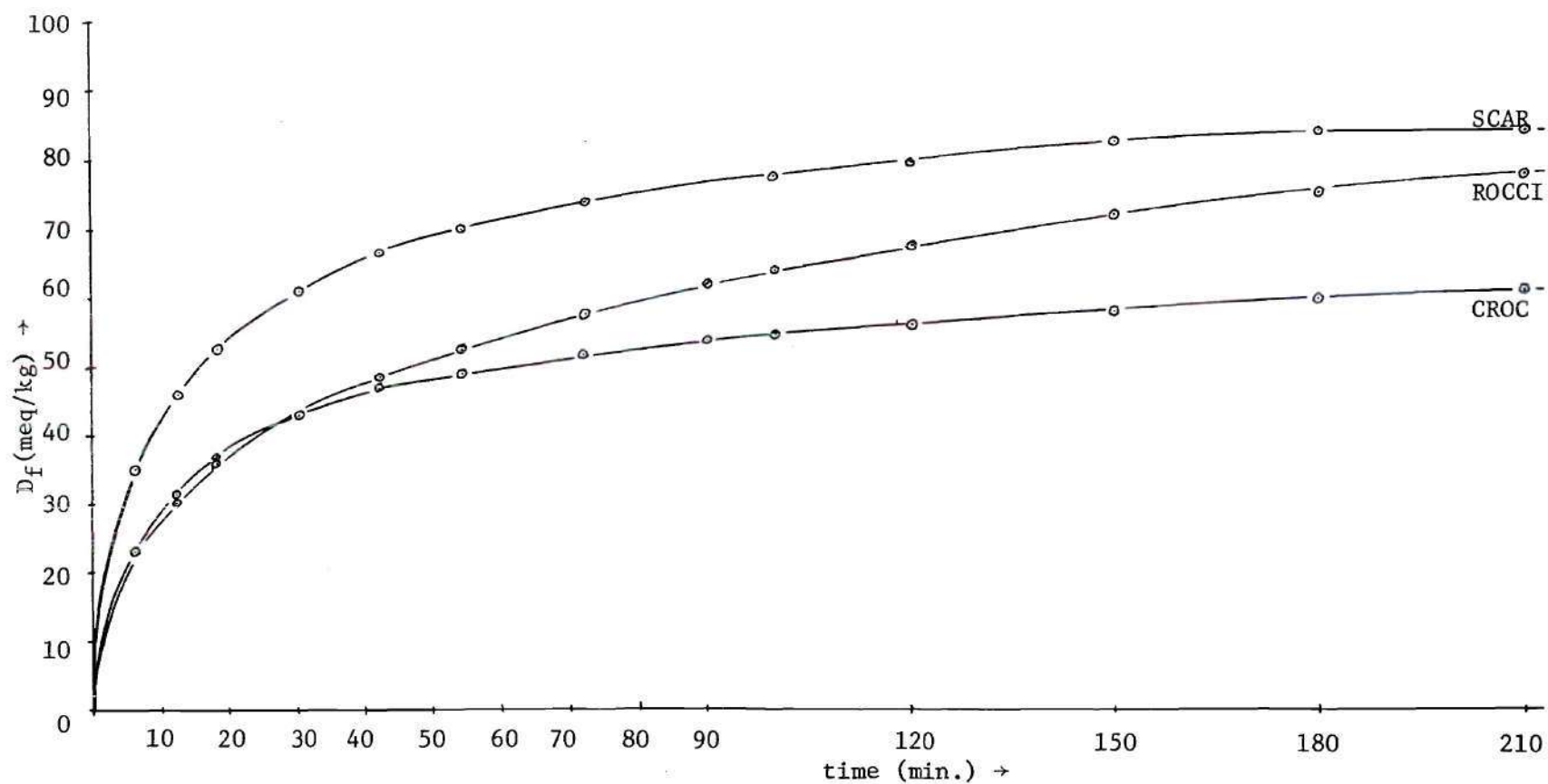


Figure 31. Rates of Dyeing with Roccelline, Croceine 3BX, and Scarlet 4RA on Fiber BB-1 (pH = 2.00, I = 0.03, T = 95°C, D_f = dye on fiber)

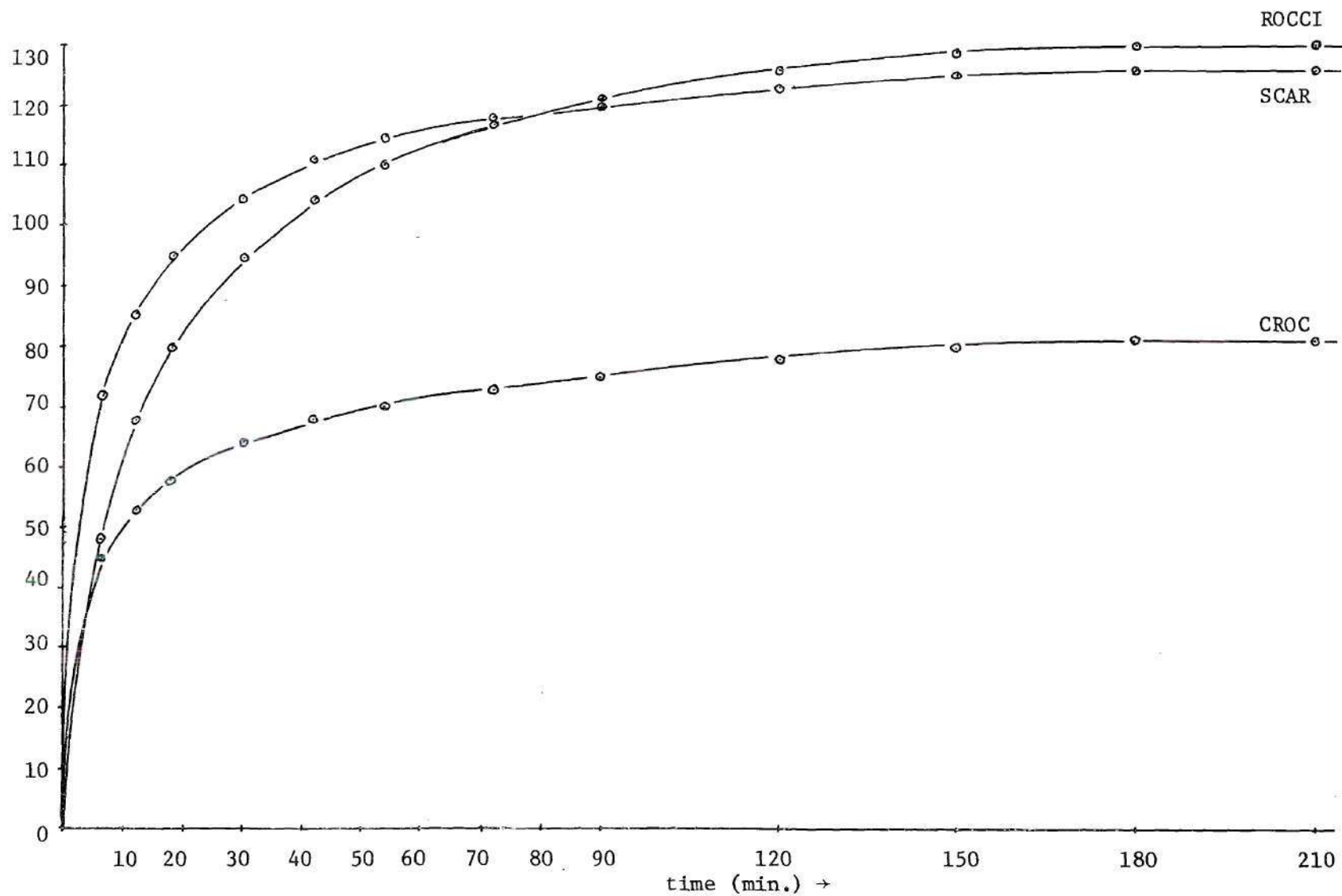
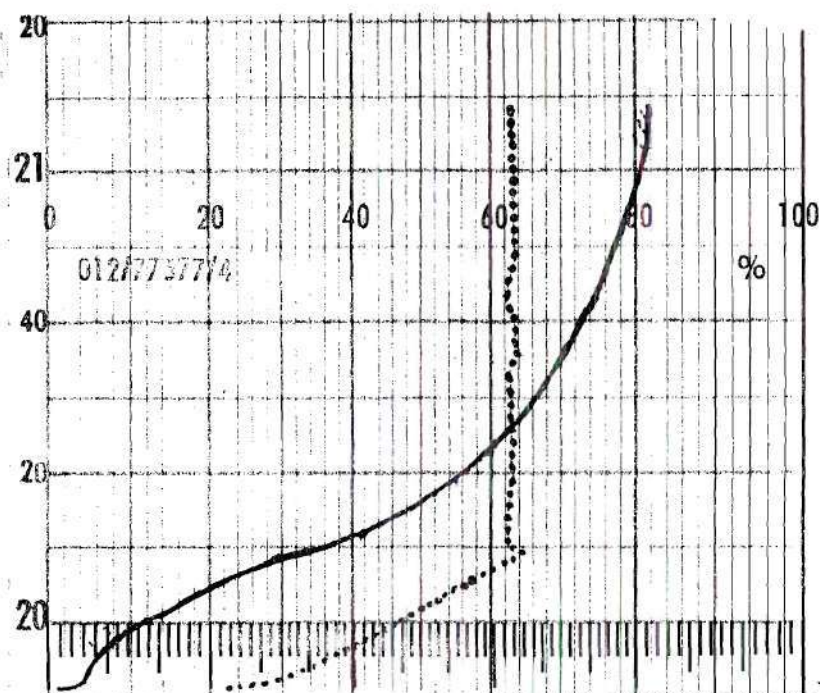
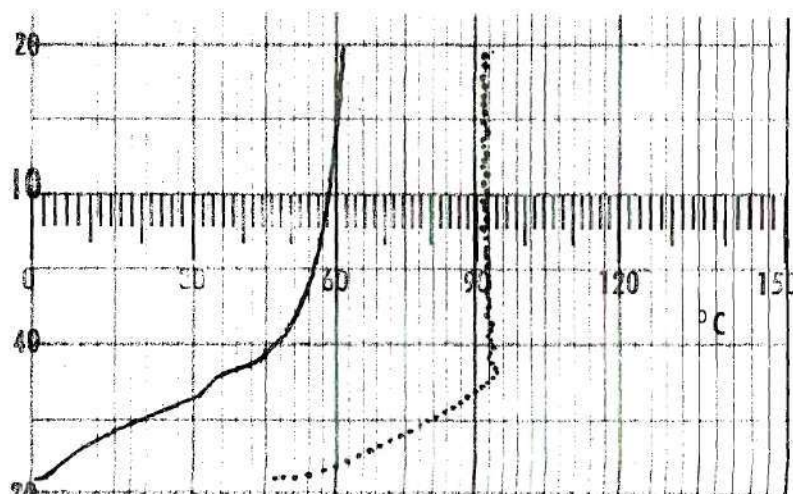


Figure 32. Rates of Dyeing with Roccelline, Croceine 3BX, and Scarlet 4RA on Fiber BB-2 (pH = 2.00, I = 0.03, T = 95°C, D_f = dye on fiber)



Example 1. Orange II on Fiber SDR-2
 Temperature = 93°C
 % Exhaustion = 82%



Example 2. Orange II on Fiber BB-1
 Temperature = 92°C
 % Exhaustion = 41%

Figure 33. Examples of Praxitest Recorder Graph
 (... = temperature; - = % Exhaustion)

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