AVAILABILITY OF AMINE END GROUPS IN NYLON 66 FOR CHEMICAL REACTION

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Herbert Alto Casey

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FOR CHEMICAL REACTION

Approved:

Chairman,

Date approved by Chairman: July 28, 1969

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CHAPTER I

INTRODUCTION

Statement of the Problem

The concentration of amine end groups in polyhexamethylene-adipamide (nylon 66) can be determined by several different analytical methods. The most common methods are based on potentiometric and conductometric titrations of the dissolved polymer with acid. These measurements are in agreement with the amount of acid (anionic) dye absorbed heterogeneously by the fiber at equilibrium. These methods are based on salt formation between the amine group of the polymer and the acid. A method involving covalent bonding employs 1-fluoro-2,4-dinitrobenzene. When the polymer is reacted with this reagent, the extent of reaction depends upon whether the reaction is carried out homogeneously or heterogeneously. The homogeneous reaction values agree with those of the procedures based on a salt formation, but the heterogeneous reaction values are significantly lower, indicating that a portion of the amine ends are tied up in the internal structure of the polymer, and not available for covalent bonding. The purpose of this work is to determine the availability of the amine groups in nylon 66 for covalent bonding with dinitrofluorobenzene both homogeneously and heterogeneously and to compare these values with the amount of acid dye absorbed heterogeneously at equilibrium. In view of the thermal and mechanical treatments to which nylon 66 (fiber form) is subjected, it

was also of interest to determine the changes in both the total amine end groups and their availability for reaction as a function of such treatments.

Nylon 66

Nylon 66 was first studied and developed by Caruthers (1) and is widely produced commercially today. It is obtained by the condensation polymerization of equal molar amounts of hexamethylenediamine and adipic acid (Table 1). This reaction proceeds until a long chain with a molecular weight of 10,000-12,000 has been produced with carboxyl and amine groups in equal numbers at the ends of the polymer chains. However, in the commercial production of nylon 66, a small amount of a monocarboxylic acid is added to control the polymerization, which it does by reacting with amine groups and terminating the growing polymer chains. The amount of acid added is not sufficient to block all the amine groups so that the finished product contains free carboxyl groups, free amine groups, and terminal amide groups (Table 1).

The determination of the concentration of each group present is useful for characterizing the nylon samples with regard to molecular weight, chemical properties, and the extent of equilibrium uptake of anionic dyes. Amine end groups are responsible for the latter as will be shown later.

Titrimetric Determinations

Several procedures for determining the amine end group content by conductometric titration of the dissolved polymer with acid have been developed. They differ in the solvent and acid used. Waltz and Taylor (2)

dissolved the polymer in a solution of phenol, ethanol, and water and titrated with hydrochloric acid. Shaefgen and Flory (3) used m-cresol as a solvent and p-toluene sulfonic acid as the titrant. Basu (4) used a mixture of phenol and small amounts of ethylene glycol as a solvent and titrated with a mixture of perchloric acid, ethylene glycol, and isopropyl alcohol. Wolf and Mobus (5) employed a mixture of m-cresol and isopropyl alcohol as a solvent and perchloric acid in ethanol as a titrant. Peters (6) used the method of Costain in which a mixture of m-cresol, methanol, and carbon tetrachloride was the solvent and hydrochloric acid the titrant.

MacInnes (7) developed a procedure for a potentiometric titration that is rarely used.

These methods give results consistent with dyeing measurements but variances can arise when the polymer samples are contaminated with other materials having acidic or basic properties. Typical interferences are caused by solvent residues in fractionated samples, acidic or basic additives used in polymer modifications, and in the reaction of end groups to form salts in hydrolysis studies and interfacial polymerization (8). For example, Morgan and Kwolek (9) noted that sodium carboxylate ends titrate as amine end groups, and Waltz and Taylor (2) observed that commercially available phenol must be treated with potassium carbonate and distilled to remove an acid impurity and then diluted considerably before titration so as to provide less chance of ambiguity in the interpretation of the titration curves.

They also proposed the theory behind these titrations. They stated that the mobility of the polymer molecules in solution is low

enough to be negligible. Until the equivalence point is reached, the addition of hydrochloric acid adds the moderately mobile chloride ion to the solution, and the conductance increases slightly in a linear manner. After passing the equivalence point, the addition of hydrochloric acid adds both the chloride ion and the highly mobile hydrogen ion to the solution, so the conductance increases sharply in a linear fashion. The intersection of the two straight lines is the equivalence point of the reaction. Typical titration curves are shown in Figure 1.

Acid Dyeing of Nylon 66

Because of superior fastness properties, acid dyes are normally used for dyeing nylon 66. Acid dyes are alkali salts of aromatic sulphonic acids which ionize in solution, with the organic component forming the anion (Table 2).

The mechanism of acid dyeing has been thoroughly studied and is generally agreed on. Palmer (10) proposed that the amount of dye that can be absorbed depends upon the pH of the dyebath (Figure 2), the number of amine end groups in the fiber, and the degree of order of the fiber.

Commercial dyeings are carried out in the pH range above three. Elod and Schachowsky (11) first studied the mechanism of acid dye absorption and their work was later clarified by Peters (6) and others (12,13). In this pH range, the nylon will combine with the carboxyl or amine groups and bring in an equivalent amount of dye anions to maintain electrical neutrality. These dye anions will orient near the terminal amine groups of the nylon as these are the only positively charged groups present and a weak salt linkage will be formed. A stoichiometric relation-

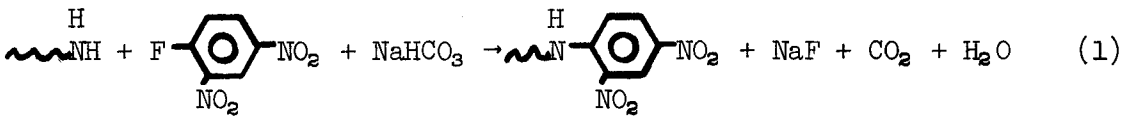
ship has been established between the amount of dye anions absorbed and the amine cations in the fiber. Since the amine content of nylon is limited, a saturation value for dye uptake is reached.

There are several sources of error in this method for amine end group determination. Peters (6) proposed that at pH values below three, the absorption increases with decreasing pH values. He attributed this to hydrogen ions being absorbed by the weakly basic amide groups and being accompanied by an equivalent number of dye anions to maintain electrical neutrality. The variance in the saturation values for different dyes was first studied by McGrew and Schneider (12). They attributed the saturation values below normal to the steric difficulty of fitting a polysulphonated dye molecule to the fiber so that all potential ionic links could be formed. Saturation values greater than normal or overdyeing were attributed by Atherton, Downey, and Peters (13) to high dye concentrations in the dyebath.

Dinitrofluorobenzene Determinations

The use of 1-fluoro-2,4-dinitrobenzene (DNFB) in determining amine ends was introduced by Sanger (14). He applied this method to the identification and estimation of free amine groups in polypeptides. The majority of his work was done with insulin.

Zahn and Rathgeber (15) first used this method for determining amine ends in nylon samples. They used an ethanolic solution of DNFB in an elaborate procedure for the heterogeneous determination of amine end groups in nylon 6 in a basic reaction medium. They proposed that a covalent bond was formed between the amine ends and DNFB as follows:



(1)

Yoshida, Nishio, and Hisazomi (16) later simplified this method and Shimizu and Miyaoka (17,18,19) combined these two with modifications in which they used ethanol for the reaction medium and dissolved the DNFB amine group conjugate with formic acid and measured the spectrum.

Garmon and Gibson (8) developed a method for reacting nylon 66 homogeneously with DNFB by dissolving the sample under reflux in an ethanolic solution of lithium bromide. They noted that the rate of reaction is dependent upon water content, the rate increasing with increasing water content up to approximately 15 percent by weight, and upon pH, with low results being obtained when the pH is adjusted from the basic side with sodium bicarbonate.

The values for the homogeneous and heterogeneous reaction differ significantly, lower results being obtained for the heterogeneous reaction. This will be discussed later.

Table 1. End Groups of Nylon 66

(1) $$n\ \underset{H}{HN}-(CH_2)_6-\underset{H}{NH} + n\ HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \underset{-H_2O}{\rightleftarrows} H\left[\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH$$

hexamethylenediamine + adipic acid nylon 66

(2) $$\sim\overset{H}{N}-H + HO-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftarrows \sim\underset{H}{N}-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O$$

nylon 66 + acetic acid terminal amide group

(3)

Group		Typical Concentration in Nylon 66
a. Carboxyl	$-\overset{O}{\overset{\|}{C}}-OH$	0.090 eq/kg
b. Amine	$-\overset{H}{N}H$	0.036 eq/kg
c. Terminal Amide	$-\overset{H}{N}-\underset{O}{\underset{\|}{C}}-CH_3$	0.063 eq/kg

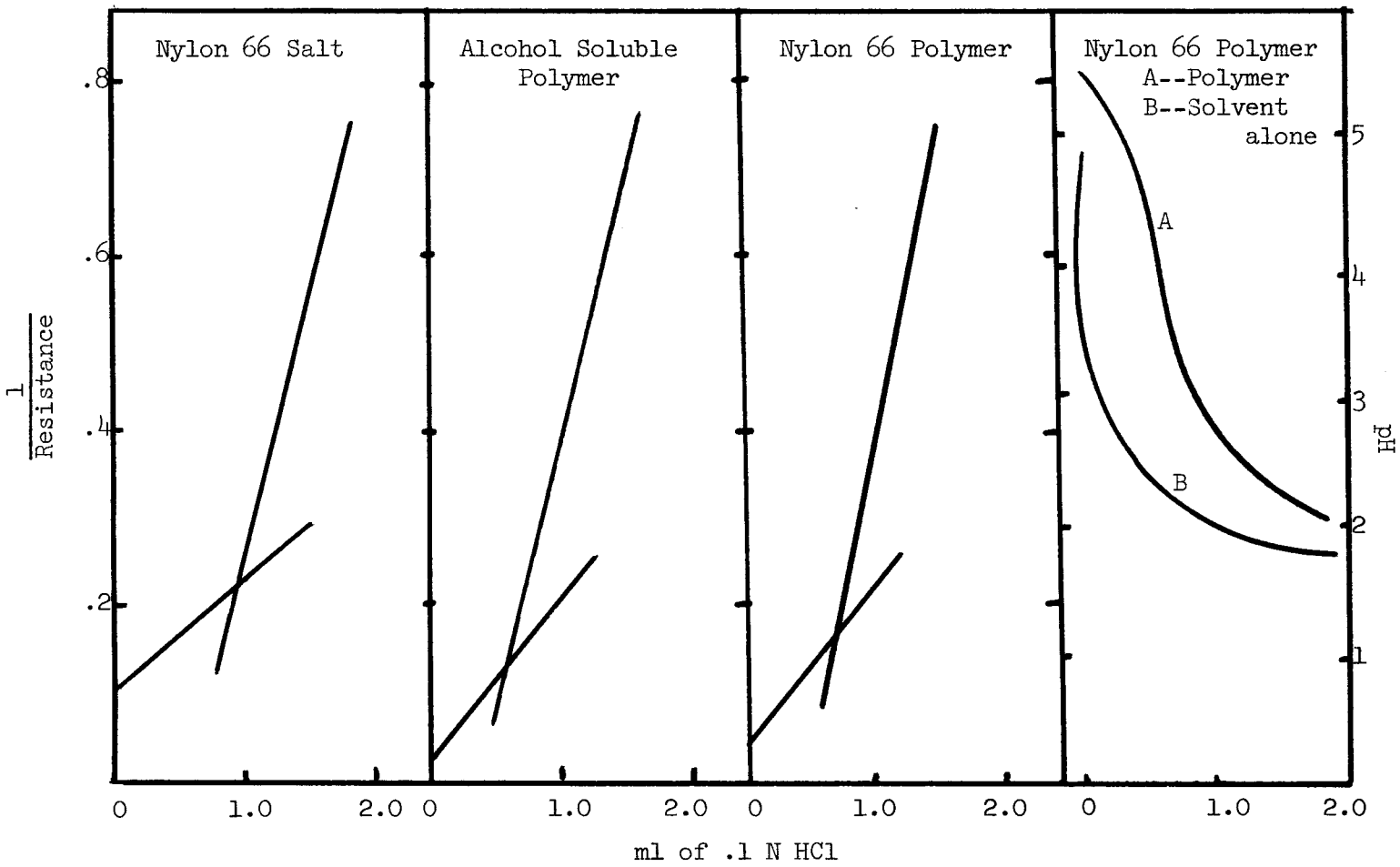
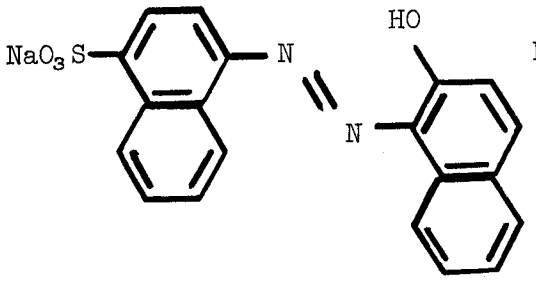
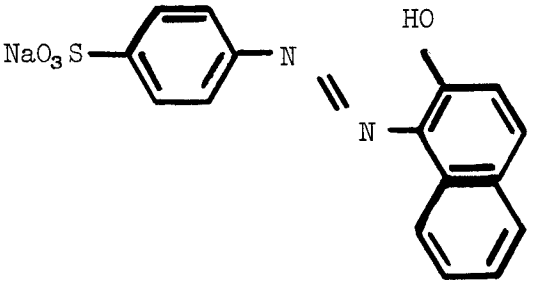


Figure 1. Typical Conductometric Titration Curves (2)

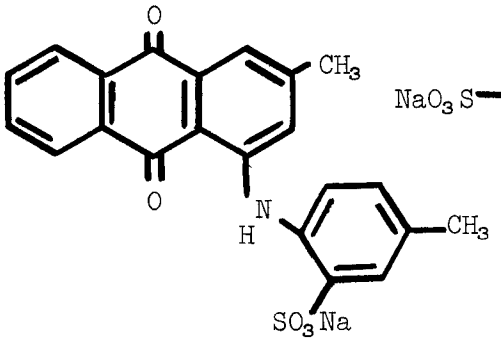
Table 2. Acid Dye Structures



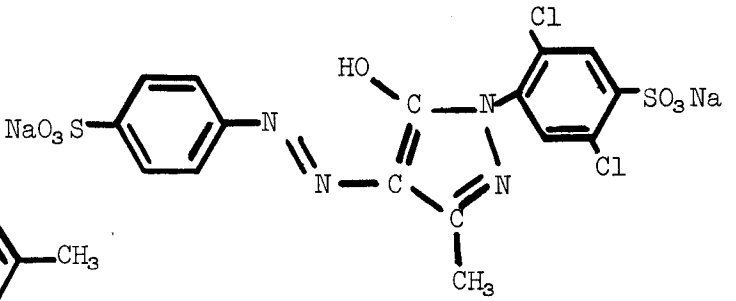
Acid Red 88(C.I. 15620)



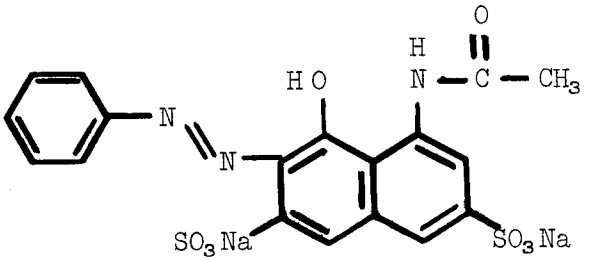
Acid Orange 7(C.I. 15510)



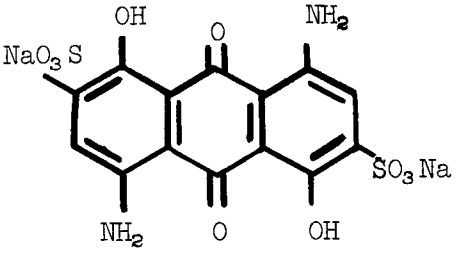
Acid Blue 47(C.I. 62085)



Acid Yellow 17(C.I. 18965)



Acid Red 1(C.I. 18050)



Acid Blue 45(C.I. 63010)

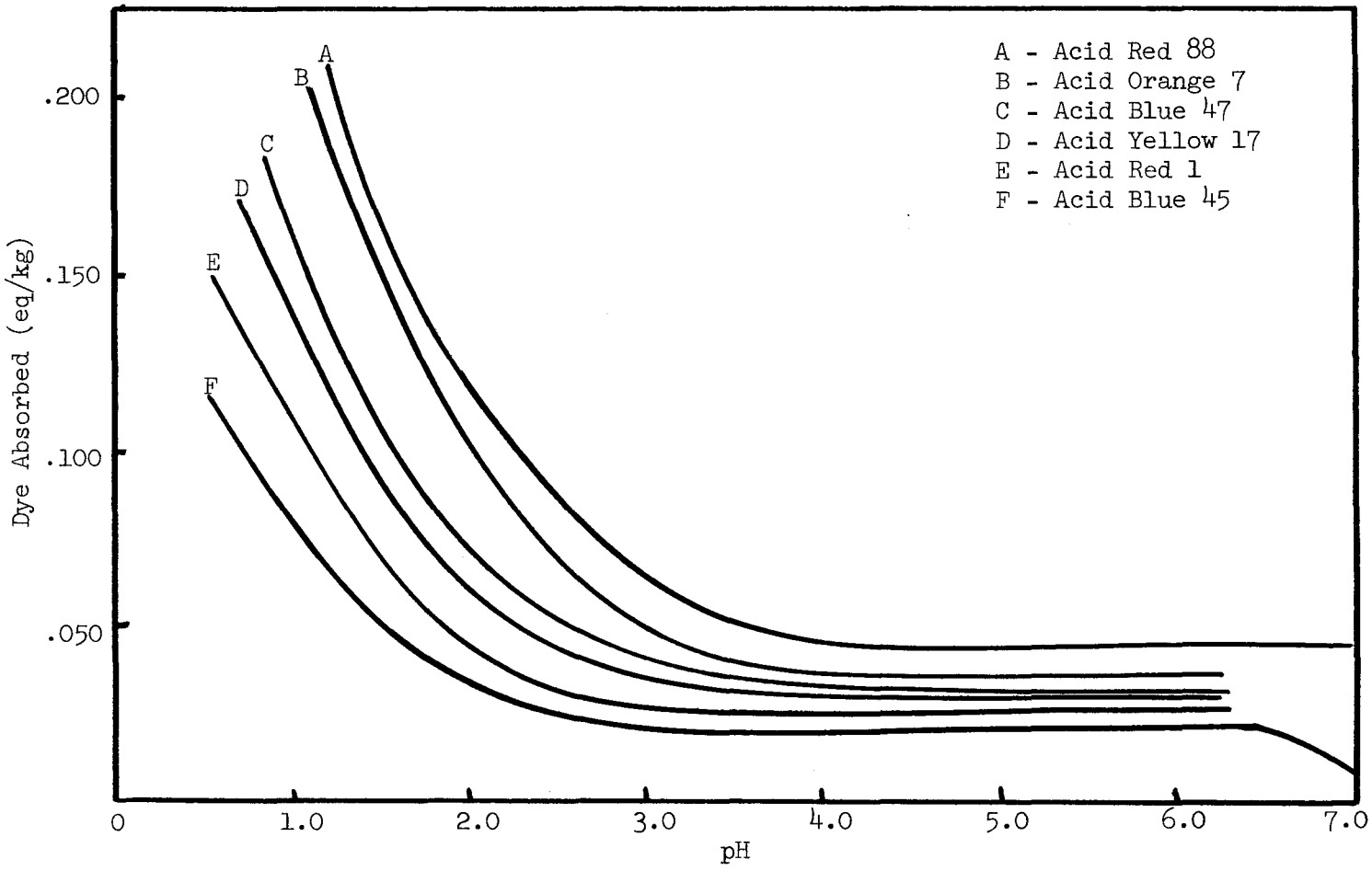


Figure 2. Variation of Equilibrium Dye Uptake with Changes in pH (6)

Review of the Literature

The stoichiometry of the acid dyeing of nylon has been studied by several workers. Peters (6) used a monosulphonated and a disulphonated acid dye and compared his results favorably with values obtained from the titrimetric method of Costain. McGrew and Schneider (12) used ten monosulphonated and disulphonated acid dyes and compared their results favorably with titrimetric values from the method of Waltz and Taylor (2). They also studied deviations from normal values and attributed low saturation values to steric hindrances involved with polysulfonated dyes. Atherton, Downey, and Peters (13) used 14 monosulphonated, disulphonated, and trisulphonated acid dyes for their work and obtained good agreement with titrimetric values from the method of Waltz and Taylor (2). They studied abnormally high saturation values or overdyeing and attributed this to high dye concentrations in the dyebath.

Munden and Palmer (20) used a disulphonated and a tetrasulphonated acid dye to study the effects of varying degrees of orientation on dye uptake. They concluded that cold drawing significantly lowered the diffusion coefficient but does not appreciably alter the equilibrium dye uptake.

Zahn and Rathgeber (15) compared their method for the heterogeneous determinations of amine groups in nylon 6 with DNFB with the amount of mineral acid absorbed heterogeneously by nylon 6 and found the values from the DNFB method to be significantly lower. They also found that dry heating the nylon 6 significantly lowered the values of the DNFB method.

Shimizu and Miyaoka (17,18,19) studied the effects of varying

crystallinity and orientation by dry heating, steam heating, and cold drawing on amine values obtained by equilibrium dye uptake of a disulphonated acid dye and heterogeneous DNFB determination. In all cases they found that values from the DNFB method were significantly lower than those of equilibrium dye uptake. They proposed that this was because some amine groups were tied up in the internal structure of the fiber and were not available for forming a covalent bond with the DNFB. However, they found that most of these amine groups were available for forming an ionic salt linkage with the dye. Generally, the DNFB values were 80 percent of the equilibrium dyeing values. They found that cold drawing decreased the diffusion coefficient of the dye, slightly increased the equilibrium dye uptake, and increased the DNFB values. The cause for this was attributed to an increase in orientation with the crystallinity remaining constant. Steam heating increased the diffusion coefficient, decreased equilibrium dye uptake, and decreased DNFB values. This was attributed to an increase in crystallinity with a decrease in orientation. Dry heating decreased the diffusion coefficient, equilibrium dye uptake, and DNFB values. This was attributed to an increase in crystallinity with orientation remaining constant. They also compared equilibrium dye uptake and titrimetric values obtained by the method of Shaefgen and Flory (3) and found the dyeing values to be significantly lower. They attributed this to crystalline regions occluding some amine groups.

Garmon and Gibson (8) used their method for the homogeneous determination of amine groups by DNFB for analyzing nylon 66 samples and compared their results favorably with titrimetric values from the method of

Waltz and Taylor (2). They also found that 83 percent of the amine ends reacted with DNFB heterogeneously (21).

From an extensive survey of the literature, there is no record of a direct comparison between the heterogeneous absorption of acid dyes by nylon 66 and both the heterogeneous and homogeneous reactions of nylon 66 with DNFB. Also, no study has been done on the effects of thermal and mechanical treatments on the homogeneous and heterogeneous DNFB reactions with nylon 66.

CHAPTER II

INSTRUMENTATION AND CHEMICALS

Absorbance measurements were made in 1.000 cm silica cells using a Beckman DB-G grating spectrophotometer in conjunction with a Beckman ten inch laboratory recorder. A magni-whirl constant temperature water bath provided the heat for the reaction and a Burrell wrist-action shaker provided continuous agitation of the samples. Weighings were made on a Mettler analytical balance.

A steaming device was made from a six inch section of heavy duty stainless steel pipe with caps on both ends. A safety valve and a pressure gauge were attached to one cap by means of a T-joint. All joints were sealed with a pipe sealing compound to make the chamber pressure tight.

The Instron tensile tester was used for stretching the nylon samples. Sonic vibration treatments were made on the ultrasonic cleaner (model G120-25 generator, heating tank model 2100-A-5, and lead zirconate transducer) produced by National Ultrasonic Corporation.

1-Fluoro-2,4-dinitrobenzene was obtained from Eastman Organic Chemicals and recrystallized from the melt. Liquid DNFB was placed in an Erlenmeyer flask and cooled until about 75 percent of the material had crystallized. The crystals were filtered on a coarse fritted glass filter, washed with absolute ethanol, air dried, and stored in a refrigerator. A DNFB reagent solution was made by dissolving 1.00 gram of DNFB in approximately seven ml of 95 percent ethanol and diluting to 10.0 ml

with distilled water.

Lithium bromide, granular, N.F., was obtained from Fisher Scientific and dried 24 hours at 110°C under vacuum. A lithium bromide reagent solution was made by dissolving 60.0 grams of lithium bromide in 300.0 ml of 95 percent ethanol and 18.0 ml of distilled water under reflux. The solution was allowed to stand overnight and was decanted from the solid residue that remained.

Fisher formic acid, 90 percent, and Baker sodium bicarbonate, 100 percent, were used.

Kiton Red 2G (Acid Red 1), 79 percent purity, was used for the dyeing measurements.

CHAPTER III

PROCEDURES

Preparation of Nylon 66 Samples

Conditioning

Undrawn nylon 66 film having a nominal thickness of 0.005 inch was obtained from The Polymer Corporation of Pennsylvania. To remove any impurities and to prevent any crystallization under reaction conditions, the samples were boiled for one hour in a solution of 0.50 gpl of Na_2CO_3, thoroughly rinsed with distilled water, and dried in a vacuum oven at 45°C. The samples were placed in a desiccator containing a H_2SO_4 solution which was adjusted to give a relative humidity of 55 percent (22) (approximately the relative humidity of the room).

Steam Heating

Steam heating of the nylon samples was performed in the steaming device described in the previous chapter. Nylon samples were placed in a test tube which in turn was placed in the steam chamber in the presence of 100 ml of distilled water. The steam chamber was lowered into a constant temperature bath. The safety valve was left open until steam was steadily produced and then closed for the specified time. Steam treatments were carried out for one hour at bath temperatures of 110°C, 120°C, and 130°C with pressures of 8, 12, and 20 psi, respectively. The samples were then dried and conditioned.

Cold Drawing

Cold drawing of the nylon film was performed on the Instron ten-

sile tester. One-half inch wide samples were used with a gauge length of one inch and a cross head (stretching) speed of one-half inch per minute. Samples with a draw ratio of 1.56, 2.19, and 2.28 were prepared. Samples with a higher draw ratio could not be prepared because of slippage of the sample in the jaws of the clamp. The draw ratio was determined by weighing one-half inch lengths of the drawn and undrawn samples and calculated as follows:

$$\text{Draw Ratio} = \frac{\text{Weight Undrawn Sample}}{\text{Weight Drawn Sample}} \qquad (2)$$

Sonic Vibration Treatment

Samples of undrawn nylon were treated in the ultrasonic cleaner at an average power of 125 watts and a frequency of 25 kilocycles per second for ten minutes at a bath temperature of 60°C. The samples were run in two media, toluene and water. Homogeneous and heterogeneous DNFB reactions were run on both types of samples after complete removal of the toluene and water followed by conditioning.

Reaction of Nylon 66 with DNFB

Homogeneous Reaction

The homogeneous reaction of DNFB with nylon 66 was described by Garmon and Gibson (8). The procedure was modified to fit the sample size used in this work and is given below:

> Weigh 0.0625 g of nylon film and place in a 25 ml volumetric flask containing 7.5 ml of lithium bromide reagent solution. Attach the flask to a water cooled condenser and reflux on a

small glass cloth heating mantel until the sample is completely dissolved. Add 0.75 ml of 0.05 N aqueous hydrochloric acid to the sample through the condenser and allow the solution to reflux an additional minute to ensure mixing and then remove from the heat. When the solution ceases to reflux, remove the condenser, add 0.5 ml of DNFB reagent solution, using a micropipet, and 0.075 to 0.125 g of solid sodium bicarbonate. Swirl gently to mix and immerse in a constant temperature bath at 80°C for 45 minutes. Agitate the samples continuously with a mechanical agitator. Before removing the sample from the bath, add 2.5 ml of formic acid. Cool the flask and dilute to volume (25 ml) with formic acid. Measure the absorbance of the sample at 440 mμ versus a reagent blank prepared in the same manner, omitting the nylon.

The choice of 440 mμ for absorbance measurements was a compromise between sensitivity and magnitude of the absorbance of the reagent blank as shown in Figure 4.

Heterogeneous Reaction

The heterogeneous reaction procedure is similar to the homogeneous reaction procedure with the differences given below:

Use 95 percent ethanol for the reaction medium. Add the DNFB and $NaHCO_3$ but omit the HCl. Allow the reaction to proceed for four hours at 80°C with constant agitation. After four hours, add 10 ml of formic acid to the flask and allow the flask to remain in the bath for ten additional minutes or until the nylon is completely dissolved. Dilutions and

measurements are made as in the homogeneous reaction procedure.

Equilibrium Dyeing

The procedure for the equilibrium dyeing measurements was described by Bell (23). Kiton Red 2G (Acid Red 1), 79 percent purity, was used at a concentration of 0.75 gpl with a 40:1 liquor ratio (ratio of volume of bath to weight of substrate). The pH was adjusted to 3.2 with formic acid. Nylon film was the substrate. The dyeings were carried out at 100°C under reflux for a minimum of five hours to ensure reaching equilibrium. The spectrum of the dyebath was taken before and after dyeing on a solution diluted 1:50 with distilled water. The absorbance at 530 mμ was used in calculations as can be seen from the spectrum for Acid Red 1 as shown in Figure 5.

CHAPTER IV

DISCUSSION OF RESULTS

The rates of the DNFB reaction with nylon, both homogeneously and heterogeneously, were studied to establish the point at which the reaction was complete. Reactions were carried out for various times as shown in Figure 3. From these curves, times for the reaction were chosen so that the reaction always reached completion. Forty-five minutes for the homogeneous reaction and four hours for the heterogeneous reaction were used throughout this work.

The conversion of absorbance measurements obtained using the DNFB method to equivalents per kilogram of polymer was made utilizing the molar absorptivity of carbon-14 labeled DNFB amine group conjugates as determined by Garmon and Gibson (8). Equations for this conversion as well as that of the equilibrium dyeing method are given in Table 3.

Homogeneous and heterogeneous DNFB measurements were made on all samples and equilibrium dyeing measurements were made on samples of the undrawn control, the samples steam heated at 130°C, and the samples drawn to a draw ratio of 2.28. The results are shown in Table 4.

The data were statistically analyzed by a randomized blocks method (24) as shown in Tables 5, 6, 7, and 8. The treatments represent different states of the nylon film and are shown as numbered in Table 4. The blocks represent identical reactions run on a particular treatment and each piece of datum represents the average of three absorbance measurements made on the sample. More data were obtained for the control

samples than the treated samples so a random number table was used to select control data for analysis.

The homogeneous DNFB method showed no significant difference between treatments. The equilibrium dyeing measurements also showed no significant difference between treated samples. Further, the homogeneous DNFB method and the equilibrium dyeing measurements are in excellent agreement.

The heterogeneous DNFB method, on the other hand, showed significant differences between treatments and between blocks. The latter was attributed to the chance of extreme values falling in the same block rather than being completely random and this was considered insignificant. Generally, steam heating lowered the extent of reaction with DNFB and gave results significantly different from the control at the 99 percent confidence level. Increasing the severity of the steam heating treatment produced much smaller effects with only the first and third treatments being significantly different from each other and this at the 98 percent confidence level. Cold drawing increased the extent of reaction with DNFB with a draw ratio of 1.56 differing from the control at the 95 percent confidence level and draw ratios of 2.19 and 2.28 differing at the 99 percent confidence level. Increasing the draw ratio produced smaller effects as they differed from each other at only the 95 percent confidence level. Too few of the sonically vibrated samples were run to do a statistical analysis, but they showed a tendency to increase greatly the extent of reaction.

Several samples were reacted with DNFB heterogeneously and then dyed heterogeneously to determine if the amine groups not available for

covalent bonding with DNFB were available for salt formation with the dye molecule. It was found that these unreacted groups do act as dye sites. Thus, the sum of the extent of the heterogeneous DNFB reaction (0.0328 eq/kg) and the dye absorption (0.0079 eq/kg) is 0.0407 eq/kg and is in good agreement with both the homogeneous DNFB reaction (0.0397 eq/kg) and the dye absorption (0.0396 eq/kg). These data are shown in Table 4.

If one assumes the dimensions of an average crystallite in undrawn nylon (50 Å x 50 Å x 50 Å), the percent crystallinity of undrawn nylon 66 (~ 40 percent) (25), and the density of crystalline nylon 66 (1.24 g/cm^3) (26), the average number of amine end groups unavailable for covalent bonding per crystallite can be calculated. The value obtained is 1.6 amine groups per crystallite. From the dimensions of a unit cell of the α form of nylon 66 (α = 17.2 Å, β = 5.4 Å, γ = 4.9 Å) (27), it can be estimated that an average crystallite contains approximately 400 unit cells. Thus, these 400 unit cells have an average of only 1.6 amine groups occluded by the crystallite.

To obtain an idea of the probability of a salt linkage forming between the dye anion and the charged amine group occluded by the crystallite, the magnitude of the energy required to move the dye anion through a water medium from an infinite distance away from the amine group to 3.0 Å away (the sum of the radii of a charged oxygen atom of the sulfonate group of the dye and that of the charged amine group of the polymer) was calculated using a form of Coulomb's law as follows:

$$\Delta E = \frac{e(-e)}{Dr} \qquad (3)$$

where ΔE is the energy change, e is the primary electric charge, D is the dielectric constant of water, and r is the distance between charges. The change in energy was calculated as -1.42 kcal/mole. Assuming the occluded amine groups are an average of 12.5 Å away from the edge of the crystallite, the energy required to move the dye anion from an infinite distance away to this distance was calculated as -.34 kcal/mole or a difference of -1.08 kcal/mole. The heat of reaction of acid dyeing is of the order of -9.1 kcal/mole (28). Therefore, if the heat of dyeings were determined for the dyeing of the available amine groups and of the occluded amine groups, the difference between these two values should be -1.08 kcal/mole providing the occluded amine groups were located at the average distance assumed. Thus, it is not surprising that the acid dye is absorbed by nylon 66 stoichiometrically even though some of the amine end groups are occluded by the crystalline portion of the polymer.

Sources of Error

Constant agitation of the DNFB reaction flasks was necessary to produce similar rates of reaction so that completion of the reaction was always reached in the specified time. However, too vigorous agitation gave inconsistent results with the homogeneous reaction by splashing portions of the dissolved polymer into the neck of the flask where it was not available for reaction.

Garmon and Gibson (8) added HCl to the homogeneous reaction to neutralize any LiOH which may have been present, as low results were obtained when the pH was adjusted from the basic side with sodium bicarbonate.

Nylon samples are induced to crystallize by hot water treatment (19), and this effect has been the cause for the low reaction temperatures of previous heterogeneous DNFB methods. In order to use a reaction temperature of 80°C, the samples were conditioned by boiling for one hour. Since these conditions are harsher than any encountered in the reaction, it was assumed that the reaction temperature induced no further crystallization.

Some previous procedures have used ground nylon as samples. Since this work was to study the effects of crystallinity on amine group availability, nylon samples were used in the form of a film. It was feared that grinding would have altered the physical structure of the polymer.

CHAPTER V

CONCLUSIONS

For the scope of the treatments used in this work, the total number of amine groups in nylon 66 remained constant. These amine groups are equally available for homogeneous reaction with DNFB and heterogeneous dye absorption. This indicates that no polymer degradation, which results in amine group formation or loss, occurred.

However, a significant portion of the amine groups (~ 17 percent) was not available for heterogeneous reaction with DNFB. The fraction of unavailable amine groups changes with various treatments of the nylon. Steam heating reduced the availability, cold drawing increased the availability, and sonic vibration of the sample resulted in an increase in their availability. As shown by Shimizu and Miyaoka (17,19), the unavailability was due to the occlusion of the end groups in the crystalline regions of the polymer, and the changes in availability were due to changes in orientation and crystallinity.

The amine groups unavailable for reaction in the heterogeneous DNFB method are quantitatively available for acting as dye sites. It may be concluded that crystallites occlude some amine groups so that covalent linkages with DNFB are impossible; however, the occluded amine groups can form salt linkages with the dye.

Calculations of the magnitude of the energies of interaction of the dye anion with both available and occluded amine end groups indicate

that stoichiometry between the amount of dye absorbed and the total amine end groups present should be obtained even though some of the end groups are occluded by the crystallites of the polymer. This is in agreement with the results obtained in this work and that of others (6,12,13).

CHAPTER VI

RECOMMENDATIONS

Only low draw ratios were obtained for this work. The effect of higher draw ratios on the availability of amine groups should be an interesting study.

The effect of dry heating of nylon 66 was not studied. This could be done by heating the nylon samples in an inert atmosphere so that no oxidation of the polymer will occur.

It would be interesting to develop a treatment that would increase the availability of amine groups to 100 percent and study any effects of such treatments on the physical properties of the polymer. Sonic vibration of the polymer showed a definite tendency in this direction, and it is possible that more severe treatments would produce this effect.

A study of the kinetics of the DNFB amine group reaction should be made.

An intriguing study would be to determine experimentally the difference in the heats of dyeing between available and occluded amine groups and determine if this corresponds to the differences calculated theoretically. This could be done by dyeing nylon 66 samples at levels below 83 percent of saturation and at saturation and determining the heats of dyeing by a desorption method. Precise technique would be necessary since small differences in small quantities are being measured.

From this difference, the approximate location of the occluded amine groups could be determined.

APPENDIX

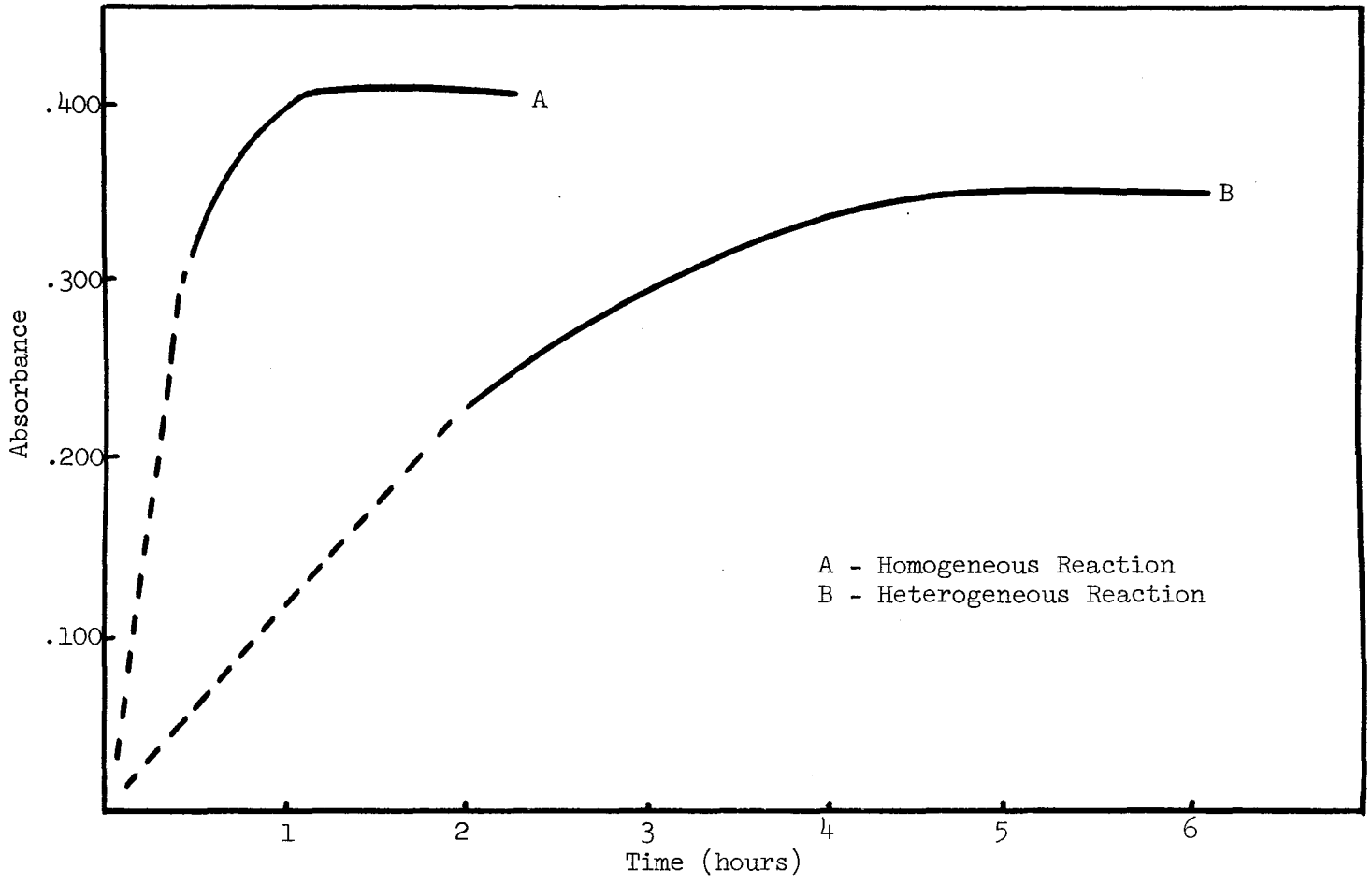


Figure 3. Extent of Reaction Curves for DNFB Reactions

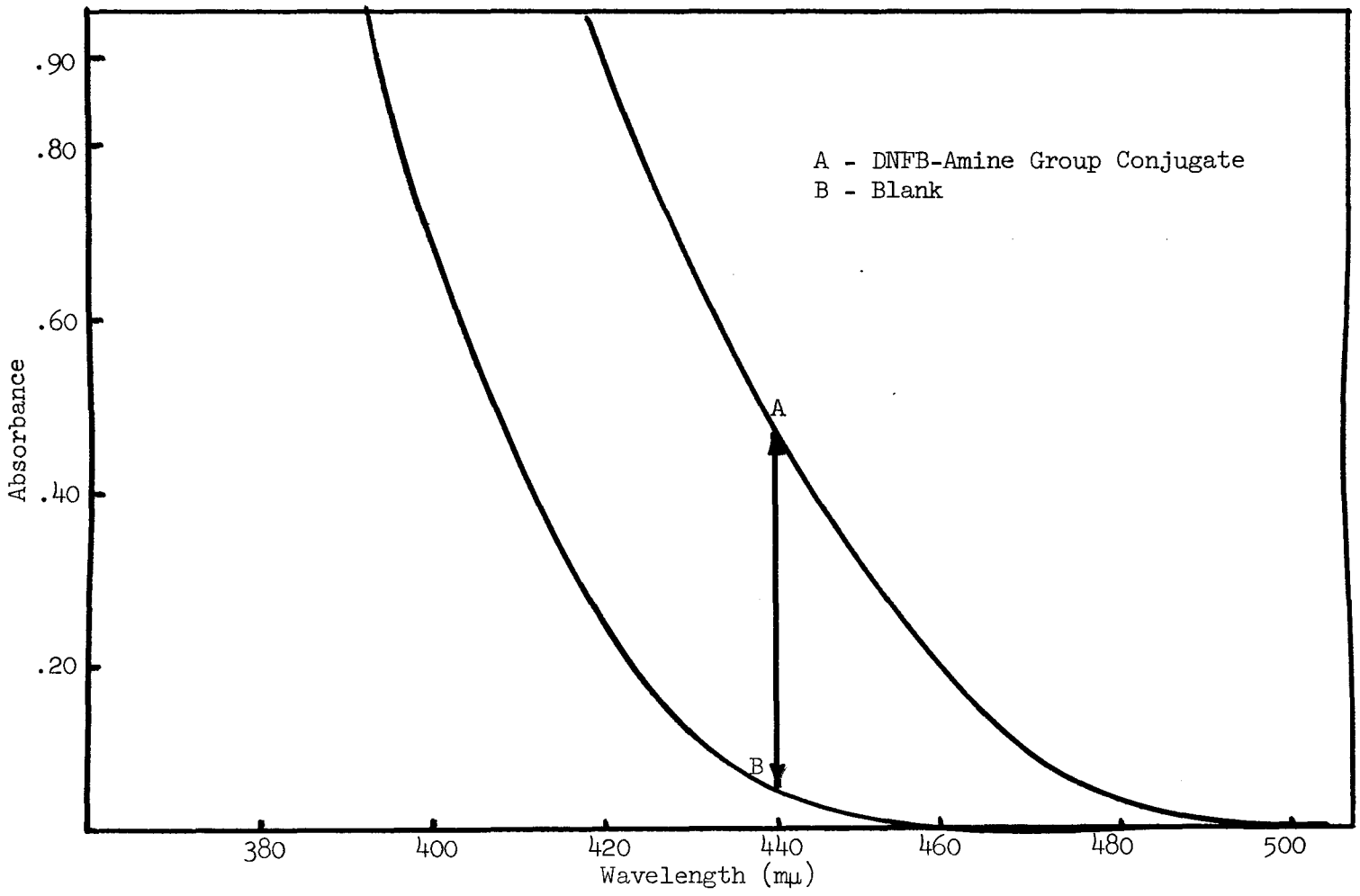


Figure 4. DNFB-Amine Group Conjugate Spectrum

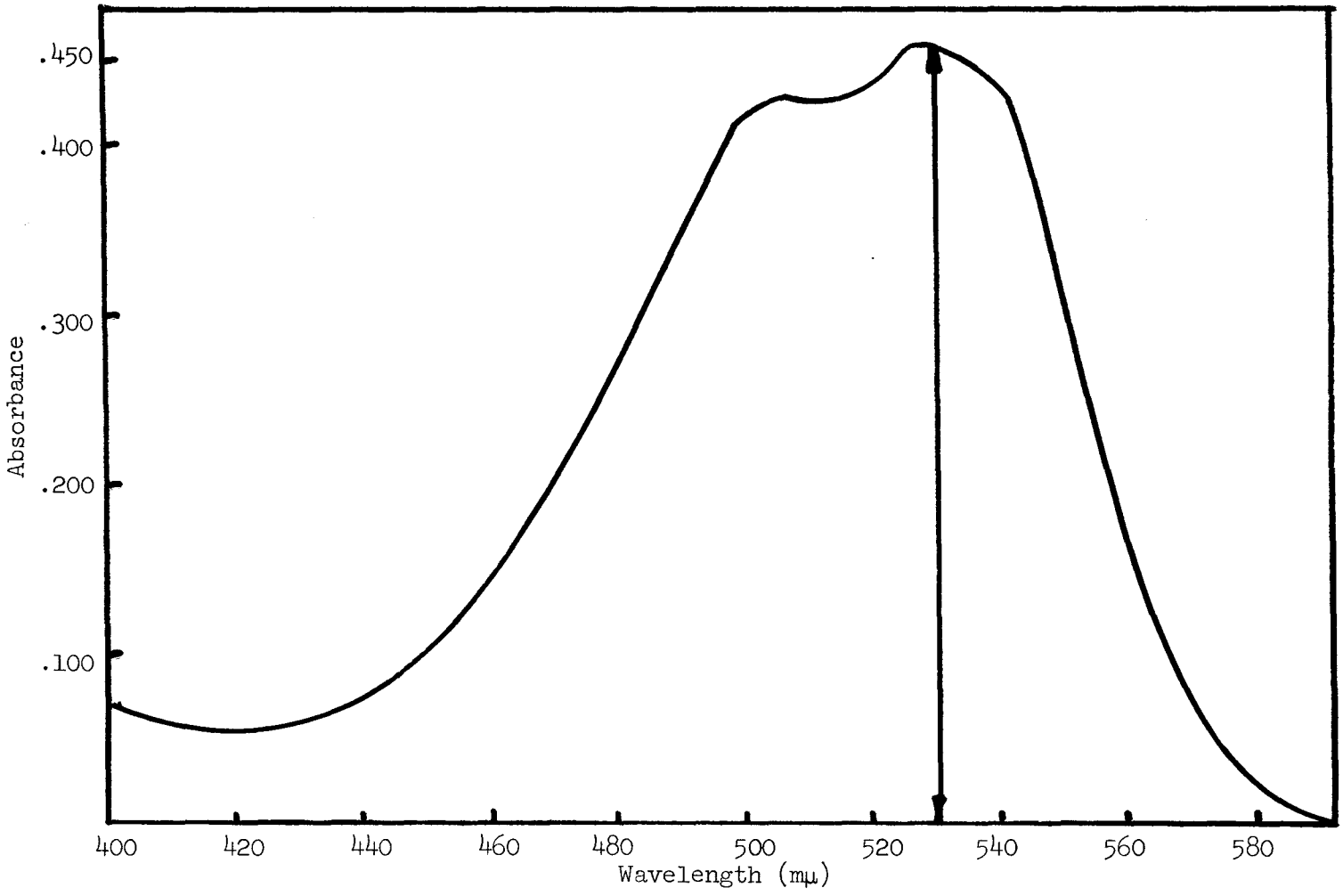


Figure 5. Spectrum of Acid Red 1

Table 3. Calculations

(1) DNFB Method

A = Absorbance at 440 mμ

V = Volume of solution (ℓ)

W = Weight of sample (kg)

ε = Molar absorptivity = 4081 ℓ $cm^{-1} mole^{-1}$

$$\text{Equivalents per kilogram} = \frac{A \times V}{\epsilon \times W}$$

(2) Equilibrium Dyeing Method

A = Absorbance at 530 mμ

P = Purity of dye = 79%

C = Concentration of dyebath = .750 gpl

V = Volume of dyebath (ℓ) = .08 ℓ

W = Sample weight (kg) = .002 kg

E = Equivalent weight of dye = 254.5 eq/kg

$$\text{Equivalents per kilogram} = \frac{P \times C \times V}{E \times W}\left[1 - \frac{A_{\text{dyed soln}}}{A_{\text{original soln}}}\right]$$

Table 4. Experimental Results

Treatment	Homogeneous DNFB eq/kg	Heterogeneous DNFB eq/kg	Equilibrium Dye Uptake eq/kg	DNFB Het. / DNFB Homo.
1. Control	.0397	.0328	.0396	.828
Standard Deviation(σ)	.0005	.0005	.0009	
2. Steamed 110°C	.0403	.0309		.767
(σ)	.0004	.0006		
3. Steamed 120°C	.0397	.0306		.771
(σ)	.0003	.0006		
4. Steamed 130°C	.0400	.0304	.0389	.760
(σ)	.0005	.0006	.0011	
5. Draw Ratio 1.56	.0398	.0333		.837
(σ)	.0004	.0005		
6. Draw Ratio 2.19	.0402	.0338		.841
(σ)	.0003	.0005		
7. Draw Ratio 2.28	.0396	.0342	.0405	.868
(σ)	.0003	.0005	.0010	
8. Sonically vibrated				
toluene	.0402	.0354		.881
water	.0400	.0350		.875
9. DNFB Het. and Dyeing			.0079	

Table 5. Statistical Analysis of Homogeneous DNFB Method

Blocks	Treatments 1	2	3	4	5	6	7
1	.0407	.0404	.0393	.0400	.0394	.0402	.0396
2	.0395	.0397	.0397	.0392	.0400	.0407	.0393
3	.0402	.0405	.0401	.0401	.0403	.0397	.0401
4	.0389	.0408	.0398	.0396	.0396	.0403	.0395

Source	df	Sum of Squares	Mean Square
Blocks	r-1	$SS_B = \frac{1}{v} \Sigma B_i^2 - CF$	$MS_B = SS_B/(r-1)$
Treatments	v-1	$SS_T = \frac{1}{r} \Sigma T_j^2 - CF$	$MS_T = SS_T/(v-1)$
Error	(r-1)(v-1)	$SS_E = SS_{To} - SS_B - SS_T$	$MS_E = SS_E/(r-1)(v-1)$
Total	(vr-1	$SS_{To} = \Sigma y^2 - CF$	

$$CF = (\Sigma y)^2/vr$$

Source	df	SS	MS	F	F 95% Confidence Level	Statistical Difference
Blocks	3	6×10^{-7}	2.00×10^{-7}	.7353	8.68	NO
Treatments	6	14×10^{-7}	2.33×10^{-7}	.8566	3.89	NO
Error	18	49×10^{-7}	2.72×10^{-7}			
Total	27	69×10^{-7}				

Table 6. Statistical Analysis of Heterogeneous DNFB Method

Blocks	Treatments 1	2	3	4	5	6	7
1	.0331	.0305	.0305	.0302	.0328	.0339	.0342
2	.0330	.0314	.0310	.0311	.0334	.0344	.0346
3	.0324	.0309	.0315	.0298	.0331	.0347	.0339
4	.0329	.0320	.0309	.0314	.0325	.0338	.0352
5	.0328	.0307	.0299	.0293	.0334	.0332	.0341
6	.0322	.0299	.0296	.0303	.0339	.0329	.0333
7	.0330	.0312	.0303	.0299	.0343	.0338	.0344
8	.0335	.0315	.0307	.0308	.0335	.0334	.0338
9	.0326	.0302	.0312	.0302	.0328	.0342	.0348
10	.0328	.0309	.0306	.0306	.0335	.0337	.0342

Source	df	SS	MS	F	F 95% Confidence Level	Statistical Difference
Blocks	9	58×10^{-7}	6.44×10^{-7}	2.556	2.05	Yes
Treatments	6	1586×10^{-7}	264.3×10^{-7}	104.881	2.27	Yes
Error	54	136×10^{-7}	2.52×10^{-7}			
Total	69	1780×10^{-7}				

Table 7. Analysis of Treatment Differences in the Heterogeneous DNFB Method Using the t Test

$$t = \frac{T_i - T_j}{\sqrt{\frac{2}{r} MS_E}}$$

Comparison	t	Confidence Level of Difference
$T_1 : T_2$	8.51	99%
$T_1 : T_3$	9.80	99%
$T_1 : T_4$	11.00	99%
$T_2 : T_3$	1.34	< 90%
$T_2 : T_4$	2.49	98%
$T_3 : T_4$	1.16	< 90%
$T_1 : T_5$	2.18	95%
$T_1 : T_6$	4.32	99%
$T_1 : T_7$	6.24	99%
$T_5 : T_6$	2.14	95%
$T_5 : T_7$	4.14	99%
$T_6 : T_7$	2.00	95%

Table 8. Statistical Analysis of Equilibrium Dyeing Method

Blocks	Treatments 1	4	7	A
1	.0400	.0385	.0408	.0407
2	.0408	.0376	.0391	.0395
3	.0391	.0405	.0418	.0402
4	.0385	.0391	.0403	.0389

Treatment A is the homogeneous DNFB value for the control.

Source	df	SS	MS	F	F 95% Confidence Level	Statistical Difference
Blocks	3	42×10^{-7}	14.0×10^{-7}	1.3462	3.86	NO
Treatment	3	52×10^{-7}	17.3×10^{-7}	1.6635	3.86	NO
Error	9	94×10^{-7}				
Total	15	188×10^{-7}				

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