A STUDY OF THE DYEING
OF WOOL PRETREATED TO PRODUCE
CONTRAST EFFECTS

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A STUDY OF THE DYEING
OF WOOL PRETREATED TO PRODUCE
CONTRAST EFFECTS

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"For, in reality, the knowledge of an effect is nothing else than the acquisition of more perfect knowledge of its cause."

SPINOZA
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Many attempts have been made to produce designs in textiles by altering the dyeing characteristics of fibers to obtain different color effects from the same dyebath. A new method (devised in the laboratory of the A. French Textile School) of producing such dyeings by pretreating wool to cause one group of fibers to absorb less dye and another group to absorb more dye, was further investigated.

The first part of this work was devoted to experimental dyeings for the purpose of acquiring the technique of the process and examining the methods in order to evaluate and improve them. The particular factors examined were: resist agents; pretreatment media; dyebath concentrations; and pH, time and temperature effects. In the second part of the work an attempt was made to explain the role of three of the components of the dyebath (the resist agent and two dyestuffs) during an actual contrast-effect dyeing.

This second phase of the work was effected by removing samples from a dyebath at frequent intervals during dyeing, and examining these spectrophotometrically. The results obtained, when combined with spectrophotometric data on each component from solutions of known concentrations, yielded estimates of the concentrations of each component at each stage of the dyeing. The mathematical operations involved were facilitated by the use of an electronic computer.

The knowledge gained in the experimental dyeings and in the study of the changes in the concentrations of the components during dyeing
was used to evolve a tentative theory of the role of each of the components studied in the contrast-effect dyeing. Detailed instructions for effecting the desired results are included.

The factors which are believed to be most important to the success of this method of dyeing are the relative affinities of the resist agent and of the dyestuffs used; these contribute most to satisfactory contrast. However, other aspects of the method, such as the chemical nature of the pretreating agent, the method of pretreatment, and the variables usually controlled in any successful dyeing -- dyebath ratio (volume of dyebath to weight of fibers being dyed), pH, concentration of dyestuffs, etc. -- also contribute to the overall success of the method. The effects of some of these variables are pointed out.

The difficulties involved when attempts are made to describe colors and color differences have been partially overcome by the inclusion, in this work, of a color photograph, which shows how the colors of two samples, dyed in the same bath at the same time, change with both time and temperature.

Although in most of the work reported here both of the dyed samples were pretreated, a method in which only one sample need be treated is proposed.

It is concluded that the dyeing method investigated in this work is an effective means for obtaining contrast effects in wool dyeing from one dyebath. The path which is judged most promising for future work is pointed out.
CHAPTER I

INTRODUCTION

Of the many ways of introducing color into textile designs, one of the most interesting is by dyeing fabrics constructed of fibers and yarns having different dyeing characteristics.

Background.—Wool has probably been studied more widely than any other fiber, and the theory of wool dyeing is no doubt the most well founded dyeing theory in existence. It is, therefore, natural that attempts have been made to alter wool in order to obtain new dyeing characteristics.

Some of the attempted methods, of which Hartley, Wood, and Lund (1) list nine, have been successful, and thousands of pieces have already been dyed in England by the chlorinated wool method. The usual methods of approach to the problem have been (a) to change the fiber structure to make it more, or less, accessible to dyestuffs, or (b) to chemically alter the number of dye sites to increase, or decrease, the total dyeing capacity of the wool (2).

A method developed by Davis (3) has many possibilities and also has the advantage of giving negligible loss in fiber strength. The most fascinating aspect of this method is that it was developed solely on the basis of wool dyeing theory.

Objectives.—The basic objectives of this work were to gain a more thorough
knowledge of the method of producing contrast effects which was devised
by Davis, to explain the dyeing mechanism of the process, and to expand
and improve the method.

Method.—The method of attack in this work was first, to explore the
pretreatment methods, the dyebath preparations, and the dyeing conditions
used by Davis in obtaining contrast effects; and second, to analyze a
typical process involving all of the elements of a contrast-effect dye-
ing.

The first part of the work consisted of several series of dyeings
which were carried out in order to study the many variables involved in
pretreatment, dyebath preparation, and dyeing conditions. The second
part was pursued by performing a typical contrast-effect dyeing and con-
ducting spectrophotometric examinations in order to determine the changes
in the concentrations of the dyebath components as the dyeing progressed.
CHAPTER II

EVOLUTION OF THE ENDEAVOR

Initial Study of the Dyeing Methods

The first part of this work was devoted to various exploratory dyeings for the purpose of developing the technique of producing contrast effects in wool dyeing and improving the methods of obtaining such effects. The methods developed by Davis \( h \) formed the basis of this work. Some of the variables which affect the pretreatment and dyeing results were investigated, as was the use of several different agents for pretreatment.

Since it appeared that the resist agent used in the pretreatment was a very important factor in determining the degree of contrast obtained in dyeing, one of the first objectives was to compare the effectiveness of several different agents. Dyeings under different dyeing conditions were made on samples pretreated with each of the resist agents. To further investigate the efficacy of the resist agents, dyeings were also conducted on samples pretreated with higher concentrations of the agents present in the pretreatment baths.

On the basis of certain dyeing results the belief was held that satisfactory contrast effects could be obtained by treating only one sample, and dyeing in the same dyebath with an untreated sample of wool. It also appeared that acids other than phenol and phosphoric could be used successfully in the pretreatment bath. Dyeings were carried out in order to verify these theories.
The results of preliminary dyeings indicated the need for a change in terminology from that used by Davis (5). The general term "Contrast Effect Method I" was considered more appropriate than the two terms "Preferred Method for Obtaining Two-Color Effects" and "Preferred Method for Obtaining Two-Tone Effects," since either method could be used to produce either type of contrast effect, depending on the dyeing conditions used. It also seemed that the title "Contrast Effect Method I" should be applied only to the dyebath preparation, rather than to the entire dyeing process, since different dyeing conditions in the same dyebath result in different color effects.

Time did not permit a systematic investigation of the effects of changes in the percentage of dye in the dyebath, the relative amounts of the two dyes, and the dyebath volume in relation to the fiber. However, these variables were surveyed to obtain an indication of their general effects and to gain a better understanding of the dyeing process. The effect of pH on the process was studied in much the same manner.

All of the initial dyeings which were carried out contributed to a better understanding and control of the over-all contrast effect process.

Investigation of the Dyeing Process

The prime objective of this work was to gain a more complete understanding of the mechanism of the acid dyeing process involved in producing contrast effects by the method being studied. It was believed that, in order to do this, the changes in the concentrations of the contrast-producing dyebath as the dyeing proceeds, must be known. The Concentration Determination Section of Chapter IV is concerned with how this knowledge was gained.
Preliminary Considerations.—Determinations of dyebath concentrations by measuring the light absorption of colored solutions depend on several considerations. These will be discussed in this section, and the methods which were used in this work to insure compliance with these conditions will be described in the next section.

The accuracy of concentration measurements on one substance in solution depends on the validity of Beer's law and of Lambert's law for the solution and for the method used in measuring the concentration. Statements of Beer's law and of Lambert's law, and the derivation of the basic formula used in spectrophotometric work from these two laws as performed by Vickerstaff (6), are contained in the Derivation of Formula in the Appendix.

The validity of Beer's and of Lambert's laws in concentration measurements depends on two primary considerations:

1. Truly monochromatic light must be used and must pass through a solution of an exactly known thickness.

2. There must be no change in the chemical or physical nature of the colored substance with changes in concentration in the solution.

The second consideration depends, in turn, on two conditions for water soluble dyes:

1. The component must not change color in aqueous solution with changes in pH. Dye color in an aqueous solution is often dependent on pH.

2. Changes in the condition of the dye must not take place during dilution due to either a change in the degree of aggregation or dissociation of the dye molecules.
The above factors must be taken into account for each dyebath component individually, since the accuracy of calculation of concentration from optical density readings for a particular dye depends on the compliance of the dye with these factors.

The terms absorbency and optical density, which are used in spectrophotometric work, both refer to the same thing, the logarithm of 100 over the per cent transmission. If the absorbency is divided by the concentration of the solution in grams per liter, the resulting value is the absorptivity. If the absorbency is divided by the concentration in mols per liter, the result is the extinction coefficient (7). At a given wavelength the ratio between two extinction coefficient gives a measure of the relative strength of absorption of light by two dyes.

Complex dye mixtures may be analyzed with the aid of plots of optical density versus wavelength, and the relative strengths determined (8). However, in dye solutions of more than one component there are additional considerations involved (9):

1. Interaction of dyes in solution must not take place. The absorption curves of certain dye mixtures may not be additive, and the fact that some are not has been demonstrated by Neale and Stringfellow (10). The evidence suggests that the effect is due to association of molecules of the two dyes to form a binary complex having an absorption spectrum different from that of the components.

2. The accuracy of concentration estimations of components in a mixture depends to a great extent on the relative shapes of the absorption curves of the components. If the curves lie close together, the
optical density readings of the standard solutions of the components may be very similar, so that the denominator in Formula 6 (See Appendix) is small and may be comparable in magnitude to the experimental error in the optical density readings. Therefore, the further apart the maximum absorption readings of the components (in wavelength), the more accurate the computation of concentrations should be.

The mathematical relationships among the terms peculiar to light absorption work, and the derivation of the formulae for spectrophotometric determinations and dye mixture analyses are contained in the Appendix. The sources for the related mathematical data, other than certain derivations performed by the author, were Vickerstaff (11) and Darbey (12).

There are other considerations which are minor only in the amount of effort required to satisfy them and not in the amount of error which can result from them. The preparation of the dye solutions must be exact. Optical density readings and extinction coefficient calculations depend entirely on concentration; therefore, dilutions for the purpose of readings on the spectrophotometer must be exact, and any evaporation of solvent must be prevented.

Verification of Compliance with Considerations.—Compliance with the considerations described in the previous section was important to this work in order that as many as possible of the sources of error might be eliminated or minimized. The validity of the first of these considerations was assured by passing monochromatic light through solutions of known thicknesses. Verification of considerations related to the dyebath components used in this work was confirmed by conducting tests to be certain that the components satisfied all conditions.
The validity of Beer's law and of Lambert's law for this work was assured by use of the Beckman Model DU Photoelectric Quartz Spectrophotometer for optical density measurements. Also, matched pairs of Beckman Absorption Cells (one Corex set and one Quartz set) were used to contain solutions. One cell of each pair was used as the standard cell and contained the solvent in all readings, while the other cell of the pair was always used for the solution being examined.

The tendency of dyes to change color with pH changes was overcome by conducting all spectrophotometric examinations on solvents and solutions which had been adjusted to an exact pH of 6.0. All pH determinations were made with a Beckman pH Meter. The tendency of dyes to change in state of aggregation may be overcome by the addition of pyridine, polyethylene oxide condensation products, alcohol, or dimethyl formamide, according to Vickerstaff (13). He further states: "The absence of change in aggregation is best established by preparing a range of solutions of the dye under test at various concentrations and confirming that a linear relationship exists between optical density and concentration." This was the method which was used in this work to verify that each component of the dyebath fulfilled the considerations.

An extension of this type of test was utilized in testing for the interaction of dyes in a multi-component dyebath. Solutions of each component, and all the components together in a representative "dummy" mixture were prepared using analogous concentrations. Optical density readings were obtained on each of the solutions and computations were made to verify the additive relationship of the optical densities of the
components in the dyebath. Optical density values for each of the dye-
bath components were converted to extinction coefficient values and
plotted in order to determine the shapes and locations of maxima for
the absorption curves.

In order to minimize experimental errors, the following precautions
were observed in all tests:

1. All fluid measurements were made with pipettes. All weighings
were carried out on analytical balance.

2. Adjustments in pH were made before the solutions were brought
to the desired volume in order to assure exact solution volumes.

3. The adjustments in pH were made with four per cent solutions
of diammonium phosphate, or of phosphoric acid, as required.

4. All containers for solutions were rinsed with water which had
been adjusted to a pH of 6.0 before use and thoroughly dried before solu-
tions were entered.

5. Solutions were tightly stoppered, and spectrophotometer read-
ings were made on the same day and as soon as possible after solutions
were prepared.

6. Distilled water which had been adjusted to a pH of 6.0 was
used for all dyebaths, solutions and dilutions.

7. Cells used to contain solutions in the spectrophotometer were
carefully cleaned and dried between each set of readings on a different
solution.
CHAPTER III

INSTRUMENTATION AND EQUIPMENT

List of Equipment Used.—The following items of special equipment were used in this work:

Christian-Becker Chainomatic Analytical Balance
Precision Scientific Mag-Mix Stirrer
Precision Scientific Vari-Speed Stirrer
Beckman pH Meter, Model H-2
Two matched Beckman Corex Absorption Cells
Two matched Beckman Quartz Absorption Cells
Beckman Spectrophotometer, Model DU
Remington Rand Univac Scientific Computer, Model 1101

The Spectrophotometer.—The sources for the information contained in this section were the instruction booklet for the Beckman Model DU Spectrophotometer (14) and Gibson and Balcolm (15). The Beckman photoelectric spectrophotometer has proved of great value in spectral transmission and absorption measurements. The essential features of the instrument are: Radiant energy from an illuminant is focused on a narrow slit by means of a concave and a plane mirror. The beam entering the slit is rendered parallel by another mirror and passes through a quartz prism to a reflecting surface. After reflection the beam returns along almost the same path to the same slit through which it entered and emerges slightly above the entrance.
bean. After passage through the sample, the beam is incident on a phototube. The photoelectric current produces a voltage drop across a phototube load resistor which is balanced by a potentiometer. While this null setting is being made, any imbalance is amplified electronically and is indicated by a milliammeter on the instrument.

The Beckman Model DU Spectrophotometer used in this work was equipped with a photomultiplier attachment which greatly increases the sensitivity of the instrument. It is capable of readings from about 200 to 1,200 millimicrons; however, the normal tungsten lamp source and corex cells may be used only above 320 millimicrons. A hydrogen discharge illuminant and quartz cells are required from 200 to 350 millimicrons. Either set-up may be used from 320 to 350 millimicrons. Since the visible region of the spectrum (from about 400 to 700 millimicrons) is most applicable for dyes, the range used for readings on the dyes was 320 to 700 millimicrons. The resist agent was examined in the region below 320 millimicrons but it was found that satisfactory results could also be obtained above 320 millimicrons.

In general, three readings are necessary to make a transmission determination at any wavelength: (1) the zero reading, in which the beam is blocked from the phototube and the galvanometer is brought to balance by a "dark current" adjustor, (2) the 100-per cent reading, in which the beam falls on the phototube after passing through the solvent or standard cell, and the milliammeter is brought to balance by adjusting the slit width, and (3) the transmission reading, in which the unknown or test sample is placed in the beam and the galvanometer is brought to
balance by turning the potentiometer dial which carries the "transmission" and "optical density" scale.

The Computer.—The Remington Rand Model 1101 Computer was used in solving the many sets of simultaneous equations with the data obtained in the dyebath concentration determinations. The source for all facts regarding the computer in this section was the Remington Rand Manual, "Introduction to Programming for the 1101 Computer."

This computer is particularly adapted to scientific work and, although the computer is today a familiar tool, its potential in work of this type has not been fully realized. The electronic computer is most complex in function, but a minimum of familiarity is required to take advantage of its possibilities.

The 1101 Computer may be divided into five sections for descriptive purposes:

(1) Memory Unit — a magnetic drum having a capacity to store 16,384 "words" of 24 "bits" each. A "bit" is merely the short name for a binary (expressed in the base of two) digit. A "word" is a group of "bits."

(2) Arithmetic Section — an accumulator and two registers which perform the arithmetic operations.

(3) Program Control — the section which governs the execution of the various instructions which make up the program. A program is the sequence of actions by which a computer handles a problem. Programming is devising a program.
(4) Input — the section which transfers numerical data and instructions from the input medium to the memory. The input medium is punched tape.

(5) Output — the section which translates the machine results into a usable form. The output medium is punched tape. The information on the tape is converted into a typed tabular form by a "Flex-o-writer" typewriter.

The parts of the computer may be roughly compared to a person using a desk calculator. The memory corresponds to the paper on which data are recorded, the arithmetic section is similar to the calculator, the program control is the brain of the operator, the input is the calculator keyboard, and the output is that part of the calculator which causes the results to appear on the proper register of the machine.

The program, "Matrix Inversion and Solution of Linear Systems," which was used for the comparatively simple problem solved in this work, was an existing general program which fitted the problem at hand. Thus, the only preparation necessary for use of the computer was conversion of gathered data into punched tape form to serve as the input medium.
CHAPTER IV

EXPERIMENTAL PROCEDURES

Exploratory Dyeings

The Materials

All of the wool dyed in this work was in the form of circularly knitted goods made from 9.88 run wool yarn with an average of ten twists per inch.

The chemical structures, molecular weights, and other pertinent information (17) regarding the principal dyebath components which were used in the dyeing tests are included in the Appendix.

Three different resist or reserve agents were investigated and evaluated. These agents were Synthrtan ACA, a condensation product of a naphthalene sulphonlric acid with formaldehyde; Tamol N, a neutral sodium salt of a complex condensed aryl organic acid; and Naccotan A, a sodium salt of a sulfonated naphthalene condensation product (18).

All pretreatments and dyeings were carried out in glass beakers of a size appropriate to the bath volume which was being used. The pretreatment and dyeing baths were agitated during each experiment by one of three means: small volume dyebaths by hand with glass stirring rods; large volume dyebaths by the Vari-Speed Stirrer; and during pH adjustments, by the Mag-Mix Stirrer. All heating was done directly over an open gas flame. Beakers were covered with watch glasses during heating.
to prevent excess loss of dyeliquor. It was necessary to remove watch glass covers frequently for access and agitation, and resulting liquor losses were not compensated for by the addition of water to the dyebaths. (The term "dyebath ratio" as employed in this account refers to the weight of dyeliquor used in relation to the weight of fiber being dyed; the abbreviation "o.w.f." designates the weight of dye used expressed as a percentage based "on the weight of fiber" which is being treated.)

The Pretreatment

Standard Pretreatment Methods.—The pretreatments developed by Davis (19) are referred to in this work as standard pretreatments. The two methods of preparing raw wool in order to produce contrast effects in dyeing were carried out in this work as follows:

Standard Pretreatment I. — Samples were treated for one hour at a gentle boil in a solution of 4 per cent phenol, containing 10 per cent resist agent (o.w.f.). The liquor to fiber ratio was 100:1. Samples were rinsed in water at room temperature and allowed to dry in the atmosphere.

Standard Pretreatment II. — Samples were treated for one hour at a gentle boil in a solution of 6 per cent phosphoric acid, containing 10 per cent resist agent (o.w.f.). The liquor to fiber ratio was 100:1. Samples were rinsed in water at room temperature and allowed to dry in the atmosphere.

Resist Agents.—The procedure used in evaluating the three resist agents is outlined below.

Each of the resist agents, Synthratan ACA, Tamol N, and Naccotan A,
was applied to samples of wool by each of the standard pretreatment methods. The pretreated samples were divided into three pairs, each pair representing two samples pretreated with the same agent, one by Standard Pretreatment I and the other by Standard Pretreatment II. A pair of each type was dyed in a different dyebath under three sets of dyeing conditions:

1. Contrast Effect Method I Dyebath (see below, under "The Dyebath") with Fast Acid Yellow GS and Alizarine Sapphire FS, dyed for 20 minutes at 160 degrees F.

2. Same dyebath preparation as in 1. Dyed for 45 minutes at 140 degrees F.

3. Contrast Effect Method I Dyebath with Fast Acid Yellow GS and Brilliant Scarlet 3R, dyed for 40 minutes at 140 degrees F.

Tamol N and Naccotan A gave less satisfactory results than Synthran ACA when the concentrations specified in the Standard Pretreatment Methods were used. To test the effectiveness of these agents at higher concentrations, samples were again pretreated as above, except that 50 per cent (rather than 10 per cent) of each agent was used.

Again, a pair of each type was dyed in a dyebath under the same conditions. The three dyebaths were each prepared by Contrast Effect Method I (see below) with Fast Acid Yellow GS and Alizarine Sapphire FS as the dyes, and dyeing conditions were varied as follows for each set of pairs:

1. Twenty minutes at 140 degrees F.

2. Sixty minutes at 140 degrees F.

3. Twenty minutes at 140 degrees F.; then, 20 minutes at 160 degrees F.; and finally, 20 minutes at the boil.
All of the resulting dyeings were compared and evaluated on the basis of the degree of contrast between samples, and the levelness of the dyeings. These evaluations are included under the "Pretreatment" section of Chapter V.

Variations of Standard Methods.—Other pretreatments were carried out and evaluated on the basis of dyeings performed with one pretreated sample and one untreated sample in the dyebath. The other pretreatment mediums used were: (a) 4 per cent formic acid, and (b) 1 per cent sulphuric acid. Pretreatments using these mediums rather than the acids specified in the Standard Pretreatments were conducted with all other conditions in accordance with the Standard Pretreatment Methods.

Samples pretreated by these new methods were dyed under various conditions in order to estimate the efficacy of the pretreatments. The descriptions of the dyebath preparations and dyeing conditions are included under the "New Methods" section of this chapter.

The Dyebath

Contrast Effect Method I.—The dyebath preparation devised by Davis (20) to obtain two color and two tone effects will be referred to in this work as Contrast Effect Method I. The dyebaths for this method were prepared as follows:

Two per cent (o.w.f.) of a level dyeing acid dye and 6 per cent (o.w.f.) of a milling or supermilling dye were entered in a dyebath at room temperature. The pretreated samples were entered and the pH of the dyebath was immediately adjusted to 6.0 by the addition of a 1 per cent
diammonium phosphate solution. The final dyebath ratio was 60:1.

Concentrations of the Dyes.--The following variables were surveyed to obtain an indication of their general effects on the dyeing process: the percentages of the dyes in the dyebath, the ratio between the two dyes, and the dyebath to fiber ratio. In each case in this series of experiments, one gram samples of wool (one pretreated by Standard Pretreatment I and one by Standard Pretreatment II) were dyed in the same dyebath. The Contrast Effect Method I Dyebath preparation was used in all cases with variations as indicated in Table 1.

All test samples cut from the wool during dyeing and the completed dyeings were washed in water at room temperature and allowed to dry in the atmosphere. The evaluation of the effects of dye ratio and concentrations was based on these samples and is included under Results and Discussion.

Effect of pH.--During the preparation of Contrast Effect Method I dyebaths using samples pretreated by Standard Methods I and II, pH determinations were made on many different dyebaths by the use of the Beckman pH Meter. For this dyebath preparation method, certain factual data were gathered and these are summarized in the following paragraph.

After the two one gram pretreated samples had been entered in the dyebath at room temperature and thoroughly agitated, the Fast Acid Yellow GS - Alizarine Sapphire FS dye combination registered a pH of 3.0, and required the addition of 1.5 ml. of a 4 per cent diammonium phosphate solution to attain a pH of 6.0. The Fast Acid Yellow GS - Brilliant
Table 1. Record of Dye Concentration Experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Milling Dye</th>
<th>Levelling Dye</th>
<th>Dyebath Ratio</th>
<th>Dyeing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>Fast Acid Yellow GS 15%</td>
<td>Alizarine Sapphire FS 1%</td>
<td>60:1</td>
<td>Heated uniformly to the boil in 30 mins. Dyed at boil for 10 mins.</td>
</tr>
<tr>
<td>A-2</td>
<td>Fast Acid Yellow GS 6%</td>
<td>Alizarine Sapphire FS 1%</td>
<td>60:1</td>
<td>Heated to 160 degrees F. in 20 mins.* Raised to boil in 15 mins.* Continued at boil 5 mins.</td>
</tr>
<tr>
<td>A-3</td>
<td>Fast Acid Yellow GS 6%</td>
<td>Alizarine Sapphire FS 2%</td>
<td>60:1</td>
<td>Heated uniformly to 190 degrees F. over a 45 min. period.</td>
</tr>
<tr>
<td></td>
<td>Fast Acid Yellow GS 3%</td>
<td>Alizarine Sapphire FS 1%</td>
<td>100:1</td>
<td></td>
</tr>
<tr>
<td>A-4</td>
<td>Fast Acid Yellow GS 6%</td>
<td>Brilliant Scarlet 3R 2%</td>
<td>100:1</td>
<td>Heated uniformly to the boil over a 45 min. period.</td>
</tr>
<tr>
<td></td>
<td>Fast Acid Yellow GS 3%</td>
<td>Brilliant Scarlet 3R 1%</td>
<td>100:1</td>
<td></td>
</tr>
<tr>
<td>A-5</td>
<td>Fast Acid Yellow GS 1%</td>
<td>Alizarine Sapphire FS 1%</td>
<td>100:1</td>
<td>Heated uniformly to 180 degrees F. in 30 mins. Dyed at 180 degrees F. for 20 mins. (*At 10 min. intervals above 160 degrees F.)</td>
</tr>
</tbody>
</table>

*Indicates points at which small sample cuts were taken from each of the two samples in the dyebath for color examination.
Scarlet 3R dye combination registered a pH of 3.2, and required the addition of 1.0 ml. of the 1 per cent diammonium phosphate solution to attain a pH of 6.0. In each case agitation was carried out for five minutes after the wool samples were entered in the dyebath and was continued during the addition of the buffer solution.

An experimental dyeing was carried out using samples pretreated by Standard Methods I and II and Fast Acid Yellow GS and Alizarine Sapphire FS in a Contrast Effect Method I dyebath without any attempt to control the pH of the dyebath. The conditions of this dyeing are summarized in Table 2.

Exactly the same dyebath preparation and dyeing conditions as above were carried out on two samples, one pretreated by Standard Method II and the other untreated, for comparative purposes. The pH of this dyebath was 3.5 throughout the dyeing period.

Evaluation of these results is contained in the Results and Discussion Chapter under "The Dyebath."

The Dyeing

Time and Temperature Effects.—Once the dyebath has been prepared, the prime variables are time and temperature. Many dyeings were conducted to determine the effects of time and temperature of dyeing on samples prepared under various pre-dyeing conditions. The pre-dyeing conditions used for these experiments are summarized in Table 3. The dyeing conditions for these experiments are detailed in the following paragraphs.

In Experiment B-1 the dyeing was begun at room temperature and the rate of heating was constant, so that the dyebath temperature
<table>
<thead>
<tr>
<th>Dyebath State</th>
<th>Dyebath Temperature Degrees Fahrenheit</th>
<th>Elapsed Time of Dyeing (Mins.)</th>
<th>pH of Dyebath</th>
</tr>
</thead>
<tbody>
<tr>
<td>No samples in dyebath</td>
<td>180</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dyebath removed from heat, samples entered</td>
<td>180</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>Dyebath being agitated</td>
<td>160</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>Dyebath returned to heat</td>
<td>140</td>
<td>10</td>
<td>3.5</td>
</tr>
<tr>
<td>Dyeing</td>
<td>180</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Dyeing</td>
<td>212</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>Dyeing</td>
<td>Boil</td>
<td>30</td>
<td>3.5</td>
</tr>
<tr>
<td>Dyeing</td>
<td>Boil</td>
<td>40</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 3. Pretreatments and Dyebaths for Time and Temperature Effect Dyeing Series

Pretreatment Methods: Standard Methods I and II for all tests.

Dyebath Preparation: Contrast Effect Method I for all tests.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Pretreatment</th>
<th>Resist Agent</th>
<th>Milling Dye</th>
<th>Levelling Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>Naccotan A</td>
<td></td>
<td>Fast Acid</td>
<td>Brilliant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Scarlett 3R</td>
</tr>
<tr>
<td>B-2</td>
<td>Tamol N</td>
<td></td>
<td>Fast Acid</td>
<td>Alizarine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Sapphire FS</td>
</tr>
<tr>
<td>B-3</td>
<td>Tamol N</td>
<td></td>
<td>Fast Acid</td>
<td>Brilliant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Scarlett 3R</td>
</tr>
<tr>
<td>B-4</td>
<td>Tamol N</td>
<td></td>
<td>Fast Acid</td>
<td>Alizarine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Sapphire FS</td>
</tr>
<tr>
<td>B-5</td>
<td>Synthratan ACA</td>
<td></td>
<td>Fast Acid</td>
<td>Brilliant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Scarlett 3R</td>
</tr>
<tr>
<td>B-6</td>
<td>Synthratan ACA</td>
<td></td>
<td>Fast Acid</td>
<td>Brilliant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Yellow GS</td>
<td>Scarlett 3R</td>
</tr>
</tbody>
</table>
gradually increased as the dyeing progressed. Samples were removed and small test patches were cut off for color determinations at the indicated intervals of elapsed dyeing time (in minutes) and dyebath temperature (degrees F.):

<table>
<thead>
<tr>
<th>Time:</th>
<th>5</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>45</th>
<th>55</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature:</td>
<td>120</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>140</td>
<td>150</td>
<td>170</td>
<td>190</td>
<td>212</td>
</tr>
</tbody>
</table>

The progressive dyeing samples from this dyeing are pictured in Figure 1.

Experiments B-2 and B-3 were run simultaneously under the same dyeing conditions. Dyeings were begun at room temperature and brought uniformly to the boil in 30 minutes. After 10 minutes at the boil, small test patches were cut from each sample. Dyeing was continued for a total of one hour at the boil.

Experiment B-4 was begun at room temperature. The dyebath temperature was brought to 140 degrees F. in 5 minutes and held at that temperature for 10 minutes. The dyebath temperature was increased to 160 degrees F. in 5 minutes and held constant for 10 minutes. This procedure was repeated at 190 degrees F. and at the boil. Small test patches were cut from the samples after each of the four temperature levels had been held for the 10 minute periods.

Experiment B-5 was begun at room temperature, and the dyebath temperature was increased uniformly until the boil was reached after 32 minutes. Dyeing was continued at the boil for 30 minutes. Pairs of small test patches were cut from the samples when the point of boil was reached and after 10 minutes at the boil.
Experiment 3-6 samples were entered after the dyebath had been brought to the boil and pairs of test patches were removed after 10 minutes and after 20 minutes at the boil. Dyeing was continued for a total of one hour at the boil.

In this series of experiments the samples were each one gram in weight (two grams in each dyebath). All small test patches and the final dyeings were rinsed in water at room temperature and allowed to dry in the atmosphere. The results are summarized in Chapter V.

Progressive Colorations in Dyeing.—During the courses of dyeings conducted it was noted that visible changes in the color of the dyebath took place which were related to the colors or shades of the samples being dyed. A series of three dyeings which was carried out for the purpose of studying this phenomenon is described in the following paragraphs.

All tests in this series were conducted with two gram samples of wool. One gram had been pretreated by Standard Method I and one gram by Standard Method II using Synthratan AGA as the resist agent in each case. Contrast Effect Method I Dyebath preparation was used for each dyeing with Fast Acid Yellow GS and Alizarine Sapphire as dyes. All test patches removed during dyeing and the completed dyeings were rinsed in water at room temperature and allowed to dry in the atmosphere. The dyeing methods are described for each experiment.

Experiment C-1 was begun with the dyebath at room temperature. The samples were entered and the temperature raised to 160 degrees F. in 15 minutes and held constant for 40 minutes. The temperature was then raised to 190 degrees F. in 10 minutes and held constant for 10 minutes.
Throughout the dyeing the dye liquor was drawn into a pipette at frequent intervals (3-5 minutes) for observation of the visible color, and then returned to the dyebath.

Experiment C-2 samples were entered at room temperature and the dyebath temperature was brought to the boil over a 45 minute period. Boiling was continued for 15 minutes. Small test patches were cut from the samples at elapsed dyeing times of 15, 25 and 40 minutes. Dye liquor color was examined as in the previous experiment.

Experiment C-3 dyebath was brought to a temperature of 180 degrees F. before the samples were entered. The dyebath was removed from the heat and samples entered. The dyebath was rapidly agitated and before the pH could be adjusted, the dyeliquor color changed from green to blue. No pH adjustment was made; dyebath was returned to the heat, and heated to the boil in 10 minutes. Dyeing was continued at the boil for 10 minutes with dye liquor examinations at five minute intervals after samples were entered. Small test patches were cut after the initial dyebath color change, before returning bath to heat, and at the point of boil.

The results of this dyeing series are reviewed in Chapter V and a typical progression of the coloration of dyeing samples is presented by Figure 1.

Reproduction of Results.—In order to assure the feasibility of obtaining reproducible results, two separate dyeings were carried out under the same set of conditions. The pretreatments for the two sets of samples were by Standard Methods I and II using Synthratan ACA as the resist agent. The two dyebaths were each prepared in accordance with Contrast
Effect Method I with Fast Acid Yellow GS and Brilliant Scarlet 3R as the dyes.

The dyeing was carried out by entering the samples at room temperature and raising the temperature up to the boil over a 30 minute period. Pairs of small test patches were cut from each bath at the point of boil. Test patches were again taken after 10 minutes at the boil, and boiling was continued for a total of 30 minutes. Results are discussed in Chapter V.

New Contrast Effect Methods.—Results of previous exploratory dyeings led to attempts to produce contrast effects by other methods. The experiments conducted in this pursuit are described in this section and the pretreatment and dyebath preparations used are summarized in Table 1. The experiment which formed the basis for most of this series of experiments is described in the following paragraph:

Two one gram samples pretreated by Methods I and II and a third one gram sample of raw wool were entered in a dyebath prepared in accordance with Contrast Effect Method I with Fast Acid Yellow GS and Brilliant Scarlet 3R as the dyes. The dye weights were based on the weight of the treated fibers only. Samples were entered at room temperature, the dyebath was raised to the boil over a 30 minute period, and held at the boil for 5 minutes. Samples were rinsed in water at room temperature and allowed to dry.

The pretreatment designated Method III was carried out in exactly the same manner as Standard Pretreatments I and II except that the acid used was one per cent sulphuric acid on the weight of the fiber treated.
Table 4. New Methods of Producing Contrast Effects

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Pretreatments</th>
<th>Dyebath Preparation</th>
<th>Dyes</th>
<th>Levelling Dye Per Cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1</td>
<td>Method III</td>
<td>No pretreatment</td>
<td>Dyebath adjusted to pH of 6.0. Ratio 100:1.</td>
<td>Fast Acid Yellow NGS 6%</td>
</tr>
<tr>
<td>D-2</td>
<td>Method III</td>
<td>No pretreatment</td>
<td>Dyebath pH not adjusted. Ratio 100:1.</td>
<td>Fast Acid Yellow NGS 6%</td>
</tr>
<tr>
<td>D-3</td>
<td>Method IV</td>
<td>No pretreatment</td>
<td>Dyebath pH adjusted to 6.0. Ratio 100:1</td>
<td>Fast Acid Yellow NGS 6%</td>
</tr>
<tr>
<td>D-4</td>
<td>Method IV</td>
<td>No pretreatment</td>
<td>Contrast Effect Method I</td>
<td>Fast Acid Yellow NGS 6%</td>
</tr>
<tr>
<td>D-5</td>
<td>Method II</td>
<td>No pretreatment</td>
<td>Contrast Effect Method I</td>
<td>Fast Acid Yellow NGS 6%</td>
</tr>
<tr>
<td>D-6</td>
<td>Method II</td>
<td>No pretreatment</td>
<td>No pH adjustment. Ratio 100:1.</td>
<td>Fast Acid Yellow GS 3%</td>
</tr>
<tr>
<td>D-7</td>
<td>Method II</td>
<td>No pretreatment</td>
<td>No pH adjustment. Ratio 60:1.</td>
<td>Fast Acid Yellow GS 6%</td>
</tr>
</tbody>
</table>

Note: The resist agent in all pretreatments was Synthratan ACA
The pretreatment designated Method IV was also carried out in exactly the same manner as Standard Pretreatments I and II except that the acid used was four per cent formic acid on the weight of the fiber treated.

In Experiments D-1, D-2, D-5, and D-7, the samples were entered at room temperature; then the temperature was raised to the boil over a 30 minute period and was held at the boil for 10 minutes. In Experiment D-3 and D-4 the same procedure was used except that the dyeing was continued at the boil for 30 minutes. The samples were entered into the dyebath at 180 degrees F. in Experiment D-6, brought to the boil in 10 minutes, and held at the boil for 10 minutes. All of the dyeings in the "D" series were made on two gram samples — one gram of each pretreated wool. All completed dyeings were rinsed and dried in the usual manner.

On the basis of this series of dyeings and other dyeings previously described, the following designations were made:

Contrast Effect Method II - Based on the total weight of the fiber to be dyed, 1 per cent of a level dyeing acid dye and 3 per cent of a milling or supermilling dye were entered in a 100:1 dyebath. While the dyebath was at room temperature and as soon as the pretreated samples were entered, the pH of the dyebath was adjusted to 6.0 by the addition of the required amount of a 1 per cent diammonium phosphate solution.

Contrast Effect Method III - This was exactly the same as Contrast Effect Method I except that no adjustment of the dyebath pH was made.

Contrast Effect Method IV - This was exactly the same as Contrast Effect Method II except that no adjustment of the dyebath pH was made.
Concentration Determinations

Preliminary Verifications

Solutions to be used in test runs for the purpose of familiarization of the operation with the spectrophotometer, verification of the absence of change of pH during dilution, and determination of optimum concentrations for satisfactory optical density readings were prepared in the following concentrations:

- Fast Acid Yellow GS - 0.25 gram in 100 ml. of aqueous solution
- Brilliant Scarlet 3R - 0.25 gram in 100 ml. of aqueous solution
- Synthratan ACA - 1.00 gram in 250 ml. of aqueous solution.

Five ml. samples of each of the prepared solutions were diluted 50 fold. The pH of each diluted solution was the same as the pH of the originally prepared solutions: 6.0. The precautions pointed out under "Verification of Compliance with Considerations" (in Chapter II) were followed in this test.

The stock solutions of the three components were taken to the spectrophotometer location and dilutions as required to obtain optical density readings at wavelengths from 320 millimicrons to 700 millimicrons were carried out at the instrument. Optical density readings were taken on each of the solutions at five millimicron intervals over the spectral range which was used.

Concentrations at which readings were obtained are listed for each of the solutions:

- Fast Acid Yellow GS - 0.625, 0.15625, and 0.0390625 grams per liter
- Brilliant Scarlet 3R - Same as for Fast Acid Yellow GS
- Synthratan ACA - 1.0, 2.0, 1.0, and 0.125 grams per liter.
The linear relationship of optical density to concentration for these components was also verified by use of the above solutions. That is, readings at one wavelength and one concentration were translated mathematically into computed optical densities at other concentrations. These results were compared to the actual optical density readings, at the same wavelength, of solutions which were of the same concentrations as were determined in the computations. Such calculations:

\[(\text{Optical Density})_2 = \frac{(\text{Concentration})_2}{(\text{Concentration})_1} \times (\text{Optical Density})_1\]

were carried out for readings at various wavelengths for each of the solutions at each of the concentrations at which optical density readings were obtained.

Generally, the results (see Sample Calculations in the Appendix) were in close agreement, in that optical density calculated with the above formula approximated the actual optical density reading at a different concentration, but at the same wavelength. The areas of disagreement were attributed to experimental errors as a result of the inexperience of the operator, plus the fact that optical density readings in the following spectrophotometric scale ranges appeared inaccurate: lower range: 0 to 0.016; upper range 1.3 to infinity. However, the over-all results of the preliminary runs supported the conclusions that the components of the dyebath to be used in this work did not change in the linear relationship of optical density to concentration at the concentrations necessary for use in the work.

In order to test for the possibility of interaction between the components of the proposed dyebath mixture and to determine the shapes
and relationships of the absorption curves, readings were made on solutions of each of the components and on a representative mixture of the components. It was necessary to make readings on the dyes and on the mixture at two different concentrations in order to obtain optical density readings over the desired ranges. The concentrations which were used in these readings and the wavelength ranges covered for each solution are contained in Table 5.

The examination of Synthatan ACA below 320 millimicrons was done using the hydrogen discharge light source and quartz cells with the spectrophotometer.

Representative extinction coefficient values for each of the solutions are contained in Table 6. Typical values obtained for extinction coefficients by calculations using Equation 8 (in the Appendix), and from actual optical density readings are contained in Table 7. Figure 2 is a graphical representation of extinction coefficients for each of the components at the wavelengths of interest. Sample calculations for these data are contained in the Appendix.

The extinction coefficient curves of Figure 2 indicate the locations of the absorption curves to be properly distributed. That is, the "peaks" of the curves are widely separated in wavelength. The absorption "peaks" were located at 420 millimicrons for Fast Acid Yellow GS, at 500 millimicrons for Brilliant Scarlet 3R, and at 320 millimicrons for Synthatan ACA.

The agreement of the actual extinction coefficient values for the "dummy" dyebath mixture with the extinction coefficient values which were
Table 5. Wavelengths and Concentrations Used in Initial Optical Density Studies

<table>
<thead>
<tr>
<th>Solution Examined</th>
<th>Wavelength Range ( \mu m )</th>
<th>Concentration</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Grams per Liter</td>
<td>Mols per Liter</td>
<td></td>
</tr>
<tr>
<td>Fast Acid Yellow GS</td>
<td>320 - 730</td>
<td>( y_o = 0.200 )</td>
<td>( C_y = 0.0004760 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>320 - 500</td>
<td>( y_o = 0.060 )</td>
<td>( C_y = 0.0001428 )</td>
<td></td>
</tr>
<tr>
<td>Brilliant Scarlet 3R</td>
<td>320 - 700</td>
<td>( r_o = 0.200 )</td>
<td>( C_r = 0.0003310 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>320 - 580</td>
<td>( r_o = 0.060 )</td>
<td>( C_r = 0.0000992 )</td>
<td></td>
</tr>
<tr>
<td>Synthratan ACA</td>
<td>215 - 675</td>
<td>( s_o = 0.800 )</td>
<td>( C_s = 0.0016900 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>320 - 510</td>
<td>( s_o = 0.160 )</td>
<td>( C_s = 0.0003380 )</td>
<td></td>
</tr>
<tr>
<td>Representative</td>
<td>320 - 675</td>
<td>( m_o = 0.320 )</td>
<td>( C_m = 0.000690 )</td>
<td></td>
</tr>
<tr>
<td>Mixture</td>
<td>320 - 510</td>
<td>( m_o = 0.064 )</td>
<td>( C_m = 0.000138 )</td>
<td></td>
</tr>
</tbody>
</table>
Table 6. Extinction Coefficients of Dyebath Components

<table>
<thead>
<tr>
<th>Wavelengths (Millimicrons)</th>
<th>Fast Acid Yellow GS $K_y$ values</th>
<th>Brilliant Scarlet 3R $K_r$ values</th>
<th>Synthratan ACA $K_g$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>--</td>
<td>--</td>
<td>1100</td>
</tr>
<tr>
<td>250</td>
<td>--</td>
<td>--</td>
<td>1135</td>
</tr>
<tr>
<td>280</td>
<td>--</td>
<td>--</td>
<td>1100</td>
</tr>
<tr>
<td>310</td>
<td>--</td>
<td>--</td>
<td>1100</td>
</tr>
<tr>
<td>320</td>
<td>3222</td>
<td>6650</td>
<td>942</td>
</tr>
<tr>
<td>340</td>
<td>3322</td>
<td>3330</td>
<td>319</td>
</tr>
<tr>
<td>360</td>
<td>4270</td>
<td>1994</td>
<td>51</td>
</tr>
<tr>
<td>380</td>
<td>6450</td>
<td>1812</td>
<td>36</td>
</tr>
<tr>
<td>400</td>
<td>9800</td>
<td>2372</td>
<td>27</td>
</tr>
<tr>
<td>420</td>
<td>10540</td>
<td>2600</td>
<td>20</td>
</tr>
<tr>
<td>440</td>
<td>9100</td>
<td>3530</td>
<td>21</td>
</tr>
<tr>
<td>460</td>
<td>6300</td>
<td>5150</td>
<td>9</td>
</tr>
<tr>
<td>480</td>
<td>3010</td>
<td>7765</td>
<td>3</td>
</tr>
<tr>
<td>500</td>
<td>1085</td>
<td>10125</td>
<td>11</td>
</tr>
<tr>
<td>520</td>
<td>290</td>
<td>9480</td>
<td>3</td>
</tr>
<tr>
<td>540</td>
<td>52</td>
<td>6949</td>
<td>6</td>
</tr>
<tr>
<td>560</td>
<td>42</td>
<td>3172</td>
<td>12</td>
</tr>
<tr>
<td>580</td>
<td>21</td>
<td>504</td>
<td>12</td>
</tr>
<tr>
<td>600</td>
<td>25</td>
<td>125</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 7. Comparison of Actual and Calculated Extinction Coefficients for the Representative Dyebath

<table>
<thead>
<tr>
<th>Wavelength (Millimicrons)</th>
<th>Optical Density Reading D</th>
<th>Extinction Coefficients - $K_m$</th>
<th>Calculated (From readings - dyebath components)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual (From Optical Density)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.330</td>
<td>2390</td>
<td>2434</td>
</tr>
<tr>
<td>340</td>
<td>0.250</td>
<td>1812</td>
<td>1867</td>
</tr>
<tr>
<td>360</td>
<td>0.310</td>
<td>2245</td>
<td>1987</td>
</tr>
<tr>
<td>380</td>
<td>0.400</td>
<td>2890</td>
<td>2862</td>
</tr>
<tr>
<td>400</td>
<td>0.570</td>
<td>4130</td>
<td>4291</td>
</tr>
<tr>
<td>420</td>
<td>0.670</td>
<td>4860</td>
<td>4633</td>
</tr>
<tr>
<td>440</td>
<td>0.590</td>
<td>4270</td>
<td>4119</td>
</tr>
<tr>
<td>460</td>
<td>0.460</td>
<td>3335</td>
<td>3039</td>
</tr>
<tr>
<td>480</td>
<td>0.280</td>
<td>2032</td>
<td>1995</td>
</tr>
<tr>
<td>500</td>
<td>0.215</td>
<td>1560</td>
<td>1393</td>
</tr>
<tr>
<td>520</td>
<td>0.750</td>
<td>1087</td>
<td>1034</td>
</tr>
<tr>
<td>540</td>
<td>0.520</td>
<td>754</td>
<td>691</td>
</tr>
<tr>
<td>560</td>
<td>0.205</td>
<td>297</td>
<td>327</td>
</tr>
<tr>
<td>580</td>
<td>0.050</td>
<td>73</td>
<td>67</td>
</tr>
<tr>
<td>600</td>
<td>0.015</td>
<td>29</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 2. Absorption Curves of Dyebath Components.

- $K_y$ - FAST ACID YELLOW GS
- $K_r$ - BRILLIANT SCARLET 3R
- $K_s$ - SYNTHRATAN ACA
calculated from the individual component readings indicated that there was no interaction of the dyebath components.

The Master Dyeing

The pretreatments of the samples of raw wool which were used in the master dyeing were carried out by Standard Methods I and II using Synthrain ACA as the resist agent. A 10 gram sample of wool was pre-treated by Standard Method I and a second 10 gram sample was pretreated by Standard Method II. Pretreatment was done in an exacting manner and samples were rinsed in water at room temperature and allowed to dry twenty-four hours in the atmosphere.

All of the precautions which were pointed out in the "Verification of Compliance with Considerations" Section of this work were closely observed in the preparation of the master dyebath. The dyes used were Fast Acid Yellow GS, 1.20 grams (6 per cent o.w.f.) and Brilliant Scarlet 3R, 0.40 gram (2 per cent o.w.f.). A dyebath ratio of 80:1 was used in order to minimize the effect on concentrations by the dye liquor removed as the dyeing proceeded. The dyebath was prepared as follows:

<table>
<thead>
<tr>
<th>Step No.</th>
<th>Volume (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dye solutions placed in beaker</td>
<td>150.0</td>
</tr>
<tr>
<td>2. Dye containers rinsed</td>
<td>150.0</td>
</tr>
<tr>
<td>3. Water added</td>
<td>1000.0</td>
</tr>
<tr>
<td>4. Dyebath agitated and pH adjusted to 6.0</td>
<td>237.5</td>
</tr>
<tr>
<td>5. Water added, pH verified at 6.0</td>
<td>1538.5</td>
</tr>
<tr>
<td>Dyebath Volume</td>
<td></td>
</tr>
<tr>
<td>6. Dyebath Sample No. 0 taken</td>
<td>5.0</td>
</tr>
<tr>
<td>Dyebath Volume</td>
<td>1533.5</td>
</tr>
<tr>
<td>7. Buffer solution added to counteract acidity of samples</td>
<td>1.5</td>
</tr>
<tr>
<td>8. Samples entered, dyebath agitated 5 minutes and buffer added to adjust pH to 6.0</td>
<td>64.5</td>
</tr>
<tr>
<td>9. Water added, agitation continued</td>
<td></td>
</tr>
<tr>
<td>10. pH checked at 6.0 Final Dyebath Volume</td>
<td>1600.0</td>
</tr>
</tbody>
</table>
The completed dyebath was placed over a constant intensity gas flame and the dyeing was carried out with constant agitation by means of the Vari-Speed Stirrer. The beaker containing the dyebath could be only partially covered and the consequent loss of dye liquor by evaporation was not replaced. The dyeing conditions and the removal of dyebath samples are summarized in Table 8.

The final dyebath sample, No. 13, was taken after the dyebath had been removed from the heat, the samples removed, and the excess dye liquor squeezed from the samples back into the dyebath. The final volume was determined by measurement.

Each of the fourteen dyebath samples (five ml. each) was placed in an individual flask and diluted twenty-five fold. The pH of the diluted solutions was checked and found to be 6.0 in each case.

The concentrations of the dyebath components, as prepared, when Sample No. 0 was taken were: Fast Acid Yellow GS — 0.78 grams per liter

Brilliant Scarlet 3R — 0.26 grams per liter

and when diluted:

Fast Acid Yellow GS — 0.0312 grams per liter

Brilliant Scarlet 3R — 0.0104 grams per liter.

The concentrations of the dyebath components when Sample No. 1 and subsequent samples were taken cannot be determined by ordinary means since the wool had absorbed some of the dyes and Synthran ACA probably had entered the dyebath from the wool as a result of the pretreatments.

The following section is concerned with the means used to estimate the concentrations of each of the dyebath components by spectrophotometric examination of the dye liquor samples taken as the dyeing proceeded.
Table 8. Record of Dyeing Conditions - Master Dyebath

<table>
<thead>
<tr>
<th>Elapsed Dyeing Time (Minutes)</th>
<th>Dyebath Temperature (Degrees F.)</th>
<th>Dyebath Sample Taken No.</th>
<th>Decrease in Dyebath Volume by Samples Removed (ml.)</th>
<th>Actual Dyebath Volume Before Sample Removed (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>85</td>
<td>1</td>
<td>5</td>
<td>1600</td>
</tr>
<tr>
<td>5</td>
<td>108</td>
<td>2</td>
<td>10</td>
<td>1595</td>
</tr>
<tr>
<td>10</td>
<td>129</td>
<td>3</td>
<td>15</td>
<td>1590</td>
</tr>
<tr>
<td>15</td>
<td>150</td>
<td>4</td>
<td>20</td>
<td>1585</td>
</tr>
<tr>
<td>20</td>
<td>168</td>
<td>5</td>
<td>25</td>
<td>1580</td>
</tr>
<tr>
<td>23</td>
<td>175</td>
<td>6</td>
<td>30</td>
<td>1575</td>
</tr>
<tr>
<td>26</td>
<td>184</td>
<td>7</td>
<td>35</td>
<td>1570</td>
</tr>
<tr>
<td>29</td>
<td>192</td>
<td>8</td>
<td>40</td>
<td>—</td>
</tr>
<tr>
<td>32</td>
<td>200</td>
<td>9</td>
<td>45</td>
<td>—</td>
</tr>
<tr>
<td>35</td>
<td>206</td>
<td>10</td>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>Boil</td>
<td>11</td>
<td>55</td>
<td>—</td>
</tr>
<tr>
<td>45</td>
<td>Boil</td>
<td>12</td>
<td>60</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>Removed from heat</td>
<td>13</td>
<td>65</td>
<td>1345</td>
</tr>
</tbody>
</table>
Computation of Concentrations

Each of the diluted dyebath samples (Numbers 0 through 13) was placed in the spectrophotometer and optical density readings were taken at 330, 350, 420, 430, 500, and 510 millimicrons. The optical densities of standard solutions of each of the dyebath components at known concentrations had been previously determined for the same wavelengths as shown in Table 6.

The optical densities of the standard solutions at the wavelengths which were to be used in the calculations of the concentrations of the master dyebath were converted to unit concentrations (see "Derivation of Formulae" in Appendix) and are shown in Table 9. The optical densities obtained for each of the dyebath samples are shown in Table 10. Tables 9 and 10 will be found in the Appendix.

The progressive concentrations of the dyebath were then determined by using these two sets of data (from Tables 9 and 10) in Formula 6 in the Appendix. In this formula as applied to this problem:

\[ D_1 - \text{optical density of a dyebath sample at 330 or 350 millimicrons} \]
\[ D_2 - \text{optical density of a dyebath sample at 420 or 430 millimicrons} \]
\[ D_3 - \text{optical density of a dyebath sample at 500 or 510 millimicrons} \]

and:

\[ Y_1, Y_2, Y_3 - \text{optical densities (at unit concentrations) of Fast Acid Yellow GS at wavelengths corresponding to those used for the dyebath} \]

and similarly for the \( R_1, R_2, R_3 \) values for Brilliant Scarlet 3R and the \( S_1, S_2, S_3 \) values for Synthratan ACA.

The optical density values for wavelengths 350, 420, and 500 were entered into the formula as described above and a desk calculator was
used to solve for the concentrations \((y, r, \text{ and } s)\) of each of the components in each of the fourteen dyebath samplings.

In order to assure accuracy and to obtain the most valid set of results, it was decided to use all possible wavelength combinations, solve all equations, and compare results. Thus, experimental error might be indicated in some sets of data, the erroneous data eliminated, and the most representative set of results used. There were eight possible combinations of sets of readings at the six wavelengths which were used with thirteen readings for each dyebath component in each set. The mathematics involved were lengthy, and there may have been errors in calculations.

In order to assure accuracy and obtain results in the fastest manner, the data were arranged in program form and the Univac Scientific 1101 Computer was used to perform the computations. Eight runs were made on the computer with the eight different sets of input data, and resulted in eight solutions for the concentrations of each component of the dyebath at each stage of the dyeing where a dyebath sample was taken.

The results from the computer for the wavelength combination of 350, 420, and 500 millimicrons agreed exactly with the results which had been computed with a desk calculator for the same wavelengths. This supported all results as to mathematical accuracy and correct machine operation.

The results of the eight sets of concentration determinations on the computer are contained in Table 11. The results are arranged in sets of wavelength combinations with the thirteen concentration estimates for each of the three dyebath components in columns. The columns represent the dyebath concentrations as the dyeing proceeded, with the first sample
results at the top of each column and the other sample results following
in order down the columns. The results of the most representative and
reliable combination of data are presented graphically in Figure 3 (in
Chapter V).

The sample pretreated by Standard Method I was dyed a medium bright
red. The sample pretreated by Standard Method II was dyed a medium bright
orange. The colors of the samples were similar to those of the final dye­
ings shown in Figure 1.

Pretreatment Measurements

This series of experiments was designed to study the behavior of
Synthrotan ACA when used as a resist agent in the pretreatment of wool
fibers. One pretreatment was carried out by Standard Method I and another
by Standard Method II with wool samples weighing 3.50 grams in each bath.
The final volumes of the two pretreatment baths were measured after the
samples had been removed and the excess liquid squeezed from them back
into the respective baths. Samples were taken from each of the final
bath liquors. Both wool samples were rinsed in water at room temperature
and allowed to dry in the atmosphere.

The dry wool samples were both entered into a bath of distilled
water and subjected to the same temperature and time of dyeing conditions
as had been used in the master dyeing. The samples were removed, excess
liquid squeezed back into the bath, the volume of the bath measured, and
a sample of the liquor taken.

Two grams of untreated wool was entered in a 120 ml. bath of dis­
tilled water and exactly the same procedure was followed as was explained
in the previous paragraph. This was termed a boil-off bath.

The above four undiluted samples were examined with the spectrophotometer at a wavelength reading of 350 millimicrons. The optical density readings were used to estimate the amount of Synthran ACA absorbed by the wool in each pretreatment and the amount which might be expected to be removed from the same samples solely by the time and temperature effects of a dyeing process. The reading on the untreated-wool bath was for the purpose of obtaining an indication of the optical density due to the impurities which might be removed from a wool sample in pretreatment. The results are summarized in Table 12 in the Appendix.
CHAPTER V

RESULTS AND DISCUSSION

No attempt will be made in this section to describe the individual samples from dyeings. Rather, the results of each series of dyeings will be summarized on the basis of the over-all results and the best judgment of the author. Contrast effects are very difficult to evaluate by visual examination. In each case, every effort was made to examine the dyeings objectively and to judge them without any consideration for eye appeal of the colors. It was concluded that levelness can be attained by using the proper dyebath preparation and dyeing conditions. Therefore, the levelness of samples from tests carried out will not be discussed unless it was an important factor in the particular test.

The Pretreatment.—On the basis of the tests conducted to compare the efficacy of three different products as resist agents in the Standard Pretreatment Methods, the decreasing order of effectiveness was indicated to be: Synthratan ACA, Tamol N, and Naccotan A. Increasing the concentrations of Tamol N and Naccotan used resulted in no visible improvement in the degree of contrast produced. Samples pretreated by each resist agent did, however, yield contrast effects. All three agents are considered satisfactory for use as resist agents. The products tested were not made for use as resist agents in wool dyeing and it is quite possible that some other product might prove even more effective than Synthratan ACA.
It was found that samples pretreated with 50 per cent Tamol N did not yield satisfactory contrast results after three days of storage following the pretreatment. Samples pretreated with Synthran ACA lost some effectiveness after ten days storage, but only to a small extent.

Samples pretreated by Standard Method I, phenol, absorbed more of the levelling acid dye faster than untreated wool. However, when untreated wool was dyed in the same dyebath with samples pretreated by each of the standard methods, the degree of contrast between the phosphoric acid pretreated sample and the untreated sample was much greater than that between the phenol pretreated sample and the untreated wool. This indicated that the contrast effects, obtained by use of the standard pretreatment methods and Contrast Effect Method I dyebath, were due primarily to the resistance of the phosphoric acid-resist agent pretreated sample to the levelling dye.

Sulfuric acid and formic acid each were satisfactory as pretreatment mediums. However, samples pretreated with solutions of these mediums did not yield as great a degree of contrast as samples pretreated by Standard Method I, phosphoric acid, and dyed under the same conditions.

The Dyebath.—The limited study of the effects of varying the dye concentrations showed that a slight improvement in contrast can be obtained by using a 100:1 dyebath ratio instead of the 60:1 ratio of Contrast Effect Method I. Contrast also appeared more definite when 3 per cent (rather than 6 per cent) of the milling or supermilling dye was used with 1 per cent (rather than 2 per cent) of the levelling dye. Changes from the 3:1 ratio between the dyes produced differences in shades rather than changes
in the degree of contrast.

The pH of the dyebath is considered to be important to the levelness of dyeings rather than the contrast attained. Samples dyed in an unbuffered dyebath showed good contrast but irregular and inadequate penetration of the dyes into the fiber. Once the dyebath is properly buffered (samples well agitated for not less than five minutes during addition of buffer solution), the pH remains constant during dyeing.

All the dyes used in this work produced good contrast and level dyeings when the standard pretreatments were used and the dyes were applied from Contrast Effect Method I dyebaths with the proper dyeing conditions.

The Dyeing.—Preliminary dyeings indicated that dyeing conditions affect not only the color, or shades of the same color, obtained from a dyeing, but also the degree of contrast produced. It was found that, for two combinations of dyes (Fast Acid Yellow GS with either Alizarine Sapphire FS or Brilliant Scarlet 3R), there is a critical temperature below which, the levelling dye did not dye the phosphoric-pretreated sample but dyed the phenol-pretreated sample lightly. Above the critical temperature, both samples were dyed by the levelling dye, but the phenol-pretreated sample was dyed to a darker shade. The milling or supermilling dye went on the fiber very rapidly above 100 degrees Fahrenheit and was almost entirely exhausted from the dyebath at the critical temperature. The critical temperature for the Fast Acid Yellow GS-Alizarine Sapphire FS combination was 170 degrees Fahrenheit. For the Fast Acid Yellow GS-Brilliant Scarlet 3R combination the critical temperature was 200 degrees Fahrenheit. The longer the dyeing was continued, the closer the two samples approached
the same shade of the same color. Samples dyed with each of the combina-
tions showed little contrast after an hour at the boil.

When the dyebath was heated above the critical temperature and the
samples entered, the milling dye was exhausted within five minutes and
the entire dyeing process was accelerated. In dyeings with Fast Acid
Yellow GS and Alizarine Sapphire FS, the change of the dyebath from green
to blue due to the exhaustion of the yellow dye was plainly visible.

Figure 1 illustrates the typical coloration of samples when pre-
treated by the standard methods and dyed in a Contrast Effect Method I
Dyebath. With either combination of dyes, two colors can be obtained by
stopping the dyeing at or just below the critical temperature. Two tones
(or shades) of the same color can be obtained by continuing the dyeing
process until the desired shades are obtained.

It was found that maximum two-color contrast was obtained by enter-
ing the samples at room temperature, bringing the dyebath up to 10 degrees
below the critical temperature over a 30 minute period, and holding the
temperature constant for 15 minutes. Optimum two-tone contrast was ob-
tained by entering the samples at room temperature, bringing the dyebath
up to a gentle boil over a 30 minute period, and holding at the boil for
15 to 30 minutes depending on the depth of shade required.

The optimum two-tone effect dyeing conditions (30 minutes at the
boil) were applied to two sets of samples pretreated by standard methods
and dyed in two separate dyebaths, prepared by Contrast Effect Method I
with Fast Acid Yellow GS-Brilliant Scarlet 3R dyes. The dyeings resulted
in two pairs of samples which were identical in contrast and in the shades
of red on the corresponding samples of each pair.
As previously stated, at the concentrations investigated, both sulfuric acid and formic acid proved inferior to phosphoric acid as a pretreating solution for use in Standard Pretreatment II. Fast Acid Yellow NGS gave good contrast effects when used as the milling dye in the New Methods tests. It is expected that most milling dyes should give good results, since the contrast obtained depends primarily on the resisting of the levelling dye by a pretreated sample (see below under "The Mechanism.") Dyeings carried out with one untreated sample and one sample pretreated by Standard Method II resulted in contrast effects which were slightly less satisfactory than when one sample was pretreated by Standard Method I and the other by Standard Method II.

The Mechanism.—The first important aspect of contrast-effect dyeing studied in this work is the pretreatment of the wool fiber. The very high affinity of phenol for wool is probably due to strong hydrogen bond formation. Alexander and Hudson (21) state that phenol replaces bound water in the wool fiber and swells the fiber to an abnormal extent. The great swelling is probably due to the size of the phenol molecule as compared to a molecule of water. Thus, the phenol-resist agent pretreatment results in greatly increased internal surface area in the fiber, and in the absorption of the resist agent which behaves essentially as a colorless dye (22).

Speakman and Stott (23) found that wool absorbs much greater quantities of weak acids than of strong acids. With weak acids the swelling increases with concentration of the acid and is not repressed by an excess as with strong acids. Swelling in strong acids is very small as compared to that caused by weak acids.
The effect of the phosphoric acid pretreatment is more complex. Steinhardt, Fugitt, and Harris (24) show that the Gilbert-Rideal theory leads to an equilibrium constant for the adsorption of hydrochloric acid which justifies the assumption that the chloride ion has no specific affinity for the wool fiber. A few acids — phosphoric, formic, and sulphamic — have abnormally low anion affinity for wool, even lower than hydrochloric (25). In the case of phosphoric acid this may be attributed to the strong hydrogen bonding action which takes place between water and the acid. Therefore, it can be concluded that as a result of the small amount of swelling that does occur, the phosphoric acid does assist in making the fiber more accessible to the resist agent, but that dye sites are not strongly occupied by the acid.

In summary, the phenol pretreated sample is swollen, and dye sites are occupied by the resist agent and by the acid. The phosphoric acid treated sample is probably little more accessible to an acid dye than normal wool in water, and the dye sites are taken up by the resist agent and loosely bonded acid. Thus, the stage is set for a difference in the rate of dyeing between the two samples in the same dyebath.

Reaction in a porous solid in contact with liquid involves the following steps (26):

(a) Transport of reactants to or products away from the surface.
(b) The sorption of reactants at the surface.
(c) The diffusion of reactants and/or products through the solid phase.
(d) Chemical reaction at the sites.
The slowest process governs the over-all rate of the reaction. It has been shown (27, 28) that steps (b) and (d) take place very rapidly as compared to the migration steps. In a dyebath with a high concentration of dye and rapid agitation, it can be assumed that step (a) will take place faster than step (c). Therefore, in the normal dyeing situation the diffusion within the fiber controls the over-all rate of dyeing for a single dye.

Vickerstaff (29) asserts that three factors influence the adsorption of dyes in a mixture:

(a) Competition between the different dye anions for the available surface.

(b) Effect of each dye in contributing to the surface charge of the fiber.

(c) Interaction between dyes in solution.

The verification of compliance with considerations for measuring light absorption indicated the absence of interaction between the dyebath components used in this work. Thus, the first two factors together with the over-all rate controlling step, must control the rate of dyeing for the dye mixture used in this work.

The last factor that will be taken into consideration is the relative affinities of the dyebath components. In general, polysulphonated dyes are adsorbed from neutral solutions to a much lower extent by wool than are monosulphonated dyes (30). Townend (31) has related the contrast producing ability of dyes to the number of sulphonic groups of the dyes. The more sulphonic groups present, the better the contrast effect. The greater affinity of monosulphonated milling and super-milling dyes can
be attributed to the fewer dye sites (ionic linkages) required for mono-
sulphonated dyes, the planar configuration of milling dyes which contrib­utes to Van der Waals attractions, and the highly hydrophobic nature of milling dyes. Meggy (32) suggests that the most important factor in determining affinity is the hydrophobic nature of the dye molecule. The dye and the wool can be visualized as linking in the hydrophobic area of the wool with a reduction in the potential energy of the dye molecule. A wool fiber dyed from a dyebath of high pH should therefore present a hydrophilic (negatively charged) surface. The rate of dyeing in a mixture is mainly dependent on the relative affinities of the dyes, and the difference in behavior between two dyes is entirely a rate effect (33).

With all of the above factors in mind, it is possible to postulate an explanation of the changes in concentrations of the dyebath components which took place in the contrast-effect dyeing process as illustrated in Figure 3.

The phenol pretreated sample is more accessible than the phosphoric acid pretreated sample. The surface dye sites and at least some of the internal sites of the wool fiber are occupied by the colorless dye (resist agent) in both samples, plus the strongly bound phenol in one case, and the weakly bound phosphoric acid in the other. The competition of the dyes for surface sites and the effect of each dye in contributing to the surface charge of the fiber form a secondary rate effect.

The affinity of Fast Acid Yellow GS is much greater than that of Brilliant Scarlet 3R or that of Synthratan ACA. The relative affinities of Brilliant Scarlet 3R and Synthratan ACA are not known, but may be
**Figure 3. Concentrations of Dyebath Components Master Dyeing.**

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>TEMP. (F.)</th>
<th>TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>108</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>129</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>168</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>175</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>184</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>192</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>206</td>
<td>35</td>
</tr>
<tr>
<td>11</td>
<td>Boil</td>
<td>40</td>
</tr>
<tr>
<td>12</td>
<td>Boil</td>
<td>45</td>
</tr>
</tbody>
</table>

**Explanation:**
- **y** = FAST ACID YELLOW GS
- **r** = BRILLIANT SCARLET 3R
- **s** = SYNTHRATAN ACA

Concentrations (grams per liter of dyebath) are plotted against sample numbers. The graph indicates the changing concentration of dye components over time during the dyeing process.
assumed to be of the same order on the basis of similar chemical configuration (see Dyebath Components and Chemical Structures in the Appendix).

For the sake of brevity these dyes will be referred to as follows: Fast Acid Yellow GS — "yellow"; Brilliant Scarlet 3R — "red"; and Synthran ACA — "Colorless".

Referring to Figure 3, when the dyeing was begun, the yellow dye began to exhaust rapidly from the dyebath onto the surface of both samples with a consequent displacement of the colorless dye from the fiber. At 168 degrees F., the colorless dye began to compete with the yellow dye for dye sites. Approximately 70 per cent of the yellow dye was on the fiber at this point and when the concentrations of the yellow and the colorless dye in solution approached the same value, the rate of dyeing of the yellow dye was retarded. The red dye concentration in the dyebath remained constant during this period.

From about 170 degrees F. up to about 181 degrees F., the colorless dye continued to compete with the yellow dye and both dyed at the same rate. At about 181 degrees F., the yellow dye again started to replace the colorless dye and this continued up to about 200 degrees F. At this point the yellow dye was about 90 per cent exhausted from the dyebath. The red dye had not appreciably exhausted from the dyebath up to this point.

At about 200 degrees F. the colorless dye again dyed the fiber at a rate similar to that of the yellow dye up to a temperature just below the boil. At this stage the red dye began to dye the fiber for the first time. The concentration of the colorless dye in the dyebath remained almost constant after the boil was attained, the red dye exhausted about
27 per cent from the solution, and the yellow dye continued to almost complete exhaustion.

The initial rapid dyeing of both wool samples and displacement of the colorless dye by the yellow dye is attributed to the high affinity of the yellow dye which caused a strong surface absorption. It would appear that at 168 degrees F., the over-all rate controlling effect of diffusion into the fiber became operative. Due to the high affinity of the yellow dye, its rate of diffusion should be slow, and possibly all of the surface sites had been occupied by the yellow dye. From this point the yellow dye began to penetrate the fiber, its dyeing rate was slowed, and the colorless dye in solution could compete for surface sites. Then, at 184 degree F. the yellow dye began to replace the colorless dye in the interior regions of the fiber. Thus, all of the surface sites were again unavailable to the colorless dye, being filled either by the yellow dye or molecules of the colorless dye which had been displaced from the interior of the fiber.

The yellow dye continued to displace the colorless dye from both the interior and the surface of the fiber until a temperature of 200 degrees F. was reached. At this point the yellow dye was almost completely exhausted from the solution. Surface sites again became available to the colorless dye and again the yellow and colorless dyes each dyed the fiber at about the same rate.

The red dye was effectively blocked from the phosphoric pretreated sample by the relatively inaccessible fiber and the colorless dye, as well as from the phenol pretreated sample by the colorless dye. As soon
as the yellow dye, which had a much stronger affinity for the surface of the wool, took up the available surface sites on both samples of wool, the red dye was blocked by the hydrophilic portion of the yellow dye which imparted a strong negative charge to the fiber surface.

Not until the yellow dye was almost exhausted (at 206 degrees F.), could the red dye successfully compete with the colorless dye and occupy the surface sites which had become available as a result of diffusion of the yellow dye into the fiber. The lack of penetration of the red dye is indicated by the last reading, taken after the samples were removed and excess liquor squeezed back into the dyebath beaker. The concentrations of the yellow and colorless dyes in solution decreased at this point while that of the red dye increased.

The preference of the red dye for the phenol pretreated sample is explained by several factors. The swollen state of the fibers due to the phenol pretreatment facilitated exit for the colorless dye molecules and entry for the larger molecules of the red dye. Since phenol has a much higher affinity for wool than phosphoric acid, it is likely that more of the sites in the phosphoric pretreated sample were occupied by the colorless dye, and more of the internal sites remained occupied during dyeing. Also, the diffusion of the yellow dye into the phosphoric sample was slower so that surface sites became available sooner on the phenol pre-treated sample. Measurements of the absorption of the resist agent (colorless dye) indicated that 63.1 per cent of the resist agent applied was absorbed by the phosphoric acid pretreated sample, as opposed to 51.7 per cent for the phenol pretreatment. These measurements cannot be considered quantitative, as will be pointed out, but should indicate the
relative amount of the resist agent absorbed by the samples.

Sources of Error.—Several sources of error could not be eliminated in this work. First, Vickerstaff (34) states that even in simple binary mixtures the accuracy of estimation of dyes in solution is much less than is the case where single dyes are involved. Therefore, the calculated concentrations of the dyebath components must be considered as estimates only.

The possibility of impurities from the wool also cannot be overlooked, as indicated by the spectrophotometric reading obtained from the boil-off of raw wool (see Table 12). However, this factor should have been negligible in dyebath readings since any impurities from the wool should have been removed in the pretreatments.

The low optical density readings for Synthran ACA in the visible region of the spectrum as compared to the readings for the two dyes is a third source of possible errors. This was the reason for the several computations of concentrations with different data. The most representative set of data for the computations was selected, but small errors in readings on the spectrophotometer can result in large errors in concentration calculations. Finally, the possibility of experimental error is always present.

The results of the concentration determinations seem reasonable and bear out the basic ideas which were held concerning the dyeing mechanism. However, the concentration results are presented as the best estimates which could be obtained and not as quantitative data. It follows, of course that the explanation of the dyeing mechanism, based on the concentration estimations, is strictly theoretical.
CHAPTER VI

CONCLUSIONS

It can be concluded that the dyeing process investigated in this work is a satisfactory method of producing contrast effects.

Synthratan ACA is the most effective resist agent of those examined. The essential pretreatment for contrast effects by this method is the phosphoric acid, Standard Pretreatment II. Good contrast results can be obtained by using untreated wool in place of Standard Pretreatment I in the dyeing process.

The use of three per cent of a milling or super-milling dye and one per cent of a levelling dye with a 100:1 bath ratio with the other specifications of Contrast Effect Method I, results in improved contrast effects. A pH of 6.0 for the dyebath retards the dyeing rate and promotes levelness.

When the Standard Pretreatments and Contrast Effect Method I Dyebaths are used the degree of contrast and the colors, or tones of the same color, obtained, are governed by the rate of dyeing. The rate effect is a function of dyeing conditions. Therefore, the time and temperature determine the results obtained.

The selection of dyes for use in this method of dyeing should be based on the affinities of the dyes for wool. The milling or super-milling dyes should possess high affinities, the levelling dyes lower affinities.
In order to obtain more pronounced contrast effects with this basic method, the most desirable solution would be an improvement in the resist treatment (such as a resist agent with a higher affinity) which would cause wool to resist levelling acid dyes more completely at ordinary dyeing temperatures.
CHAPTER VII

RECOMMENDATIONS

It is recommended that the framework of information established in this work be used as the base for a systematic study designed to develop the best possible contrast effect method. The best method in this case will be the one best suited to commercial purposes as far as expense, simplicity, and uniformity of results are concerned.

The first approach should be to improve the pretreatment so that the maximum degree of contrast can be attained. Although theoretical considerations indicate that a phosphoric acid solution is the best pretreatment medium, comparative studies with such acids as sulfuric, formic and hydrochloric should be undertaken in order to confirm the indication.

After the best pretreatment medium has been established, the concentration of that acid which produces maximum contrast without appreciable damage to the wool fiber should be ascertained. A similar systematic elimination should be followed to evaluate some of the more recent commercial products which indicate good possibilities as resist agents. When the best resist agent has been determined, further tests should be made to discover the optimum concentration for use with the selected application medium to produce the best contrast results.

Once the method of producing maximum contrast has been found, any additional studies of dyebath preparation and dyeing conditions which might be necessary, should be fairly simple. The principal questions
involving the dyebath preparation which remain to be answered are the actual value of pH control and the most desirable pH to be used in dyeing. The latter topic should be investigated as related to levelness of dyeing results.

No extensive investigation of dyeing conditions for the dyes which have been used should be necessary unless a radical change in pretreatment is made.

After the above studies have been completed, the range of each type of acid dyes which may be used in producing contrast effects should be expanded and the developed process evaluated as to general applicability.
APPENDIX
Table 9. Optical Densities at Unit Concentrations for Dyebath Components Used in Master Dyeing

(Unit Concentration Refers to a Solution Containing One Gram Per Liter).

<table>
<thead>
<tr>
<th>Wavelengths (Millimicrons)</th>
<th>Fast Acid Yellow GS</th>
<th>Brilliant Scarlet 3R</th>
<th>Synthratan ACA</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>$Y_1 = 10.2500$</td>
<td>$R_1 = 12.0000$</td>
<td>$S_1 = 3.87500$</td>
</tr>
<tr>
<td>350</td>
<td>$Y_1 = 12.5000$</td>
<td>$R_1 = 5.4500$</td>
<td>$S_1 = 1.03125$</td>
</tr>
<tr>
<td>420</td>
<td>$Y_2 = 33.1250$</td>
<td>$R_2 = 6.2500$</td>
<td>$S_2 = 0.06250$</td>
</tr>
<tr>
<td>430</td>
<td>$Y_2 = 31.4375$</td>
<td>$R_2 = 7.1250$</td>
<td>$S_2 = 0.06250$</td>
</tr>
<tr>
<td>500</td>
<td>$Y_3 = 3.0625$</td>
<td>$R_3 = 22.5000$</td>
<td>$S_3 = 0.06250$</td>
</tr>
<tr>
<td>510</td>
<td>$Y_3 = 1.8750$</td>
<td>$R_3 = 24.1250$</td>
<td>$S_3 = 0.31250$</td>
</tr>
</tbody>
</table>
Table 10. Optical Density Readings of Master Dyebath Samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$\frac{330}{D_1}$ Values</th>
<th>$\frac{350}{D_1}$ Values</th>
<th>$\frac{420}{D_2}$ Values</th>
<th>$\frac{430}{D_2}$ Values</th>
<th>$\frac{500}{D_3}$ Values</th>
<th>$\frac{510}{D_3}$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4150</td>
<td>0.4300</td>
<td>1.0550</td>
<td>1.0450</td>
<td>0.3000</td>
<td>0.2810</td>
</tr>
<tr>
<td>1</td>
<td>0.4100</td>
<td>0.4000</td>
<td>0.9800</td>
<td>0.9000</td>
<td>0.3100</td>
<td>0.2810</td>
</tr>
<tr>
<td>2</td>
<td>0.4000</td>
<td>0.4200</td>
<td>1.0000</td>
<td>0.9800</td>
<td>0.3250</td>
<td>0.2900</td>
</tr>
<tr>
<td>3</td>
<td>0.3950</td>
<td>0.4100</td>
<td>0.9000</td>
<td>0.9600</td>
<td>0.3300</td>
<td>0.2960</td>
</tr>
<tr>
<td>4</td>
<td>0.3100</td>
<td>0.3250</td>
<td>0.7350</td>
<td>0.7200</td>
<td>0.2850</td>
<td>0.2750</td>
</tr>
<tr>
<td>5</td>
<td>0.2500</td>
<td>0.2100</td>
<td>0.3750</td>
<td>0.3550</td>
<td>0.2650</td>
<td>0.2700</td>
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<tr>
<td>6</td>
<td>0.2300</td>
<td>0.1800</td>
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<td>7</td>
<td>0.1875</td>
<td>0.1350</td>
<td>0.2450</td>
<td>0.2600</td>
<td>0.2500</td>
<td>0.2500</td>
</tr>
<tr>
<td>8</td>
<td>0.1700</td>
<td>0.1150</td>
<td>0.1600</td>
<td>0.1600</td>
<td>0.2450</td>
<td>0.2450</td>
</tr>
<tr>
<td>9</td>
<td>0.1750</td>
<td>0.0950</td>
<td>0.1500</td>
<td>0.1100</td>
<td>0.2350</td>
<td>0.2350</td>
</tr>
<tr>
<td>10</td>
<td>0.1400</td>
<td>0.0800</td>
<td>0.0925</td>
<td>0.1000</td>
<td>0.2250</td>
<td>0.2250</td>
</tr>
<tr>
<td>11</td>
<td>0.1250</td>
<td>0.0800</td>
<td>0.0800</td>
<td>0.0900</td>
<td>0.2000</td>
<td>0.2000</td>
</tr>
<tr>
<td>12</td>
<td>0.1050</td>
<td>0.0575</td>
<td>0.0600</td>
<td>0.0650</td>
<td>0.1700</td>
<td>0.1700</td>
</tr>
<tr>
<td>13</td>
<td>0.1025</td>
<td>0.0550</td>
<td>0.0525</td>
<td>0.0625</td>
<td>0.1750</td>
<td>0.1750</td>
</tr>
</tbody>
</table>
Table 11. Results of Concentration Determinations by the Computer
(All concentrations are in grams per liter in the dilute samples used for spectrophotometer readings).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Concentrations</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( y ) ( r ) ( s )</td>
<td>( y ) ( r ) ( s )</td>
</tr>
<tr>
<td>1 -</td>
<td>0.02769</td>
<td>0.01000</td>
</tr>
<tr>
<td>2 -</td>
<td>0.02819</td>
<td>0.01062</td>
</tr>
<tr>
<td>3 -</td>
<td>0.02504</td>
<td>0.01126</td>
</tr>
<tr>
<td>4 -</td>
<td>0.02031</td>
<td>0.00989</td>
</tr>
<tr>
<td>5 -</td>
<td>0.00933</td>
<td>0.01089</td>
</tr>
<tr>
<td>6 -</td>
<td>0.00815</td>
<td>0.01039</td>
</tr>
<tr>
<td>7 -</td>
<td>0.00544</td>
<td>0.01038</td>
</tr>
<tr>
<td>8 -</td>
<td>0.00281</td>
<td>0.00989</td>
</tr>
<tr>
<td>9 -</td>
<td>0.00261</td>
<td>0.00967</td>
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<tr>
<td>10 -</td>
<td>0.00093</td>
<td>0.00987</td>
</tr>
<tr>
<td>11 -</td>
<td>0.00073</td>
<td>0.00878</td>
</tr>
<tr>
<td>12 -</td>
<td>0.00039</td>
<td>0.00719</td>
</tr>
<tr>
<td>13 -</td>
<td>0.00012</td>
<td>0.00776</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>y</th>
<th>r</th>
<th>s</th>
<th>y</th>
<th>r</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02770</td>
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<tr>
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<td>0.01117</td>
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</tr>
<tr>
<td>4</td>
<td>0.02030</td>
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<td>0.01704</td>
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<td>5</td>
<td>0.00929</td>
<td>0.01041</td>
<td>0.03602</td>
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<td>6</td>
<td>0.00813</td>
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</tr>
<tr>
<td>7</td>
<td>0.00678</td>
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<td>0.00684</td>
<td>0.00989</td>
<td>-0.00121</td>
</tr>
<tr>
<td>8</td>
<td>0.00282</td>
<td>0.01014</td>
<td>0.02216</td>
<td>0.00297</td>
<td>0.00960</td>
<td>0.02474</td>
</tr>
<tr>
<td>9</td>
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<td>0.01007</td>
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<td>0.00911</td>
<td>0.00924</td>
</tr>
<tr>
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<td>0.00091</td>
<td>0.00987</td>
<td>0.01457</td>
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<td>0.00073</td>
<td>0.00873</td>
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<td>0.00789</td>
<td>0.02521</td>
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<td>0.00050</td>
<td>0.00683</td>
<td>0.01363</td>
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<td>0.00010</td>
<td>0.00773</td>
<td>0.01120</td>
<td>0.00023</td>
<td>0.00706</td>
<td>0.01325</td>
</tr>
</tbody>
</table>

Table 11. Results of Concentration Determinations by the Computer
(continued)

(All concentrations are in grams per liter in the dilute samples used for spectrophotometer readings).
Table 12. Results of Pretreatment Measurements

<table>
<thead>
<tr>
<th>Bath</th>
<th>Initial Volume (ml)</th>
<th>Final Volume (ml)</th>
<th>Optical Density</th>
<th>Calculated Concentration (grams/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment I</td>
<td>350</td>
<td>198</td>
<td>0.880</td>
<td>0.8533</td>
</tr>
<tr>
<td>Pretreatment II</td>
<td>350</td>
<td>213</td>
<td>0.620</td>
<td>0.6012</td>
</tr>
<tr>
<td>Dyebath Minus Dye</td>
<td>120</td>
<td>350</td>
<td>0.070</td>
<td>0.0679</td>
</tr>
<tr>
<td>Boil-off bath</td>
<td>120</td>
<td>76</td>
<td>0.790</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath</th>
<th>Synthratan ACA Originally in Bath (grams)</th>
<th>Synthratan ACA in Bath After Treatment (grams)</th>
<th>Synthratan ACA on Fiber (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment I</td>
<td>0.350</td>
<td>0.1690</td>
<td>.1810</td>
</tr>
<tr>
<td>Pretreatment II</td>
<td>0.350</td>
<td>0.1281</td>
<td>.2219</td>
</tr>
<tr>
<td>Dyebath Minus Dye</td>
<td>0.0</td>
<td>0.0238</td>
<td>.3791</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bath</th>
<th>% Synthratan ACA in Bath Absorbed by Fiber</th>
<th>% Synthratan ACA on Fiber Desorbed to Bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment I</td>
<td>51.7</td>
<td>-</td>
</tr>
<tr>
<td>Pretreatment II</td>
<td>63.4</td>
<td>-</td>
</tr>
<tr>
<td>Dyebath Minus Dye</td>
<td>-</td>
<td>5.9</td>
</tr>
</tbody>
</table>
DYEBATH COMPONENTS AND CHEMICAL STRUCTURES

FAST ACID YELLOW GS (C.I. 145)
A MONOAZO MONOSULPHONATED DYE
MOLECULAR WEIGHT – 474.2

ALIZARINE SAPPHIRE FS (C.I. 1054)
AN ANTHRAQUINONE DISULPHONATED DYE.
MOLECULAR WEIGHT – 474.2

BRILLIANT SCARLET 3R (C.I. 185)
A MONOAZO TRISULPHONATED DYE.
MOLECULAR WEIGHT – 604.28

SYNTHRATAN ACA
ESTIMATED MOLECULAR WEIGHT – 472.2

Figure 1. Dyebath Components and Chemical Structures.
DERIVATION OF FORMULAE

The Basic Spectrophotometric Formula-Laws of Light Absorption (5)

Lambert's law - The fraction of light absorbed by a substance is independent of the intensity of the light.

Expressing the law in terms of the thickness of the absorbing medium:

$$I_t = I_o \left( e^{-ad} \right)$$

Where:

- $I_t$ = the intensity of light transmitted through a solution or solid
- $I_o$ = the intensity of light incident on the absorbing body
- $a$ = a constant
- $d$ = thickness of the solution or solid

********

Beer's law - The absorption of light by a colored solution is proportional to the number of molecules of absorbing substance through which the light passes.

Mathematically:

$$I_t = I_o \left( e^{-bc} \right)$$

Where:

- $b$ = a constant
- $c$ = the concentration of the colored solution

********

Combining the mathematical statements of the two laws:

$$I_t = I_o \left( e^{-kcd} \right)$$

Where:

- $k$ = a constant

*******
Optical density, $D$, is defined by the equation:

$$D = \log_{10} \frac{T_0}{T_t}$$

Combining this equation with the next previous one:

$$D = kcd$$  \hspace{1cm} (1)

The basic formula in spectrophotometric work is (14):

$$D = kcd = (-\log_{10} \frac{T}{100})$$  \hspace{1cm} (1)

Where:

- $D$ - Optical density (read from spectrophotometer)
- $k$ - Extinction coefficient
- $c$ - Concentration of sample in solution (mols per liter)
- $d$ - Light path of the cell (centimeters)
- $T$ - Per cent transmission (read from spectrophotometer)

Rearranging formula (1):

$$k = \frac{D}{cd}$$

A constant value of 1.00 cm. being assumed for $d$, then:

$$k = \frac{D}{c}$$  \hspace{1cm} (1a)

*******

Density of Mixture Expressed in Terms of the Mixture Components

Where:

$D$ - Optical density of a mixture (In this case Fast Acid Yellow plus Brilliant Scarlet 3R plus Synthran ACA)
Y - Optical density of Fast Acid Yellow GS
R - Optical density of Brilliant Scarlet 3R
S - Optical density of Synthran AGA

\( y_0 \) - Concentration of Fast Acid Yellow GS in a known standard solution (grams per liter)

\( r_0 \) - Concentration of Brilliant Scarlet 3R in a known standard solution (grams per liter)

\( s_0 \) - Concentration of Synthran AGA in a known standard solution (grams per liter)

\( m_0 \) - Concentration of a known standard mixture (grams per liter)

\( y \) - Concentration of Fast Acid Yellow GS in unknown mixture (grams/liter)

\( r \) - Concentration of Brilliant Scarlet 3R in unknown mixture (grams/liter)

\( s \) - Concentration of Synthran AGA in unknown mixture (grams/liter)

Then:

\[
D = \frac{Y}{y_0} y + \frac{R}{r_0} r + \frac{S}{s_0} s
\]  

Conversion of equation (2) to terms of extinction coefficient:

When:

\( C_y \) - Concentration of Fast Acid Yellow GS in standard solution (mols per liter)

\( C_r \) - Concentration of Brilliant Scarlet in standard solution (mols per liter)

\( C_s \) - Concentration of Synthran AGA in standard solution (mols per liter)

\( C_m \) - Concentration of Mixture (mols per liter)

\( K_Y \) - Extinction coefficient of Fast Acid Yellow GS

\( K_R \) - Extinction coefficient of Brilliant Scarlet 3R

\( K_S \) - Extinction coefficient of Synthran AGA

\( K_m \) - Extinction coefficient of Mixture
Combining equations (1) and (2) and substituting capital letters for the usual lower case designations of $k$ and $c$; so that:

$$D = K_c \quad Y = K_y y \quad R = K_r r \quad S = K_s s$$

Then:

$$K_{cm} = \frac{V}{y_0} (K_{cy} y) + \frac{r}{r_0} (K_{ry} r) + \frac{s}{s_0} (K_{sy} s)$$

(3)

Determination of Concentrations of Components of a Dyebath from Optical Density Readings (Ternary Mixture)

If:

- $A_1$ - Wavelength of maximum absorption for one component
- $A_2$ - Wavelength of maximum absorption for a second component
- $A_3$ - Wavelength of maximum absorption for the third component

Then the Optical Densities of the mixture of these components at $A_1$, $A_2$, $A_3$ respectively (see Vickerstaff (5)):

$$D_1 = \frac{V}{y_0} y_1 + \frac{r}{r_0} R_1 + \frac{s}{s_0} S_1$$

$$D_2 = \frac{V}{y_0} y_2 + \frac{r}{r_0} R_2 + \frac{s}{s_0} S_2$$

$$D_3 = \frac{V}{y_0} y_3 + \frac{r}{r_0} R_3 + \frac{s}{s_0} S_3$$

(4)

If the divisions $\frac{y_1}{y_0}$, $\frac{R_1}{r_0}$, $\frac{S_1}{s_0}$, $\frac{y_2}{y_0}$, $\frac{R_2}{r_0}$, $\ldots$ etc. are carried out, the resulting values represent the Optical Densities of a solution of each of the components (at each of the three wavelengths) which contains one gram per liter of the component. Thus, $y_1$, $y_2$, $y_3$; $R_1$, $R_2$, $R_3$; $S_1$, $S_2$, $S_3$ may be placed in the following equations, if it be recognized that
for this case the values must be based on solutions of unit concentration:

\[ D_1 = y Y_1 + r R_1 + s S_1 \]
\[ D_2 = y Y_2 + r R_2 + s S_2 \]
\[ D_3 = y Y_3 + r R_3 + s S_3 \]

A set of three simultaneous equations containing three unknowns; in this case, the concentrations of the components of a ternary dye bath mixture.

(5)

Expansion of equation set (5):

Equation set (5) may be expanded into the form below for ease of solution:

\[ y = \frac{D_1 (R_3 S_2 - R_2 S_3) + D_2 (R_1 S_3 - R_3 S_1) + D_3 (R_2 S_1 - R_1 S_2)}{K'} \]
\[ r = \frac{D_1 (S_3 Y_2 - S_2 Y_3) + D_2 (S_2 Y_3 - S_1 Y_2) + D_3 (S_3 Y_1 - S_1 Y_2)}{K'} \]
\[ s = \frac{D_1 (Y_3 R_2 - Y_2 R_3) + D_2 (Y_1 R_3 - Y_3 R_1) + D_3 (Y_2 R_1 - Y_1 R_2)}{K'} \]

Where \( K' = y_1 (R_3 S_2 - R_2 S_3) + y_2 (R_1 S_3 - R_3 S_1) + y_3 (R_2 S_1 - R_1 S_2) \)

Extinction Coefficients

Concentration in mols per liter equals concentration in grams per liter divided by the molecular weight of the solute.

Therefore, from the molecular weights of the dye bath components:

\[ C_y = \frac{y_0}{120.3} \quad C_r = \frac{r_0}{604.2} \quad C_s = \frac{s_0}{172.2} \]

Substituting the above values for \( C_y \), \( C_r \), and \( C_s \) in equation (3) and cancelling:
\[ K_m = \frac{yK_y}{420.3} + \frac{rK_r}{604.2} + \frac{sK_s}{472.2} \]

Let:

\[ M_y = \text{Concentration of Fast Acid Yellow GS in a Mixture} = \frac{y}{420.3} \]

(in mols per liter)

\[ M_r = \text{Concentration of Brilliant Scarlet 3 R in a Mixture} = \frac{r}{604.2} \]

(in mols per liter)

\[ M_s = \text{Concentration of Synthran in a Mixture} = \frac{s}{472.2} \]

(in mols per liter)

Then:

\[ K_m = M_yK_y + M_rK_r + M_sK_s \] (7)

And, since concentration of the dyebath must equal the sum of the concentrations of the components:

\[ K_m = \frac{M_yK_y + M_rK_r + M_sK_s}{M_y + M_r + M_s} \] (8)
SAMPLE CALCULATIONS

\[ (O.D.)_2 = \frac{(\text{Concentration})^2}{(\text{Concentration})_1} \times (O.D.)_1 \]

Fast Acid Yellow GS

\[ (O.D.)_2 = \frac{.15625}{.03906} \times .17 \]

\[ (O.D.)_2 = .68 \text{ (computed) } \quad \text{Actual O.D. = .70} \]

Brilliant Scarlet 3R

\[ (O.D.)_2 = \frac{.15625}{.03306} \times .19 \]

\[ (O.D.)_2 = .76 \text{ (computed) } \quad \text{Actual O.D. = .78} \]

Synthran ACA

\[ (O.D.)_2 = \frac{2.0}{1.0} \times .7 \]

\[ (O.D.)_2 = 1.4 \text{ (computed) } \quad \text{Actual O.D. = 1.46} \]

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Comparison of Calculated and Actual Extinction Coefficients in

Formula 8:

\[ K_m = \frac{M_y K_y + M_r K_r + M_s K_s}{M_y + M_r + M_s} \]

\[ K_m = \frac{D}{m_o} \]

\[ K_m = \frac{.011 \times K_y + .096 \times K_r + .19 \times K_s}{.011 + .096 + .190} \]

\[ K_m = \frac{.400}{.000138} \]
\[ K_m = \frac{\text{l}_{14}(61.50) + .096(1812) + .49(36)}{1.000} \]

\[ K_m = 2890 \text{ (actual)} \]

\[ K_m = 2862 \text{ (computed)} \]
LITERATURE CITED


4. Ibid., pp. 18, 20-21.

5. Ibid., pp. 20-21.


8. Loc. cit.


30. Ibid., p. 393.


34. Ibid., p. 47.