STUDY OF A CONTRAST DYEING

PROCESS FOR WOOL

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SUMMARY

In recent years, many attempts have been made to produce unusual effects in textile materials by altering the dyeing characteristics of the fibers to obtain contrast in color-effects from the same dyebath.

A new method (devised in the laboratory of the A. French Textile School) of producing such effects on wool was achieved by pretreating two samples of wool to cause one group of fibers to absorb less dye and another to absorb more dye. Later work along these lines included further development of the dyeing process and, subsequently, an attempt to determine the behavior of each dyebath component (two dyes and the pretreating agent) in the dyebath as the dyeing proceeded. The latter phase of the work was effected by removing dyebath samples at intervals during the dyeing, analyzing them spectrophotometrically, and, from the data obtained, determining the concentrations of each component in the dyebath during the dyeing.

Further work, consisting of examining the variables of the contrast-dyeing method, was performed and the original method was improved considerably, the greatest improvement being in the pretreatment method; only one of the samples

of wool was pretreated and it, along with an untreated sample, was dyed in a bath containing two selected acid dyes.

The work herein is concerned with the determination of the behavior of the dyebath components during the contrast dyeing. The first phase of the work consisted of repeating the previously mentioned experiment in which the dyebath samples from a contrast dyeing were analyzed spectrophotometrically, and the concentrations of each component determined. The results of this experiment supported the previous findings; the behavior of the dyebath components (particularly the pretreating agent) in the bath during the dyeing was quite unexpected.

Since these findings certainly warranted further investigation, the second phase of this work consisted of a study of the improved method of achieving contrast. It was concerned with the determination of the concentrations of each component on both fabrics as well as in the bath during the dyeing. This was effected by removing small samples of each of the fabrics, as well as bath samples, from the dyebath at intervals during the dyeing. The dye was stripped from the fabrics and the stripped solutions were analyzed spectrophotometrically. The data obtained were used to compute (using an electronic computer) the concentrations of each of the components in the bath and on both fabrics.

While previous investigations gave information concerning the behavior of the components in the dyebath only, the investigations included in this work gave insight as to the distribution of the components on the fabrics as well as in the bath.

CHAPTER I

INTRODUCTION

The problem of producing contrast effects on wool was first brought to the attention of a graduate student (Davis, J.) in the A. French Textile School by Peerless Woolen Mills, a Division of The Burlington Industries, Inc. Peerless desired a method of dyeing nubbed woolen fabrics which would yield a color contrast between the nubs and the body of the fabric.

Work of a similar nature has been carried out by Fosse Dyeworks, Ltd., in England to produce ingrain or fleck effects and similar melange effects in woolen fabrics.

Earlier attempts to achieve contrast effects on wool were accomplished with varied success by using the chlorinated wool method as is explained by Hartley, Wood, and Lund (1). This method has disadvantages however, the major one being that the wool is degraded to some extent and considerable loss in fiber strength results.

The usual approaches to the problem have been: to change the chemical structure of the fiber, making it more or less accessible to dyestuffs or, to chemically alter the number of available dye sites and thus increase or decrease the total dyeing capacity of the wool (2).

A method based on dyesite availability was developed by Davis (3). The desired results were obtained by pretreating two samples of wool with a resist agent; one in the presence of phenol, and the other with phosphoric acid. These two samples were then dyed in a buffered bath containing two carefully selected acid dyes.

This work was extended by Anderson (4) who studied, spectrophotometrically, the change in concentration of the dyes and the resist agent in the dyebath as the dyeing proceeded. The results obtained during this investigation were quite unexpected and rather interesting, thus it was decided to repeat this phase of Anderson's work.

Parikh (5) continued the investigation initiated by Davis and extended by Anderson. He investigated the variables of the contrast-producing method and improved it considerably. The major improvement, which had been suggested by Anderson, was in the pretreatment; only one of the samples of wool was pretreated and it, along with an untreated sample, was dyed in a buffered bath containing two selected acid dyes.

The results of Anderson's investigations gave only an overall picture of what takes place in the dyebath during the contrast dyeing. In order to get a more complete understanding of the dyeing process, that is, to be able to determine "what is going where and when", it was necessary

to determine the amounts of each of the dyebath components
on both samples of the fabric as well as in the bath. This
was achieved by removing small pieces of both the treated
and the untreated fabric samples at the same intervals that
each of the samples of the dyeliquor was removed. The dyes
were stripped from the fabric samples and the concentration
of each of the components was determined by spectrophoto-
metric means.

The work reported herein, in addition to being a
check on Anderson's work, is an investigation of Parikh's
improved method of achieving contrast. It is concerned
with the determination of the changes in concentrations of
the dyebath components, both in the bath and on the fiber
as the dyeing proceeds.

CHAPTER II

EXPERIMENTAL PROCEDURES

Pretreatment and Dyeing Procedures

The Preparation

All woolen goods to be dyed and pretreated were initially prepared by boiling in an 80:1 bath of water, the pH of which had been adjusted to that to be used in the subsequent dyeing.*

The Pretreatments

The pretreatment methods developed by Davis and investigated by Anderson shall be referred to in this work as Standard Pretreatment I and Standard Pretreatment II. The improved method developed by Parikh shall be referred to as the Improved Pretreatment.

Standard Pretreatment I.--The woolen samples, which were circularly knitted goods, were treated for one hour at a gentle boil in a 4 per cent solution of phenol, containing 10 per cent Synthratan ACA (owf**). The liquor to fiber ratio

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*All adjustments in pH were made with 4 per cent solutions of diammonium phosphate or of phosphoric acid.
**On weight of fiber.

was 100:1. The samples were then rinsed in distilled water at room temperature.

Standard Pretreatment II.--Samples were treated for one hour at a gentle boil in a 6 per cent solution of phosphoric acid, containing 10 per cent Synthratan ACA (owf). The liquor to fiber ratio was 100:1. The samples were then rinsed in distilled water at room temperature.

Improved Pretreatment.--The samples, which were woven woolen blanket material, were treated for 45 minutes at a gentle boil in a 17 per cent solution of phosphoric acid, containing 40 per cent Synthratan ACA (owf). The liquor to fiber ratio was 100:1. The samples were then rinsed in distilled water at room temperature.

Parikh found that for best results, the pretreated goods should be dyed within 24 hours after the pretreatment.

The Dyeings

The dyebath preparation devised by Davis and investigated by Anderson shall be referred to as the Contrast Dyeing Method. This dyeing method which was improved by Parikh shall be referred to as the Improved Contrast Dyeing Method.

Contrast Dyeing Method.--Two samples of circularly knitted woolen goods, one pretreated by Standard Pretreatment I and the other by Standard Pretreatment II, were dyed in an 80:1

bath, containing 6 per cent (owf) Fast Acid Yellow GS
(Similar to C. I. Acid Orange 1) and 2 per cent (owf)
Brilliant Scarlet 3R (C. I. Acid Red 18). Both dyestuffs
and the pretreating agent were used as received from the
manufacturers, without purification. The pH of the bath had
been adjusted to 6.0. The goods were entered at room
temperature and the bath was brought to the boil during
15 minutes. The goods were dyed at the boil for 30 minutes;
rinsed in distilled water at room temperature; and dried.

Improved Contrast Dyeing Method.--Two samples of woven
woolen blanket material, one untreated and the other pre-
treated by the Improved Pretreatment, were dyed in a 70:1
bath, containing 3 per cent (owf) Fast Acid Yellow GS and
1 per cent (owf) Brilliant Scarlet 3R. The pH of the bath
had been adjusted to 3.0. The goods were entered at room
temperature and the bath was brought to the boil during 15
minutes. The goods were dyed at the boil for 30 minutes;
rinsed in distilled water at room temperature; and dried.

The Stripping

Stripping Method.--The most effective stripping method
developed to extract the dyebath components from the fabric
samples was carried out in this work as follows: The samples
were treated in a Soxhlet Extractor with 150 ml. of 10 per
cent aqueous pyridine solution at the boil for from 2 to 10

hours, depending on the amount of dye on the goods. The Soxhlet Extractor was heated with an electric heating mantle.

Concentration Determinations

Preparation of Standard Curves for Each Dyebath Component

The master dyeing performed by Anderson and repeated initially in this work shall be referred to as The Master Dyeing. The master dyeing based on Parikh's improved methods of pretreatment and dyeing shall be referred to as The Improved Master Dyeing.

The Master Dyeing.--In order to check Anderson's standard curves of the dyebath components, test runs were made on solutions prepared as follows:

Fast Acid Yellow GS - 0.25 gram was dissolved in 100 ml. of distilled water (in the case of this particular dye, heating to about 180° F. was necessary for complete dissolution) and the pH of the solution was adjusted to 6.0. A five ml. sample was diluted with water of pH 6.0, to give a concentration of 0.06 gram per liter.

Brilliant Scarlet 3R - Same as given for Fast Acid Yellow GS (without heating).

Synthratan ACA - 0.40 gram was dissolved in water and the pH of the solution adjusted to 6.0. Dilutions were made to give concentrations of 0.20 and 4.00 grams per liter.

The optical densities of the prepared solutions were determined at five millimicron intervals over the range 320 to 520 millimicrons with the aid of a Beckman Model DU Spectrophotometer.

As expected, the data obtained verified the linear relationship of optical density to concentration. That is, readings at one wavelength with a known concentration were mathematically computed to optical density values at another wavelength, using the following formula:

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

In general, the results were in close agreement.

The standard absorption curves of the dyebath components determined by Anderson and checked in this work indicate that the peaks of each of the compounds are properly distributed, that is, widely separated along the wavelength axis. The absorption peaks are located at 410 millimicrons for Fast Acid Yellow GS, at 500 for Brilliant Scarlet 3R, and at 320 for Synthratan ACA. Optical density values for each solution at the above wavelengths are given in Table 3 in the Appendix.

The Improved Master Dyeing.--Since the dyeing in this procedure was to be carried out at a pH of 3.0, it was desired to run the spectrophotometric analyses of the samples from the dyebath at the same pH. Standard absorption curves of

each of the components in solution at a pH of 3.0 were run
in order to obtain the necessary data for the computations
of the concentrations of the components in the dyebath.
The optical density values of the components at the critical
wavelengths (320, 410, and 500 millimicrons) are given in
Table 3 in the Appendix. (It had been previously determined
that changing the pH did not affect the position of the
absorption maxima.)

When it was attempted to prepare the components in a
10 per cent aqueous pyridine solution (the stripping
medium), a precipitate formed in the solution at a pH of
about 4.5. It was thus decided to run the standard curves
of the components in the pyridine medium at a pH of 6.0.
Standard solutions of the components, containing 10 per cent
pyridine and ½ per cent Triton X-100 (a non-ionic surfactant
used to prevent turbidity in the sample solutions), were
prepared and adjusted to a pH of 6.0. Optical density values
for these solutions were determined at the critical wave-
lengths (320, 410, and 500 millimicrons) in order to obtain
the data necessary for the computations of the concentra-
tions of the components on the fabrics. The optical density
values are included in Table 3 in the Appendix.

The Dyeings

The Master Dyeing.--A ten gram sample of prepared wool
(circularly knitted) was pretreated by Standard Pretreatment

I and a second ten gram sample was pretreated by Standard Pretreatment II. The samples were dyed by the Contrast Dyeing Method, the bath being prepared as follows:

Step No.	Volume (ml.)
1. Dye solutions placed in beaker	150.0
2. Dye containers rinsed	150.0
3. Water added	1000.0
4. Bath agitated and pH adjusted to 6.0	1.0
5. Water added, pH 6.0	237.5
DYEBATH VOLUME	1538.5
6. Sample No. 0 removed	- 10.0
DYEBATH VOLUME	1528.5
7. Samples entered, agitated 5 minutes and buffer added to adjust pH to 6.0	7.0
8. Water added, agitation continued	64.5
FINAL DYEBATH VOLUME	1600.0

The completed dyebath was placed over a constant intensity gas flame and the dyeing was carried out with constant agitation using a Vari-Speed stirrer. Any subsequent loss by evaporation as the dyeing proceeded was replaced by predetermined amounts of water. Details of time and temperature of sample removal are given in Table 1.

Each of the seventeen dyebath samples (10 ml. each) was placed in an individual flask and diluted twenty-five fold with water of pH 6.0. Optical density values were obtained at each of the desired wavelengths (320, 410, and 500 millimicrons). These values are given in Table 4 in the Appendix.

The concentrations of the dyebath components when Sample No. 0 was taken were:

Table 1. Record of Dyeing Conditions
The Master Dyeing

Dyebath Sample No.	Dyebath Temperature (Degrees F.)	Elapsed Dyeing Time (Minutes)
0	79	0
1	79	12
2	91	16
3	106	20
4	122	24
5	137	28
6	149	32
7	161	36
8	172	40
9	180	44
10	187	48
11	192	52
12	198	56
13	Boil	60
14	Boil	64
15	Boil	68
16	Boil	72

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 subsequent samples were taken cannot be determined by ordinary calculations since some of the dyes had been absorbed by the wool and some of the Synthratan ACA had been desorbed from the pretreated sample of wool into the bath.

The Improved Master Dyeing.--Before pretreatment, the prepared pieces of woven woolen blanket material were cut and weighed as follows, in order to distinguish the pretreated fabric from the untreated fabric in the dyebath:

Set One - One ten gram sample and thirteen rectangular-shaped 0.2 gram samples.

Set Two - One ten gram sample and thirteen square-shaped 0.2 gram samples.

The ten gram samples remained in the dyebath throughout the dyeing, while the smaller samples were removed at the appropriate time intervals.

The samples from Set Two were pretreated using the Improved Pretreatment and were dyed, along with the untreated samples (Set One), using the Improved Contrast Dyeing Method. The dyebath was prepared as follows:

Step No.		Volume (ml.)
1.	Dye solutions placed in beaker	150.0
2.	Dye containers rinsed	150.0
3.	Water added	1000.0
4.	Bath agitated and pH adjusted to 3.0	10.0
5.	Water added, pH 3.0	454.0
	DYEBATH VOLUME	1764.0
6.	Sample No. 0 removed	- 10.0
	DYEBATH VOLUME	1754.0
7.	Samples entered, agitated 5 minutes and buffer added to adjust pH to 3.0	8.0
8.	Water added, pH 3.0, and agitation continued.	7.0
	FINAL DYEBATH VOLUME	1769.0

The methods of heating and stirring were exactly as those used in The Master Dyeing. Details of time and temperature of sample removal are given in Table 2.

Each of the fourteen dyebath samples (10 ml. each) was placed in an individual flask and diluted ten fold with water of pH 3.0. The diluted solutions were analyzed with the spectrophotometer and optical density values were obtained at the appropriate wavelengths (320, 410, and 500 millimicrons). These values are given in Table 5 in the Appendix.

The concentrations of the dyebath components when Sample No. 0 was taken were:

Fast Acid Yellow GS - 0.4285 grams per liter

Brilliant Scarlet 3R - 0.1428 grams per liter

and when diluted:

Fast Acid Yellow GS - 0.04285 grams per liter

Brilliant Scarlet 3R - 0.01428 grams per liter

Table 2.   Record of Dyeing Conditions
The Improved Master Dyeing

Sample No. (Bath and Fabric)	Dyebath Temperature (Degrees F.)	Elapsed Dyeing Time (Minutes)
0	87	0
1	87	6
2	100	9
3	118	12
4	136	15
5	150	18
6	161	21
7	169	24
8	180	27
9	190	30
10	Boil	33
11	Boil	36
12	Boil	39
13	Boil	42

Each of the twenty-six fabric samples (thirteen pre-treated and thirteen untreated) was stripped of the dyebath components by treating them separately in a Soxhlet Extractor containing 150 ml. of 10 per cent aqueous pyridine solution. The samples were treated until they showed no further traces of dye and the fresh pyridine solution in the Soxhlet tube showed no coloration. The time of this stripping treatment ranged from two hours for the lighter dyed samples to ten hours for the heavier dyed samples. The stripped solutions were allowed to cool and, because they showed slight signs of turbidity, it was necessary to add a few drops of Triton X-100, a non-ionic surfactant, to each to clear the solution.

Each of the solutions was adjusted to a pH of 6.0 and diluted with water of pH 6.0, to give a final volume of 100 ml.* The diluted solutions were placed in the spectrophotometer and optical density values were obtained on each at the desired wavelengths (320, 410, and 500 millimicrons). These values are shown in Tables 6 and 7 in the Appendix.

Computations

The Master Dyeing.--The concentrations of the dyebath components in the Master Dyeing were determined by means

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*Before the dye solution was removed from the Soxhlet system, the Soxhlet tube was allowed to fill up with distilled pyridine solution, thus the remaining volume of dye-pyridine solution removed was less than 100 ml.

of the formula (6) in the Appendix, using the optical
density values in Table 4 and the calculated optical density
values at unit concentration (one gram per liter) for the
components (calculated from the values given in Table 3)
in Table 8. (All of these Tables are included in the
Appendix.)

In order to assure accuracy and obtain the results
in the fastest manner, the data were arranged in program
form and a Univac Scientific 1101 Computer was used to per-
form the computations. (Random sets of data were picked
and the computations were performed on a desk calculator.
The results were then compared with the results obtained
from the computer. This served as a check on the correctness
of the programming for the computer.)

The data from the computer (expressed as grams per
liter) were converted to concentrations in the bath by
multiplying the data by 25, the dilution factor. The con-
centrations obtained are given in Table 9 in the Appendix.

The Improved Master Dyeing.--The concentrations of the com-
ponents in the dyebath in this dyeing were determined by
means of the formula in the Appendix, using the data in
Tables 5 and 8. The data from the computer were converted
to concentrations in the bath by multiplying by 10, the
dilution factor. The concentrations obtained are given in
Table 10 in the Appendix.

The concentrations of the components in the solutions stripped from the fabrics were determined by means of the same formula, using the data in Table 6 (for the pretreated fabrics) and Table 7 (for the untreated fabrics) with the data in Table 8. These computer data (grams per liter) were converted to grams of each component on the samples removed by multiplying by 100 ml./1000 ml. per liter. (The stripped solutions were brought to a total volume of 100 ml. before spectrophotometer readings were taken.) The results obtained are given in Table 11 (for the pre-treated fabrics) and Table 12 (for the untreated fabrics) in the Appendix.

In order to convert the concentrations of the components in the dyebath for Sample 1, from grams per liter to grams, the data in Table 10 were multiplied by 1.769, the total number of liters in the bath initially. For subsequent samples, this factor was progressively decreased by 0.010 to account for the volume (10 ml.) of each sample removed.

In order to convert the weights of the components on each fabric from grams on the sample removed to total grams on the particular fabric, the following formula was used:

$$\text{Total weight on each fabric} = \frac{W \times T}{0.2}$$

where W = weight from Table 11 (or Table 12)

T = total grams of particular fabric in bath immediately prior to time of sample removal

0.2 = gram of sample removed at each time interval

These converted data are summarized in the Appendix as follows: Fast Acid Yellow GS in Table 13; Brilliant Scarlet 3R in Table 14; Synthratan ACA in Table 15. The figures given in column 5 in each of these Tables are the cumulative amounts of the component that were removed with bath and fabric samples as the dyeing proceeded.

CHAPTER III

RESULTS AND DISCUSSION

Introduction

This work was initially undertaken because of interest in the rather peculiar results obtained by Anderson during his investigations of the changes in the concentrations of the dyebath components in the dyebath as the dyeing proceeded (7).

Investigation of the behavior of the dyebath components was begun in this work by repeating Anderson's Master Dyeing (8) in order to check the validity of his results. The results (See Table 9) of this investigation agreed closely with Anderson's findings. The established peculiar behavior of the dyebath components (particularly Synthratan ACA) during the dyeing, certainly warranted further investigation of this reaction.

Since Anderson's investigations were concerned strictly with the pretreatment and dyeing methods devised by Davis, and Parikh had later developed a superior method for achieving contrast, it was decided to restrict further investigations in this work to Parikh's method. At the same time, the investigation was extended by determining the

amounts of the dyebath components absorbed by both the pretreated and the untreated fabrics as well as the changes in the concentrations in the bath. These results are given in Tables 10, 11, and 12, and are summarized in Tables 13, 14, and 15.

From the summary tables of each of the components, the reproducibility of the determinations may be approximated by comparing the calculated total grams of dye present in the system at each time interval with the known initial concentration of the dye. The average calculated total amount of Fast Acid Yellow GS as given in Table 13, agrees within 1% with the actual weight of the dye used. The smallest value obtained, 0.7351 gram (Sample 4), is 3% low, while the largest value, 0.7639 (Sample 10), is 1% high. In the case of Brilliant Scarlet 3R, the average calculated total amount as given in Table 14 agrees within 5% with the actual weight of dye used. The smallest value obtained, 0.2091 (Sample 2), is 17% low, while the largest value obtained, 0.2521 (Sample 5), is the actual weight of dye used. This 17% error is probably due to a slight error in optical density readings, for this is beyond the range of experimental error. The larger overall error for this dye compared to the yellow dye is due to the fact that the optical density range for the values of the red dye (absorption peak 500 millimicrons) was smaller than that required

for greatest accuracy.

Since the original concentration of the Synthratan ACA on the pretreated fabric was unknown, the error for this component could not be calculated. The concentration of the Synthratan ACA in the system was calculated to be 1.9256 grams, the average of the total calculated grams of the component present in the system at each time interval. Since the original amount of Synthratan ACA used in the pretreatment was known to be 5.04 grams, and the average amount absorbed by the fabric was 1.9256 grams, the exhaustion of the pretreatment bath was calculated to be 38%.

Interpretation of Results

Analysis of the changes in the concentrations of the components as the dyeing proceeds is more readily carried out if the data are presented in the form of curves expressed as concentration versus time of dyeing. The curves for the Improved Master Dyeing were prepared from the data contained in Tables 10 through 12 and are shown in Figures 1 through 6.

The following discussion is a presentation of the interpretation of the individual sets of curves and no attempt is made to explain the dyeing reaction on the basis of a single set of these curves.

The Yellow Dye (Figure 1).--As the curve indicates, the dye in the bath began to exhaust immediately, with the rate of

exhaustion increasing to a maximum between points 2 and 5.
At 7, the dye was almost completely exhausted from the bath
and little change in concentration was noted past this
point.

The dye was absorbed essentially equally by both the
pretreated and the untreated fabrics from points 0 to 1.
From 1 to 4 the untreated fabric absorbed the dye very
rapidly, while the pretreated fabric absorbed dye very
slowly. From 4 to 5 the untreated fabric continued to
absorb dye at a rapid rate but the pretreated fabric suddenly
began to absorb dye at a similar rapid rate. From 5 to 7
the untreated fabric continued to absorb dye, but at a
slightly decreasing rate, while the concentration of dye
on the pretreated fabric remained practically constant.
From 7 to 8 the untreated fabric absorbed dye rapidly as
the pretreated fabric desorbed dye at a similar rate.
Little significant change in the amounts of dye on either
fabric was noted from point 8 to the end of the dyeing.

In summary, the yellow dye exhausted from the bath
at a rapid rate, reaching maximum exhaustion at point 7.
The pretreated fabric absorbed dye slowly except for rapid
absorption from interval 4 to 5. The dye was absorbed
readily by the untreated fabric to point 7. At this point,
dye was desorbed by the pretreated fabric and absorbed by
the untreated fabric. After point 8, little change took
place in the concentrations of yellow dye in the bath or on
either fabric.

The Red Dye (Figure 2).--The dye in the bath exhausted very slowly until point 5. From 5 until 11, the dye exhausted very rapidly and from point 11 to the end of the dyeing, exhausted more slowly.

Very little dye was absorbed by the pretreated fabric throughout the course of the dyeing. The small amount that was absorbed by the pretreated sample went on the fabric very slowly from points 7 to 12. Little dye was absorbed by the untreated fabric until point 5. At this point, the dye was absorbed by the fabric until the end of the dyeing at approximately the same rate it exhausted from the bath.

Overall, the pretreated fabric absorbed very little red dye. The untreated fabric absorbed dye from point 5 to the end of the dyeing.

The Colorless Dye (Synthratan) (Figure 3).--During the initial six minutes of the dyeing, the Synthratan was desorbed rapidly from the pretreated fabric and was taken up by the bath and the untreated fabric. From point 1 to point 3, the pretreated sample regained this colorless dye rapidly as it was given up from the bath and the untreated sample. From 4 to 5, the agent was desorbed rapidly from the pre-treated fabric and went into the bath and onto the untreated fabric. From 5 to 8, the concentration on the pretreated sample remained essentially constant, while from 5 to 6, the untreated sample absorbed Synthratan from the bath.

From 8 to 9, the bath took up the agent as it was desorbed from the pretreated sample. From 9 to 11, the untreated fabric absorbed Synthratan rapidly from the bath. At point 11, the component was seemingly approaching equilibrium in the system, as little change in the concentration in the bath or on either fabric was noted after this point.

The Dyes in the Dyebath (Figure 4).--As indicated by the curve, the yellow dye exhausted rapidly from the bath until point 6, at which point it was almost completely exhausted and thus the concentration remained practically constant during the rest of the dyeing.

The red dye exhausted very slowly until the yellow dye approached maximum exhaustion. At this point, 6, the red dye began to exhaust rapidly and continued to exhaust at essentially the same rate until point 10. From 11 to the end of the dyeing, the concentration of the red dye remained practically constant.

The colorless dye (Synthratan) went into the bath rapidly from points 0 to 1, 4 to 5, and 7 to 9 while it was exhausted from the bath from points 1 to 4, 5 to 7, and 9 to 10.

The Dyes on the Pretreated Fabric (Figure 5).--(Due to the much larger concentration of Synthratan on the pretreated fabric, it was necessary to use a different scale when plotting the concentrations of this component. This must

be kept in mind when analyzing the relationships of the curves in this and subsequent figures.)

From point 0 to point 5, the yellow dye was absorbed by the fabric, with rapid exhaustion from 4 to 5. The concentration of this dye remained constant from 5 to 7, but was desorbed rapidly from 7 to 8. After point 8, the concentration of the yellow dye on this fabric remained constant to the end of the dyeing.

The Synthratan was rapidly desorbed from the fabric from point 0 to point 1, but from 1 to 3, the agent was partially regained by the sample. The fabric desorbed Synthratan rapidly from 4 to 5 (the same interval during which it absorbed yellow dye) and desorbed it again from 8 to 10. From 5 to 8 and 10 to 13, the concentration of Synthratan on the fabric remained constant.

Very little red dye was absorbed by the pretreated fabric throughout the dyeing.

The Dyes on the Untreated Fabric (Figure 6).--In general, the figure indicates that all three components were absorbed readily by the untreated fabric. It is significant that the red dye began to be absorbed only after the yellow dye had practically reached maximum absorption.

The Synthratan was absorbed readily during the initial interval. During the second interval, however, it was desorbed from the fabric (whether or not it was displaced by

yellow dye is questionable). The fabric absorbed Synthratan rapidly from point 4 to point 11, with a slight deviation in the rate of absorption from points 8 to 9.

The yellow dye was absorbed rapidly from point 1 to point 8, with a slight deviation in the rate occurring from 6 to 7. At 8, the fabric was apparently approaching maximum yellow dye absorption and thus little dye was absorbed after this point.

The red dye was absorbed very slowly by the untreated fabric until point 6. At this time, the red dye began to be absorbed rapidly and continued to be taken up at this rate until point 10. From 10 to the end of the dyeing, red dye absorption continued at a very slow rate.

The Dyeing Reaction

The explanation of the overall dyeing reaction is based on a logical interpretation of the combined sets of curves of the dyebath components (Figure 7) and the individual sets of curves previously analyzed.

Due to the complexity of the behavior of the components during the dyeing, the overall process is interpreted in a stepwise manner, based on the changes which took place during the thirteen intervals between the times at which samples were removed for analysis.
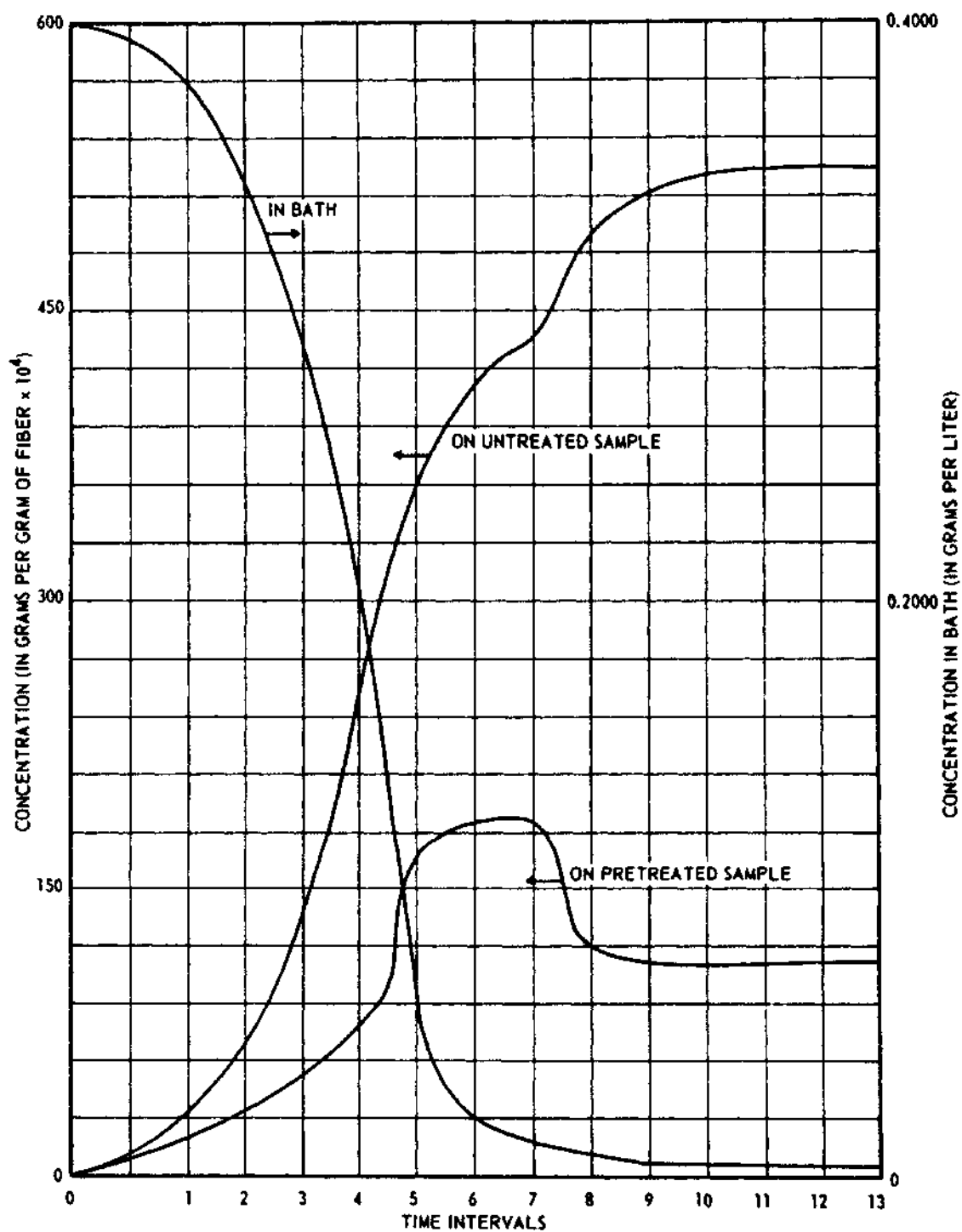
Figure 1. The Yellow Dye.
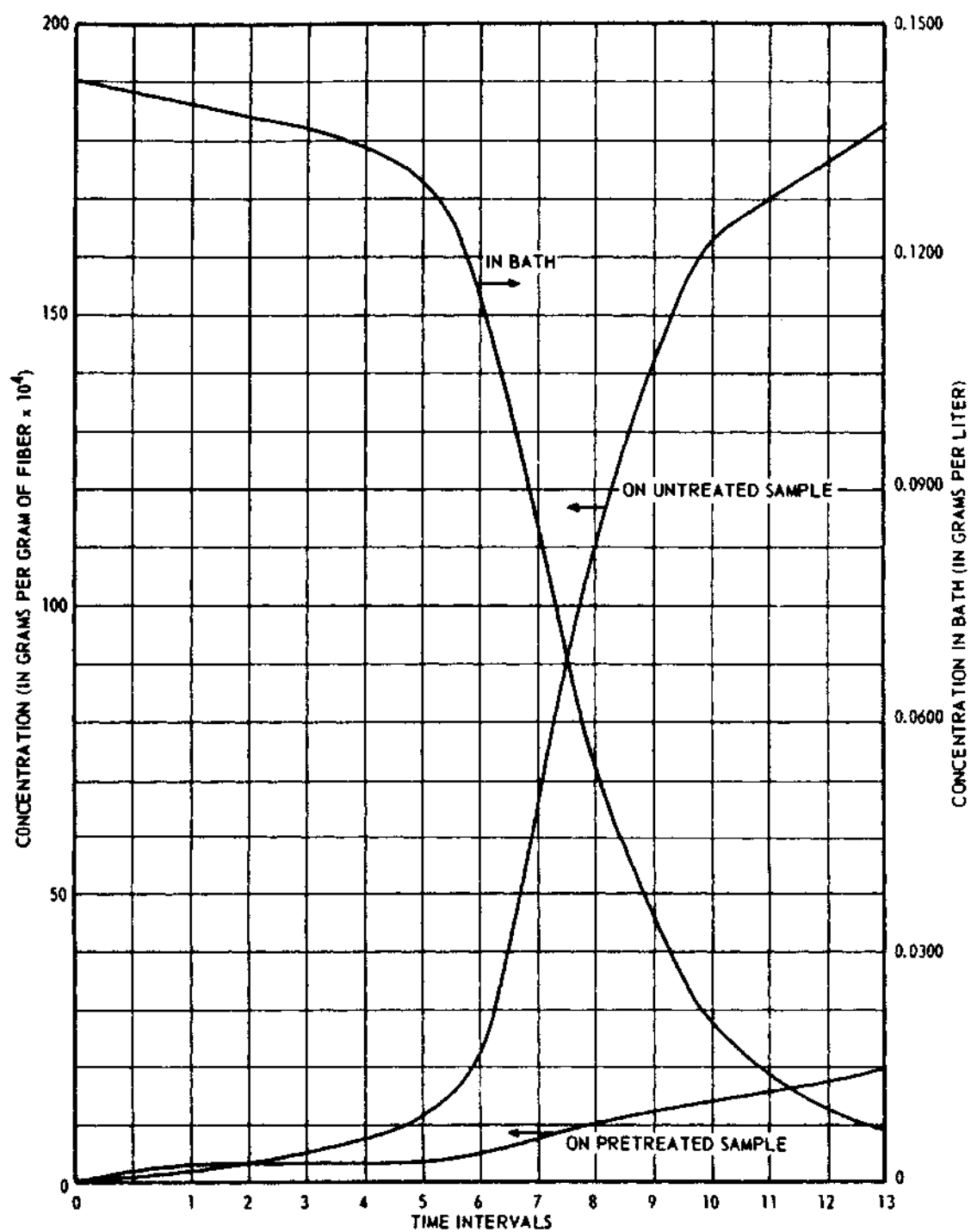
Figure 2. The Red Dye.
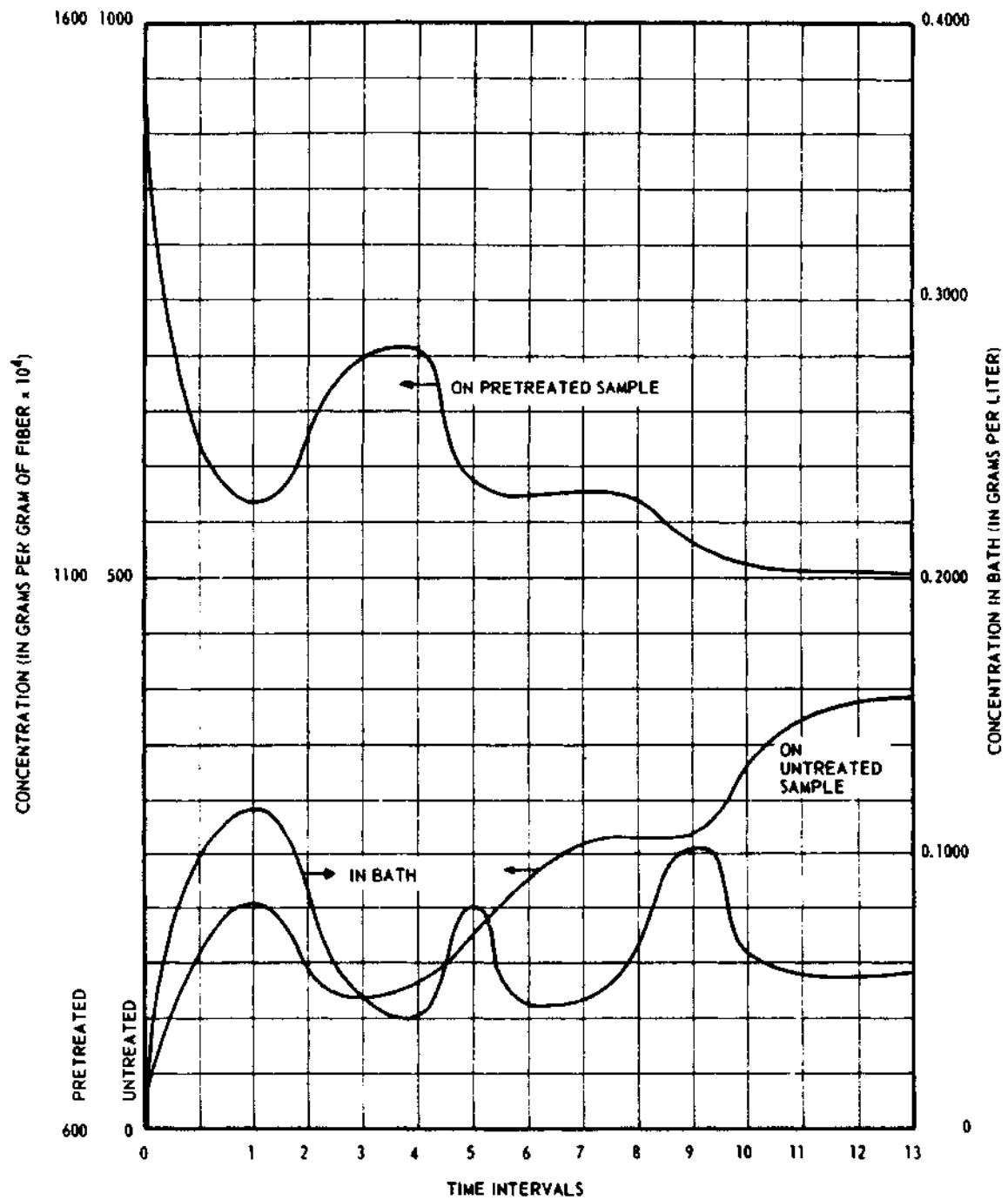
Figure 3. The Colorless Dye.
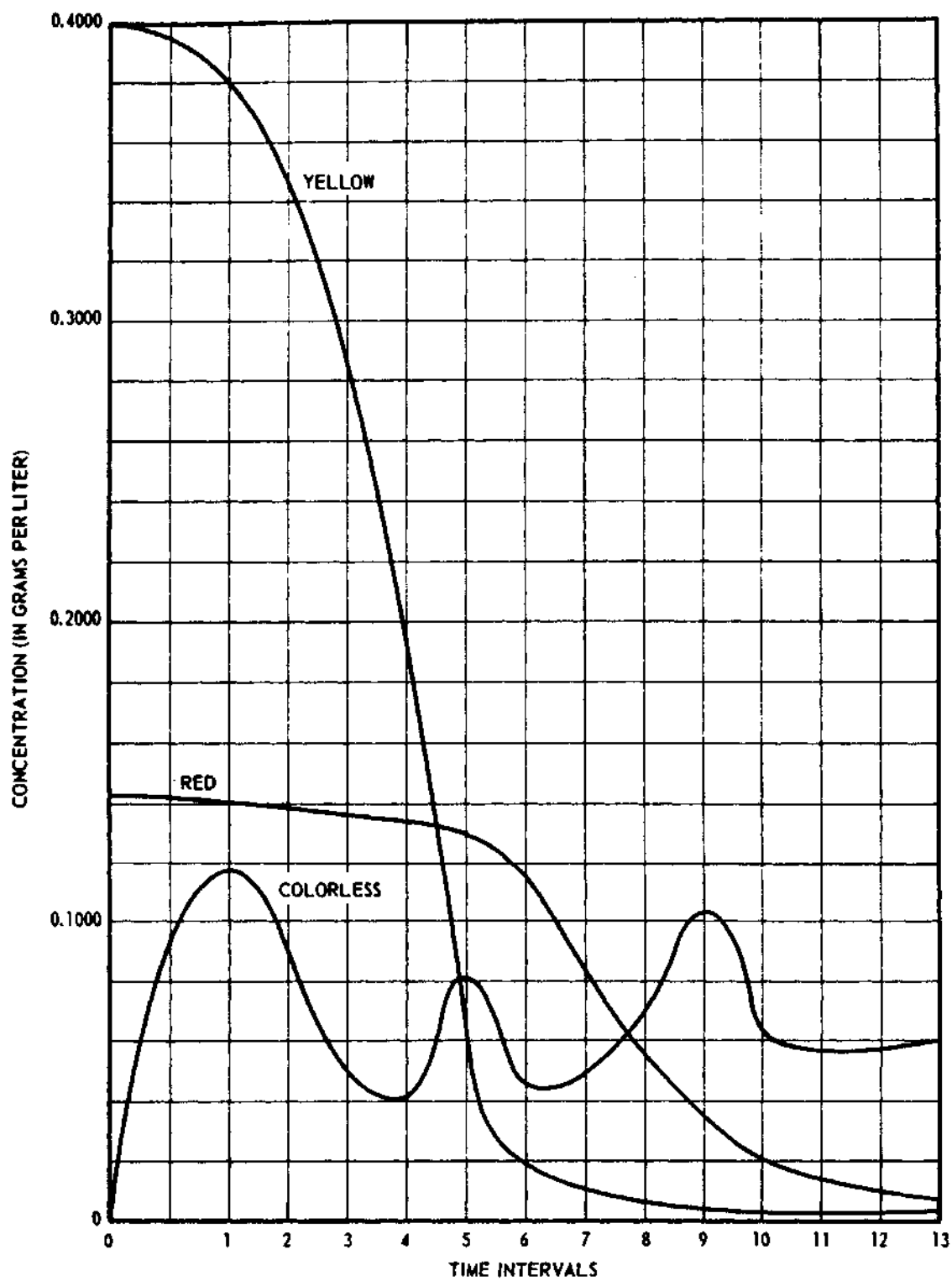
Figure 4.   Components in the Dyebath.
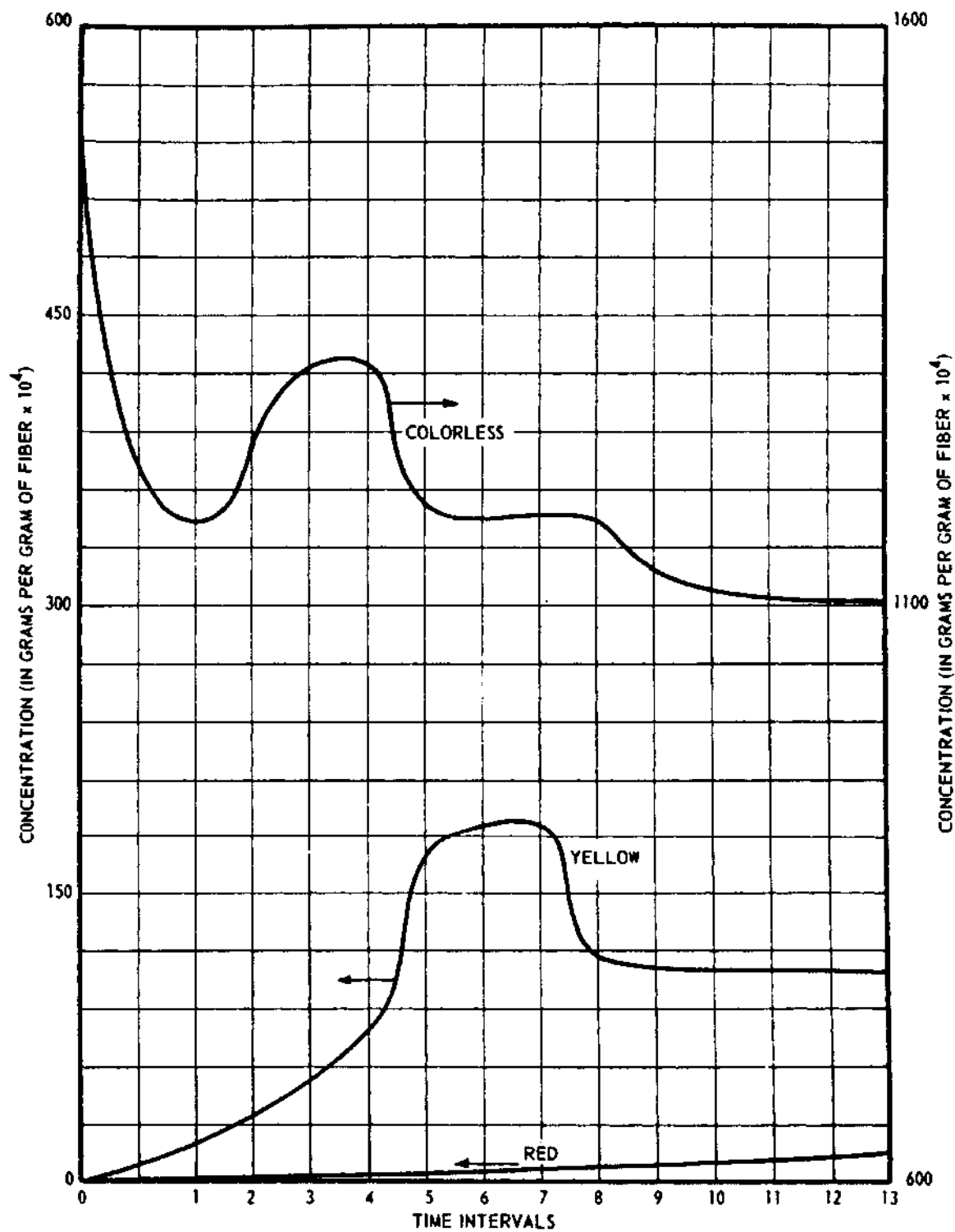
Figure 5. Components on Pretreated Fabric.
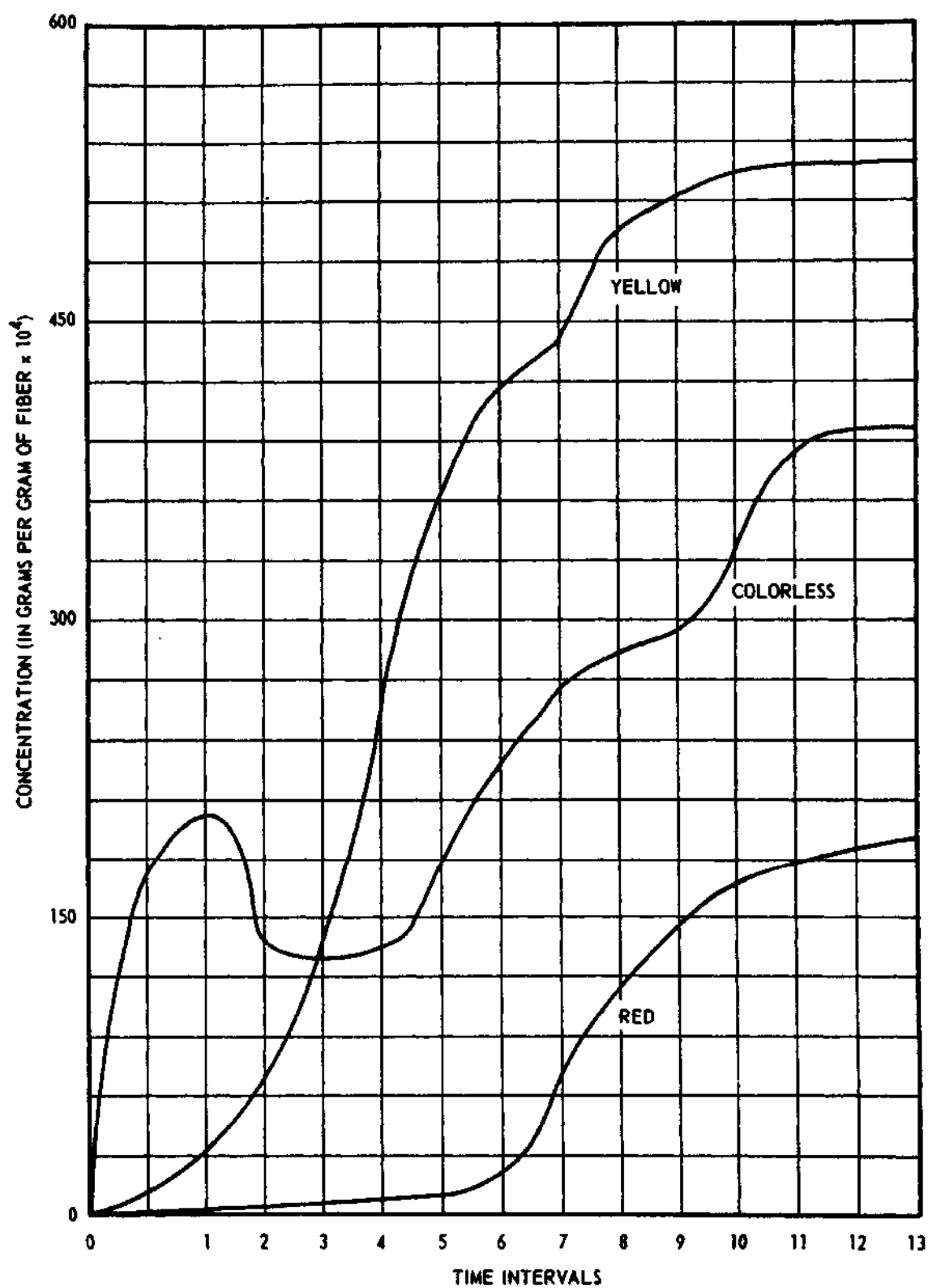
Figure 6. Components on Untreated Fabric.

Interval 0 to 1 (Six minutes).--The yellow dye began to exhaust from the bath and was absorbed by both fabrics, with approximately twice as much dye going on to the untreated fabric. The pretreated fabric, apparently having absorbed an excess of Synthratan in the pretreatment, desorbed this agent readily; the desorbed material was taken up by the bath and the untreated fabric. Essentially, the red dye did not begin to exhaust from the bath before interval 4 to 5.

Interval 1 to 2*.--The yellow dye continued to exhaust from the bath, being absorbed by both fabrics at the same rate as during the first interval. However, the Synthratan was no longer desorbed from the pretreated sample but was, in fact, absorbed by this fabric as it was lost from both the bath and the untreated fabric.

Interval 2 to 3.--The yellow dye continued to exhaust rapidly, being absorbed at a similar rate by the untreated fabric and slowly by the pretreated fabric. The Synthratan continued to exhaust from the bath, being rapidly absorbed by the pretreated sample.

Interval 3 to 4.--The yellow dye continued to exhaust rapidly from the bath, being absorbed quickly by the untreated fabric

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*This and all subsequent intervals are of three minutes' duration.

and slowly by the pretreated fabric. The pretreated fabric continued to absorb Synthratan from the bath.

Interval 4 to 5.--The yellow dye continued to exhaust rapidly but, during this interval, was absorbed at essentially equal rates by both fabrics. The sudden increase in the absorption rate of the yellow dye by the pretreated fabric may be due to the increasing affinity of this dye for the fabric as the temperature rises, and also a decrease in the affinity of the Synthratan at the higher temperatures. The displaced Synthratan was taken up by the bath and the untreated sample. The red dye began to be absorbed slowly by the untreated fabric.

Interval 5 to 6.--The yellow dye continued to exhaust from the bath, being absorbed rapidly by the untreated fabric and slowly by the pretreated fabric. Synthratan was absorbed by the untreated sample as it was given up by the bath. The red dye was absorbed slowly by the untreated sample while the pretreated sample remained resistant to this dye.

Interval 6 to 7.--As the yellow dye approached maximum exhaustion from the bath, it was absorbed by the untreated fabric at a decreasing rate, and remained constant on the pretreated fabric. The Synthratan continued to be absorbed by the untreated sample as it was given up by the bath. The red dye, as it exhausted from the bath, began to be rapidly absorbed by the untreated fabric.

Interval 7 to 8.--At this point, the yellow dye had reached maximum exhaustion from the bath. This dye, having a greater affinity for the untreated fabric (which had a greater number of available dyesites) than the pretreated fabric, desorbed from the latter and was quickly absorbed by the former. The red dye continued to be absorbed by the untreated fabric at a rapid rate, and was absorbed to a slight extent by the pretreated fabric. The concentration of Synthratan in all phases remained constant.

Interval 8 to 9.--A small amount of yellow dye continued to transfer from the pretreated to the untreated sample. Synthratan was suddenly desorbed from the pretreated sample and taken up by the bath. The red dye continued to be absorbed by the untreated fabric as it exhausted from the bath.

Interval 9 to 10.--From point 9 to the completion of the dyeing, the concentration of the yellow dye in the bath and on both fabrics remained constant, and it may be assumed that this component had essentially reached equilibrium in the system. The Synthratan was absorbed by the untreated sample as it was lost rapidly by the bath and slowly by the pretreated sample. The red dye continued to be absorbed by the untreated sample as it exhausted from the bath.

Interval 10 to 11.--As the red dye in the bath approached maximum exhaustion, it continued to be absorbed by the

untreated fabric but at a decreasing rate. The pretreated sample continued to absorb red dye only slightly. The Synthratan was absorbed by the untreated fabric as it exhausted from the bath.

Interval 11 to 12.--The red dye continued to be absorbed slowly by the untreated fabric. The untreated sample continued to absorb Synthratan as it exhausted from the bath. By this time, all curves began to level out.

Interval 12 to 13.--The red dye continued to be absorbed very slowly by the untreated fabric as the dye in the bath reached maximum exhaustion. It may be assumed that, by the end of the dyeing, equilibrium of red dye in the system had been established. From the final levelness of the Synthratan curves, it may be assumed that this component was also approaching a state of equilibrium in the system.
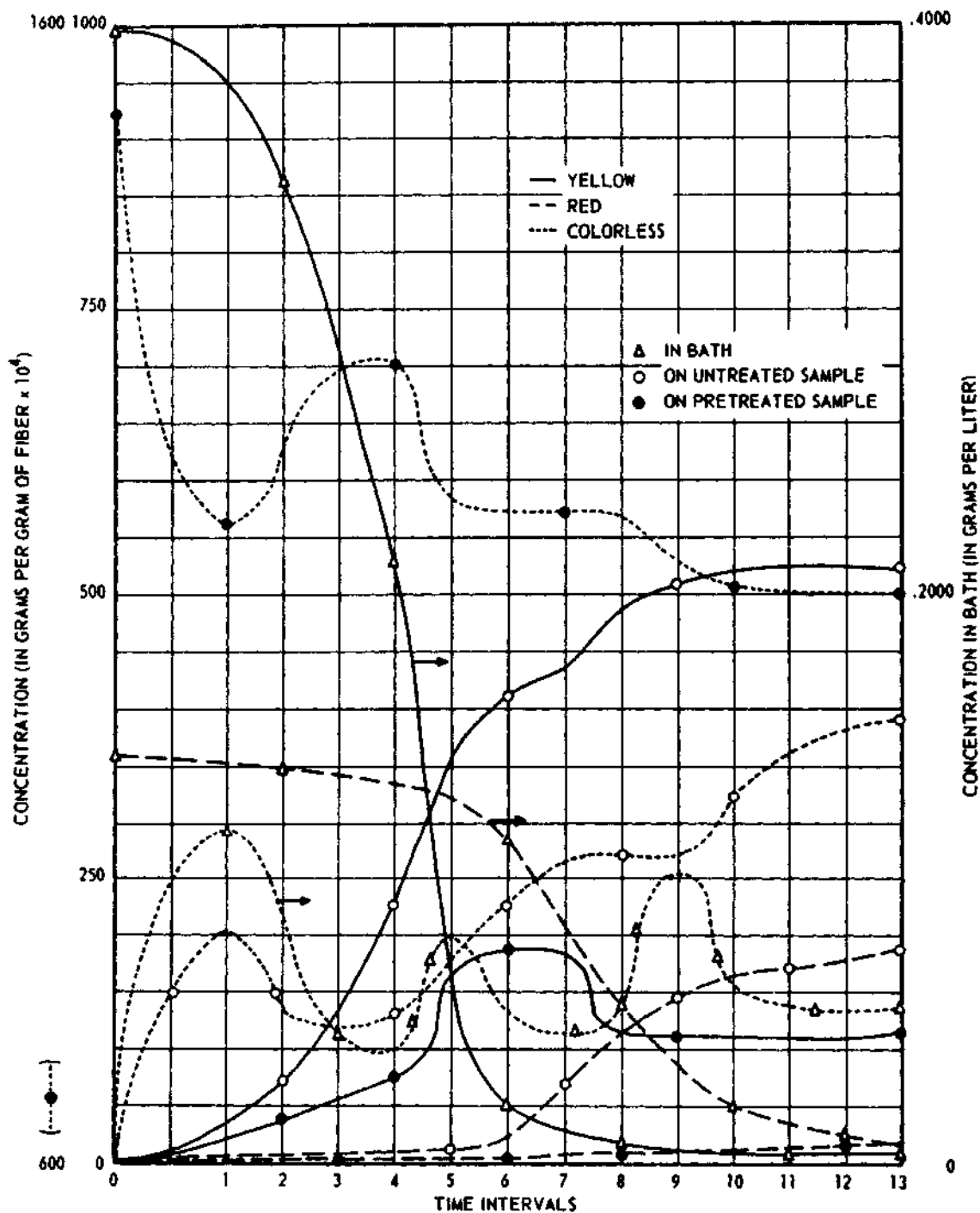
Figure 7. Figures 1-6 Combined

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

It is concluded that a rather unique reaction takes place when dyeing wool to produce contrast effects. This reaction may be summarized as follows:

In general, under the conditions of this experiment, the yellow dye exhausted from the bath rapidly, with much more being absorbed by the untreated fabric than the pretreated fabric. When the yellow dye reached maximum exhaustion from the bath, yellow dye was desorbed from the pretreated fabric and absorbed by the untreated fabric until the latter seemingly reached maximum yellow dye absorption.

The red dye exhausted very little from the bath on to either fabric until the yellow dye approached maximum exhaustion. When this occurred, the red dye was absorbed almost entirely by the untreated fabric as it exhausted from the bath. The pretreated sample remained essentially resistant to the red dye throughout the dyeing.

The reaction of the colorless dye followed no general trend, except that overall it was desorbed from the pretreated fabric into the bath and onto the untreated fabric.

It is concluded that, in general, the achieving of contrast effects on wool is dependent on the relative affinities of the dyebath components for the wool and on the relative rates of dyeing of the components. Based on dyeing behavior of the components in this work, the affinity of Fast Acid Yellow GS is assumed to be much greater than that of Brilliant Scarlet 3R or Synthratan ACA. The relative affinities of Brilliant Scarlet 3R and Synthratan ACA are not known, but may be assumed to be of the same order.

It is recommended that, since the activity of the Synthratan ACA in the system seems to control the degree of contrast, and since this activity seems to be dependent on temperature, this work be repeated at selected constant temperatures. It is also recommended that different dye-stuffs and other pretreating agents be used in further investigations in order to determine if the unusual behavior of the components is characteristic of this process.

APPENDIX

Formula Used in Calculating Concentrations of Mixtures of Dyes by Spectrophotometric Means

The formula:

$$y = \frac{D_1 (R_3 S_2 - R_2 S_3) + D_2(R_1 S_3 - R_3 S_1) + D_3(R_2 S_1 - R_1 S_2)}{K}$$

$$r = \frac{D_1 (S_3 Y_2 - S_2 Y_3) + D_2(S_1 Y_3 - S_3 Y_1) + D_3(S_2 Y_1 - S_1 Y_2)}{K}$$

$$s = \frac{D_1 (Y_3 R_2 - Y_2 R_3) + D_2(Y_1 R_3 - Y_3 R_1) + D_3(Y_2 R_1 - Y_1 R_2)}{K}$$

where $K = Y_1(R_3 S_2 - R_2 S_3) + Y_2(R_1 S_3 - R_3 S_1) + Y_3(R_2 S_1 - R_1 S_2)$

In the formula as applied to problems in this work:

D_1 = optical density of a solution at 320 millimicrons

D_2 = optical density of a solution at 410 millimicrons

D_3 = optical density of a solution at 500 millimicrons

and:

Y_1, Y_2, Y_3 = optical densities (at unit concentration)

of Fast Acid Yellow GS at 320, 410, and

500 millimicrons,

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.

Table 3. Optical Density Values of Standard Solutions

A. Components in water, pH 6.0. (The Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS 0.06*	Brilliant Scarlet 3R 0.06*	Synthratan ACA 0.20*	4.00*
320	0.344	0.651	0.865	--
410	1.106	.332	--	0.260
500	.091	1.470	--	.260

B. Components in water, pH 3.0. (The Improved Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS 0.10*	Brilliant Scarlet 3R 0.05*	Synthratan ACA 0.16*	8.00*
320	0.555	0.559	0.883	—
410	1.852	.281	—	0.116
500	.179	1.245	—	.032

C. Components in 10% aqueous pyridine solution, containing 1% Triton X-100, pH 6.0. (The Improved Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS 0.10*	Brilliant Scarlet 3R 0.05*	Synthratan ACA 0.16*	8.00*
320	0.516	0.516	0.875	--
410	1.882	.249	--	0.120
500	.160	1.153	--	.032

*Concentration expressed in grams per liter

Table 4. Optical Density Values
The Master Dyeing

Sample No.	Wavelength (millimicrons)		
	320	410	500
0	0.309	0.672	0.307
1	.290	.577	.284
2	.297	.593	.288
3	.290	.559	.285
4	.280	.513	.276
5	.266	.482	.283
6	.249	.407	.268
7	.246	.332	.267
8	.205	.254	.257
9	.209	.215	.252
10	.194	.183	.249
11	.190	.156	.250
12	.194	.147	.251
13	.198	.154	.252
14	.210	.153	.259
15	.212	.144	.256
16	.206	.145	.263

Table 5. Optical Density Values
The Improved Master Dyeing
Solutions from Dyebath

| Sample No. | Wavelength (millimicrons) | | |
	320	410	500
0	0.382	0.811	0.403
1	.418	.775	.385
2	.365	.703	.335
3	.335	.602	.386
4	.288	.461	.372
5	.231	.210	.339
6	.165	.101	.293
7	.130	.073	.218
8	.106	.055	.143
9	.086	.037	.097
10	.060	.021	.053
11	.049	.015	.038
12	.051	.017	.029
13	.047	.012	.018

Table 6.   Optical Density Values
The Improved Master Dyeing
Solutions from Pretreated Samples

Sample No.	Wavelength (millimicrons)		
	320	410	500
1	1.320	0.117	0.040
2	1.439	.147	.032
3	1.467	.230	.035
4	1.498	.230	.040
5	1.382	.643	.052
6	1.362	.711	.043
7	1.386	.718	.091
8	1.408	.446	.093
9	1.337	.438	.107
10	1.367	.435	.121
11	1.317	.419	.123
12	1.308	.448	.140
13	1.320	.432	.114

Table 7. Optical Density Values
The Improved Master Dyeing
Solutions from Untreated Samples

Sample No.	Wavelength (millimicrons)		
	320	410	500
1	0.263	0.131	0.021
2	.224	.276	.047
3	.318	.510	.075
4	.399	.936	.099
5	.363	1.340	.110
6	.457	1.597	.154
7	.561	1.733	.412
8	.830	1.940	.679
9	.828	2.020	.867
10	.874	2.070	1.000
11	.876	2.080	.980
12	1.026	2.020	1.059
13	.975	2.100	1.076

Table 8. Calculated Optical Densities at
Unit Concentrations of Dyebath
Components

(Unit concentration refers to a solution containing one gram
per liter.)

A. In water, pH 6.0. (The Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS	Brilliant Scarlet 3R	Synthratan ACA
320	5.7333	10.8500	4.3233
410	18.4333	5.5333	0.0625
500	1.5167	24.4667	0.0625

B. In water, pH 3.0. (The Improved Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS	Brilliant Scarlet 3R	Synthratan ACA
320	5.550	11.1800	5.5200
410	18.5200	5.6200	0.0145
500	1.7900	24.9000	0.0040

C. In 10% aqueous pyridine solution, containing ½% Triton
X-100, pH 6.0. (The Improved Master Dyeing)

Wavelength (millimicrons)	Fast Acid Yellow GS	Brilliant Scarlet 3R	Synthratan ACA
320	5.1600	10.3200	5.4700
410	18.8200	4.9300	0.0150
500	1.6000	23.0600	0.0040

Table 9.   Calculated Concentrations of
Dyebath Components
The Master Dyeing

Sample No.	Fast Acid Yellow GS (g/l)	Brilliant Scarlet 3R (g/l)	Synthratan ACA (g/l)
0	0.803	0.264	----
1	.682	.248	0.099
2	.703	.251	.106
3	.657	.250	.126
4	.598	.245	.164
5	.554	.255	.105
6	.458	.245	.163
7	.356	.250	.272
8	.254	.246	.165
9	.203	.244	.270
10	.161	.244	.235
11	.124	.247	.251
12	.111	.249	.289
13	.121	.249	.301
14	.117	.257	.360
15	.105	.254	.396
16	.104	.261	.336

Table 10. Calculated Concentrations of
Dyebath Components
The Improved Master Dyeing
Solutions from Dyebath

Sample No.	Fast Acid Yellow GS (g/l)	Brilliant Scarlet 3R (g/l)	Synthratan ACA (g/l)
0	0.397	0.131	----
1	.380	.127	.118
2	.346	.111	.089
3	.284	.135	.049
4	.208	.134	.040
5	.074	.131	.079
6	.019	.116	.044
7	.013	.087	.047
8	.013	.057	.065
9	.008	.038	.101
10	.005	.021	.061
11	.004	.015	.055
12	.006	.011	.064
13	.004	.007	.067

Table 11. Calculated Weights of Dyebath
Components Stripped from Pre-
treated Samples
The Improved Master Dyeing

Sample No.	Fast Acid Yellow GS (grams)	Brilliant Scarlet 3R (grams)	Synthratan ACA (grams)
1	0.0006	0.0001	0.0234
2	.0007	.0001	.0246
3	.0012	.0001	.0256
4	.0012	.0001	.0262
5	.0033	.0001	.0238
6	.0037	.0001	.0234
7	.0037	.0002	.0236
8	.0023	.0002	.0240
9	.0022	.0003	.0226
10	.0022	.0003	.0233
11	.0021	.0003	.0224
12	.0023	.0004	.0221
13	.0022	.0003	.0224

Table 12. Calculated Weights of Dyebath
Components Stripped from Un-
treated Samples
The Improved Master Dyeing

Sample No.	Fast Acid Yellow GS (grams)	Brilliant Scarlet 3R (grams)	Synthratan ACA (grams)
1	0.0007	0.0001	0.0041
2	.0014	.0001	.0027
3	.0027	.0002	.0033
4	.0049	.0002	.0026
5	.0070	.0003	.0035
6	.0082	.0004	.0045
7	.0087	.0014	.0053
8	.0097	.0022	.0065
9	.0101	.0029	.0052
10	.0104	.0033	.0064
11	.0103	.0034	.0062
12	.0101	.0036	.0095
13	.0104	.0038	.0078

Table 13. Calculated Distribution of
Fast Acid Yellow G8
The Improved Master Dyeing

Sample No.	In the Bath (g)	On the Pretreated Sample (g)	On the Untreated Sample (g)	Total Removed with Samples (g)	Total (g)
0	0(.7560)*	--	--	--	0(.7560)*
1	.6717	0.0368	0.0429	0.0004	.7508
2	.6084	.0452	.0884	.0021	.7441
3	.4971	.0725	.1618	.0045	.7359
4	.3619	.0701	.2944	.0087	.7351
5	.1273	.1938	.4101	.0150	.7462
6	.0330	.2135	.4743	.0252	.7460
7	.0224	.2105	.4934	.0371	.7634
8	.0212	.1280	.5457	.0495	.7444
9	.0140	.1236	.5570	.0615	.7561
10	.0082	.1203	.5615	.0739	.7639
11	.0058	.1129	.5465	.0865	.7517
12	.0095	.1192	.5245	.0919	.7521
13	.0071	.1127	.5291	.1113	.7602

Average: 0.7465

*Actual weight of dye used.

Table 14.   Calculated Distribution of
Brilliant Scarlet 3R
The Improved Master Dyeing

Sample No.	In the Bath (g)	On the Pretreated Sample (g)	On the Untreated Sample (g)	Total Removed with Samples (g)	Total (g)
0	0(.2520)*	--	--	--	0(.2520)*
1	.2252	0.0082	0.0027	0.0001	.2362
2	.1951	.0059	.0078	.0003	.2091
3	.2354	.0050	.0108	.0007	.2519
4	.2337	.0062	.0092	.0011	.2502
5	.2262	.0077	.0168	.0014	.2521
6	.1999	.0048	.0258	.0019	.2324
7	.1480	.0117	.0784	.0025	.2406
8	.0960	.0124	.1256	.0042	.2382
9	.0647	.0142	.1577	.0069	.2435
10	.0351	.0155	.1782	.0099	.2387
11	.0250	.0182	.1786	.0135	.2353
12	.0186	.0186	.1854	.0172	.2398
13	.0114	.0148	.1916	.0212	.2390

Average: 0.2399

*Actual weight of dye used.

Table 15. Calculated Distribution of
Synthratan ACA
The Improved Master Dyeing

Sample No.	In the Bath (g)	On the Pretreated Sample (g)	On the Untreated Sample (g)	Total Removed with Samples (g)	Total (g)
0	--	(1.9256)*	--	--	(1.9256)*
1	0.2079	1.4710	0.2570	--	1.9359
2	.1562	1.5256	.1660	0.0276	1.8754
3	.0848	1.5618	.2002	.0550	1.9018
4	.0699	1.5733	.1573	.0838	1.8843
5	.1373	1.4030	.2063	.1127	1.8593
6	.0756	1.3560	.2611	.1400	1.8327
7	.0802	1.3460	.2993	.1678	1.8933
8	.1104	1.3420	.3649	.1966	2.0139
9	.1704	1.2420	.2862	.2271	1.9257
10	.1029	1.2560	.3452	.2550	1.9591
11	.0915	1.1860	.3279	.2846	1.8900
12	.1060	1.1490	.4942	.3132	2.0624
13	.1102	1.1440	.3997	.3448	1.9987
				Average:	1.9256

*Assumed value.

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