THE DEVELOPMENT OF A LABORATORY PROCEDURE FOR DYEING NYLON
KNITS FOR REPRODUCIBILITY OF SHADES AND LEVELNESS
USING A MIXTURE OF THREE ACID DYES

by

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CHAPTER I
INTRODUCTION

In the past few years there has been a tremendous growth in tex­turized knit fabrics. Nearly all the texturized filament nylon consumed in 1972 was used in knitwear (1). In addition to this increased consumer demand for knits, the consumer has also been increasing his demands for durability and utility in the fabrics he buys. The durability and utility included dyefastness properties of adequate colorfastness and acceptable levelness of dyeing (2). Because of the great amount of nylon used in knitwear and the consumer demand for higher quality, the problems associated with nylon have become increasingly important.

Although by present standards, nylon is considered a relatively easy fiber to dye (2), there are still unsolved problems in the dyeing of nylon. The dyer can only go so far in obtaining uniformity and fast­ness. It is important that he understand the limitations with which he is confronted and know when he is getting the best results for a given fabric (3).

The textile dyer is faced with the problem of either knowing of, or selecting, a simple laboratory dye procedure that will give reproducibility in shade and levelness (4). "Despite common use of laboratory dyeings for many purposes, there is surprisingly little in the technical literature on exactly how to go about it (5)." The AATCC*

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*American Association of Textile Chemists and Colorists
Technical Manual offers no standard procedure (6), and manufacturers of laboratory dye apparatus leave the procedure up to the user. Many laboratories have their own standard procedures which they use and trust, but nowhere in the textile literature can there be found any standard dyeing procedure that will guarantee repeatable and reliable results (5). Due to the lack of such a procedure, the dyers are having little success in correlating and exchanging dye results between laboratories (4).

A standard laboratory dyeing procedure which will give repeatable and reliable results is needed to allow for measurements of the fiber dyeability, for comparisons of dyes or dye auxiliaries in a sequence of tests, and for programming for evaluation of shade matching (5)(7).

With these purposes in mind, this researcher became interested in attempting to develop a standard laboratory procedure for dyeing nylon.

The objective of this research were:

1. To evaluate the effects of and to determine the pH of the dyebath, the amount of dye assistant to be used, and the starting or preheating temperature and the final dyeing temperature required to give optimum dye results.

2. To develop a laboratory procedure for dyeing nylon doubleknit fabric using the Launder-Ometer as a dye machine (4).

3. To reproduce dye results for accuracy of shade for a given color and levelness using the dye procedure to be developed (4).

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Launder-Ometer—Trademark for Atlas Electric Device Company
CHAPTER II

REVIEW OF LITERATURE

The fiber structure, the influence of the physical and chemical factors of nylon on its dyeability, and the dyeing mechanism must be reviewed to achieve an understanding of the dyeing problems associated with nylon (2).

Fiber Structure

Nylon, discovered by W. H. Carothers and initially manufactured by E. I. duPont de Nemours and Co., Inc. about 1938, was the first synthetic fiber built up from nonpolymeric starting materials (8). The term "nylon" is now regarded as a generic one and refers to a broad class of synthetic polyamides which can be spun into fibers and yarns (8)(9)(10).

A polyamide is a polymer in which the characteristic repeating unit is -CONH-. Polyamides can be formed by either a reaction between a diamine and a dicarboxylic acid, or suitable derivatives,

\[ n\text{NH}_2(CH)x\text{NH}_2 + n\text{HOOC(CH}_2)y\text{COOH} = \]
\[ \text{NH}_2(CH)_x\text{NHCO(CH}_2)y\text{CONH...(CH}_2)y\text{COOH} + (2n-1)\text{H}_2\text{O} \]

or by self-condensation of an amino acid or derivative thereof.

\[ n\text{NH}_2(CH)_x\text{COOH} = \text{NH}_2(CH)_x\text{CONH(CH}_2)x\text{CO...NH(CH}_2)x\text{COOH} + (n-1)\text{H}_2\text{O} \]

Both of the above reactions are reversible, but equilibrium greatly favors the polymeric side. The average length of the polymer chain has
an important influence on its physical characteristics, behavior during melt spinning, and on the fiber properties. Therefore, it is necessary to employ the use of chain stoppers or stabilizers, which are usually mono-functional materials such as acetic acid, to limit and control the degree of polymerization (8)(11).

The polymer chains are also in reversible equilibrium with low molecular weight cyclic compounds, which can sometimes have an important influence on polymer properties. As a result, a polynamide comprises a mixture of polymer chains of various lengths having terminal or end groups which may be -NH₂, -COOH, or stopper groups such as -NHCOCH₃, together with a greater or lesser amount of cyclic monomeric, dimeric, and, in some cases, trimeric material (11).

The two most important polynamides for fibers are Nylon 66 and Nylon 6 polymers (11). Nylon 66 is obtained by polymerization of the salt of adipic acid and hexamethylenediamine to give the structure [-NH(CH₂)₆NHCO(CH₂)₄CO-]ₙ, where n varies within a range of 50-90. Nylon 6 is made by the polymerization of caprolactam by heating under pressure with or without the addition of water. It has a structure [-NH(CH₂)₅CO-]ₙ, where n has a value of about 200 (8).

**Physical and Chemical Characteristics of Nylon**

For many years after its discovery the dyeing of nylon presented considerable difficulties arising from the physical and chemical variations in the fiber structure (12). The physical yarn differences are in what is known as the fine structure of the fiber, which generally refers to crystallinity, orientation, heat history, draw ratio, and other factors that affect the accessibility of the dye to fiber. "Some gross
differences may even introduce differences in the optical appearance of the undyed fiber. This extreme difference cannot be changed by dyeing (3)." The physical variations or the fine structure differences arise mainly from differences in drawing, spinning, bulking, crimping, fabric manufacture, and heat-setting. Chemical yarn differences are associated with differences in the proportion of free amino groups in the polymer chains composing the fiber which depends upon the molecular weights of the polymers (3)(12)(13). The amine end group differences affect only those dyes which have an affinity for these groups, such as acid dyes. The physical differences influence all types of dyes to a greater or lesser degree (12).

These differences in fibre structure make it exceedingly difficult to obtain level dyeings with conventional dyes which at the same time possess adequate fastness to wet treatments, level dyeings usually having only moderate fastness and fast dyeings having a tendency to show 'barrasses,' i.e., light and dark streaks in weft or warp direction (12).

Therefore, barre' or fabric streaks fall into two categories: (1) streaks due to configurational or physical defects; i.e., nondye defects; and (2) true-dye-on fiber differences. Defects due to bulk or twist differences, nondye defects are generally a minor problem in knit goods. Barre' due to variations in amine ends or dye sites is extremely rare with today's nylons of improved quality and uniformity. However, the differences in the fiber porosity, which determines the accessibility of the dye sites and is determined by the total tension-temperature history of the fiber, are responsible for most of the barre' problems in the industry today (1).

To gain a better understanding of the influence of these physical and chemical variations, it is necessary to discuss in further detail
the processes involved in the manufacture of nylon from fiber to yarn to fabric. As previously mentioned, nylon fibers can be formed by spinning any long chain synthetic polyamide (2). Whether the fiber is produced from a polymer of caprolactam, or of hexamethylenediamine and adipic acid, the individual polymer molecules must be aligned to develop useful properties. As the polymer is extruded from the spinneret, the molecules are in random arrangement (1). Therefore, a drawing operation is performed during the manufacturing process to develop final fiber properties, such as tenacity (1)(2)(11). The drawing orients the polyamide molecules and arranges the crystallites in a parallel manner. This would be like pulling the molecules through a funnel and aligning them. The degree of molecular orientation determines the fiber's properties and thus determines how readily dye can penetrate the fiber (2). Unless this drawing has been carried out in a uniform manner, differences in orientation will result in uneven dyeing (11). The more highly oriented the fiber, the more difficult it is for dye to penetrate it. One theory is that the highly oriented parts of the fiber are crystalline in nature and the less oriented are amorphous. The amorphous regions allow the dye to penetrate readily, whereas the crystalline areas resist dye penetration (2)(11).

Another important factor that will affect dyeability is the concentration of the amino groups in the terminal positions of the molecular chains (11). "The nylon molecule is a flexible chain of carbon atoms in the form of methylene groups with amide groups located at intervals along its axis (1)." The amine groups in the fiber provide sites for acid dyes (1). In other words, the polyamide molecules end in either ammonium cations or carboxylate anions and the ammonium cations serve as dye sites
for anionic acid dyes. The accessibility number, and uniformity of the dye sites determines the dye distribution and the depth of shade that can be obtained with acid dyes (2). As a result, it is necessary to use a uniform procedure for stabilizing the product during the polymerizing step. By rigorously controlling all the steps used in the manufacture of nylon fibers and yarns, a product having uniform dyeing characteristics can be made consistently. To do this, it is necessary to apply rigorous quality control procedures to the production of the required chemical intermediates, as well as during the polymerizing and spinning operations (11).

Therefore, there are two important fiber conditions which influence the dyeability of nylon. The first condition is the degree of crystallinity which is related to uniform drawing and the heat history of the fiber. The second condition is the number and location of amino groups in the fiber, and this is related to the control of polymerization and fine fiber structure. Variables are encountered in milling which influence fiber dyeability because of their effect upon these two conditions. The two major variables encountered many times in milling prior to dyeing are heat and tension (2).

These two fiber conditions and two milling variables help explain why all nylon fibers are not necessarily dyed to the same degree even though exposed to a dyebath under identical conditions. They affect the dye rate and the dye capacity which are two important factors that account for a given product's dyeability. "Dye rate is the speed of dye take-up by the fiber and is influenced by many factors including fiber structure, size and shape of the dye molecule, and dyeing conditions
The dye rate is a function of yarn orientation and this is related to the degree of drawing or mechanical working of the fiber and the amount of heat to which it has been exposed (14). Dye capacity is the total amount of dye that a fiber can absorb (9). It is a function of the chemistry of the polymer. Some fibers are produced to have more amine ends per molecule than others. The ones with higher numbers of amine ends will dye more rapidly and have a higher saturation level than the lower ones. Also, the fine structures of the polymer and the polymer density will affect the accessibility of the amine ends for the dye. These can be changed by heating (14).

In nylon the polar groups of one molecule are strongly attached to those of another molecule by hydrogen bonds. These bonds are released and rearranged when the yarn is heat-set either in dry heat or steam. This rearrangement takes place in dry heat at approximately 400°F or in steam at about 250°F. Fabrics or yarns heat-set by either method retain their geometric configuration even when processed in a boiling dyebath (1). However, a heat-set fabric will not dye as deeply under competitive conditions as an unheat-set fabric (14).

The heat-settability of nylon has led to the development and growth of most of the yarn texturizing processes which have had such an impact on the whole textile industry. The textured yarn is so desirable because it gives a fabric made from such a yarn better hand, improved comfort, stretch characteristics, ease of care properties, and a smoother, more uniform appearance. Nylon yarns have the ability to be heat-set because they are thermoplastic. Because they soften when heated, they are sensitive to the combination of heat and tension in the texturizing processes.
"The total tension-temperature history of the yarn—i.e., in fiber manufacturing and in texturing—determines the degree of orientation in the textured yarns (1)." This affects the fiber "porosity" in terms of accessibility of the dye ions to the dye sites. Tension and temperature must be carefully controlled in texturing to maintain the dye uniformity built into the fiber in manufacture (1).

Therefore, dye rate and dye capacity are determined by fiber manufacturing conditions and by the degree of tensions and/or heat treating the fiber has encountered prior to dyeing. Processing variables which influence the dyeability of nylon, and their effects are:

1. "Stretching or processing tensions encountered in a textile process such as winding, warping, or weaving reduce the dye rate; therefore, yarn tensions should be kept as uniform and as low as possible.
2. Heat-setting in the recommended temperature range significantly affects dyeing characteristics. Dry heat-setting reduces the dye rate and decreases the apparent dye capacity; whereas steam setting under pressure increases the dye rate, but has no significant effect on dye capacity (9)."

**Dyeing Mechanism**

**Preparation for Dyeing**

The increasing use of the texturized nylon fabrics makes it important that a superior dyeing technique be available for application of acid dyes (2). However, before nylon is dyed or bleached, it is necessary to prepare the yarns or fabric by scouring them. "Nylon yarns are sized with polyacrylic acid, polyvinyl alcohol, glue, oils, or waxes (15)." Scouring is necessary to remove these sizes and the processing assistants applied by the textile manufacturer. The purpose of scouring is also to
remove yarn lubricants and/or processing assistants applied during yarn manufacture, and soils (9) or any foreign matter from the fabric so that these materials do not interfere with the dyeing process or detract from the final appearance of the fabric (3). Scouring is also essential to insure uniform dyeing and good shade reproducibility from batch-to-batch (16). Scouring should be done before heat-setting to eliminate materials that might contribute to yellowing under heat-setting conditions. Nylon should be scoured with mild agitation at moderate temperatures such as 120° to 140°F (50° to 60°C). The effectiveness of the scour can be increased by higher temperatures, but care must be taken to prevent wrinkles or creases which can be set in the fabric and may be impossible to remove later (9). The requirements of a scouring product are wetting, soil removal or detergency, soil suspension without redeposition, and no adverse effect on dye sites or dye dispersion. Most scouring baths use a scouring assistant and are made more effective by the addition of alkalis such as TSPP (Tetrasodium pyrophosphate) and TSP (Tetrasodium phosphate). The usual formula uses one pound of detergent and two pounds of alkali per 100 gallons. The use of some alcohol sulfates or other strong anionic materials should be avoided in scouring nylon. These substances tend to react with the amine ends on nylon and block the dye sites. Therefore, shade depth cannot be obtained. This does not present a problem when disperse dyes are used, but strong anionic agents should be avoided where fabric is prepared for inventory with the dyeing procedure to be decided later (3).

According to Richardson (3), it is safer to scour nylon at temperatures below 160°F discarding the bath containing the suspended soils
since some soils have affinity for nylon at high temperatures. Due to
the wide variety of soils, pilot tests should be run to determine the
best method and temperature for scouring.

Occasionally nylon fabrics may yellow with excessive exposure
during heat-setting. If this discoloration cannot be removed by scour­
ing, the fabric may require bleaching (17).

Dyeing Conditions

After scouring, and bleaching if necessary, the fabric is prepared
for dyeing. Since the mechanical operations and heat treatments to
which the yarns are subjected in texturing increase the chances of vari­
ations in these yarns, care must be taken in selecting the dyeing con­
ditions and dyeing procedures for knit fabrics of textured yarns if
level, streak-free dyeing are to be obtained (17). Also the different
available types of nylon have varying degrees of dyeability. This makes
it necessary to adjust dyeing conditions to obtain reasonable color ex­
haustion when dyeing different fiber types (2). The conditions which
influence dyeing results are:

1. Dye selection
2. Type and amount of auxiliary
3. pH of dyebath
4. Temperature, $T_{START}$ and $T_{DYEING}$
5. Dyeing time at maximum temperature (18)

These conditions are reviewed to gain a better understanding of their ef­
flect on the dyeing of nylon.
Dye Selection.---Nylon has receptivity for many classes of dyes (9)(11), but most dyes currently used on nylon can be classified as either nonionic or anionic. The nonionic class includes the disperse dyes. The anionic class includes level dyeing acid dyes, milling or reserving acid dyes, neutral dyeing and acid dyeing pre-metalized dyes, chrome dyes, and direct dyes (1). For most purposes, however, the dyes selected are either disperse or acid dyes (9)(11).

The disperse dyes are the easiest dyes to apply to nylon (3). They have excellent leveling and transfer properties and normally yield level, streak-free dyeings (17). If dyeing is carried out at reasonable temperatures, the levelness of these dyes is seldom affected by the physical differences in the fiber nor the amine end differences. Disperse dyes are composed of small molecules which penetrate the fibers and are held by a solution mechanism within the fiber. However, the saturation levels for disperse dyes are low and this makes it difficult to obtain dark shades (3). As a result, the use of disperse dyes are usually limited to light shades (17). Even though these dyes are easily applied, this advantage is offset by their ease of removal as reflected in their poor wet fastness (3).

Both of these deficiencies encountered with disperse dyes can be overcome with the level dyeing acid dyes (1). Acid dyes contain sulfonic acid groups and are dissociable sodium salts. They are water soluble and the dissolved dye ion from the bath enters the fiber and reacts to form a salt with the polymer ammonium ion formed from the amine end groups. The reverse reaction also occurs, thus a state of equilibrium exists. The rate of the reverse reaction determines the
leveling characteristics of a given dye. The equilibrium permits the dye to cover streaks due to differences in the initial dye rate (3).

Due to the relatively strong bond formed between the ionic pair and the dye site, acid dyes provide improved washfastness. They also generally dye brighter than disperse dyes. Acid dyes are more resistant to fading from atmospheric gases and have superior light fastness. However, they are more sensitive to barre' (1)(17), because they are sensitive to both physical and chemical differences between yarns (3).

A combination of several dyes is often required to produce a particular color. If the dyes exhaust simultaneously, i.e., as time increases the dyed material shows an increase in depth but not a change in hue, the dyes are considered to be compatible in that particular combination and under those dyeing conditions used (18)(19). If the dyes used in combination are compatible, they have the following advantages over incompatible dyes:

... Dyeing conditions can be chosen which are optimum—in rate of exhaustion—for all dyes present; compatible dyes dye quicker and with better reproducibility.

... Non-uniform conditions of flow, temperature, dyeability of material result in differences in depth only—not in hue, as with incompatible dyes. Differences in depth only are more easily to level than those in hue; compatible dyes dye more level, less leveling agent is required (18).

However, according to another source (20), in combinations individual dyes exhaust nearly independent of each other, i.e., there is generally no influence of one dyestuff on the exhaustion of another.

Dye Assistants.—Over the years attempts have been made to develop dyeing methods and chemical assistants that would improve the quality of levelness on nylon with acid dyes. From these attempts it was determined that a dyeing assistant was needed which would
compete with the specific dyes to mask minor site variations within the fiber and a dyebath additive was necessary to assist in promoting the required transfer (2). The levelness of dyeing depends on the speed of exhaustion. If this speed is suitably slow, level dyeings are obtained from the beginning without migration (20). Dyebath additives used to control leveling fall into two classes, anionic and cationic (9). Anionic agents are used to slow the dye strike. They operate within the nylon fiber, not in the dyebath. The anionic additives are colorless surface active agents whose anions, when placed in the dyebath, compete with the dye for the positively charged dye sites in the fiber (1)(3)(9). These anions make it more difficult for the dye ions to find points of attachment during the initial stages of dyeing and thus retards the rate of dyeing to achieve level results (1).

The colorless cations of the cationic additives operate in the dyebath (1) to complex with the dye anions. This complex gradually dissociates and releases the dye anions in low concentration as the dyeing temperature is approached. This condition favors level dyeing of the fiber (9).

Various dyeing procedures have incorporated dye assistant concentrations as low as 0.5% owf\(^1\) (21) to as high as 2% owf (9) depending upon conditions employed.

\textbf{pH of Dyebath.--} In dyeing nylon, control of the dyebath pH is important to achieve the best possible dye results, but the specific pH

\(^1\)The term "owf" denotes "on weight of fabric" and is used in the abbreviated form in this research.
preferred will vary with different dyeing conditions and fabrics (2). Dyeing conditions should be selected which give reasonable exhaustions of the dye and adequate leveling. Since the distribution of the anionic dyes depends upon the pH of the dyebath, a pH should be selected that will be as stable as possible to allow maximum reproducibility (22).

The pH of the dyebath can influence the strike rate of the dye, the transfer of the dye, and the total color value obtained. Care must be exercised with the many acid dyes available to select a bath pH that will not allow the dye to strike too rapidly. Although many dyes depend upon a high pH to achieve good transfer and levelness, this high bath pH can cause a sacrifice in color value. However, without the addition of some acid to the dyebath, it is often difficult to obtain efficient dye exhaustion. According to Turner, Newby, and Speck (2) it has been established that a pH of 4 is suitable for achieving good dye exhaustion for most usable acid dyes. This pH can be employed if other dyebath considerations do not dictate otherwise.

Improved levelness of dyeing can sometimes be attained by dyeing at a pH of 6.0-6.5. Sufficient dye exhaustion can be attained at this pH with light shades. However, gradual additions of acid can be made in the case of heavy shades. These additions will help obtain a more complete exhaust of the dye, without any serious loss of dye transfer (2).

Another procedure (9) recommends a pH of 5.5 or lower for certain acid dyes, but suggests using a pH range of 6.0 to 7.0 for more difficult dyeing problems. Other procedures (21) list pH's of 5.0, 8.5,
and 10 depending upon the dyes used.

**Dyeing Temperature and Time.**—The levelness of acid dyeings can be improved by slowing the rate of dye strike and improving the dye transfer at the final dyeing temperature. The rate of dye strike can be controlled by the combination of the proper selection of suitable dyeing assistants and a gradual increase of temperature and decrease in pH. If the temperature rise exceeds 3°F per minute, the dye strike will be too fast. In addition, if the final dyeing temperature does not reach 205°F, the amount of dye transfer will be reduced. Both a too rapid dye strike and a reduced amount of dye transfer adversely affect the levelness and streak coverage of the resultant dyeing (17).

One source (11) says that high temperature dyeings have more rapid and more thorough penetration, better leveling, improved shade built up and increased wet fastness. Light to medium shades can be produced with acid dyes by normal boiling, starting with baths at 100-110°F, raising to the boil in 30 minutes, and adding extra acetic acid to complete the exhaust.

Another approach (9) states that the transfer and leveling of most acid dyes are promoted by increasing the dyeing temperature to 250°F (120°C) in pressurized equipment. The benefits from this temperature are increased fiber penetration and improved wet fastness.

According to Schmidlin (23),

Optimum results in the dyeing of synthetic fibres can be obtained by dyeing at temperatures above 100°C, i.e., under pressure, or by dyeing under normal pressure and observing the following three points: keeping the temperature as close as possible to 100°C, applying a dye accelerator (carrier), and using longer dyeing times.
The amount of acid dye transfer is increased by both an increased time at dyeing temperature and a higher dyeing temperature. For the more difficult shades and fabric styles, the total time at the dyeing temperature should be raised to 90 minutes. If the dyeing equipment allows, the dyeing should be carried out at a temperature of 230°F. This will help streak coverage on unheat-set fabric (17).

Other procedures suggest various temperatures and times range from 30 minutes at 205°F (17) to 45 minutes at 200°F (24) to one to two hours at the boil (9).

Liquor Ratio.--The literature makes little mention of the liquor ratio to be used in dyeing. One source (16) does state that for good shade reproduction from lot-to-lot, the ratio of dye liquor to fabric weight should be constant. A few other procedures use ratios of 10:1, 20:1 (24), and 30:1 (25). Other sources (26) (27), concerning dyeing nylon carpet, recommend that the bath-to-carpet ratio should be constant within the range of 20:1 to 40:1 to insure shade reproduction from lot-to-lot.

Laboratory Dyeing of Nylon Knits

Very little literature is found regarding laboratory dyeing (5). The dyeing theories and procedure reviewed thus far, relate to industrial processing.

Variables for Consideration.--A laboratory dyeing procedure must consider many variables some of which are weight of sample, liquor ratios, percent auxiliaries added, pH of dyebath, starting dyeing temperature, maximum dyeing temperature, the dyeing equipment used, post
dyeing operations, and evaluation instruments (2)(4).

The equipment and instruments used in developing a laboratory procedure for polyester were a low-temperature Launder-Ometer, because of its availability in most U.S. textile laboratories, a spectrophotometer, and a Hunter Color Difference MeterR (4)(5).

Methods of Dye Result Evaluation.--A color defect is an unwanted color difference (28), and these color differences are important in determining how good a match one fabric is for another (29).

One color defect is unlevelness. There are several types of unlevelness, such as side to side, side to center, end to end, and skitteriness. Side to side unlevelness occurs when the color on one edge of the cloth is not the same color as that on the opposite edge. Side to center unlevelness means that there is an objectionable color difference from the edge to the center of the fabric. End to end unlevelness means that the beginning of the piece of cloth is different in color from the end of the bolt. Skitteriness is unlevelness on a micro scale and is not satisfactory dyeing when a solid shade is desired (28).

Color is usually the first attribute noticed in a textile product. It is often influential in determining the salability of that product. Prior to 1930 nearly all work in the textile industry concerning color involved visual determinations. Since that time instruments, such as spectrophotometers and computers, have been developed to help in the evaluation of color in dyeing (28)(29).

The Spectronic 20R spectrophotometer measures the percentage of
light transmittance through a solution, as a function of a standardized wavelength (4). "An analytical wavelength is a wavelength selected for measurement. Usually this is the point of maximum absorption (minimum reflectance factor) (30)." The Spectronic 20 was used in previous work (4) to determine the concentration of dyes in the dyebath solution. The Hunter Color Difference Meter was also used to measure the light reflected by the fabric specimen. This instrument reports its measurements in terms of $L$ (lightness), $a$ (red-green), and $b$ (yellow-blue) values. The $L$ value is a measurement of color in units of approximate visual uniformity throughout the colored material (30).

In order to obtain accurate and precise dye evaluation results using the Spectronic 20 and the Hunter Color Difference Meter, it is imperative that certain variables be controlled. The dye solution should contain a dye sample weighing at least one gram or more and this sample should be weighed on an analytical balance. Pipets and volumetric flasks should be used in preparing the stock solutions and dilutions. The substrate samples must be weighed accurately to ± 1%, and for all practical purposes, they must be chemically and physically identical. The pH, liquor ratios, and additions of necessary chemicals must be closely controlled. In exhaust dyeing, the temperature and time of the dye cycle must also be controlled very closely to give identical conditions (31).

In measuring the strength of the dye solution, it is necessary to be careful if a mixture of dyes is contained in the solution. The absorption curve of a mixture of dyes is normally expected to be the
sum of the absorption curves of the individual dyes. This is assuming that each dye in the mixture is acting independently. Sometimes, however, the dyes in a mixture interact, resulting in a totally unpredictable mixture curve. An error in the amount of each dye present in the mixture would be the result of a hasty analysis of the absorption curve (32).

In taking measurements on the fabric samples it is important that (1) the samples be evenly dyed and clean, (2) the sample completely cover the sample part, and (3) a sufficiently thick sample be measured to prevent light passing through the sample and reflecting off the sample holder (31).
CHAPTER III

PROCEDURE

This research involved the development of a laboratory dyeing procedure using a standard Launder-Ometer for exhaust dyeings of nylon knits. This work considered the various steps in the dyeing procedure and such important variables as: (1) starting temperature, (2) final dyeing temperature, (3) percentage of dye assistant, and (4) pH of the dyebath in order to obtain optimum results and level dyeings.

Initial Dyeing Procedure

The initial dyeing procedure (24) used for experimentation on nylon knit fabric was as follows:

**Apparatus:** Launder-Ometer, AATCC IIA Wash Test sized cups

**Dyes:** 0.2% owf Acid Yellow 40—Supernylite Yellow 3G\(^R\)*
0.2% owf Acid Red 266—Merpacyl Red BR\(^R\)*
0.2% owf Acid Blue 25—Alizarine Supra Blue AR\(^R\)*

**Auxiliaries:** 2% owf Alkanol NDR\(^R\)—Dyeing assistant
2% owf Ammonium Sulfate*

*The use of these specific chemicals and dyes in this research does not imply recommendation of these agents to the exclusion of others which are equally effective.

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Supernylite Yellow 3G\(^R\)—Trademark for Crompton and Knowles Corporation.
Alizarine Supra Blue AR\(^R\)—Trademark for Verona, division of Baychem Corp.
Alkanol NDR\(^R\)—Trademark for E. I. du Pont de Nemours and Company, Inc.
A stock solution of 1% dyestuff was prepared for each dye by weighing out one gram of dye onto a watch glass on an analytical balance, transferring this dye into a 100 ml. volumetric flask, and adding hot distilled water to make the volume up to 100 ml. After cooling, distilled water was added to remake the volume up to 100 ml. Also a stock solution of 1% was made for each auxiliary by weighing out 10 grams of chemical, transferring the chemical to a 1000 ml. volumetric flask, and making up the volume to 1000 ml. by adding distilled water as above.

Procedure:

Weight of fabric sample .................. 10.0 grams
Liquor ratio (dyebath to fabric) ........... 20:1
Add dyes using volumetric pipets .......... 2 ml. each
Add auxiliaries using volumetric pipets ... 20 ml. each
Add distilled water and mix completely ... 154 ml.
Preheat the dyebath in the Launder-Ometer containers using the Launder-Ometer preheating table to 100°F.
Add fabric sample to container, wet completely using glass stirring rod
Carefully seat a dome Mason jar lid on top of each container, checking the lip for nicks or particles that might cause a leak
Place a cap with neoprene gasket on top and clamp tight
Weigh each complete container
Load containers on the Launder-Ometer racks
Turn on rotor and raise temperature to 200°F at a rate of 2° per minute
After bath reaches 200°F continue dyeing for 45 minutes
Turn off heat but continue rotor
Cool bath to 140°F, 3° per minute, by opening the top of the Launder-Ometer tank
Stop rotor and remove containers
Wipe and reweigh each container to check for leakage
Open containers and remove samples
Thoroughly rinse samples with distilled water
Squeeze samples using a wringer
Air dry samples
Description of Test Fabric

To be able to evaluate a developed dye procedure for reproducibility of shade and uniform dyeing, it is necessary to use a standard form of textile material. Variations in the fabric samples as to the form of fiber, yarn, or fabric would result in differential dyeing (4).

In this research all dyeings were performed on a white 100% nylon doubleknit fabric, weighing approximately 6.2 ounces per square yard. The size of a 10 gram swatch was determined by trial, and a cardboard template was made slightly oversize. The template was placed over several layers of fabric and rough swatches were cut out. Each sample was weighed on a direct reading balance. Edges were snipped off until each swatch weighed 10.0 grams.

Description of Dyestuff

A mixture of the following three acid dyestuffs was used in all the dyeings of this research:

1. Supernylite Yellow 3G is listed under Acid Yellow 40 (24). According to the Colour Index (33), Acid Yellow 40 is in the chemical class of monoazo dyes for wool, and can be used on nylon with the addition of ammonium sulfate. Acid Yellow 40 is soluble in water, slightly soluble in ethanol and acetone, and insoluble in other organic solvents.

2. Merpacyl Red B, listed under the generic name of Acid Red 266 in the Colour Index (33), is in the chemical class of azo dyes. On nylon it gives a bright bluish red hue. It is claimed that the group of dyes under the trademark, Merpacyl, in
combination with Alkanol ND perform with maximum effectiveness to minimize the most severe dyehouse problems of levelness or streakiness and also provides high light fastness (2).

3. Alizarine Supra Blue A comes under the generic name of Acid Blue 25. It is in the chemical class of the anthraquinone dyes for wool, acetate, silk, and nylon. Acid Blue 25 is soluble in acetone and alcohol, slightly soluble in benzene and tetrahydronaphthalene, and insoluble in nitrobenzene and xylene. In concentrated sulfuric acid it gives a dull blue, and on dilution it gives a blue precipitate (33).

**Description of Auxiliaries**

Alkanol ND is listed in Products/74 (34) as a sodium aryl sulfonate, used as a leveling agent in dyeing of nylon. Other sources (1)(2)(3)(9) state that the Alkanol ND dyeing assistant is an anionic dyebath additive. It is claimed that Alkanol ND gives superior dye transfer and is a retarder for dye rate which accounts for improved levelness of dyeing (1)(2)(3)(17).

**Experimental Dyeing Procedure**

1. Prior to sample cutting and dyeing, the nylon fabric was scoured at 160°F for 30 minutes in a Najort® reversible wash-wheel machine with 12% owf AATCC detergent. The fabric was thoroughly rinsed, spun in a centrifugal extractor, and air dried.

Najort®—Trademark for Robert Ewing and Sons, Inc.
2. Test samples were cut to weigh 10 grams according to the directions under Description of Test Fabric.

3. The preparation of the stock solutions were made as directed in the initial dyeing procedure.

4. The following variations made in the dyeing conditions of the initial dyeing procedure were:
   --Starting or preheating temperature, 100°F and 140°F
   --Final dyeing temperature, 180°F and 200°F
   --pH of dyebath, 4.05-4.30 and 5.10-5.50
   --Amount of dyeing assistant, 1% and 2% owf

One drop of a 14% acetic acid solution was used when desired to lower the pH to 4.05-4.30.

5. All samples were dyed at the final dyeing temperature for 45 minutes and were cooled at a rate of 3° per minute to 140°F. The cooling process took about 20 minutes.

6. All dyeing were done in a Launder-Ometer with AATCC IIA Wash Test sized containers without steel balls. Each of the containers was marked. These were marked instead of the samples to prevent any variation that might occur in the dyeing of the sample due to marking. Samples were later marked after dyeing. Both KerrR and BallR jar lids were used to help prevent leakage in the containers.

7. Each container was weighed after dyeing, samples were then removed, rinsed with distilled water, and air dried according to the initial dyeing procedure. The dyebaths were saved and labeled for later

BallR—Trademark for Ball Brothers Company
percentage of transmittance readings.

Evaluation Procedures

1. Using the Spectronic 20 spectrophotometer, a sample solution, collected after dyeing from each dyebath, was measured for percentages of transmittance to estimate the percentage of exhaustion. The wavelengths of maximum absorbance for each of the dyes was determined by making twelve dyebaths, four separate dyebaths for each of the three dyes. The four dyebaths of each color were prepared as follows:

<table>
<thead>
<tr>
<th>Dyebath</th>
<th>pH Range</th>
<th>Percentage of Alkanol ND</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.05-4.30</td>
<td>1%</td>
</tr>
<tr>
<td>2</td>
<td>4.05-4.30</td>
<td>2%</td>
</tr>
<tr>
<td>3</td>
<td>5.10-5.50</td>
<td>1%</td>
</tr>
<tr>
<td>4</td>
<td>5.10-5.50</td>
<td>2%</td>
</tr>
</tbody>
</table>

Percentage of transmittance readings were taken on each color at each of the above combination of variables, at the original undiluted concentrations of 0.02 gram of dye per 200 ml. of dyebath or 0.01%. The wavelengths of maximum absorbance determined were 397.5 nm. for Acid Yellow 40, 495 nm. for Acid Red 266, and 610 nm. for Acid Blue 25. Neither the above difference in pH's nor the different amounts of Alkanol ND made any variation in the wavelength of maximum absorbance for any of the three dyes.

Since the dyebath solutions to be measured were mixtures of the three dyes, measurements of percentage of transmittance were taken at each of the above predetermined wavelengths on three
concentrations of dyebath solutions representing the standard mixtures used in the dyeings. Again the variations in pH and amounts of Alkanol ND seemed to have little or no effect on the percentage of transmittance readings. Therefore, a standard dyestuff solution including the mixture of all three dyes was diluted to give solutions that would represent 0%, 50%, 75%, 87.5%, 93.75%, 96.87%, 98.44%, 99.22%, and 100% exhaustion. Percentage of transmittance readings were recorded at each of the above dilutions at each of the three predetermined wavelengths. A curve was plotted on Graph I by taking the logarithm of the percentage transmittance readings on the ordinate versus the corresponding solutions diluted to known degrees on the abscissa. Dyebath solutions collected at the end of each dyeing were measured individually for their percentage transmittance value. The corresponding percentage of exhaustion for each dye could be estimated from Graph I.

The spectrophotometer was calibrated with distilled water prior to taking measurements on each set of dyeings. The instrument was often checked during the measuring to prevent errors in readings due to instrumental drift.

2. Reflectance measurements were taken on the dyed samples using the Hunter Color Difference Meter, Model D25. The samples were conditioned at 70°F and 65% relative humidity. The instrument was standardized against a calibrated white plate. Four layers of fabric were placed under the two inch diameter sample port. Care was taken that the sample did not pillow into the sample port. Readings on the $L$ (lightness), $a$ (red-green), and $b$ (yellow-blue)
GRAPH I. Calibration curve for evaluating % dye exhaustion relative to the logarithm of the % transmittance values of the dye solution measured on a spectrophotometer: (A) Acid Red 266; (B) Acid Blue 25; (C) Acid Yellow 40.
scales were recorded. Each sample was turned 90 degrees in between readings, and averages of each value were expressed as recommended by the manufacturer (30).

**Data Analysis Procedures**

Data was obtained for a $4 \times 2 \times 2$ factorial design with the factors and respective levels denoted with the symbols as follows:

**Factor 1:**
- $T_1$ for starting temperature of 100°F and final dyeing temperature of 200°F
- $T_2$ for starting temperature of 100°F and final dyeing temperature of 180°F
- $T_3$ for starting temperature of 140°F and final dyeing temperature of 200°F
- $T_4$ for starting temperature of 140°F and final dyeing temperature of 180°F

**Factor 2:**
- $P_1$ for pH range of 4.05-4.30
- $P_2$ for pH range of 5.10-5.50

**Factor 3:**
- $A_1$ for 1% owf Alkanol ND
- $A_2$ for 2% owf Alkanol ND
CHAPTER IV

RESULTS AND DISCUSSION

Data for the following statistical analysis was obtained according to the procedures described in Chapter III. For dyebath exhaustion, the percentage of transmittance values were recorded and analyzed using the analysis of variance as described below. \( L \) (lightness), \( a \) (red-green), and \( b \) (yellow-blue) values were recorded for the analysis of variance on reflectance.

Observations During Data Collection

The following observations were recorded prior to and during testing but could not be analyzed statistically:

1. Even though Richardson (3) and Wiberley (35) warned against the use of anionic agents like AATCC detergent and temperatures as high as 160°F for scouring, scouring the test fabric in AATCC Test detergent 124 at 160°F did not seem to affect the levelness of dyeings in this research.

2. Since the distilled water used was observed to be slightly acidic no adjustments were needed to obtain the dyebath pH of 5.10-5.50.

3. With the pump switch on, it took approximately 70 to 85 minutes to heat the water in the Launder-Ometer from 100°F to 200°F. If the pump was turned off, it only took 60 to 65
minutes. Therefore, to save time in dyeing it was decided to
turn the pump off during the heating to the final dyeing
temperature. With the pump off the temperature rise did not
exceed the 3° limit cautioned against by one source (17).

4. From observations made in the weighing of dyestuff and its
transfer to volumetric flasks, it was concluded that the most
successful technique was to weigh out the one gram of dye
onto a watch glass and then transfer the dye from the watch
glass to the 100 ml. volumetric flask by gradually scraping
the dye, in its powdered form, with a spatula into a glass
funnel placed in the flask without first making a paste with
the dye. Hot distilled water was used to rinse the remaining
dye particles off the watch glass and spatula and into the
funnel. Attempts to weigh the dye into a beaker or a weigh­
ing bottle, making a paste by adding hot distilled water, and
then transferring the dye paste into the volumetric flask
were often unsuccessful. It was difficult to transfer all
the dye paste out of the beaker or weighing bottle without
adding more than 100 ml. of water. Difficulty was found in
going the dye paste out of the corners of the beaker or
weighing bottle. It was also easy to lose drops of the dye
solution by this transfer method.

5. It was observed that the Acid Blue 25 dyestuff would settle
to the bottom of the flask upon storage. Therefore, it was
considered very important to shake the dyes well before use.

6. For greater accuracy, volumetric pipets were used in measuring
out the dye solution and auxiliaries. It was observed that using volumetric pipets rather than graduated cylinders made a considerable savings in the time it took to prepare the dye-baths.

7. Initial attempts were made to vary the time of dyeing at the final dyeing temperature by removing containers from the rotor after 30, 45, and 60 minutes. However, regardless of the temperatures or times used, all the samples showed obvious signs of unlevelness. It was therefore assumed that the gradual cooling of the containers in the dye machine, as described in Chapter III, was necessary to insure level dyeings.

8. In collecting exhaust solutions, it was observed that the solutions contained tiny nylon fibers which would eventually settle. Therefore, it was decided not to shake the solutions before pouring off samples for transmittance readings to prevent fibers from getting into the sample and interfering with the readings.

9. As stated in Chapter III, the amount of difference in pH and in percentages of dye assistant used in the dyebaths did not seem to significantly vary the transmittance readings.

10. Depending upon the temperatures used, it took two to two and a half hours to run a dye experiment in the Launder-Ometer.

11. Even though there was a variance in the reflectance measurements, the amount of variance could not be detected by the eye as not being a color match. With more study in this area, a correlation of the Hunter Color Difference Meter readings
and the eye sight may be possible.

12. Both the Kerr and Ball jar lids were used. It was observed that the Kerr lids worked just as well as the Ball lids in stopping leakage. It was also observed that the Ball lids could often be reused, without leakage occurring, provided the lids appeared to be in good condition. However, neither lid controlled leakage completely. Leakage occurred in 8 out of the 96 containers used in this research. It might therefore be advisable to use new lids or used lids in very good condition to help control leakage in the Launder-Ometer IIA sized cups. Yet, leakage could still be a problem even with new lids if they are not placed properly on the container. Even though great care was taken to seat the lids properly on the containers occasional slippages did occur. It was also noticed that a neoprene gasket which fit very tightly into the container tops helped stop leakage better than those gaskets which did not have a snug fit. Therefore, the leakage problem might possibly be eliminated with the right combination of jar lid and gasket.

13. It was observed that some Launder-Ometer containers had dye-bath to leak out while others had water from the Launder-Ometer tank to leak into the containers. Neither type of leakage had a significant influence on the dyeings. Therefore, it was assumed that in those cases where dye-bath leaked out that the dyeing of the sample had taken place prior to the leakage. In those cases where water leaked into the
containers, it was assumed that dilution did not alter the dyeings.

14. All samples dyed at T₄P₁A₁, T₄P₁A₂, and two samples dyed at T₄P₂A₁ were observed to show unlevelness. However, the Hunter Color Difference Meter did not seem to detect the unlevelness. It was assumed that this instrument should not be used to determine unlevelness in dyeings.

15. From visual observations of the exhaust solutions, exhaustion of all treatment combinations appeared to be almost perfectly clear. Percentage of exhaustion values derived from Graph I indicated that the exhaustions of (1) the Acid Yellow 40 dye ranged from a low of 88.5% to a high of 98.0%, (2) the Acid Red 266 dye ranged from a low of 90.5% to a high of 98.5%, and (3) the Acid Blue 25 dye ranged from a low of 93.5% to a high of 99.0% exhaustion. The exhaustion readings seemed to indicate that the Acid Blue 25 had slightly higher percentages of exhaustion than the Acid Red 266, and that the Acid Red 266 had slightly higher percentages of exhaustion than the Acid Yellow 40 in most instances.

**Data Analysis**

Three replications of each of the sixteen treatment combinations were made in duplicate. The following data was analyzed using an analysis of variance.

**Exhaustion**

The percentage of transmittance was recorded for each exhaust
solution at each of the three predetermined wavelengths. The higher the percentage of transmittance, the higher was the percentage of exhaustion.

Results for each dyestuff were tabulated in Tables 4.1, 4.2, and 4.3. These results indicated that the A_1 treatment had a significantly higher percentage of transmittance than did A_2 for each of the three colors. There was no significant difference in transmittance values due to the variations in pH and starting and final dyeing temperatures used in this research.

Reflectance

The L, a, and b values were recorded for each fabric sample. An analysis of the data was tabulated in Tables 4.4, 4.5, 4.6, and 4.7. The results indicated that:

1. The samples dyed in a dyebath at P_1 had significantly lower L values than those dyed at P_2.
2. The samples dyed in a dyebath at A_1 had significantly lower L values than those dyed in a dyebath at A_2.
3. The samples dyed at T_4 had significantly lower L values than those dyed at any of the other temperature combinations tested. There was no significant difference between T_1, T_2 and T_3 as to L values.
4. The samples dyed at T_3 had significantly higher a values than those dyed at any of the other temperature combinations tested.
5. The samples dyed at T_1 had significantly higher b values than those dyed at T_3 or T_4, but did not differ significantly from samples dyed at T_2.
TABLE 4.1

Analysis of Variance Table for Transmittance Percentages
-Acid Yellow 40-

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>371.48</td>
<td>123.83</td>
<td>1.96</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>253.50</td>
<td>253.50</td>
<td>4.01</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>2646.00</td>
<td>2646.00</td>
<td>41.81**</td>
</tr>
<tr>
<td>(T x P)</td>
<td>3</td>
<td>203.94</td>
<td>67.98</td>
<td>1.07</td>
</tr>
<tr>
<td>(T x A)</td>
<td>3</td>
<td>4.44</td>
<td>1.48</td>
<td>--</td>
</tr>
<tr>
<td>(P x A)</td>
<td>1</td>
<td>32.67</td>
<td>32.67</td>
<td>--</td>
</tr>
<tr>
<td>(T x P x A)</td>
<td>3</td>
<td>214.55</td>
<td>71.52</td>
<td>1.13</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>2025.17</td>
<td>63.29</td>
<td>2.80**</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>1085.75</td>
<td>22.62</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>6837.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** Significant at the 0.01 level
**TABLE 4.2**
Analysis of Variance Table for Transmittance Percentages

-Acid Red 266-

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>163.97</td>
<td>54.66</td>
<td>1.34</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>48.16</td>
<td>48.16</td>
<td>1.18</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>1093.50</td>
<td>1093.50</td>
<td>26.81**</td>
</tr>
<tr>
<td>(T x P)</td>
<td>3</td>
<td>154.45</td>
<td>51.48</td>
<td>1.26</td>
</tr>
<tr>
<td>(T x A)</td>
<td>3</td>
<td>3.65</td>
<td>1.22</td>
<td>--</td>
</tr>
<tr>
<td>(P x A)</td>
<td>1</td>
<td>20.17</td>
<td>20.17</td>
<td>--</td>
</tr>
<tr>
<td>(T x P x A)</td>
<td>3</td>
<td>136.39</td>
<td>45.46</td>
<td>1.11</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>1305.31</td>
<td>40.79</td>
<td>2.61**</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>749.99</td>
<td>15.62</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>3675.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Significant at the 0.01 level**
### TABLE 4.3
Analysis of Variance Table for Transmittance Percentages

- **Acid Blue 25-**

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>77.97</td>
<td>25.99</td>
<td>1.10</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>39.40</td>
<td>39.40</td>
<td>1.66</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>658.88</td>
<td>658.88</td>
<td>27.82**</td>
</tr>
<tr>
<td>((T \times P))</td>
<td>3</td>
<td>70.54</td>
<td>23.51</td>
<td>--</td>
</tr>
<tr>
<td>((T \times A))</td>
<td>3</td>
<td>0.73</td>
<td>0.24</td>
<td>--</td>
</tr>
<tr>
<td>((P \times A))</td>
<td>1</td>
<td>16.25</td>
<td>16.25</td>
<td>--</td>
</tr>
<tr>
<td>((T \times P \times A))</td>
<td>3</td>
<td>66.42</td>
<td>22.14</td>
<td>--</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>757.73</td>
<td>23.68</td>
<td>3.17**</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>373.64</td>
<td>7.78</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>2061.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Significant at the 0.01 level**
**TABLE 4.4**

Analysis of Variance Table for Reflectance—\(L\) Values

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T)</td>
<td>3</td>
<td>1.1824</td>
<td>0.3941</td>
<td>6.3056**</td>
</tr>
<tr>
<td>(P)</td>
<td>1</td>
<td>1.2489</td>
<td>1.2489</td>
<td>19.9824**</td>
</tr>
<tr>
<td>(A)</td>
<td>1</td>
<td>0.7021</td>
<td>0.7021</td>
<td>11.2336**</td>
</tr>
<tr>
<td>((T \times P))</td>
<td>3</td>
<td>0.4243</td>
<td>0.1414</td>
<td>2.2624</td>
</tr>
<tr>
<td>((T \times A))</td>
<td>3</td>
<td>0.1387</td>
<td>0.0462</td>
<td>-</td>
</tr>
<tr>
<td>((P \times A))</td>
<td>1</td>
<td>0.0883</td>
<td>0.0883</td>
<td>1.4128</td>
</tr>
<tr>
<td>((T \times P \times A))</td>
<td>3</td>
<td>0.0788</td>
<td>0.0263</td>
<td>-</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>1.9988</td>
<td>0.0625</td>
<td>2.0695*</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>1.4477</td>
<td>0.0302</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>7.3100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Significant at the 0.05 level
**Significant at the 0.01 level
### TABLE 4.5

Analysis of Variance Table for Reflectance--a values

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>1.4076</td>
<td>0.4692</td>
<td>4.0942 *</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>0.4648</td>
<td>0.4648</td>
<td>4.0558</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>0.4760</td>
<td>0.4760</td>
<td>4.1536</td>
</tr>
<tr>
<td>(T x P)</td>
<td>3</td>
<td>0.4190</td>
<td>0.1397</td>
<td>1.2190</td>
</tr>
<tr>
<td>(T x A)</td>
<td>3</td>
<td>0.0986</td>
<td>0.0329</td>
<td>-</td>
</tr>
<tr>
<td>(P x A)</td>
<td>1</td>
<td>0.0963</td>
<td>0.0963</td>
<td>-</td>
</tr>
<tr>
<td>(T x P x A)</td>
<td>3</td>
<td>0.0345</td>
<td>0.0115</td>
<td>-</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>3.6678</td>
<td>0.1146</td>
<td>5.8173 **</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>0.9439</td>
<td>0.0197</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>7.6085</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Significant at the 0.05 level
** Significant at the 0.01 level
TABLE 4.6

Analysis of Variance for Reflectance--b values

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f.</th>
<th>Sums of Squares</th>
<th>Mean Squares</th>
<th>F-Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>3</td>
<td>0.88</td>
<td>0.29</td>
<td>4.14*</td>
</tr>
<tr>
<td>P</td>
<td>1</td>
<td>0.27</td>
<td>0.27</td>
<td>3.86</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>(T x P)</td>
<td>3</td>
<td>0.43</td>
<td>0.14</td>
<td>2.00</td>
</tr>
<tr>
<td>(T x A)</td>
<td>3</td>
<td>0.24</td>
<td>0.08</td>
<td>1.14</td>
</tr>
<tr>
<td>(P x A)</td>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>(T x P x A)</td>
<td>3</td>
<td>0.05</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>Within Samples</td>
<td>32</td>
<td>2.36</td>
<td>0.07</td>
<td>3.50**</td>
</tr>
<tr>
<td>Between Duplicates</td>
<td>48</td>
<td>0.99</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>5.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Significant at the 0.05 level
**Significant at the 0.01 level
TABLE 4.7
Means of Reflectance Values for Temperature Combinations

<table>
<thead>
<tr>
<th>REFLECTANCE VALUES</th>
<th>TEMPERATURE COMBINATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (lightness)</td>
<td>$T_4^*$ T_2 T_3 T_1</td>
</tr>
<tr>
<td></td>
<td>34.87 35.09 35.11 35.16</td>
</tr>
<tr>
<td>$+a$ (redness)</td>
<td>$T_2$ $T_1$ $T_4$ $T_3^*$</td>
</tr>
<tr>
<td></td>
<td>5.22  5.26  5.28  5.53</td>
</tr>
<tr>
<td>$-b$ (blueness)</td>
<td>$T_3$ $T_4$ $T_2$ $T_1^*$</td>
</tr>
<tr>
<td></td>
<td>11.04 11.04 11.18 11.27</td>
</tr>
</tbody>
</table>

*The difference between two means not underscored by the same line are significant at the 0.05 level*
The need of the textile dyer to achieve reliability and reproducibility in dye results necessitated the development of a standard detailed laboratory dyeing procedure (4)(5). Since there were still unsolved problems in the dyeing of nylon (3), the three objectives of this research were to evaluate the effects of and to determine the various dyeing conditions necessary to give optimum dye results; to develop a laboratory procedure for dyeing nylon doubleknit fabric using the Launder-Ometer as a dye machine; and to reproduce dye results for accuracy of shade for a given color and levelness using the dyeing procedure developed.

Dyeings were carried out using 0.2% owf Acid Yellow 40, 0.2% owf Acid Red 266, and 0.2% owf Acid Blue 25 dyes, 1% and 2% owf Alkanol ND dyeing assistant, and 2% owf ammonium sulfate. All fabric to be dyed and all chemicals used were each obtained as a single type and from a single source.

Exhaustion data was obtained using the percentage of transmittance of the exhaust solutions. Reflectance data was obtained by measuring the \( L \) (lightness), \( a \) (red-green), and \( b \) (yellow-blue) values of the dyed fabric samples.

An analysis of variance was conducted to determine statistically
significant differences between the combinations of the various dyeing conditions investigated.

**Major Findings**

Results of the analysis indicated the following major findings:

1. The $A_1$ dyebath treatment resulted in significantly higher percentages of transmittance of the exhaust solutions than did $A_2$. Also those samples dyed at $A_1$ had significantly lower $L$ values than those dyed at $A_2$. The lower $L$ value indicated a darker sample. Thus, it was concluded that higher percentages of exhaustion and dye fixation could be obtained by using 1% owf rather than 2% owf dyeing assistant.

2. There was no significant difference in the percentage of transmittance between the dyebath treatments $P_1$ and $P_2$. It was concluded that lowering the pH of the dyebath from 5.10-5.50 to 4.05-4.30 was unnecessary to achieve good dye exhaustion. However, those samples dyed in a dyebath at $P_1$ had significantly lower $L$ values than those dyed at $P_2$. This meant that the samples dyed at $P_1$ were darker in color and therefore had a higher percentage of dye fixation. Thus, it was concluded that a dye bath with a pH of 4.05-4.30 would give better dye results than would a pH of 5.10-5.50.

3. Since no significant difference in the transmittance percentages was found in the temperatures used, no conclusion could be made as to which temperature combination would give the better exhaustion. The fabric samples dyed at $T_4$ did show significantly lower $L$ values and thus, higher percentages of dye fixation than
did those samples dyed at any other of the temperature combinations tested. However, all samples dyed at $T_4 P_1 A_1$ and $T_4 P_1 A_2$ showed obvious signs of unlevelness. Two samples dyed at $T_4 P_2 A_1$ also showed slight unlevelness. Due to these results it was concluded that this temperature combination should only be used with dyebath solutions at $P_2 A_2$. Since this pH and percentage of dyeing assistant did not give as good results as did $P_1 A_1$, it was concluded that $T_4$ did not give optimum dye results and should be eliminated from further consideration for a recommended dyeing procedure. It was also concluded that the Hunter Color Difference Meter should not be used to detect unlevelness in dyed samples. The lower $L$ values obtained at $T_4$ could have resulted if the area of the unlevel samples tested happened to have more dye in the two inch diameter covered by the sample port.

4. No significant difference was found between $T_1$, $T_2$, and $T_3$ as to $L$ values, indicating that these three temperature combinations gave good, reproducible dye results. However, samples dyed at $T_3$ had significantly higher $a_+$ (redness) values, indicating a higher percentage of fixation of the Acid Red 266 dye at this temperature combination. Samples dyed at $T_1$ had significantly higher $b_-$ (blueness) values, indicating higher percentages of fixation of the Acid Blue 25 dye at this particular temperature combination. Even though $T_1$ gave higher $b_-$ values than did $T_3$, $T_1$ was not significantly higher than $T_2$. However, since $T_1$ took more time than any of the other
combinations, it was eliminated from further consideration.

The choice for a recommended temperature combination was then between T₂ and T₃. Since there was no significant difference between T₂ and T₃ as to \( -b \) values, and since T₃ did show significantly higher \( +a \) values, it was concluded that T₃ should be used for the recommended dyeing procedure.

**Recommended Dyeing Procedure for Nylon Knit Fabrics**

The results of this research indicated that a dyeing procedure for nylon knits, incorporating the optimum levels of variables and giving reliable and reproducible results, could be recommended with the following major limitations. In this research the leakage of the Launder-Ometer cups was observed to be 8.3% of the experiments. If this procedure is followed it must be understood that absolute control of the leakage of the Launder-Ometer cups is imperative.

The use of the anionic AATCC Test detergent 124 and a temperature of 160°F for scouring in this research did not appear to affect the levelness of nylon dyeings as warned against by Richardson (3) and Wiberley (35), however it might be advisable, just for a precaution, not to use the AATCC detergent and a temperature as high as 160°F for scouring in future dyeings with nylon.

Since the time of dyeing at the final temperature and the rate of cooling were held constant throughout this research, further work is needed to determine the optimum levels for these two variables.

With these limitations firmly in mind, the following procedure is recommended:
I. Scouring:

A. Scour the fabric with a nonionic agent for 30 minutes in hot water (140°F).

B. Suggested equipment: Najort washer or automatic washer

II. Preparation of Stock Solutions:

A. Dye Solutions: Make up a 1% dye solution by weighing a watch glass on an analytical balance and adding, with a spatula, exactly 1.000 gram of Supernylite Yellow 3G dyestuff. Transfer dyestuff carefully to a 100 ml. volumetric flask using a glass stirring rod and a small glass funnel. Rinse watch glass and rod with hot distilled water until all dye particles are washed into the flask. Make up to 100 ml. and mix well. When ready to use, remake up to the mark if the volume has contracted on cooling. Shake well before each use. Repeat for Merpacyl Red B and Alizarine Supra Blue A.

B. Auxiliary Solutions: Make up a 1% Alkanol ND dyeing assistant solution by weighing out 10 grams, transferring to a 1000 ml. volumetric flask, and making up to the mark following the above procedure for dyestuff solutions. Repeat for the 1% ammonium sulfate solution.

III. Dyeing:

Weight of fabric sample ........................................ 10 grams
Liquor ratio .................................................. 20:1
(volume of liquor to weight of fabric)

Add dyes and auxiliaries using volumetric pipets:

0.2% owf Supernylite Yellow 3G (1% sol'n.) ........ 2 ml.
0.2% owf Merpacyl Red B (1% sol'n.) .......... 2 ml.
0.2% owf Alizarine Supra Blue A (1% sol'n.) .... 2 ml.
1.0% owf Alkanol ND dyeing assistant (1% sol'n.).. 10 ml.
2.0% owf Ammonium Sulfate (1% sol'n.) ........ 20 ml.

Dilute with distilled water ................................. 164 ml.

Adjust pH of 200 ml. dyebath solution
using 14% acetic acid ................................. 4.05-4.30

Preheat the dyebath solution in the Launder-Ometer containers
(AATCC IIA sized cups) with tops on but not clamped to
140°F

Add sample to container using glass stirring rod
Carefully seat dome Mason jar lid on top of each container
Place caps with neoprene gaskets on top and clamp
Weigh each complete container
Load containers on racks in Launder-Ometer
Turn on rotor, raise temperature at a rate of 2°F per minute
to 200°F and hold for 45 minutes

Turn off heat, continue rotor, and open the top of the Launder-
Ometer tank to reduce the temperature to 140°F, 3°F per minute (approx.)
Stop rotor and remove containers from rack, wipe exterior, re-weigh to check for any liquor loss.

IV. Rinsing and Drying:

A. Remove samples and rinse well with warm distilled water. Squeeze samples using wringer. Air dry flat.

Measure the remaining dye liquor for dye transmittance percentage to determine percentage of exhaustion. Measure the dyed sample for color value.
REFERENCES


VITA

Gail Ferguson Cook was born on December 18, 1950 in Richmond, Virginia. After graduation from Midlothian High School, Midlothian, Virginia in 1969, she attended Virginia Polytechnic Institute and State University in Blacksburg, Virginia.


She received her Bachelor of Science degree in Clothing, Textiles and Related Art, Textiles Option, in June 1973. She entered graduate school as a dual registrant in January 1973. While in graduate school she worked as a lab technician in the Clothing, Textiles and Related Art Department. She completed the Master of Science, Clothing, Textiles and Related Art degree requirements at Virginia Polytechnic Institute and State University in July 1974.

Gail Ferguson Cook
This research developed a laboratory procedure for dyeing nylon doubleknit fabric that would insure reproducibility of shade and levelness using a mixture of three acid dyes by evaluating the effects of the following dyeing conditions: (1) starting temperature; (2) final dyeing temperature; (3) pH of dyebath; and (4) concentration of dyeing assistant. The fabric samples were dyed in a Launder-Ometer. A mixture of Acid Yellow 40, Acid Red 266, and Acid Blue 25 dyes, Alkanol ND dyeing assistant, and ammonium sulfate were used.

Dye results were evaluated by comparing the percentage of transmittance of the exhaust solutions and the Hunter $L$, $a$, and $b$ color values of the dyed samples. The dye results were statistically analyzed.

Major findings of this research were:

1. Samples dyed at the starting and final dyeing temperature combinations of 100°F to 200°F, 100°F to 180°F, and 140°F to 200°F gave level and reproducible results at the dyebath pH's and the amount of dye assistant used in this research.

2. Samples dyed in a dyebath with a pH of 4.05-4.30 gave the best
reflectance ($L$ value) results

3. Samples dyed with 1% owf dyeing assistant gave the best dye exhaustion and reflectance ($L$ value) results.