To the Graduate Council:

I am submitting herewith a thesis written by Irene Lois Barnes entitled "The Properties of Cellulose Dyed with Fiber Reactive Dyes." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Textiles and Clothing.

Leona Kocher

Leona Kocher, Major Professor

We have read this thesis
and recommend its acceptance:

Tyrone L. Vigo

A. Alan Lowry

Accepted for the Council:

L. Evans Reed

Vice Chancellor
Graduate Studies and Research

THE PROPERTIES OF CELLULOSE DYED WITH FIBER REACTIVE DYES

A Thesis

Presented for the

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Degree

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Irene Lois Barnes

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ABSTRACT

The thermal and physical properties of reactive dyed cotton fabric were investigated, and the results were compared among the dyed fabrics, as well as to those properties exhibited by undyed cotton fabrics. A 2 X 2 X 2 factorial design was used to evaluate the effects of dye type, dye concentration, and method of dye combination on temperature at onset of thermal degradation, degradation peak temperature, and heat of decomposition. A 2 X 2 X 2 factorial design was used to evaluate the effects of dye type, dye concentration, and fabric direction on breaking tenacity, breaking extension, wrinkle recovery, and flexural rigidity. A 2 X 2 factorial design was used to evaluate the effect of dye type and dye concentration on moisture content and moisture regain; fiber swelling; and fiber breaking tenacity, breaking elongation, and initial modulus. The reactive dyed cotton fabrics included both a monochlorotriazinyl and dichlorotriazinyl structure (Procion H and MX, respectively); two dye concentrations (1 and 4%); all of one color (Brilliant Blue). Testing was carried out through use of a differential scanning calorimeter (DSC), Instron tester, Monsanto wrinkle recovery method, Shirley stiffness tester, and methods developed for this study to measure moisture content, moisture regain, and fiber swelling.

The DSC findings revealed onset of degradation began at lower temperatures for the bifunctional dye and for fabrics dyed at a 4% concentration. Increasing dye concentration also resulted in lower degradation peak temperatures, especially with the bifunctional dyes. Heat of decomposition was affected only by the method in which the dye

was combined with the fabric (via chemical or physical means) with the physical combinations requiring slightly less energy to decompose than the chemical combinations. The undyed fabrics were found to degrade at higher temperatures than the dyed fabrics. There were no differences in heat of decomposition between dyed and undyed fabrics.

The results of the physical tests revealed that the property of fabric wrinkle recovery is improved by increasing dye concentration. Any effects due to the presence of dyes in fabric tensile properties or flexural rigidity were overshadowed by the dominant effects of fabric direction. Initial modulus of fibers removed from dyed fabrics was lowered by the effect of the bifunctional dye as compared to the monofunctional dye or the absence of dye. Breaking tenacity and elongation of the fibers were found to be affected by the presence of dye, although the source of this effect was not determined. There were no differences in the amount of swelling of fibers removed from any of the dyed or undyed fabrics. Moisture sorption properties of the fabrics were also relatively unaffected by the presence of dye, although a useful procedure for evaluation of these properties was developed.

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CHAPTER I

INTRODUCTION

The effect of dyes on the flammability behavior of textile materials has been the subject of several recent studies (16,29,33,36). Various dyes of known structure have been examined as potential flame retardants or as additives in combination with flame retardants to reduce the amount of flame retardant incorporated into textiles. Flammability parameters investigated have generally not shown large variability when tested against dye effects, although statistically significant differences have been observed.

The effect of dyes on the physical properties of textile materials has received limited attention in current research studies. A flammability study which included an investigation of the tensile strength of dyed cotton fabrics revealed small but significant variations due to the amount of dye contained in the fabric (16).

The question as to whether such subtle dye effects on thermal and physical properties of fabrics may have any practical importance is still unanswered. An investigation of flammability parameters of cotton fabric dyed with fiber reactive dyes reported that the amount of dye in cellulose is the most important factor in heat transfer during burning (43). The same study reported reactive dyed cellulose decomposition to be closely related to the chemical structure and uptake of the dye.

Reactive dyes, unlike other dyestuffs, combine chemically with the cellulose molecule; chemical modification of cellulose is known to

have an effect on fiber, yarn, and fabric properties. Thus, in the present study, changes in properties associated with modification of cotton cellulose by reactive dyes were investigated. This paper presents an evaluation of the thermal behavior of cotton fabric treated with reactive dyes through chemical, as well as physical, means and various properties of that fabric based on moisture sorption, elastic recovery, and tensile strength.

I. OBJECTIVES

1. To determine the effect of dye type, dye concentration, and method of combination of dye and fabric on temperature at onset of degradation, degradation peak temperature, and heat of decomposition of reactive dyed cotton fabric.

2. To determine the effect of dye type, dye concentration, and fabric direction on breaking tenacity, breaking extension, wrinkle recovery, and flexural rigidity of reactive dyed cotton fabric.

3. To determine the effect of dye type and dye concentration on moisture content and moisture regain of reactive dyed cotton fabric and on swelling, breaking tenacity, breaking elongation, and initial modulus of fibers removed from reactive dyed cotton fabric.

4. To determine the difference between undyed and reactive dyed cotton fabric with respect to temperature at onset of degradation; degradation peak temperature; heat of decomposition; breaking tenacity and breaking extension; wrinkle recovery; flexural rigidity; fiber breaking tenacity, breaking elongation, and initial modulus; fiber swelling; and moisture content and moisture regain.

II. ASSUMPTIONS

1. The determination of differences in thermal and physical properties of reactive dyed cotton cellulose may contribute to an increased understanding of the practical significance of dyes in cotton fiber.

2. The fiber reactive dyes used in this study, as well as the concentrations used, are representative of those used commercially on cotton fabric.

III. LIMITATIONS

1. Fabrics of 100% cotton will be the only fabric tested.

2. Only plain weave fabric of one weight will be used.

3. Only two fiber reactive dyes, representing two chemically different structures, and one color will be used.

4. Fabrics will be dyed at only two concentrations.

5. All thermal testing will be conducted on a differential scanning calorimeter; all tensile testing on an Instron tensile testing machine; wrinkle recovery by the Monsanto method; flexural rigidity on a Shirley stiffness tester; and fiber swelling, moisture content, and moisture regain by methods developed for this study.

IV. DEFINITIONS

Breaking Tenacity--The maximum force applied to a specimen in a tensile test carried to rupture expressed as force per unit linear density of the unstrained specimen.

Shirley Stiffness Tester--An instrument which measures bending length of fabrics based on the cantilever principle from which flexural rigidity can be calculated.

Differential Scanning Calorimeter--An apparatus which measures the heat energy per unit time necessary to maintain a sample and an inert reference material at the same temperature during an interval of programmed temperature rise.

Dye Concentration--Amount of dye on the fabric expressed as a percentage of fabric weight.

Elongation at Break, Percent--The increase in length of a specimen which corresponds to the rupture of the last component of the specimen expressed as a percentage of the original length.

Flexural Rigidity--A measure of stiffness associated with handle.

Heat of Decomposition--A calorimetric measurement of the energy absorbed by a substance in order to cause decomposition.

Initial Modulus--Initial resistance to extension of a textile material.

Instron Tensile Testing Machine--An apparatus which measures the force required to break a fabric under tension by maintaining a rate of increase of specimen length which is uniform with time.

Moisture Content--The amount of water in a material determined under prescribed conditions and expressed as a percentage of the mass of the moist material.

Moisture Regain--The amount of water in a material determined under prescribed conditions and expressed as a percentage of the mass of the water-free specimen.

Planimeter--A mechanical device which measures area under a curve by tracing the perimeter of the curve.

Sample--Total number of specimens required per replication for a test method.

Specimen--Individual component of a sample cut to specific dimensions as specified for a test method.

Wrinkle Recovery--That property of a fabric which enables it to recover from folding deformations.

CHAPTER II

REVIEW OF LITERATURE

Recent literature contributing to the subject of the properties of cotton cellulose when dyed with fiber reactive dyes was reviewed in the following categories: Chemical Reaction Between Cellulose and Reactive Dyes, Effect of Dyes in Cellulose Combustion and Decomposition, and Physical Properties of Cellulose.

I. CHEMICAL REACTION BETWEEN CELLULOSE AND REACTIVE DYES

The cellulose molecule consists of a chain of several thousand anhydroglucose units and has an empirical formula of $(C_6H_{10}O_5)_n$. Each repeating unit is composed of a β-d-glucose molecule linked together at the carbon atoms in the 1 and 4 positions, as shown in Figure 1.

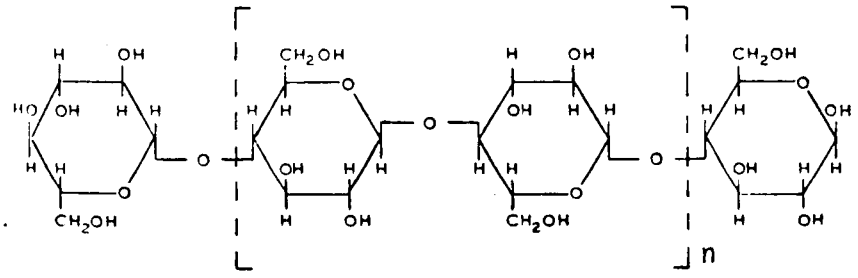


Figure 1. Structural Formula for Cellulose.

Source: Trotman, E. R. Dyeing and Chemical Technology of Textile Fibers. Charles Griffin and Company, Ltd., London, 1975.

In the fibrous form of cellulose, many individual chain molecules are packed closely together. The chain molecules are joined by crosswise hydrogen bonds between hydroxyl groups which exist along the fringe of the chain. In the crystalline regions, the number of these hydrogen bonds is high, producing a highly oriented structure and restricting penetration by outside substances such as dyes. The amorphous regions, however, have fewer connecting bonds, leaving the hydroxyl groups accessible for combination with outside molecules (6,37,38).

Dyestuffs which were capable of covalently bonding with cellulosic molecules were developed in the 1950's. Such dyestuffs created a new method of attaching dyes to cellulosics. In 1956, ICI marketed the first commercial reactive dye under the trade name "Procion." By the 1970's, the range of reactive dyes had grown extensively as other companies began manufacturing them (3,22).

In general, reactive dyes can be represented by the formula:

S - F - T - X

where S represents one or more sulfonic acid groups which impart solubility to the dye, F is the chromophoric group responsible for the shade and brilliance of the dyeing and determines the light fastness and stability of the product, T represents the carrier of the reactive group which contributes to the reacting capacity of the dye, and X is the reactive group which forms a covalent bond with the functional group of the fiber. The X component may be present in one or more groupings (6,22).

The original Procion dyes were developed to react with cellulose by nucleophillic substitution. In this type of reaction, a leaving

group from the dye, a halogen atom, is replaced by the attaching base, a cellulosate ion (O^-) from the fiber. The substitution reaction occurs when nitrogen containing atoms in the aromatic ring of the carrier group of the dyestuff activate the system due to their electronegativity. Attack can occur by the hydroxyl groups at either the 2-, 3-, or 6-carbon positions, although the major part of the reaction is said to occur at the C-6 position, where the primary hydroxyl group is located (22). One of the most commercially important systems of this type is the dichloro-s-triazinyl group, which is the basis for the Procion MX dyes by ICI. The leaving group (X) in this case is chlorine. These dyes are highly reactive, to the extent that one chlorine can be replaced by a hydroxyl group of the fiber at room temperature. The second chlorine, however, reacts only at higher temperatures and may result in crosslinking. An alteration in the leaving group substituent where one chlorine is replaced by an amine group is the basis for the Procion H dyes by ICI. This monochloro-s-triazinyl structure has a lower reactivity than that of the Procion MX dyes and, thus, requires higher temperatures, in a range similar to those required to react the second chlorine atom in the dichloro-s-triazinyl compound (35).

Substituent chlorine atoms in diazines, while less reactive than those in triazines, form the basis for di- and trichloropyrimidinyl reactives. These dyes, which have proven satisfactory for printing and hot continuous dyeing, are known as the "Reactone" range by Ciba-Geigy and as the "Drimarene" range by Sandoz.

The "Remazol" dyes introduced to the market by Hoechst contain a sulphatoethylsulphonyl group which is transformed into a vinyl sulfone

by treatment with a mild alkali. Vinyl sulfones are capable of undergoing addition reactions, and dyes containing these substituents can react with cellulose under slightly alkaline conditions to form covalent bonds. At higher temperature and under more concentrated alkaline conditions, a β-hydroxyethylsulphonyl compound is formed and functions as the reactive system of the Remazol dyes.

A β-sulphatoethylsulphamoyl group is the basis of the "Levafix" dyes by Bayer which form a cyclic compound capable of reacting with cellulose to form a bond similar to the type found in ethers. The "Levafix E" dyes, having enhanced reactivity, employ a halogenated benzodiazine reactive system. A large number of other reactive systems are described in patent literature, although those mentioned here may be considered representative of the most important commercial reactive dyes (3,13).

II. EFFECT OF DYES IN CELLULOSE COMBUSTION AND DECOMPOSITION

Fundamental studies investigating the mechanism of thermal degradation of cellulose suggested the cause of flammability of the polymer is the decomposition of levoglucosan yielding volatile and flammable products (28). Research efforts led to the theory that chemical modification of the cellulose molecule at the 6-carbon position of the anhydroglucose unit should prevent the formation of levoglucosan and, thus, result in decreased flame and thermal hazards. Introduction of known flame-retardant elements, such as the halogens, into the cellulose molecule could be accomplished by means of a substitution reaction.

A report on subsequent investigations found that the presence of a flame retardant on the cellulosic material caused levoglucosan to be degraded to a heavier char than when this intermediate product of cellulose was degraded alone. This supports the previously suggested mechanism that levoglucosan formation is the principal source of combustible products from cellulose degradation (18). Chemical modification of the cellulose molecule to inhibit the formation of levoglucosan thus appeared to offer a possible strategy for providing protection from thermal hazards.

Interest in the effect of alkali metal bases on cotton cellulose at high temperatures prompted a study by Mack and Donaldson (21) which evaluated the effect of added base at temperature ranges associated with cellulose degradation. A comparison of the data determined by differential scanning calorimetry (DSC) and differential thermal analysis (DTA) revealed that an increase in the concentration of base on cotton cellulose altered the pattern of the thermogram by reversing the endotherm to an exotherm. The transition temperature and the ΔH of pyrolysis were determined to be lowered, suggesting the base functioned as a catalyst during one of the pyrolysis reactions. Thermogravimetric analysis (TGA) provided the additional information that the same effect also produced an increase in the amount of char formation or percent residue during degradation.

The earliest report of the effect of dyes on flame and thermal parameters of cellulose was that of Reeves, et al. (29) from an investigation of the chemical and physical properties of aminized cotton. Aminized fabric dyed with acidic azo dyes acquired a low degree of combustibility due to the phosphate or sulfo groups in the dye and the

nitrogen present in the aminized cotton. Direct dyes are also capable of imparting flame resistance in this manner.

Research investigating the effect of dyes on the flammability of untreated cotton fabric was first reported in 1974 in a study by Timpa, et al. (36). A measure of the degree of flammability of cotton dyed with indigo and bromine- and/or chlorine-substituted dyestuffs indicated that higher concentrations of dye increased the oxygen index (OI) to a slight extent. An even greater effect of these dyestuffs on thermal degradation was observed by thermogravimetric analysis, although it did not correlate well with increased OI values. Increasing halogen substitution shifted the TGA curves to progressively lower decomposition temperatures, with bromine having a greater effect than chlorine.

Segal, et al. (33) investigated the effect of representative dyes from other classes on all cotton fabric. Oxygen index values were lowered slightly by reactive dyes, although the changes could not be clearly related to percent add-on. The greatest changes in pyrolysis toward lower decomposition temperatures as shown by TGA were demonstrated with the reactive dyes, a pentabrominated indigo dye, and acid dyes on aminized cotton.

An explanation for a reduction in flammability of dyed aminized cotton, where the acid dye becomes a substituent through attachment to the amino group, has been offered in the previous study by Reeves, et al. (29). Although the pentabrominated indigo dye is not chemically bound to cotton cellulose, its effectiveness can be attributed to the well known flame-retardant effects of bromine. In combining with the cotton fiber, the reactive dyes form a cellulose derivative in which the dye,

now a substituent group bound by covalent bonds, interferes with the pyrolysis of cellulose to levoglucosan (33).

The effect of fiber reactive dyes on flammability and other thermal parameters was further investigated by Hopkins and Buchanan (16) in a study using a series of cotton/polyester fabrics dyed at several levels with two Procion fiber reactive dyes. These dyes were chosen to determine whether or not different reactivities of the dye molecule at the hydroxyl groups of cellulose might result in different flammability behavior. Different levels of reactivity were exhibited by a Procion H-GR dye which contained one chlorine atom and by a Procion M-R dye which contained two chlorine atoms. Increasing dye level in the fabrics resulted in lower OI values, a confirmation of earlier results (33). Average ignition time (obtained with the Mushroom Apparel Flammability Tester [MAFT]) was also reduced, which agrees with previous reports that thermal decomposition temperatures in cotton fabrics are lowered by the presence of dyes (29,33,36). Although dye level did not affect maximum heat transfer rate, this result was attributed to difficulties in obtaining reproducible results since the fabrics emitted considerably greater amounts of heat than what the MAFT apparatus was designed to measure.

A recent study by Westlake (43) investigated the effect of dye type, dye level, and dye color on the flame and thermal properties of reactive dyed cotton fabric. Total heat transfer as measured by the MAFT was found to be affected by all three parameters, with the Procion H dyes, the 4% level, and the blue color producing the highest values for heat transfer. Flammability hazard as determined by an analysis of the

heat/time relationship for this MAFT data suggests that fabrics dyed at the 4% level transfer heat more slowly than those dyed at the 1% level, but they ultimately transfer more heat. This finding, when compared with the Derkson injury curve, showed that a greater level of dye lowered the flammability hazard of the fabrics during the initial stages of burning. Rate of flame spread (measured by a 45° angle tester) revealed that as the dye level increased, longer flame spread times occurred. This finding was consistent with the above MAFT results. Although heat of decomposition determined by differential scanning calorimetry was unaffected by dye level, the thermal decomposition temperatures were reported as being lowered by the increasing amount of dye in the fabric.

III. PHYSICAL PROPERTIES OF CELLULOSE

An observation of the burning behavior of fabrics on the MAFT in which shrinkage during burning was reported to progressively increase as the amount of dye in the fabric increased raises questions about the physical, as well as thermal, properties of reactive dyed cellulose (43). Physical properties of cotton fibers are exhibited in response to mechanical forces. The various structural aspects of the fiber, such as molecular chain length, accessibility, crystallinity, etc., contribute to the responses the fiber makes. These may be collectively referred to as its "physical behavior."

Strength of textile materials, expressed in terms of tenacity, represents the number of unit lengths of the textile material which can be supported before rupture. The naturally occurring hydrogen bonds between unmodified cellulose chains are an important factor in cotton

cellulose tenacity. Chain slippage, which contributes to fiber weakness, is prevented in the crystalline areas due to a high degree of hydrogen bonding; however, in the frequently occurring amorphous areas, tenacity is dependent only on primary valence bonds and any naturally existing crosslinking. Additional crosslinking achieved by chemical modification can severely reduce tenacity since the cellulose chains are no longer free to move in order to relieve any imposed stress (37).

The degree of crystallinity and the accessibility of the molecular chain are important in determining strength loss during degradation. A cellulose molecule with molecular chains accessible to an attacking reagent will experience a greater degree of chain scission and, thus, a reduction in tenacity. A cellulose molecule which has more crystalline regions will be stronger than one which has fewer, although larger, crystalline areas. This is the process by which mercerization increases cotton tenacity (20,25,26,37).

Other chemical modifications of cotton demonstrate the diverse ways in which tenacity can be affected. While partial acetylation tends to decrease tenacity, the trend reverses when acetyl contents are increased (9,24). Although various explanations have been suggested, this finding may be due to non-uniformity of the extent of reaction at the fiber level; the unequal composition of products formed would lead to poor stress distribution and lower breaking strength (37). The application of resin treatments on cotton results in a severe loss of strength if the cotton is in a relaxed state when treated. If the treatment is applied under tension, however, significant increases in breaking strength can be obtained. Immobilizing the molecular chains in the

positions they occupy when relaxed curtails their ability to shift during stress. When immobilized in the position occupied under tension, the added strength due to crosslinking can be fully realized (27,37).

Research investigating the effect of the chemically bound reactive dye on the physical properties of cotton is extremely limited. Hopkins and Buchanan (16) found that dye level had a significant, although small, effect on breaking strength by producing higher values in the warp direction. No significant change of breaking strength was observed in the filling direction. Likewise, in the case of tear strength, the only statistically significant effect of dye level occurred when the warp yarns were involved in the deformation. Tear strength values were slightly decreased in the filling direction as dye level increased.

Elongation is a measurement of the extension of a material when stressed to the point of rupture and is normally expressed as a fraction of the unstressed length (37). A study by Weiss, et al., investigating the elongation of flame retardant cotton yarns and fabrics during combustion, determined that increases in length were observed up to 300°C; at higher temperatures, contraction occurred (42). The presence of crosslinking will tend to reduce elongation; since crystallinity may be regarded as a type of crosslinking by hydrogen bonds and van der Waals forces, those celluloses with a higher degree of crystallinity usually have lower elongation (37). Grant, et al. (8) determined definite lower elongation at break in processed fibers. When stretching or tension was applied, an even greater effect was observed in lowering elongation.

The physical properties involved in the crease recovery of cotton fabrics are a reflection of the internal morphology of the fibers.

Permanent set, as well as elasticity and elongation discussed previously, are influenced by the freedom of motion possessed by the cellulose chains, the individual microfibrils, and the individual cell-wall lamellae. It has been determined that slippage of any of these structural elements of the fiber permit crease formation and that stabilization of the elements yield crease recovery (30,31). The effect of crosslinks in providing this stabilization influence is quite clear. Electron microscope studies investigating the behavior of reactive dyes applied to cotton cellulose revealed that the monofunctional dye left the lamellar structure of the cotton intact, while the bifunctional dye caused it to completely collapse (4). This reaction is similar to that of a crosslinking agent in which the collapse of the lamellae is due to formation of crosslinks between adjacent chains. Thus, the bifunctional dye treatment appears to result in such a crosslinked structure which serves to increase the dimensional stability, wrinkle resistance, and resiliency of the fabric.

Wrinkle resistance and resiliency can be clarified in terms of three components: elastic recovery, which is immediate recovery from deformation involving a reaction from primary valence bonds; viscoelastic recovery, a time-delayed recovery reflecting movement of large segments of the molecule; and plastic recovery, the irreversible breakage of introduced and natural bonds. The conversion of plasticity into elasticity is the more effective means of improving recovery (41).

An evaluation of the effect of parchmentization of reactive dyed cotton fabrics with sulfuric acid revealed that in the case of the monofunctional dye, a significant alteration in the stiffness of the treated

fabric toward higher flexural rigidity is possible. This is due to the fact that the acid is able to sufficiently penetrate the fibers. The bifunctional dyes, however, restrict acid penetration due to the presence of crosslinks and resulted in a softer fabric with a lower flexural rigidity (4).

Reeves, et al. (29), after investigating the physical properties of aminized cotton, reported that a slight increase in stiffness is one of the more profound changes in physical behavior compared to that of the untreated fabric.

Moisture sorption and swelling of cotton fiber are complex phenomena dependent on many variables such as the percentage of amorphous cellulose, density, and the presence of impurities (10,34). The extent of reaction between cotton fibers and intended swelling solutions depends on the accessibility of the intrafiber structure and upon the space available to accommodate the expanding structure. In chemically modified cottons, the reagent can alter the intrafiber spaces, and if any cross-linking occurs, restrict the mobility of the structural elements and, thus, prevent access to portions of the intrafiber structure. Both factors can then affect the swelling and sorptive capacity of the cotton (15,34).

Swelling, as measured by cadoxen retention values (4), was reduced slightly for cotton fabrics dyed with a monofunctional dye. Significantly greater reduction was achieved by bifunctional dyes, with the result being attributed to the formation of crosslinks which prevent the penetration of solvent into the fiber.

In another study (9), moisture regain of chemically modified cotton was found to depend on both the type of modification and the

conditions of treatment. Cotton treated with sodium hydroxide, as in mercerization, was able to achieve higher moisture regain values than untreated cotton. The increases were slightly less when tension was applied to the yarns.

When an entirely new compound was formed by a chemical reaction, the moisture regain was reported as being dependent on the chemical groups formed (9). For example, in the case of carboxymethylation, as degree of substitution of anhydroglucose units increased, so did moisture regain. On the other hand, for acetylated cottons, as the degree of substitution increased, the moisture regain decreased.

CHAPTER III

METHODOLOGY

Reported in this chapter are the experimental design and description of the fabrics, dyes, and method of sample preparation. The procedures for conducting the physical and thermal tests are explained, along with the method for obtaining the statistical analysis of the data.

I. EXPERIMENTAL DESIGN

A 2 X 2 X 2 fully-crossed and balanced design was used to test the effect of dye type, dye concentration, and method in which the dye and fabric were combined (independent variables) on three dependent thermal degradation variables (temperature at onset of degradation, degradation peak temperature, and heat of decomposition). In addition, the undyed fabric was tested for comparison with the dyed fabric. The thermal degradation variables were measured with a DSC.

A 2 X 2 X 2 fully-crossed and balanced design was used to test the effect of dye type, dye concentration, and fabric direction (independent variables) on the following dependent variables: fabric breaking tenacity, breaking extension, wrinkle recovery, and flexural rigidity. In addition, the undyed fabric was tested for comparison with the dyed fabric. The Instron tensile testing machine was used to determine fabric breaking tenacity and breaking extension. Wrinkle recovery was measured by the Monsanto recovery angle method, and flexural rigidity was calculated from a measurement of bending length as determined by the Shirley stiffness tester.

A 2 X 2 fully-crossed and balanced design was used to test the effect of dye type and dye concentration (independent variables) on the following dependent variables: moisture content, moisture regain, fiber swelling, fiber breaking tenacity, breaking elongation, and initial modulus. In addition, the undyed fabric was tested for comparison with the dyed fabric. Moisture content and moisture regain were measured on the basis of fabric weight. Amount of fiber swelling was measured in eye-piece scale divisions on the basis of fiber width. The Instron (constant-rate-of-extension type) tensile testing machine was used to determine the three dependent tensile variables for the cotton fibers.

II. FABRIC

A single weight of 100% plain woven cotton obtained from Test-fabrics, Inc., Middlesex, New Jersey was used in this study. The fabric was characterized in a previous study at this university (43) according to the following physical properties:

Fabric Weight--Fabric weight was determined as specified by ASTM Method D 1910-64 (2). Ten randomly selected, 5.08-cm squares were weighed on a Mettler balance. The weight in grams was converted to ounces per square yard and grams per square meter.

Fabric Thickness--Fabric thickness was determined according to ASTM Method D 1777-64 (2). Ten randomly selected, 5.08-cm squares were measured on an electric low-pressure thickness gauge to the nearest 0.001 of an inch.

Fabric Count--Procedures specified in ASTM Method D 1910-64 were used to determine fabric count (2). The mean number of warp ends and

filling picks of five randomly selected, one-inch areas were counted and recorded.

Cotton Count--Fabric strips measuring 10 X 45 cm were cut from the warp and filling direction of the fabric, and ten yarns from each direction were removed. A Shirley Crimp Tester was used to remove yarn crimp under a tension of four grams. Yarns were cut to a length of 40 cm during crimp removal and then weighed on a Mettler balance. Denier was calculated using the following formula:

$$\frac{W \text{ X } 9000}{L}$$

where W = the weight in grams of the specified length of yarn, and L = the length of the yarn in meters. Denier was converted to cotton count (CC) as follows:

$$CC = \frac{5314.87}{\text{denier}}$$

Fabric Cover--Fabric cover (K) was calculated from fabric count and cotton count as follows:

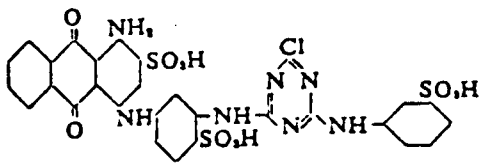
$$K_w = \frac{N_w}{\sqrt{CC_w}} \qquad K_f = \frac{N_f}{\sqrt{CC_f}}$$

$$K_{fabric} = K_w + K_f$$

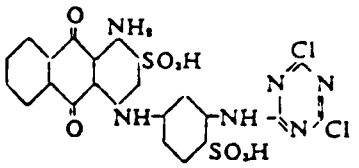
where N = number of threads designated either warp (w) or fill (f), and CC = cotton count, warp or fill.

III. DYES

Two types of reactive dyes were used to dye the cotton fabric: CI Reactive Blue 5 (Procion Brilliant Blue H-GR), a monochlorotriazinyl structure, and CI Reactive Blue 4 (Procion Brilliant Blue MX-R), a dichlorotriazinyl structure (Figure 2). Dyeing was done at Kimtex, Inc.,



PROCION BRILLIANT BLUE H-GR
(C.I. Reactive Blue 5)



PROCION BRILLIANT BLUE MX-R
(C.I. Reactive Blue 4)

Figure 2. Chemical Structures of Reactive Dyes.

Source: The Society of Dyers and Colourists. Colour Index, Volume 4. Lund Humphries, London, 1971.

Patterson, New Jersey. Two dye levels, expressed as a percentage of fabric weight, were used to obtain the following dye variants for the fabric:

1. Procion MX dye--1% concentration,
2. Procion MX dye--4% concentration,
3. Procion H dye--1% concentration,
4. Procion H dye--4% concentration, and
5. Control (undyed).

The undyed fabric was run through a mock dyeing process.

IV. SAMPLE PREPARATION

Fabrics were laundered once prior to cutting specimens for all tests according to the procedure given in AATCC Test Method 124-1978 (1). Fabric specimens were cut so as to assure randomness for each sample. A random sample of fibers for both the swelling and tensile tests was obtained in the following manner. Ten 5 X 4-inch specimens were cut from each fabric, five with the long dimension in the warp direction and five with the long dimension in the filling direction. For each test, ten adjacent yarns were removed from each warp specimen, making a total of 50 warp yarns. One fiber was removed from each yarn. The filling specimens were prepared in the same way, with the exception that every tenth yarn was removed from each specimen until ten yarns per specimen were obtained. Specimens for all physical tests were conditioned for 24 hours at a temperature of 21 $\pm$ 1°C and a relative humidity of 65 $\pm$ 2%.

DSC samples were prepared from the cotton fabric by grinding in a Wiley mill. A specimen consisting of ground dyed fabric was regarded as a chemical combination of dye and fabric. Physical combinations were prepared by weighing an arbitrary amount of ground undyed fabric, determining the appropriate weight of dye required to produce either a 1% or 4% concentration, and mixing the two components in a mortar and pestle. Control specimens were prepared from ground undyed fabric and from each type of dye in powder form.

V. THERMAL TESTING

DSC

A sample consisted of two specimens from each treatment combination. Aluminum sample pans were used for testing. The pan and lid were weighed together to the nearest 0.1 mg. Approximately 8 mg of fabric were added to each pan. After crimping the entire container closed with the press designed for that purpose, the sample was weighed again and the specimen weight determined by the difference.

DSC analyses were performed using a Perkin-Elmer DSC 1B. Temperature calibration was completed with a 12.3-mg tin reference sample. Each specimen was heated from 340°K to 750°K at a scan rate of 20 K/minute. The DSC was operated in a range of 16 mcal/second under a nitrogen atmosphere and at a chart speed of 1.0 inch/minute. After completion of each test, the container was re-weighed and weight of the residue determined.

An approximation to a linear baseline was drawn on each DSC curve according to a method outlined by Frederick and Mentzer (7). The temperature at onset of degradation and the temperature at which the transition was proceeding at a maximum rate were read from the thermogram. A measurement of the area under the curve was obtained with a mechanical planimeter (44). The integrated area was converted to calories by multiplying by a conversion factor equivalent to the number of calories per area unit of the known ΔH_f for the tin reference standard. Heat of decomposition was determined by dividing the area under the curve (in calories) by the calculated change in mass of the specimen (in grams).

VI. PHYSICAL TESTING

Fiber Tensile Testing

Individual fiber specimens were mounted according to a procedure developed by Wyatt (45) in order to ensure minimal fiber slippage. A sample consisted of 100 randomly selected specimens from each treatment combination.

Fiber tensile tests were conducted using a table model Instron tensile testing machine with the AJ jaws and the corresponding A load cell installed. Calibration of the system was completed using a 10-gm calibration weight. The instrument was operated at the one-pound load range with a crosshead speed and chart speed of five and 50 inches/minute, respectively. Gauge length was set at 12.7 mm.

After determination of a mean fiber diameter representative of all specimens tested, fiber denier (D) was calculated according to the following formula (23):

$$D = \frac{\pi \varrho d^2 L}{4}$$

where π is equivalent to 3.1416, ϱ represents the known density of cotton at 65% relative humidity, d represents mean fiber diameter in cm, and L represents length equivalent to 9000 m.

Breaking load and elongation-at-break were read from each stress-strain curve. In addition, the load and elongation associated only with the initial portion of that curve was determined by a method outlined by Ko (17). Breaking tenacity, percent elongation at break, and initial modulus for the cotton fibers were calculated as follows:

$$\text{Breaking tenacity (gm/denier)} = \frac{\text{breaking load (gm)}}{\text{denier}}$$

$$\text{Breaking elongation (\%)} = \frac{\text{elongation-at-break (mm) X 100}}{\text{gauge length (mm)}}$$

$$\text{Initial modulus (gm/denier)} = \frac{\text{load (gm)/denier}}{\frac{\text{elongation (mm)}}{\text{gauge length (mm)}} \cdot \frac{\text{crosshead speed}}{\text{chart speed}}}$$

Fabric Tensile Testing

All fabrics were tested according to the specifications in ASTM Method D 1682-64 for the ravel-strip load/elongation test (2). A sample consisted of five randomly selected specimens from each of the ten treatment combinations. Each specimen consisted of a strip measuring 6 X 1½ inches, from which ¼ inch of the width had been raveled from each edge in the long dimension.

Fabric tensile tests were conducted using a table model Instron tensile testing machine with the CJ jaws and corresponding CT load cell installed. Calibration of the system was completed using a five-pound calibration weight. The instrument was operated in the 200-pound range with a crosshead speed and chart speed of five and 50 inches/minute, respectively. Gauge length was set at 76.2 mm.

After determination of area density for each fabric category in gm/m^2, fabric tex in gm/m was obtained by multiplying each value by the specimen width, excluding the fringed edges, expressed in meters (12). Breaking load and elongation-at-break were read from each stress-strain curve. Breaking tenacity and percent breaking extension were calculated as follows:

$$\text{Breaking tenacity (kg/tex)} = \frac{\text{breaking load (kg)}}{\text{tex}}$$

$$\text{Breaking extension (\%)} = \frac{\frac{\text{crosshead speed}}{\text{chart speed}} \quad \text{elongation-at-break (mm)}}{\text{gauge length (mm)}} \times 100$$

Wrinkle Recovery

Wrinkle recovery angle in degrees was measured as specified in AATCC Test Method 66-1978 (1). A sample consisted of six randomly chosen specimens from each of the ten treatment combinations. Each specimen measured 15 X 40 mm. Since differences between face-to-face and back-to-back values for each fabric category were <15°, no distinction between sides of the fabric was made in reporting the results.

Flexural Rigidity

All fabrics were tested according to the specifications in ASTM Method D 1388-64 (2). A sample consisted of four randomly chosen specimens from each of the ten treatment combinations. Each specimen measured 25 X 150 mm. A Shirley stiffness tester was used to obtain four readings of overhang length for each specimen, measured in centimeters. After determination of a mean overhang length for each specimen, bending length was obtained by dividing each value by 2. Flexural rigidity was calculated using the following formula:

$$\underset{\text{(mg-cm)}}{\text{Flexural rigidity}} = \left[\underset{\text{(mg/cm}^2\text{)}}{\text{fabric weight}}\right] \left[\underset{\text{(cm)}}{\text{bending length}}\right]^3$$

Fiber Swelling

Individual fibers were viewed through an AO-Spencer Microscope at a magnification of 450X. True fiber diameter in microns was obtained

by determining the width of the fiber in eyepiece scale divisions and multiplying by a calculated micrometer value obtained through calibration of the instrument with a stage micrometer (5,14,40).

Each individual specimen was prepared by mounting a single fiber on a slide, securing both ends with tape, and applying a coverslide. A sample consisted of 100 randomly selected specimens from each treatment combination. Original fiber diameter was determined from measuring the fiber width in the wide area of the convolutions at five arbitrary locations and obtaining a mean value. Fibers were swollen by adding a drop of 1% NaOH solution at the edge of the coverslide (39). After a 60-second interval, the diameter of the fiber was re-measured in the same fashion. A change in fiber diameter was calculated for each specimen by subtracting the original diameter from that in the swollen state, and percent swelling was calculated by the following formula:

$$\text{Fiber swelling (\%)} = \frac{\text{change in diameter } (\mu)}{\text{original diameter } (\mu)} \times 100$$

Moisture Content and Moisture Regain

A sample consisted of five specimens measuring 6 X 6 inches, from each fabric tested. Each specimen was coded with a ziploc-type plastic bag (size: 168 X 149 mm) and the weight of each bag recorded. After conditioning under standard atmospheric conditions for 24 hours, each specimen was placed in its respective bag and the weight of the unit recorded. Initial weight (IW) of the fabric was calculated from this value be subtracting the weight of the bag. While taking care to handle the specimen and bag with tweezers only, the specimen was oven-dried for 30 minutes at 105 $\pm$ 2°C, then cooled in a desiccator with its bag for an additional 30 minutes. Each specimen was re-weighed in its bag,

and dried fabric weight (FW) was determined by subtracting the weight of the bag. Moisture content as a percentage of initial weight was calculated according to the following formula:

$$\text{Moisture content (\%)} = \frac{IW - FW}{IW} \times 100$$

To determine moisture regain, specimens were conditioned for an additional 24 hours. Following conditioning, each specimen was transferred to its bag and re-weighed. Regain weight (RW) of the fabric was obtained by subtracting the weight of the bag from the combined weight of bag and fabric, and percent moisture regain was determined as follows:

$$\text{Moisture regain (\%)} = \frac{RW - FW}{FW} \times 100$$

VII. STATISTICAL ANALYSIS

A test for normal distribution of data for each dependent variable specified in the experimental design was performed through a Shapiro-Wilk W statistic for populations ≤ 50 and through a modified Kolmogorov-Smirnov D statistic for populations >50. A check for homogeneity of variance of each population was made through use of a Bartlett-Box F statistic. A one-way analysis of variance with orthogonal contrasts to test for dye main effects (dye type and dye concentration), interaction effects, and dyed vs. undyed fabric was used for fiber swelling and fiber initial modulus. A one-way analysis of variance with orthogonal contrasts to test for main effects (dye type, dye concentration, and fabric direction), interaction effects, and dyed vs. undyed fabric was used for fabric wrinkle recovery, flexural rigidity, fabric breaking

tenacity, and breaking extension. A one-way analysis of variance with orthogonal contrasts to test for main effects (dye type, dye concentration, and method of dye application), interaction effects, and dyed vs. undyed fabric was used for the thermal variables (onset of degradation, degradation peak temperature, and heat of decomposition). Further examination of all possible pairwise comparisons of treatment means for those dependent variables which produced a significant overall F test was carried out with a Tukey post hoc procedure.

A nonparametric one-way analysis of variance was carried out by means of a Kruskal-Wallis test for those dependent variables which violated the homogeneity of variance assumption (fiber breaking tenacity, breaking elongation, moisture content, and moisture regain). Further analysis of treatment means through planned comparisons investigating the effects of dye type, dye concentration, and interaction of the two was conducted with a Mann-Whitney U rank sum test for those dependent variables which had produced a significant chi-square statistic.

A significance level of 0.10 was used for all tests, with the exception of the Mann-Whitney U test, where a level of 0.03 was used.

The preciseness of all experimental procedures used was evaluated by means of a coefficient of variation as follows: For those tests producing a significant overall F statistic, a coefficient of variation (percent) was determined for each treatment combination by dividing the standard deviation by each treatment mean and multiplying by 100. For those tests with a nonsignificant overall F statistic, a single coefficient of variation was determined through use of the grand mean and following the same procedure. A precise procedure was indicated by values in the range of 5-10% and no greater than 15% (19).

CHAPTER IV

RESULTS AND DISCUSSION

Reported in this chapter are the results for the physical properties of weight, thickness, fabric count, and fabric cover for each test fabric. In addition, the results for all thermal and physical tests are reported for each test fabric.

The effect of dye type, dye concentration, method of dye combination, and dyed vs. undyed fabric on temperature at onset of degradation, degradation peak temperature, and heat of decomposition is reported. Also included is the effect of dye type, dye concentration, fabric direction, and dyed vs. undyed fabric on breaking tenacity and breaking extension; wrinkle recovery; and flexural rigidity. In addition, the effect of dye type, dye concentration, and dyed vs. undyed fabric on moisture content and moisture regain; fiber swelling; and fiber breaking tenacity, breaking elongation, and initial modulus is reported. Coefficients of variation have been determined for each test method and are listed with the summary of test results for each dependent variable.

I. DYED FABRICS

Characterization of Fabrics

The mean results for the physical properties of weight, thickness, fabric count, cotton count, and fabric cover as determined during a previous study using these fabrics (43) are listed in Table I. The findings indicate that the cotton fabrics are equivalent in physical properties despite processing with reactive dyes of varying types and concentrations.

Table I. Physical Properties of Fabrics.[a]

Fabric[b,c]	Weight		Thickness[d] (in Mills)	Fabric Count[e]	Cotton Count[f]	Cover Factor[g]
	oz/yd^2	gm/m^2		Warp / Fill	Warp / Fill	
MX 1%	3.84	130	15	130 / 80	42 / 44	31.99
MX 4%	3.91	132	15	130 / 80	41 / 44	32.36
H 1%	3.85	130	15	130 / 80	44 / 43	31.70
H 4%	3.89	132	15	130 / 80	43 / 44	31.89
Undyed	3.91	132	15	130 / 82	43 / 42	32.47

[a]Westlake, Betsy Carolyn. "The Effect of Selected Reactive Dyes on the Flammability Behavior of Cotton." Unpublished Master's Thesis, The University of Tennessee, Knoxville, 1980.

[b]All fabrics were purchased from Testfabrics, Inc., Middlesex, New Jersey and dyed at Kimtex, Inc., Patterson, New Jersey.

[c]Identified according to dye type and dye concentration.

[d]Determined according to standard procedure ASTM Method D 1777.

[e]Determined according to standard procedure ASTM Method D 1910.

[f]5314.87/denier (the number of 840-yard hanks per pound of yarn).

[g]K (warp) + K (filling) = K (fabric cover).

DSC Tests

The mean results for the DSC tests are given in Table II. The Bartlett-Box F statistic calculated for each dependent variable were nonsignificant, which permitted the assumption that variances were equal in all populations. A one-way analysis of variance with orthogonal contrasts was used to test for differences in main effects (dye type, dye concentration, and method of dye combination) and interaction effects on the temperature at onset of degradation, degradation peak temperature, and heat of decomposition. Results of the three analyses are shown in Tables III-V. Each of these dependent variables will be discussed separately.

Temperature at onset of degradation. The temperatures at onset of degradation were significantly different for the dyed fabrics due to dye type, dye concentration, method in which the dye was combined with the fabric, and the two-way interaction of type and method (Table III). Tukey post hoc analysis indicated that fabrics dyed with Procion MX dyes began to degrade at lower temperatures than did fabrics dyed with Procion H dyes. Onset of degradation also began at a lower temperature for fabrics dyed at a 4% concentration than for those dyed at the 1% concentration. No consistent differences between the physical and chemical combinations of dye and fabric were shown by this analysis.

Because of the significant type x method interaction, the means were graphed to provide an understanding of the differences (Figure 3). Lower onset of degradation temperatures for dye types were exhibited when the dye was applied by a chemical, rather than a physical, means.

Table II. Summary of DSC Test Results.[a]

Fabric[b]	Temperature at Onset of Degradation		Degradation Peak Temperature		Heat of Decomposition	
	(°K)	C.V. (%)[c]	(°K)	C.V. (%)[c]	(cal/gm)	C.V. (%)[c]
MX 1% Physical	583	0.78	637	1.1	87.4	20.7
MX 4% Physical	557	0.82	586	1.2	35.2	51.3
H 1% Physical	573	0.79	637	1.1	52.5	34.4
H 4% Physical	560	0.81	613	1.9	47.4	38.1
MX 1% Chemical	560	0.81	628	1.2	95.3	19.0
MX 4% Chemical	549	0.83	617	1.2	83.2	21.7
H 1% Chemical	572	0.80	630	1.2	80.1	22.6
H 4% Chemical	561	0.81	618	1.2	88.8	20.3
Undyed	594	0.77	639	1.4	83.2	21.7

[a]Mean values for all variables; N = 2.

[b]Identified according to dye type, dye concentration, and method in which dye was applied to the fabric.

[c]Coefficient of variation for each treatment combination.

Table III. Analysis of Variance for Temperature at Onset of Degradation.

Source	df	Sum of Squares	Mean Square	F
Model	8	3183.78	397.97	19.51*
Contrast				
Type	1	81.00		3.91*
Concentration	1	930.25		44.89*
Method	1	256.00		12.35*
Dyed vs. Undyed	1	1534.03		74.03*
MX vs. Undyed	1	1600.23		77.22*
H vs. Undyed	1	1177.23		56.81*
Type x Concentration	1	36.00		1.74
Type x Method	1	240.25		11.59*
Concentration x Method	1	64.00		3.09
Type x Concentration x Method	1	42.25		2.04
Error	9	186.50	20.72	
Total	17	3370.28		

*Significant at the 0.10 level.

Table IV. Analysis of Variance for Degradation Peak Temperature.

Source	df	Sum of Squares	Mean Square	F
Model	8	4533.0	566.63	10.69*
Contrast				
Type	1	210.25		3.97*
Concentration	1	2450.25		46.23*
Method	1	100.00		1.89
Dyed vs. Undyed	1	600.25		11.33*
MX vs. Undyed	1	744.40		14.61*
H vs. Undyed	1	348.10		6.57*
Type x Concentration	1	156.25		2.95
Type x Method	1	144.00		2.72
Concentration x Method	1	676.00		12.75*
Type x Concentration x Method	1	196.00		3.70*
Error	9	477.00	53.00	
Total	17	5010.00		

*Significant at the 0.10 level.

Table V. Analysis of Variance for Heat of Decomposition.

Source	df	Sum of Squares	Mean Square	F
Model	8	7420.71	927.59	2.84*
Contrast				
Type	1	260.82		0.80
Concentration	1	918.09		2.82
Method	1	3893.76		11.94*
Dyed vs. Undyed	1	256.00		0.79
MX vs. Undyed	1	101.40		0.31
H vs. Undyed	1	411.50		1.26
Type x Concentration	1	1152.60		3.53*
Type x Method	1	42.90		0.13
Concentration x Method	1	723.61		2.22
Type x Concentration x Method	1	172.92		0.53
Error	9	2934.89	326.10	
Total	17	10355.60		

*Significant at the 0.10 level.

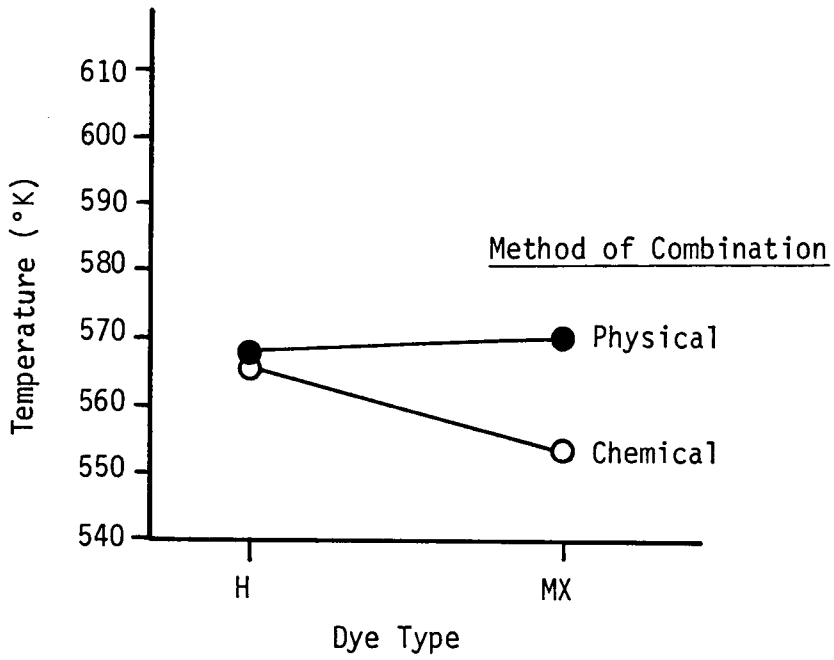


Figure 3. Mean Values of Temperature at Onset of Degradation for Dye Type and Method of Combination.

The coefficients of variation for each fabric tested are shown in Table II in order to give an indication of the precision of the experimental procedure used. Values for onset of degradation are very low, meaning a high degree of reproducibility was obtained during this test.

Degradation peak temperature. The main effects of dye type and dye concentration, the interaction of concentration x method, and the interaction of type x concentration x method were significant for degradation peak temperature (Table IV). As with onset of degradation, the Tukey procedure indicated that the temperature at the peak of degradation was lower for fabrics dyed at the 4% concentration than at the 1% concentration. No consistent differences were determined for dye type.

A graph of means for the concentration x method interaction (Figure 4) illustrates the effect of increasing dye concentration in lowering the degradation peak temperatures. At the 1% concentration, the lower values were produced by the chemically combined dye and fabric, while at the 4% concentration, the physical combination had lower temperatures. This latter effect is further illustrated in Figure 5, where the type x concentration x method interaction is shown. For both dye types, the chemical combination of dye and fabric produced the most consistent results in lowering degradation temperatures as dye concentration increased. The coefficient of variation values reported in Table II again indicated a very precise experimental procedure.

Heat of decomposition. The values for heat of decomposition for the dyed fabrics were significantly different due to the effect of method in which the dye was combined with the fabric and to the interaction of

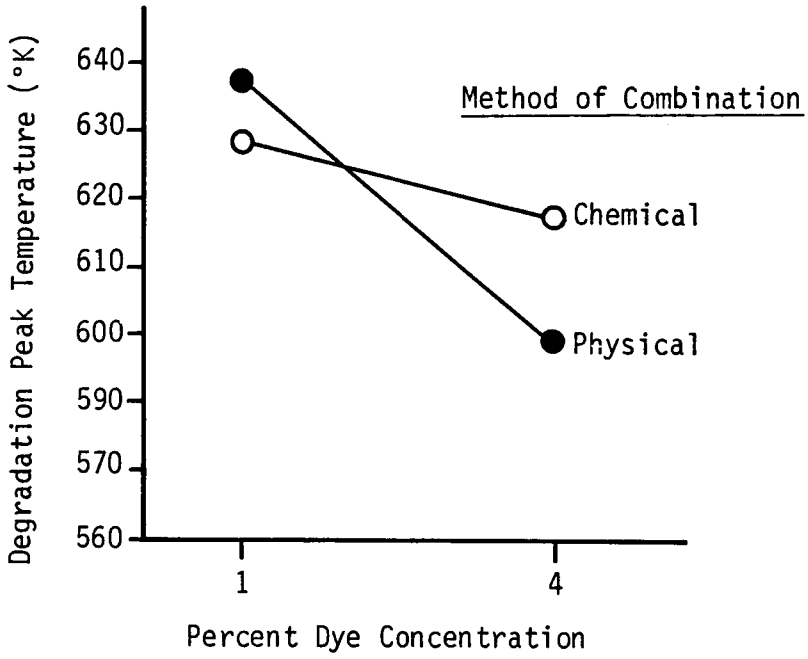


Figure 4. Mean Values of Degradation Peak Temperature for Dye Concentration and Method of Combination.

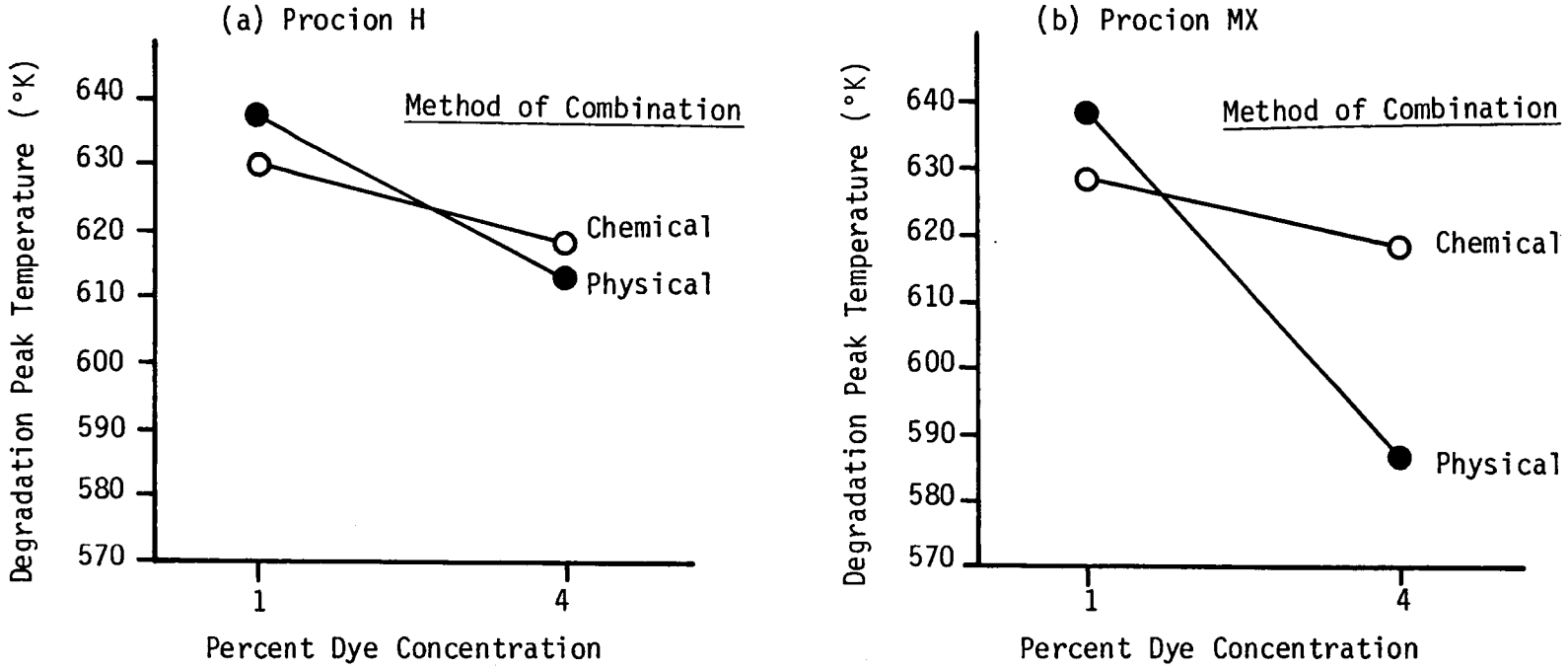


Figure 5. Mean Values of Degradation Peak Temperature for Dye Type, Dye Concentration, and Method of Combination.

dye type and dye concentration (Table V). No further information concerning the effect of method of combination was given by a Tukey post hoc analysis.

A graph of means for the type x concentration interaction is shown in Figure 6. Heat of decomposition decreased from Procion H to Procion MX dyed fabrics at the 4% concentration. At the 1% concentration, however, an increase was shown from the Procion H to the Procion MX dye types. Coefficient of variation values (Table II), unlike those for the degradation temperatures, indicated an imprecise experimental procedure. Since data for all dependent thermal variables was derived from the same DSC curves, this result can best be attributed to human error in drawing the approximations to the baselines on these curves.

Fabric Tensile Testing

The mean results for the fabric tensile tests are listed in Table VI. The Shapiro-Wilk W statistic calculated as a test for normality was nonsignificant for each dependent variable, indicating each population was normally distributed. The Bartlett-Box F statistic used to determine homogeneity of variance was also nonsignificant in each case, indicating the population variances were equal. A one-way analysis of variance with orthogonal contrasts was used to test for difference in main effects (dye type, dye concentration, and fabric direction) and interaction effects on fabric breaking tenacity and breaking extension. Results of the two analyses are shown in Tables VII and VIII. Each of these dependent variables will be discussed separately.

Fabric breaking tenacity. Significantly different values in breaking tenacity for the dyed fabrics were produced by fabric direction

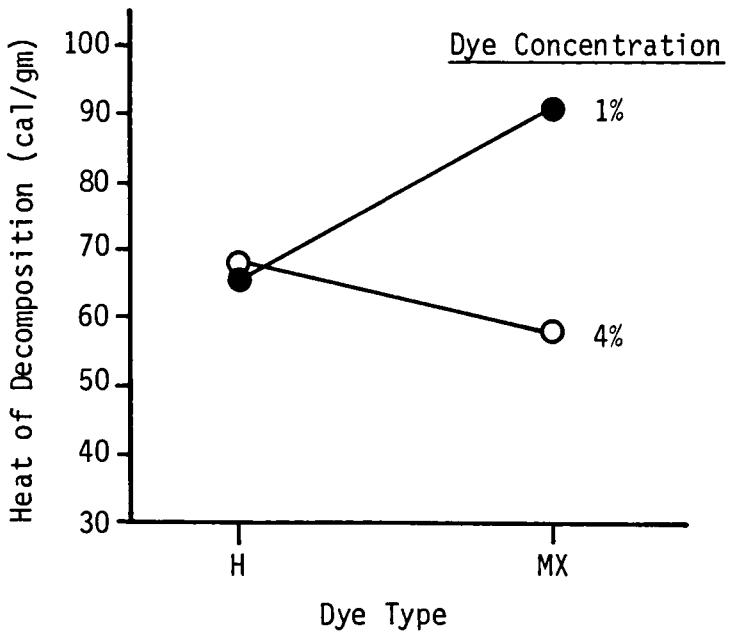


Figure 6. Mean Values of Heat of Decomposition for Dye Type and Dye Concentration.

Table VI. Summary of Fabric Tensile Test Results.[a]

Fabric[b]	Breaking Tenacity (kg/tex)	Breaking Tenacity C.V. (%)[c]	Breaking Extension (%)	Breaking Extension C.V. (%)[c]
MX 1% Warp	9812.1	8.0	14.7	14.8
MX 1% Filling	5854.5	13.4	14.5	15.0
MX 4% Warp	10088.2	7.8	17.2	12.6
MX 4% Filling	4970.6	15.8	10.4	20.9
H 1% Warp	9442.4	8.3	17.0	12.7
H 1% Filling	5442.4	14.5	8.5	25.5
H 4% Warp	9600.0	8.2	15.3	14.1
H 4% Filling	4976.5	15.8	7.1	30.6
Undyed Warp	9364.7	8.4	12.5	17.3
Undyed Filling	4305.9	18.3	6.2	34.8

[a]Mean values for all variables; N = 5.

[b]Identified according to dye type, dye concentration, and fabric direction.

[c]Coefficient of variation for each treatment combination.

Table VII. Analysis of Variance for Fabric Breaking Tenacity

Source	df	Sum of Squares	Mean Square	F
Model	9	267421270.65	29713474.52	48.03*
Contrast				
Type	1	998876.02		1.61
Concentration	1	524639.03		0.85
Direction	1	298954634.03		418.57*
Type x Concentration	1	56055.17		0.09
Type x Direction	0	NON EST[a]		
Concentration x Direction	1	1988268.10		3.21*
Type x Concentration x Direction	1	179935.40		0.29
Dyed vs. Undyed	1	3787137.29		6.12*
MX vs. Undyed	1	4772116.82		7.71*
H vs. Undyed	1	1872737.33		3.03*
Error	40	24746666.19	618666.65	
Total	49	292167936.84		

*Significant at the 0.10 level.

[a]Nonestimated contrast due to error in writing contrast coefficients.

Table VIII. Analysis of Variance for Breaking Extension.

Source	df	Sum of Squares	Mean Square	F
Model	9	740.94	82.33	17.50*
Contrast				
Type	1	47.74		10.15*
Concentration	1	14.04		2.98*
Direction	1	452.40		96.14*
Type x Concentration	1	1.48		0.31
Type x Direction	0	NON EST[a]		
Concentration x Direction	1	25.76		5.47*
Type x Concentration x Direction	1	30.10		6.40*
Dyed vs. Undyed	1	109.37		23.24*
MX vs. Undyed	1	152.96		32.51*
H vs. Undyed	1	45.24		9.61*
Error	40	188.23	4.71	
Total	49	929.16		

*Significant at the 0.10 level.

[a]Nonestimated contrast due to error in writing contrast coefficients.

and by the interaction of dye concentration and fabric direction (Table VII). Tukey post hoc analysis indicated fabric specimens cut in the warp direction produced much greater values for breaking tenacity than filling specimens in all cases.

The warp specimens were also responsible for the significant interaction of concentration x direction shown by the graph of means in Figure 7. Only slight changes in tenacity across the concentrations of dye were determined; the values for warp specimens were higher than those for filling specimens. The coefficients of variation shown in Table VI indicated the experimental procedure for determining breaking tenacity was fairly precise.

Breaking extension. Breaking extension of dyed fabrics was significantly affected by all main effects, the interaction of concentration x direction, and the interaction of type x concentration x direction (Table VIII). No consistent differences for dye type or dye concentration were shown by Tukey post hoc analysis. The same procedure indicated that, generally, warp specimens produced higher values for breaking extension than did filling specimens.

The graph of means in Figure 8 illustrates the concentration x direction interaction. The higher values for the warp specimens are shown as having contributed to the significant interaction effect. In addition, values for breaking extension decreased with greater dye concentration for the filling specimens.

The type x concentration x direction interaction is shown by a graph of means in Figure 9. Breaking extension values at the 1 and 4% concentration were greater for warp specimens of both dye types, which

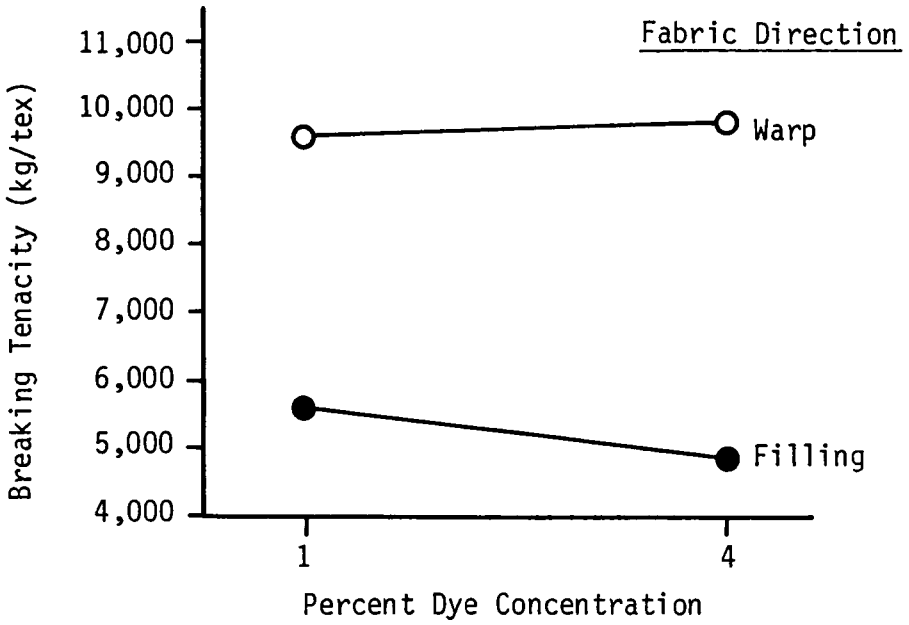


Figure 7. Mean Values of Fabric Breaking Tenacity for Dye Concentration and Fabric Direction.

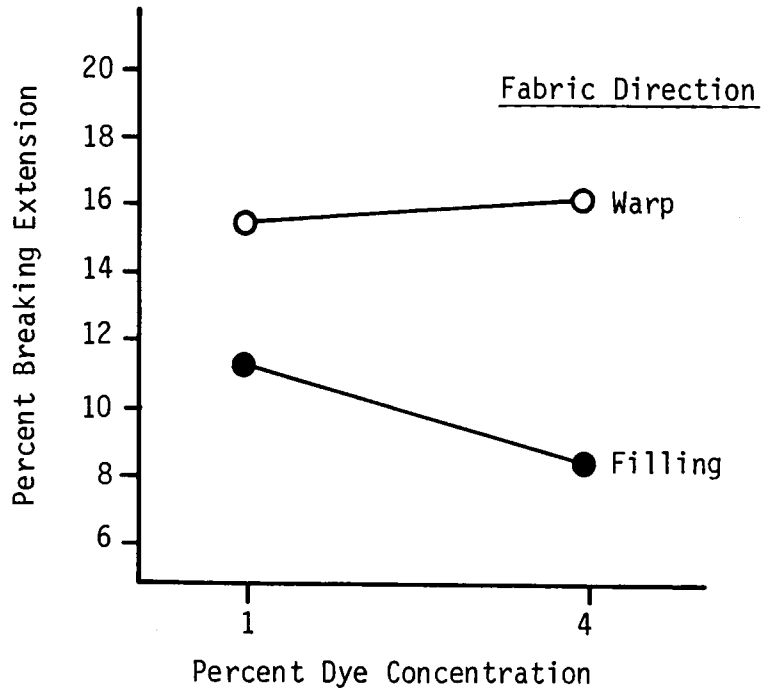


Figure 8. Mean Values of Percent Breaking Extension for Dye Concentration and Fabric Direction.

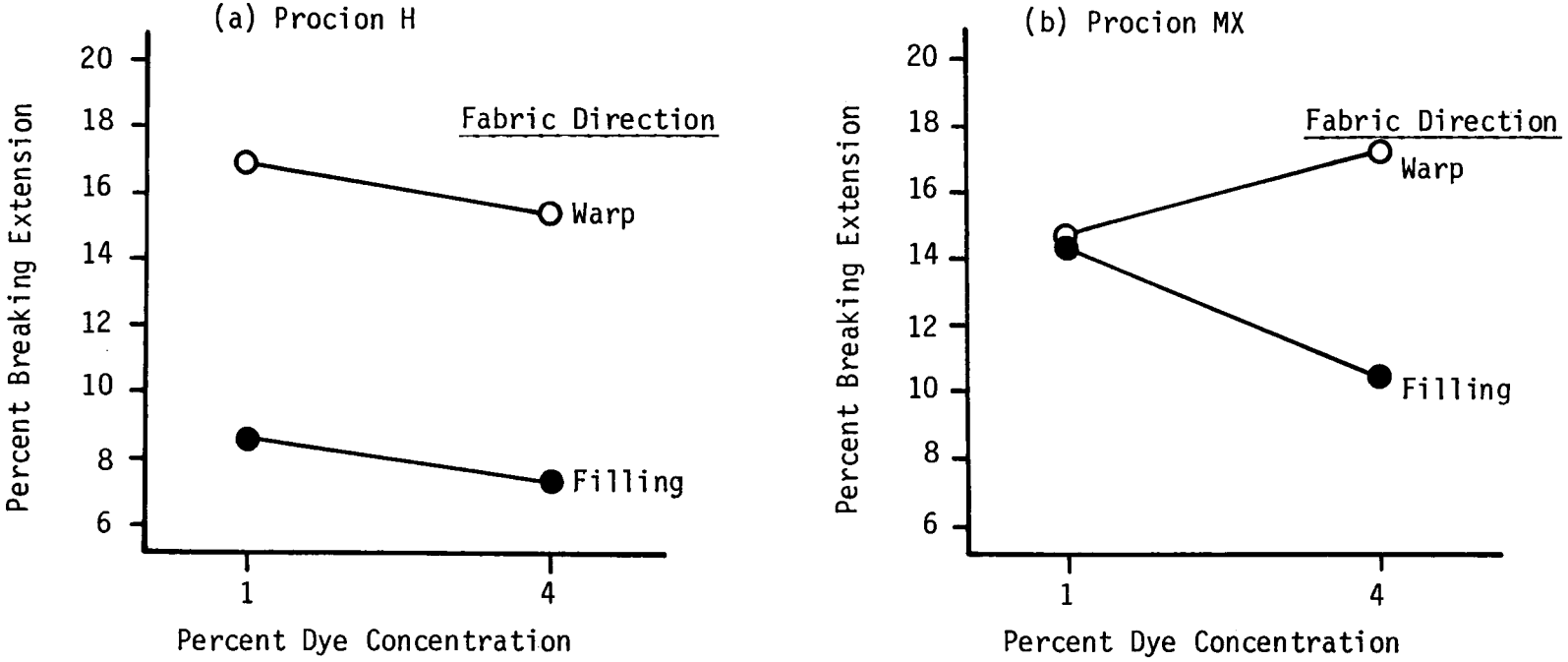


Figure 9. Mean Values of Percent Breaking Extension for Dye Type, Dye Concentration, and Fabric Direction.

again indicated the importance of fabric direction on this dependent variable. The coefficient of variation values shown in Table VI indicated the experimental procedure for breaking extension was slightly more imprecise than that for breaking tenacity.

Wrinkle Recovery

The mean results for the wrinkle recovery tests are given in Table IX. The assumptions of normal distribution of data and homogeneity of variances were made since the Shapiro-Wilk W statistic and the Bartlett-Box F statistic were both determined to be nonsignificant. A one-way analysis of variance with orthogonal contrasts was used to test for differences in main effects (dye type, dye concentration, and fabric direction) and interaction effects on wrinkle recovery. Results of the analysis are shown in Table X.

Dye concentration, fabric direction, and the interaction of type x concentration x direction caused significantly different responses in wrinkle recovery for the dyed fabrics (Table X). Tukey post hoc analysis indicated the 4% dye concentration produced higher values for wrinkle recovery than the 1% concentration. No consistent differences in results due to fabric direction were shown.

The graphs in Figure 10 illustrate the type x concentration x direction interaction. The filling specimens produced higher values for wrinkle recovery for both dye types and both dye concentrations. However, the greatest increase in values for this dependent variable were shown by an increase in dye concentration. This result applied for both dye types and in both fabric directions. The coefficient of variation

Table IX. Summary of Wrinkle Recovery Results.[a]

Fabric[b]	Wrinkle Recovery Angle (°)	Coefficient of Variation[c] (%)
MX 1% Warp	102	6.3
MX 1% Filling	103	6.3
MX 4% Warp	107	6.0
MX 4% Filling	112	5.7
H 1% Warp	92	7.0
H 1% Filling	104	6.2
H 4% Warp	109	5.9
H 4% Filling	112	5.7
Undyed Warp	92	7.0
Undyed Filling	109	5.9

[a]Mean values for all variables; N = 6.

[b]Identified according to dye type, dye concentration, and fabric direction.

[c]Coefficient of variation for each treatment combination.

Table X. Analysis of Variance for Wrinkle Recovery.

Source	df	Sum of Squares	Mean Square	F
Model	9	2951.48	327.94	7.92*
Contrast				
Type	1	42.19		1.02
Concentration	1	1150.52		27.77*
Direction	1	904.82		21.84*
Type x Concentration	1	82.69		2.00
Type x Direction	0	NON EST[a]		
Concentration x Direction	1	11.02		0.27
Type x Concentration x Direction	1	117.19		2.83*
Dyed vs. Undyed	1	222.34		5.37*
MX vs. Undyed	1	264.50		6.38*
H vs. Undyed	1	120.13		2.90*
Error	50	2071.50	41.43	
Total	59	5022.98		

*Significant at the 0.10 level.

[a]Nonestimated contrast due to error in writing contrast coefficients.

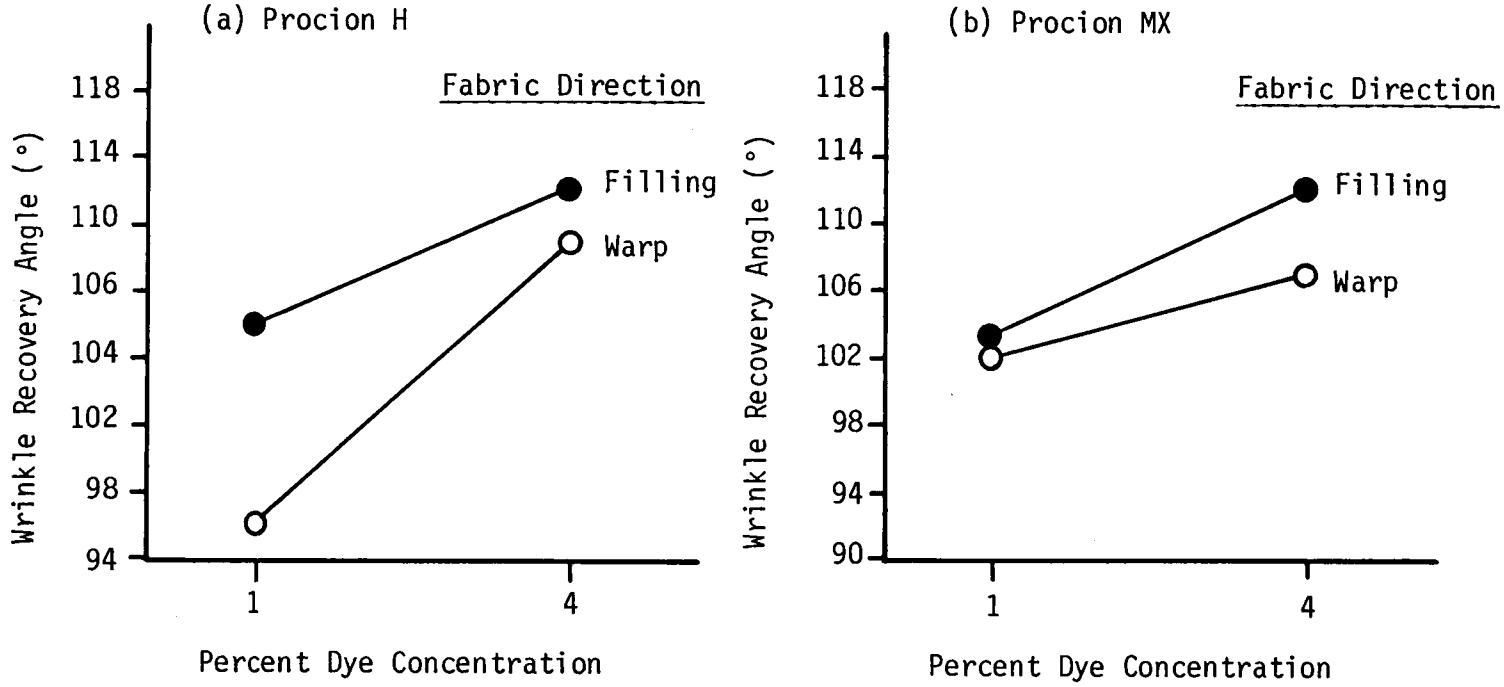


Figure 10. Mean Values of Wrinkle Recovery Angle for Dye Type, Dye Concentration, and Fabric Direction.

values listed in Table IX indicate the experimental procedure used to determine wrinkle recovery was very precise.

Flexural Rigidity

The mean values for flexural rigidity of the dyed fabrics are listed in Table XI. A nonsignificant Shapiro-Wilk W statistic and Bartlett-Box F statistic indicated that the population was normally distributed with equal variances. A one-way analysis of variance with orthogonal contrasts was used to test for differences in main effects (dye type, dye concentration, and fabric direction) and interaction effects on flexural rigidity. Results of the analysis are shown in Table XII.

Dye concentration, fabric direction, and the interaction of type x concentration x direction were found to be significant for flexural rigidity (Table XII). Tukey post hoc analysis revealed warp specimens produced higher values for flexural rigidity than filling specimens. The same procedure indicated there were no consistent differences in results for this dependent variable due to dye concentration.

The graphs of means in Figure 11 indicate flexural rigidity increased to some extent as dye concentration increased; however, the significant interaction of type x concentration x direction was mainly due to higher values for warp specimens than for filling specimens. The coefficient of variation values listed in Table XI indicate a reproducible procedure was used to determine flexural rigidity.

Fiber Tensile Testing

The mean values for the fiber tensile tests are given in Table XIII. A test for normality using a modified Kolmogorov-Smirnov D

Table XI. Summary of Flexural Rigidity Results.[a]

Fabric[b]	Flexural Rigidity (mg-cm)	Coefficient of Variation[c] (%)
MX 1% Warp	162.75	6.5
MX 1% Filling	103.00	10.3
MX 4% Warp	186.72	5.7
MX 4% Filling	107.37	9.9
H 1% Warp	148.93	7.1
H 1% Filling	102.32	10.4
H 4% Warp	166.42	6.4
H 4% Filling	127.21	8.3
Undyed Warp	159.91	6.6
Undyed Filling	121.47	8.7

[a]Mean values for all variables; N = 4.

[b]Identified according to dye type, dye concentration, and fabric direction.

[c]Coefficient of variation for each treatment combination.

Table XII. Analysis of Variance for Flexural Rigidity.

Source	df	Sum of Squares	Mean Square	F
Model	9	32858.60	3650.96	32.36*
Contrast				
Type	1	111.94		0.99
Concentration	1	2500.48		22.16*
Direction	1	27739.18		245.86*
Type x Concentration	1	98.60		0.87
Type x Direction	0	NON EST[a]		
Concentration x Direction	1	74.45		0.66
Type x Concentration x Direction	1	364.30		3.23*
Dyed vs. Undyed	1	43.25		0.38
MX vs. Undyed	1	2.84		0.03
H vs. Undyed	1	106.56		0.94
Error	30	3384.71	112.82	
Total	39	36243.31		

*Significant at the 0.10 level.

[a]Nonestimated contrast due to error in writing contrast coefficients.

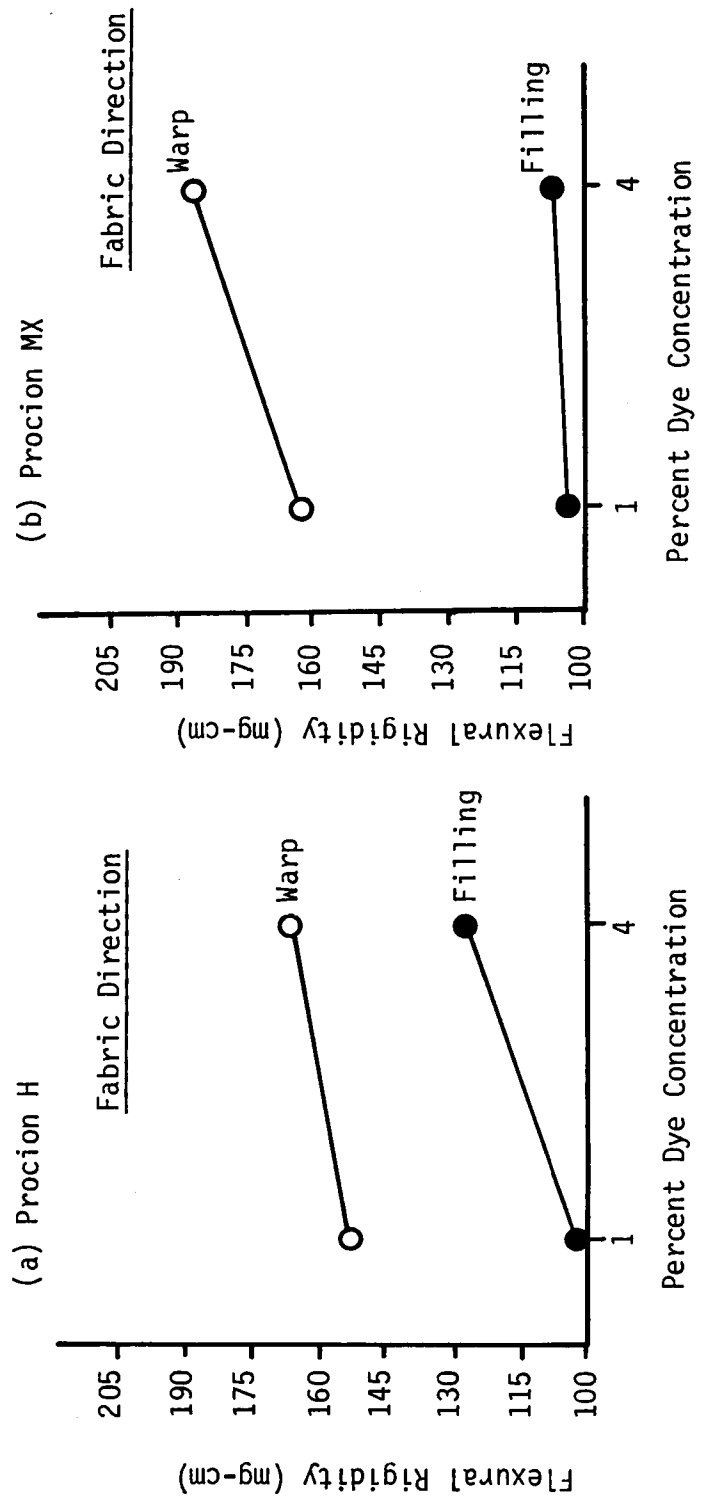


Figure 11. Mean Values of Flexural Rigidity for Dye Type, Dye Concentration, and Fabric Direction.

Table XIII. Summary of Fiber Tensile Test Results.[a]

Fabric[b]	Breaking Tenacity		Breaking Elongation		Initial Modulus	
	(gm/denier)	C.V. (%)[c]	(%)	C.V. (%)[c]	(gm/denier)	C.V. (%)[c]
MX 1%	0.749	57.2	72	33.4	11.9	21.9
MX 4%	0.820	52.3	73	32.8	12.3	21.1
H 1%	0.884	48.5	80	30.1	12.2	21.3
H 4%	0.844	50.8	79	30.5	12.9	20.1
Undyed	0.950	45.1	87	27.6	12.9	20.1

[a]Mean values for all variables; N = 100.

[b]Identified according to dye type and dye concentration.

[c]Coefficient of variation for each treatment combination.

statistic was found to be significant for each dependent variable. This result, which indicated a skewed population in each case, was accepted on the basis that the F statistic is robust with respect to departures from normality. A test for homogeneity of variance using a Bartlett-Box F statistic was found to be significant for fiber breaking tenacity and breaking elongation, indicating unequal population variances. The Bartlett-Box F statistic was nonsignificant for fiber initial modulus. A nonparametric one-way analysis of variance (Kruskal-Wallis Test) was used to test for differences in overall treatment effects on fiber breaking tenacity and breaking elongation. Planned comparisons by means of a Mann-Whitney U test were used to test for differences in main effects (dye type and dye concentration) and the interaction effect on each of these dependent variables. A one-way analysis of variance with orthogonal contrasts was used to test for differences in main effects (dye type and dye concentration) and the interaction effect on fiber initial modulus. Results of the three analyses are shown in Tables XIV-XVI. Each of these dependent variables will be discussed separately.

Fiber breaking tenacity. Breaking tenacity for fibers removed from dyed fabrics was significantly affected by the overall treatment effect (Table XIV). The Mann-Whitney U test, however, indicated no significant differences could be attributed to either main effect of dye type or dye concentration, nor was the interaction effect significant according to this procedure. The coefficient of variation values reported in Table XIII were extremely high, which indicated a high degree of inaccuracy existed in the procedure used to evaluate fiber breaking tenacity.

Table XIV. Kruskal-Wallis and Mann-Whitney U Tests for Fiber Breaking Tenacity

Chi-Square Statistic	Prob. Chi-Square	Comparison	U-Statistic	Prob. U-Value
8.11*	0.0877	Type	28552.5	0.3584
		Concentration	29222.5	0.6218
		Interaction	29712.0	0.8550

*Significant at the 0.10 level.

**Significant at the 0.03 level.

Table XV. Kruskal-Wallis and Mann-Whitney U Tests for Breaking Elongation.

Chi-Square Statistic	Prob. Chi-Square	Comparison	U-Statistic	Prob. U-Value
18.35*	0.0011	Type	27824.0	0.1680
		Concentration	28369.5	0.3016
		Interaction	28854.5	0.4680

*Significant at the 0.10 level.

**Significant at the 0.03 level.

Table XVI. Analysis of Variance for Fiber Initial Modulus

Source	df	Sum of Squares	Mean Square	F
Model	4	91.04	22.76	3.38*
Contrast				
Type	1	23.52		3.49*
Concentration	1	34.69		5.15*
Type x Concentration	1	2.22		0.33
Dyed vs. Undyed	1	30.60		4.54*
MX vs. Undyed	1	49.42		7.33*
H vs. Undyed	1	9.43		1.40
Error	495	3337.31	6.74	
Total	499	3428.35		

*Significant at the 0.10 level.

Breaking elongation. The overall treatment effects produced significant differences in values for breaking elongation of fibers removed from dyed fabrics (Table XV). As in the case of breaking tenacity, however, no significant differences were shown for either main effect or the interaction effect by analysis of the planned comparisons. Coefficient of variation values reported in Table XIII have shown the preciseness of the procedure for obtaining breaking elongation to be somewhat improved over that for breaking tenacity.

Initial modulus. Initial modulus of fibers removed from dyed fabrics was significantly affected by dye type and dye concentration but not by the interaction of these effects (Table XVI). No consistent differences for either main effect were indicated by Tukey post hoc analysis. The coefficients of variation listed in Table XIII indicated some degree of inaccuracy existed in the experimental procedure, although an improvement over those values for both breaking tenacity and breaking elongation was indicated.

Fiber Swelling

The mean values for the fiber swelling test are listed in Table XVII. A test for normality using a modified Kolmogorov-Smirnov D statistic was found to be significant for each treatment combination. The normal probability plots from this analysis indicated only a slightly skewed population, which is acceptable since the F statistic is relatively unaffected by departures from normality. A test for homogeneity of variance using a Bartlett-Box F statistic was found to be nonsignificant, which indicated population variances were equal. A one-way

Table XVII. Summary of Fiber Swelling Results.[a]

Fabric[b]	Fabric Swelling (%)	Coefficient of Variation[c] (%)
MX 1%	10.2	65.8
MX 4%	10.8	
H 1%	11.9	
H 4%	11.9	
Undyed	12.3	

[a]Mean values for all variables; N = 100.

[b]Identified according to dye type and dye concentration.

[c]Coefficient of variation for overall treatment effect.

analysis of variance with orthogonal contrasts was used to test for differences in main effects (dye type and dye concentration) and the interaction effect on fiber swelling. A Kruskal-Wallis test was used to confirm results of the analysis of variance. Results of the analyses are shown in Tables XVIII and XIX.

There were no significant differences in the swelling of fibers removed from the five fabrics tested (Tables XVIII and XIX). The coefficient of variation reported for the overall effect of treatments on fiber swelling (Table XVII) was extremely high, which indicated a high degree of irreproducibility existed in the experimental procedure.

Moisture Content and Moisture Regain

The mean values for moisture content and moisture regain are given in Table XX. The Shapiro-Wilk W statistic calculated as a test for normality was nonsignificant for both dependent variables, which indicated both populations were normally distributed. The Bartlett-Box F statistic used to determine homogeneity of variance was significant in both cases, violating the assumption that population variances were equal. A nonparametric one-way analysis of variance (Kruskal-Wallis Test) was used to test for differences in overall treatment effects on moisture content and moisture regain. Planned comparisons by means of a Mann-Whitney U test were used to test for differences in main effects (dye type and dye concentration) and the interaction effect on moisture content. Results of the two analyses are given in Tables XXI and XXII. Each dependent variable will be discussed separately.

Table XVIII. Analysis of Variance for Fiber Swelling.

Source	df	Sum of Squares	Mean Square	F
Model	4	317.77	79.44	1.40
Contrast				
Type	1	195.16		3.44
Concentration	1	9.61		0.17
Type x Concentration	1	10.30		0.18
Dyed vs. Undyed	1	102.70		1.81
MX vs. Undyed	1	223.63		3.95
H vs. Undyed	1	12.59		0.22
Error	495	28057.92	56.68	
Total	499	28375.69		

*Significant at the 0.10 level.

Table XIX. Kruskal-Wallis Test for Fiber Swelling.

Chi-Square Statistic	Probable Chi-Square
7.57	0.1087

*Significant at the 0.10 level.

Table XX. Summary of Moisture Content and Moisture Regain Results.[a]

Fabric[b]	Moisture Content (%)	Moisture Content C.V. (%)[c]	Moisture Regain (%)	Moisture Regain C.V. (%)[d]
MX 1%	5.17	14.6	5.88	9.9
MX 4%	5.66	13.3	5.96	
H 1%	5.86	12.9	5.78	
H 4%	5.77	13.1	6.05	
Undyed	5.78	17.3	6.59	

[a]Mean values for all variables; N = 5.

[b]Identified according to dye type and dye concentration.

[c]Coefficient of variation for each treatment combination.

[d]Coefficient of variation for overall treatment effect.

Table XXI. Kruskal-Wallis and Mann-Whitney U Tests for Moisture Content.

Chi-Square Statistic	Prob. Chi-Square	Comparison	U-Statistic	Prob. U-Value
8.25*	0.0829	Type	42.5	0.0709
		Concentration	48.0	0.1438
		Interaction	42.5	0.0709

*Significant at the 0.10 level.

**Significant at the 0.03 level.

Table XXII. Kruskal-Wallis Test for Moisture Regain.

Chi-Square Statistic	Probable Chi-Square
6.18	0.1862

*Significant at the 0.10 level.

Moisture content. Moisture content of the fabrics tested was found to be significantly affected by the overall treatment effect (Table XXI). No significant differences were shown for dye type, dye concentration, or the interaction type x concentration. The coefficients of variation listed in Table XX indicate the experimental procedure used to determine moisture content was fairly precise.

Moisture regain. There was no difference in the moisture regain of the fabrics tested (Table XXII). A coefficient of variation reported for the overall treatment effect (Table XX) determined the procedure for obtaining moisture regain of the fabrics test was fairly precise.

II. DYED VS. UNDYED FABRICS

Thermal Degradation Variables

The mean results for DSC testing of both dyed and undyed fabrics are given in Table II, page 34. The analysis of variance procedure used for the dyed fabrics included three orthogonal contrasts to compare the dyed and undyed fabrics. Results of differences between the dyed and undyed fabrics, the MX dyed and undyed fabrics, and the H dyed and undyed fabrics are given for degradation temperatures and heat of decomposition in Tables III-V, pages 35-36. The three contrasts were significant for temperature at onset of degradation and for degradation peak temperature, with the undyed fabric exhibiting the highest values of any fabrics tested. No significant differences in heat of decomposition were shown between dyed and undyed fabrics.

Physical Variables

The mean results for breaking tenacity and percent breaking extension of both dyed and undyed fabrics are given in Table VI, page 43. The results of orthogonal contrasts to test the differences in these dependent variables for dyed and undyed fabrics are given in Tables VII and VIII, pages 44-45. Significantly different values in breaking tenacity and in percent breaking extension were found to exist for each of the three comparisons: dyed vs. undyed, MX dyed vs. undyed, and H dyed vs. undyed. The undyed filling specimens had the lowest values of all filling specimens for breaking tenacity and breaking extension. The same results also applied to the undyed warp specimens, although the latter produced significantly higher values for both dependent variables than the undyed filling specimens due to the influence of fabric direction.

The mean results for the wrinkle recovery test are given in Table IX, page 51. The three comparisons (Table X, page 52) of dyed vs. undyed and each of the two dye types vs. undyed caused significantly different responses in values for fabric wrinkle recovery. The undyed warp specimens exhibited the lowest values for wrinkle recovery for the warp specimens and for all fabrics tested. The undyed filling specimens did not produce significantly different values from other filling specimens and fell in the middle of the range of mean values for these fabrics.

The mean values for both dyed and undyed fabric flexural rigidity are listed in Table XI, page 55. The three contrasts evaluating the effect of the undyed fabrics on this dependent variable (Table XII, page 56) indicated there were no significant differences in flexural rigidity due to the presence or absence of dye in the fabrics.

The mean values for the fiber tensile tests of both the dyed and undyed fabrics are listed in Table XIII, page 58. The Mann-Whitney U tests (Tables XIV and XV, page 60) investigating the effects of various planned comparisons on breaking tenacity and percent breaking elongation did not include a contrast comparing fibers removed from dyed and undyed fabrics. The orthogonal contrasts for initial modulus, shown in Table XVI, page 61, revealed significant differences existed between an average of all dyed fabrics compared to the undyed fabrics and between fabrics dyed with the Procion MX dyes compared to undyed fabrics. No significant differences were produced by the Procion H dyed fabrics and the undyed fabrics. Fibers removed from undyed fabrics were responsible for the highest values of initial modulus of all fabrics tested.

Fibers removed from the undyed fabrics exhibited the highest amount of swelling of all fibers tested (Table XVII, page 63); however, the overall effect of the dye treatments on percent fiber swelling was determined to be statistically nonsignificant (Tables XVIII and XIX, page 65).

The mean results for moisture content and moisture regain of both the dyed and undyed fabrics are given in Table XX, page 66. Although the undyed fabrics produced the highest values for moisture regain, the overall effect of the treatments applied on this dependent variable was reported as nonsignificant. As in the case of the fiber tensile tests, the Mann-Whitney procedure used to evaluate the effect of planned comparisons on moisture content did not include a contrast comparing the undyed vs. dyed fabrics.

CHAPTER V

SUMMARY AND CONCLUSIONS

The purpose of this study was to investigate the thermal and physical properties of reactive dyed cotton fabric and to compare these results to the thermal and physical properties of undyed cotton fabric. A 2 X 2 X 2 factorial design was used to evaluate the effects of dye type, dye concentration, and method of dye combination on temperature at onset of thermal degradation, degradation peak temperature, and heat of decomposition. A 2 X 2 X 2 factorial design was used to evaluate the effects of dye type, dye concentration, and fabric direction on breaking tenacity, breaking extension, wrinkle recovery, and flexural rigidity. A 2 X 2 factorial design was used to evaluate the effect of dye type and dye concentration on moisture content and moisture regain; fiber swelling; and fiber breaking tenacity, breaking elongation, and initial modulus. The reactive dyed cotton fabrics included two dye types (Procion H and MX), two dye concentrations (1 and 4%), all of one color (Brilliant Blue). Testing was carried out through use of a differential scanning calorimeter, Instron tester, Monsanto wrinkle recovery method, Shirley stiffness tester, and methods developed for this study to measure moisture content, moisture regain, and fiber swelling. The undyed fabric was also tested for comparison with the dyed fabrics.

I. THERMAL PROPERTIES

Dye type and dye concentration significantly affected the temperatures at which degradation occurred and at which the process proceeded

at its maximum rate. In addition, the method in which dye was combined with the fabric (via physical or chemical means) had a significant effect on the onset of degradation. Heat of decomposition, however, was affected only by method of dye combination, although the interaction of dye type and concentration did produce significant results.

Onset of degradation began at lower temperatures for the Procion MX dyes and for fabrics dyed at a 4% concentration. The effect of increasing dye concentration also resulted in lower degradation peak temperatures, especially with the Procion MX dyes. No consistent differences in method of dye combination could be determined for degradation temperatures. Although the overall effect of method of combination was determined significant for heat of decomposition and mean results appear to indicate lower values were produced by the physical combinations, an order relationship among treatment means could not be established for this variable.

The undyed fabrics were found to degrade at higher temperatures than the dyed fabrics. There were no significant differences in heat of decomposition between the dyed and undyed fabrics. Although the above results are consistent with those reported in a previous study (43), the earlier observation that the dyed fabrics produced two degradation peaks as compared to a single peak by the undyed fabrics was not consistently observed in the present investigation.

While the physical combinations of dye and fabric produced a rather broad peak in which two shoulders of approximately equal height were visible, the chemical combinations of dye and fabric, as well as the undyed fabric, produced a single, strong peak with no evidence of a

smaller shoulder. All curves produced a single endotherm with the chemical combinations and the undyed fabrics also producing a small exotherm at the completion of degradation. Representative DSC curves for the undyed fabric and for both physical and chemical combinations of one of the dyed fabrics are shown in Figure 12.

Conclusions

Generally, the result of lower degradation temperatures due to the effect of dye in the fabric, especially the amount of dye, has been shown. This is a confirmation of earlier findings for Procion dyes (16,33,43). The comparison of a physical vs. chemical combination of these dyes with the fabric seems to further indicate that it is the amount of dye in the fabric and not the fact that it is a chemically bound dye which interferes with the thermal degradation of cellulose.

II. PHYSICAL PROPERTIES

Breaking tenacity and breaking extension of the fabrics tested were significantly affected by fabric direction. In addition, dye type and dye concentration were found to have a significant effect on breaking extension.

The effect of fabric direction on tensile properties is well established; therefore, the higher values of both dependent variables for specimens cut in the warp direction was to be expected. A very slight but statistically significant increase in breaking tenacity with dye concentration was observed. Warp specimens displayed a small increase in breaking extension as dye concentration increased, while filling specimens exhibited a decrease at the 4% concentration compared

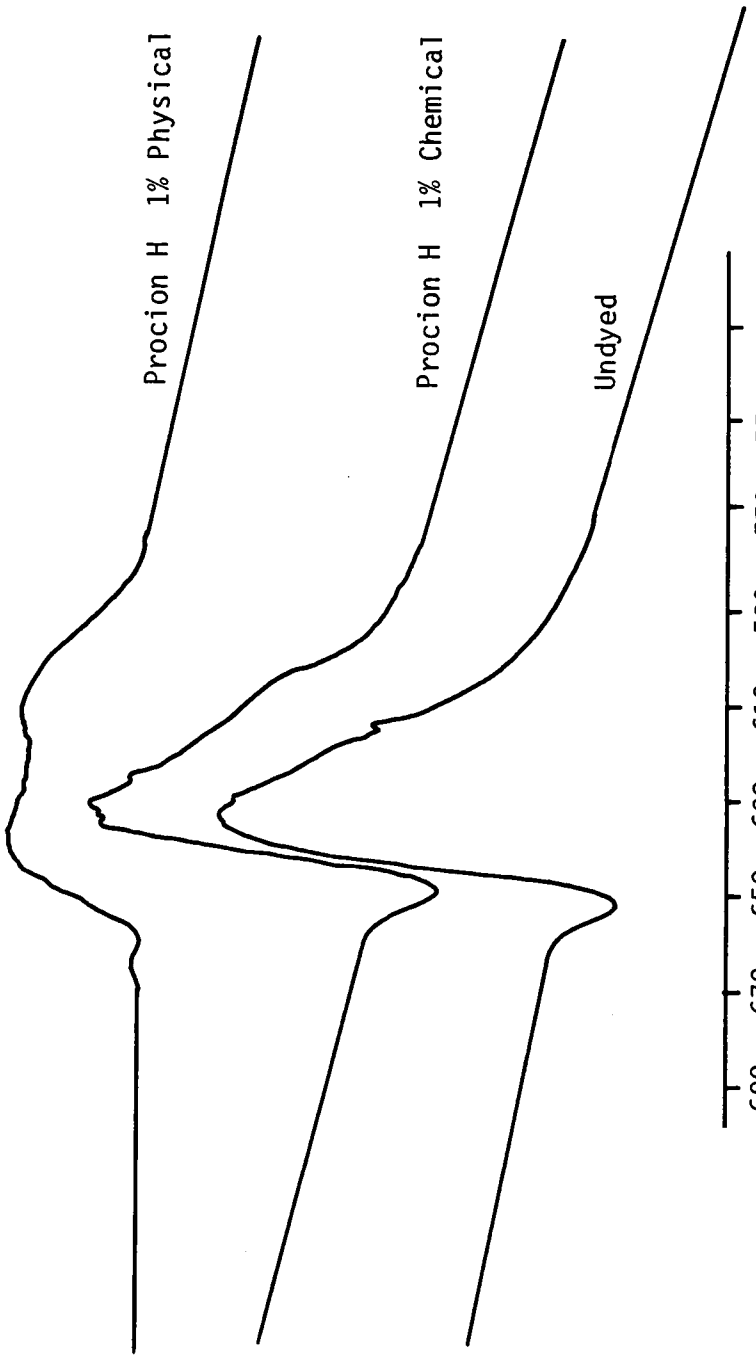


Figure 12. Representative DSC Curves for Dyed and Undyed Fabrics.

to the 1% concentration. These observations regarding fabric breaking extension were largely attributed to the Procion MX dyes over the Procion H dyes.

The undyed fabrics were found to produce lower values for both breaking tenacity and breaking extension than the dyed fabrics. All significant effects, however, were clearly tied to fabric direction. In summary, the presence of dye in the fabric does tend to increase breaking tenacity and extension, but fabric direction is the contributing factor in making these effects significant.

Dye concentration, as well as fabric direction, were responsible for significant differences in wrinkle recovery of the reactive dyed cotton fabrics. The greatest improvement in wrinkle recovery was shown by the 4% fabrics, and this effect was fairly constant between the two dye types. Although the analysis did not establish an order relationship for treatment means due to fabric direction, the filling specimens appeared to produce higher values for wrinkle recovery angle than the warp specimens.

The undyed fabrics did produce lower values for wrinkle recovery in the warp direction than the dyed fabrics. This effect did not apply to the filling specimens. The effect of increasing dye concentration, then, seems to be the most important factor in the improvement of wrinkle recovery for reactive dyed cotton fabrics. Fabric direction has a less important role with filling specimens exhibiting somewhat improved recovery over warp specimens.

As is the case with wrinkle recovery, fabric flexural rigidity was significantly affected by dye concentration and fabric direction.

Unlike the wrinkle recovery test, however, fabric direction appeared to be the dominant factor with the warp specimens producing much higher values for this dependent variable than filling specimens. Increasing dye concentration raised these values to some extent, creating stiffer fabrics, but the effect was tied to the influence of fabric direction. The undyed fabrics did not produce statistically significant differences than the dyed fabrics, which further indicates it is fabric direction which has the greatest influence on this property.

The breaking tenacity and elongation of fibers removed from the reactive dyed fabrics were found to be significant, although the analysis used did not identify either dye type, dye concentration, or interaction of the two as the source of this significance. It is possible that unimportant differences could produce a significant F statistic due to a large sample size; this may have been the case in this test, where N = 500. Confirmation of such a result would require further investigation and improvement in the experimental method, which was shown to be imprecise by the coefficients of variation.

Initial modulus of these fibers was determined to be significantly affected by dye type and dye concentration, with the Procion MX dyes and the 1% concentration having the greatest effect in lowering values for this variable. The interaction of these two factors, however, was not shown to be significant. The undyed fabrics produced the highest values for initial modulus and further confirmed the influence of dye type (especially the Procion MX dyes) as being the most important factor influencing this variable.

There were no significant differences in the percent swelling of fibers removed from the fabrics tested, although the undyed fabrics did

exhibit the highest mean value for this variable, while the Procion MX dyed fabrics displayed the lowest mean value. The nonsignificant overall F statistic may be attributed to a large degree of within-cell variation, which is highly possible due to the handling of fibers when removed from fabrics and when mounted on slides. The overall coefficient of variation (65.8%) indicates a low degree of precision existed in the experimental procedure. Since fibers removed from fabrics in the same manner for the tensile tests produced a similar degree of inaccuracy (45.1 to 57.2%), it is suggested that handling of the fibers and tension applied in removing them from the yarns appear to be contributing factors to the impreciseness of the fiber swelling, as well as the tensile test, results. It is likely that more accurate testing could be done with cotton fibers not yet made into yarns and fabrics.

Moisture content of the fabrics tested was found to be significantly affected by the overall treatment effect, although the analysis did not show any significant differences due to the planned comparisons of dye type, dye concentration, or the interaction of the two factors.

Moisture regain was not significantly affected by the overall treatment effect. The undyed fabrics, however, appeared to exhibit the highest values for this dependent variable. Coefficients of variation were slightly high for moisture content (12.9 to 17.3%) but within the acceptable range (9.9%) for moisture regain. Unlike the swelling procedure developed for this study, this procedure appeared to be fairly precise. Even greater assurance of accurate results could be obtained by repeating the drying and weighing procedure used to obtain the dried fabric weight for figuring moisture content of each specimen until a

constant weight was obtained. Likewise, the regain weight of fabrics could be more carefully found by repeating the conditioning and weighing procedure until this weight was determined to be constant. Although the independent variables of this study did not have an important effect on moisture sorption properties of the fabrics tested, the development of a procedure for measuring these properties which is reliable in light of the above suggestions is a worthwhile contribution.

Conclusions

The results of the physical tests have revealed that the property of fabric wrinkle recovery is improved by an increasing amount of dye in the fabric. Any effects due to the presence of dyes in fabric tensile properties or flexural rigidity are overshadowed by the dominant effects of fabric direction. Initial modulus of fibers removed from dyed fabrics is lowered by the effect of Procion MX dyes over that of Procion H dyes and the absence of dye. Swelling and moisture sorption properties of fabrics are not affected to a great extent by the presence of dyes in the fabric, although a useful procedure for evaluation of moisture properties has been developed.

III. IMPLICATIONS FOR FURTHER STUDY

Swelling and moisture sorption properties of cotton were determined to be generally unaffected by the presence of reactive dye in the fabric in this study. However, the availability of a large number of reactive dyestuffs, as well as various procedures for evaluating moisture sorption properties of textiles, raises questions as to whether the present findings are representative of reactive dyes in general.

Evaluation of swelling through cadoxen retention values is suggested in recent literature (4) to provide more accurate results than those determined with the more common swelling agents (alkalis and acids) when the inhibition of swelling is thought to be due to crosslinking. A comparison of the effectiveness of various swelling agents in evaluating crosslinking finishes of cotton (32) has shown various acids and organic solvents to be unable to distinguish between crosslinking among samples. The use of sodium hydroxide as a swelling agent is reported to give inaccurate results in some cases; e.g., cotton fabrics treated with a resin which forms long crosslink-bridges (aminoaldehydes) exhibit swelling which is only slightly reduced from that of the untreated material. The ability of cadoxen to reveal even small differences in degree of crosslinking is said to be due to its large molecular size (1 cadium to 3 ethylenediamine molar units). These molecules can penetrate the larger spaces found with the cotton fiber. The size of these spaces is decreased by crosslinking until they are no longer accessible to the cadoxen molecules.

Determination of evidence for the formation of crosslinks between adjacent cellulose chains in cotton dyed with bifunctional vs. monofunctional reactive dyes might be better accomplished through swelling tests in a cadoxen solvent. Practical implications of such a finding lie in the correlation of crosslinking with crease recovery angle and wash/wear performance. The centrifuge test could be employed as a supplement to existing procedures for testing wrinkle behavior of cotton in the textile laboratory.

Fabric stiffness, as well as the tensile properties of tenacity and elongation, may also be affected by a high degree of crosslinking

between cellulose chains. Further information on the presence of cross-linking in reactive dyed cotton fabric might be obtained through a more detailed study of swelling behavior of a variety of reactive dyes applied through varying application techniques.

LIST OF REFERENCES

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VITA

Irene Lois Barnes was born in Gallipolis, Ohio on April 27, 1954. She graduated from Meigs High School, Pomeroy, Ohio in 1972. Undergraduate studies were undertaken at Ohio University, Athens, Ohio. In 1976, she received her Bachelor of Science degree in Home Economics. From 1976 through 1979 she taught Vocational Home Economics at Gallia Academy High School, Gallipolis, Ohio.

In the fall of 1979, she was awarded a two-year Agricultural Experiment Station research assistantship and entered Graduate School at The University of Tennessee, Knoxville, in the Department of Textiles, Merchandising, and Design of the College of Home Economics. In August of 1981, she received her Master of Science degree with a major in Textiles and Clothing and a minor in Statistics.

The author is a member of the American Association of Textile Chemists and Colorists, Phi Upsilon Omicron honor society, and the American Association of University Women.