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Title: NITROGEN CONTENT AND PERFORMANCE OF SHIRT FABRIC DURABLE PRESS FINISHED WITH DIMETHYLOLDIHYDROXYETHYLENEUREA

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A procedure is described for analyzing the nitrogen content of durable press cotton fabric at the rate of 20 samples per hour using the Technicon Kjeldahl AutoAnalyzer equipped with a continuous digestor. This method was as good as or better than conventional micro-Kjeldahl techniques.

Durable press cotton fabric from the earlier W103 Western Regional study was laundered for 0, 1, 12, 24, 36 and 48 times at 140 F followed by a 104 F rinse and tumble drying. An additional sample at each laundry level was both steam pressed and laundered. The fabric was then analyzed for total percent add-on of finishes, total nitrogen, durable press rating, wrinkle recovery angle, bursting strength and Elmendorf tear resistance. Percent add-on and decreases in nitrogen content due to extraction with perchloroethylene,

ethanol, water and 0.1 N HCl were also determined.

Steam pressing in addition to laundering did not significantly affect any of the physical properties studied. Bursting strength did not change significantly during laundering. Tear resistance decreased significantly through 36 launderings.

Significant decreases occurred during the first laundering and up to the twelfth laundering for percent add-on, durable press rating and wrinkle recovery angles. Total nitrogen content showed a significant quadratic effect on durable press ratings with increased launderings. This was related only to the 0.1 N HCl extractable nitrogen containing fraction. Major decreases in other nitrogen containing and most percent add-on fractions occurred only during the first laundering. No other relationships were shown between nitrogen content and observed physical properties.

Nitrogen Content and Performance of Shirt Fabric Durable Press Finished with Dimethyloldihydroxyethyleneurea

by

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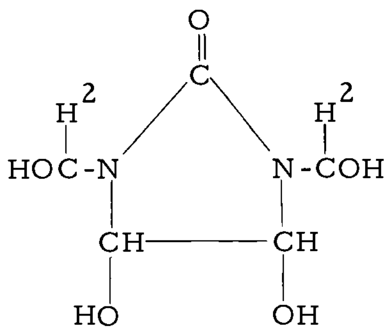
NITROGEN CONTENT AND PERFORMANCE OF SHIRT FABRIC DURABLE PRESS FINISHED WITH DIMETHYLOLDIHYDROXYETHYLENEUREA

INTRODUCTION

Dimethyloldihydroxyethyleneurea (DMDHEU), also referred to as 1,3-dimethylol-4,5-dihydroxy-2-imidazolidinone,



is the major resin used in the durable press finishing of textile fabrics (19,37). DMDHEU is used with the Koratron and many related finishing processes.

Western Regional Project W103 showed that DMDHEU durable press finished men's white shirts of 100 percent cotton and 65/35 polyester/cotton become more wrinkled after laundering and after wear and laundering (31). Similar observations have been noted by Consumer Bulletin (29), Vail, et al. (49) and Stover (45).

Portions of shirts from project W103 which were laundered and worn tended to be less wrinkled than those which were laundered only. This might have been due to body moisture and warmth.

The W103 observations have not been related to changes in or loss of DMDHEU or other finishes present on the shirts.

The Technicon Kjeldahl AutoAnalyzer has been used for determining the nitrogen content of plant materials (47, 53). Although the Kjeldahl method is frequently used for nitrogen analysis of textiles, the author has found no published procedures or reported use of the Technicon apparatus for determining the nitrogen content of fabrics and finishes.

Objectives

This study was based on three major objectives:

1. To establish a procedure for using the Technicon Kjeldahl AutoAnalyzer on the 100 percent cotton DMDHEU durable press finished shirt fabric used in Western Regional Project W103 or similar fabric.
2. To study the nitrogen content (total and extractable) in this fabric after increased numbers of launderings.
3. To determine if a relationship exists between nitrogen content (total and extractable) and observed performance (appearance and durability) characteristics of the 100 percent cotton shirt fabric or a similar fabric.

Hypotheses

The following are the null hypotheses (H_o) tested in this study.

1. The total nitrogen content of the yardage fabric does not differ among blocks.
2. Total percent add-on will not change after laundering 0, 1, 12, 24, 36 and 48 times.
3. Total nitrogen in the fabric will not change after laundering 0, 1, 12, 24, 36 and 48 times.
4. Ironing prior to laundering 0, 1, 12, 24, 36 and 48 times has no additional effect after laundering on
   a. total nitrogen content.
   b. percent add-on.
   c. bursting strength.
   d. Elmendorf tear resistance in the warp or filling direction.
   e. wrinkle recovery angles.
   f. durable press appearance ratings.
5. Laundering 0, 1, 12, 24, 36 and 48 times does not affect bursting strength of the fabric.
6. There is no linear or quadratic relationship between total nitrogen and bursting strength after laundering 0, 1, 12, 24, 36 and 48 times.

7. Laundering 0, 1, 12, 24, 36 and 48 times does not affect Elmendorf tear resistance in either the warp or filling direction.
8. There is no linear or quadratic relationship between total nitrogen and Elmendorf tear resistance in either the warp or filling direction after laundering 0, 1, 12, 24, 36 and 48 times.
9. Laundering 0, 1, 12, 24, 36 and 48 times does not affect the wrinkle recovery angles of the fabric.
10. There is no linear or quadratic relationship between wrinkle recovery angles after laundering 0, 1, 12, 24, 36 and 48 times and
    a. total nitrogen remaining in the fabric.
    b. nitrogen extractable with perchloroethylene.
    c. nitrogen extractable with ethanol after perchloroethylene extraction.
    d. nitrogen extractable with water after extraction with perchloroethylene and ethanol.
    e. nitrogen remaining after extraction with perchloroethylene, ethanol and water.
11. Laundering 0, 1, 12, 24, 36 and 48 times does not affect the durable press appearance rating of the fabric.

12. There is no linear or quadratic relationship between durable press appearance rating after laundering 0, 1, 12, 24, 36 and 48 times and
    a. total nitrogen remaining in the fabric.
    b. nitrogen extractable with perchloroethylene.
    c. nitrogen extractable with ethanol after perchloroethylene extraction.
    d. nitrogen extractable with water after extraction with perchloroethylene and ethanol.
    e. nitrogen remaining after extraction with perchloroethylene, ethanol and water.

Delimitations

A temperature of 140 F was used for laundering since this was the temperature used throughout the Western Regional Project W103 (31).

Assumptions

Laundering and ironing do not convert finish compounds to compounds with N-N or N-O linkages.

Definitions

Blocks: areas within the length of yardage from which samples were taken for laundering.

Sample: one yard length of fabric receiving a specified number of launderings or ironing and launderings.

Specimen: fabric on which a single observation for a specific test was made.

Nitrogen content: milligrams (mg) nitrogen per gram (gm) of fabric.

Percent add-on: weight in gm extracted by any one solvent in the sequence per gm of fabric after extraction with all four solvents x 100.

Total nitrogen: mg nitrogen per gm fabric present before extraction with any solvent.

Total percent add-on: total weight in gm extracted with perchloroethylene, ethanol, water and 0.1 N HCl in that sequence per gm of fabric after extraction with these four solvents x 100.

REVIEW OF LITERATURE

Consumer satisfaction with durable press garments is based on several performance factors in addition to the no-iron property. These factors include good wrinkle recovery during wear, permanence of finish, shrinkage control, acceptable tensile and tear strength, good abrasion resistance, stain resistance and soil removal (55).

Men's dress shirts are a major enduse where consumers encounter problems related to durable press (39,44,55).

Steiniger and Dardis (44) noted that the majority of faults with durable press occurred during laundering. Consumer related problems include loss of finish or increased wrinkling after laundering, low strength and abrasion resistance and differential shrinkage of component parts.

Care of Durable Press Garments

Although laundering instructions for durable press garments vary, small wash loads and warm wash water followed by warm or cold rinses and tumble drying are generally recommended (11, 14, 26).

Knoepfler, *et al*. (24) found that wash water temperature was more significant than drying temperature when samples were tumble dried to five percent moisture content. Consumer Reports (54) observed that use of a clothes dryer has a greater effect on appearance of durable press items than conditions in the washer. Wham (55) and Consumer Reports (54) reported water temperature was important if durable press items were to be line dried.

If hot wash water is used, cooler rinses are recommended (10, 12, 54). Whirlpool has permanent press or wash-and-wear cycles that use hot wash water, but with reduced agitation and partial replacement of the wash water by cold water before spinning at a reduced speed and a final cold rinse (10).

The length of the wash period at 180 F was found not to affect wrinkling when followed by a short spin dry (27). The load to water ratio was important.

Consumer Reports (11, 30) sent durable press shirts to a commercial laundry ten and 20 times. Although this involved hotter laundering temperatures than home laundering and included pressing, when these shirts were then washed in warm water they looked as good a shirts washed the recommended way the same number of times.

Consumer Reports (11), Foy (14) and Eastman Chemical Products (12) recommended hot water if durable press garments are heavily soiled or dingy. However, Martin and Wood (28) found ease of stain removal from durable press fabrics depended on the soil release finish, not on the presence of phosphate in the detergent or on the wash temperature (120 F and 140 F).

Strength and Abrasion Resistance

Durable press finishing with DMDHEU and other resins reduces strength and abrasion resistance of cotton fabrics (20,23,36,38,55). Resin stripping of these fabrics will result in increased strength (42). Considerable research has been directed toward developing durable press cotton fabrics with better abrasion resistance and strength.

The abrasive damage observed in the W103 study was due to washing and drying rather than wear (32). The damage increased with increased launderings.

Wylie and Erickson (57), reporting on the same project, found that tear resistance was significantly lower for laundered only shirts compared with laundered and worn shirts. The ball bursting strength was slightly lower for worn and laundered 100 percent cotton shirts compared to laundered only shirts. Bursting strength of cotton shirts did increase during the first 12 laundering cycles with little change during the next 12 cycles.

Cotton shirts in Stover's (45) study retained 63 to 83 percent of the original tear resistance and 84 to 100 percent of the original breaking strength after 72 wear laundering cycles.

Durable Press Appearance

Decreases in durable press appearance ratings and seam pucker of both cotton and cotton/polyester men's shirts from Western Regional project W103 were noted after the first 12 launderings (31, 32). Twelve additional launderings resulted in little change of these properties. The unlaundered controls in this study were steam pressed before evaluation. The magnitude of difference between shirt backs worn and laundered and laundered only was 0.2 or less. Pockets, cuffs and collars were rated markedly lower and did show a decrease in appearance ratings from 12 to 24 launderings. Significantly higher appearance ratings were noted for worn and laundered shirts over laundered only shirts for pockets and collars. There was no significant difference in the mean of durable press ratings among the five locations where the study was carried out.

Stover's (45) study included three types of durable press cotton shirts and four with various blend levels of polyester and cotton. The durable press ratings of the three types of cotton shirts decreased through 40 wear launderings. Then two types increased until their durable press appearance after 72 wear launderings was almost as good as after the eighth.

Consumer evaluation showed that the greatest change in fabric appearance occurred some time during the first eight wearings and launderings (45). Consumers were satisfied and felt pressing was not necessary at the 3.0+ durable press appearance rating and wrinkle recovery angles of 270° (W + F). Franklin, Madacsi and Rowland (17) stated that 280° (W + F) wrinkle recovery angles were required for satisfactory performance.

Opinions vary on the number of wearings or launderings a shirt should undergo to test various properties. Handy, et al. (20) stated that a good shirt wear test involves a minimum of six months. Consumer Reports (11,30) used 18 wear launderings. Consumer Bulletin (29) found that if a shirt had a good smooth appearance after one washing, it was likely to keep on looking well for a fairly long time. They did note a few instances where pressing was needed after 20 washings. Stover's study (45) extended over a period of 72 wearings and launderings.

Wrinkle Recovery Angle

Stover (45) found that consumer satisfaction was best related to wrinkle recovery angle and air permeability. Over a period of 72 wear launderings, the wrinkle recovery angles of cotton shirts decreased 20 to 30° (W + F).

The Gulf Coast Section of AATCC (2) studied the relationship of wrinkle recovery angles and durable press ratings on various DMDHEU treated cotton fabrics. A good linear correlation was found between tumble dry durable press ratings and conditioned wrinkle recovery angles of print cloth receiving different DMDHEU finishing processes. These correlations showed little difference after five launderings and tumble dryings. It was pointed out that wrinkle recovery angle and fabric smoothness ratings are both related to the resiliency of the fabric.

Dimethyloldihydroxyethyleneurea

Hall (19) said DMDHEU is perhaps the most important cross-linking agent used in preparing cotton fabrics with a crease resistant finish. Although more costly than many cross linking agents, it is not chlorine retentive and reacts better with cotton in the swollen state (56). Its slow reaction rates make it advantageous for use in delayed cure processes (6, 19). Franklin, Madacsi and Rowland (15, 16) found DMDHEU to be the preferred agent for recurable durable press fabrics.

Durability of Finish

The durability of durable press finish is mentioned as an explanation of appearance changes. Consumer Reports (11) said that the finish does not last indefinitely. Stover (45) suggested that downward trends in consumer evaluations might indicate a loss in durable press finish. However, since none of the shirts required pressing after 72 wear launderings, this was indicative that little deterioration of the durable press finish had occurred.

Wylie and Erickson (57) in their report on the W103 study concluded "that there was more loss of durable press finish in the worn and laundered shirts" than in the laundered only shirts. "As the amount of durable press finish decreases, the strength of cotton increases."

Vail, et al. (49) measured the wrinkle recovery angle and nitrogen content of cotton fabrics treated with DMDHEU before and after five AATCC launderings and after ten home launderings at 130 to 140 F in the presence of 0.02 percent available chlorine during a 15 minute wash period. The wrinkle recovery angle was markedly lower for the home laundering procedure. Some of the AATCC launderings showed no decrease while home laundering resulted in a 20 to 30° (W + F) decrease.. Nitrogen changes varied from no change to 0.9 mg loss per gm of fabric. They felt this slight or no loss of nitrogen might be due to partial cleavage of crosslinks, resulting in more pronounced losses in wrinkle recovery angles than in nitrogen content.

Nitrogen Analysis

The Kjeldahl technique is most frequently used for nitrogen analyses of textiles.

At present there is no reported use of the Technicon Auto-Analyzer equipped with a continuous flow digestor for determining the nitrogen content of fabrics and finishes. This Technicon apparatus has been used for determining the nitrogen content of plant materials (47, 53). The Technicon continuous flow AutoAnalyzer first digests the nitrogen containing compound, then mixes the digest with phenol and hypochlorite. In an alkaline solution, this mixture developes a blue color (Berthelot reaction) that is measured spectrophotometrically and automatically recorded. The color relates directly to the amount of nitrogen present. Twenty to 30 samples can be digested and analyzed per hour.

Another method of nitrogen analysis using the Technicon Auto-Analyzer has been described by Schuman, Stanley and Knudsen (41) in which the digestion is effected in an aluminum block equipped with a heating mechanism which can accommodate 40 samples. The digested samples are then fed into the AutoAnalyzer without the digestion helix and digestion fluids for spectrophotometric analysis.

Nitrogen Content and Textile Research

Harper and Bruno (21) used nitrogen content to show quantitatively where DMDHEU reacts in polyester/cotton blends.

Rowland, et al. (40) utilized CHO/N ratio to establish the structural form of DMDHEU in crosslinked cotton. They found that methylol crosslinks constitute a significant fraction of the crosslinkages.

Vail (50), Vail and Verburg (51) and Vail and Pierce (52) have concluded that most N-methylol and similar agents react during curing with cotton undergoing little, if any, structural modification or loss of methylols. In their research, they utilized both wrinkle recovery angles and nitrogen content. Nitrogen provided the more accurate and reproducible data. When nitrogen was removed by hydrolysis, the wrinkle recovery developed during curing was lost.

Fiebig and Rezk (13) state that nitrogen is a measure of reagent bound to the fiber, while dry (conditioned) crease recovery angles are indications of the extent of crosslinking. Kullman and Reinhardt (25) noted that in both dehydration curing and pad-dry-cure finishing, the nitrogen content and wet recovery angle increased with increased curing times while the conditioned recovery angle did not.

Grant, et al. (18) observed that both wet and conditioned wrinkle recovery angles increased non-linearly with increased add-on. The greatest increases occurred between 0.5 and 1.0 percent nitrogen add-on.

Fiebig and Rezk (13) noted that the nitrogen content and wet recovery angle of both fabrics studied did not decrease after ten launderings. The conditioned wrinkle recovery angle decreased 17° (W + F).

Vail and Pierce (52) followed nitrogen content after one and after four launderings. The loss in nitrogen content ranged from 0.1 to 0.4 mg nitrogen per gram of fabric.

Nitrogen content of durable press fabrics in the above studies and other reports (5, 6, 7, 22, 33, 34, 49) is used primarily as a measure of bound resin.

MATERIALS AND METHODS

Fabric

Three fabrics were used in this research. Preliminary studies were carried out on fabric from shirts of 100 percent cotton and 65/35 polyester/cotton. Yardage fabric of 100 percent cotton was used in the final series of investigations. The three fabrics are described in Table 1 and the following discussion.

Table 1. Comparison of thread count and weight of yardage and shirt fabrics.

	100 Percent Cotton		65/35 Polyester/Cotton
	Yardage	Shirts*	Shirts*
Yarns per inch:			
Warp	141	140	131
Filling	61	61	71
Ounces per square yd:	4.0	4.4	3.1

*Morris, et al. (31).

The men's white long sleeved dress shirts were among those obtained for Western Regional Research Project W103. The 100 percent cotton broadcloth shirts had a precured Nevapress (M. Lowenstein and Sons) durable press finish accounting for a 5.5 percent add-on. The 65/35 polyester/cotton fabric was from shirts with a Koratron (Koratron Company) durable press finish. Both blended and 100 percent cotton shirts were Sanforized and had a soil release finish.

The yardage obtained from the shirt manufacturer was 100 percent mercerized cotton broadcloth, the same as used for the shirts according to the manufacturer. It was precured by the Masterprest process resulting in a 5.5 percent durable press finish add-on. The yardage was 45.7 inches wide and 49.5 yards long.

Sampling

The yardage was sampled in three blocks, each eight yards in length. The sampling blocks were eight yards apart and no less than four yards from either end of the bolt (Appendix A). The first 2.5 yards were reserved for use as standards in the Technicon Kjeldahl analysis. One sample at random from each of the three blocks was used for each period of laundering. Only one sample at each period of laundering was used for the ironed and laundered samples.

From each sample, specimens for testing were selected according to one of three predetermined randomized patterns (Appendix A and Appendix B). This was to minimize testing the same warp or same filling yarns at the same distance from any one edge. Specimens were taken no closer than one-tenth the width of the fabric from either the selvage or cut edges.

Laundry Procedure

The laundry equipment used in this and the W103 study consisted of a Whirlpool Mark XII (LSA 9920) washer and Whirlpool Mark XII dryer (LSE 9920) obtained in 1968.

The laundry load consisted of the equivalent of eight shirts (4 lbs 6 oz to 4 lbs 8 oz). Samples were laundered at regular intervals on a rotating basis with ironed and laundered samples or cotton shirts from one of two lots bringing each load to weight. Samples were laundered a maximum of once every 22 hours.

The washing was carried out at 140 ± 5 F. After the tub was filled and agitated for 1.0 minute, Tide detergent was added in the amount of 1.2 cups and agitation continued for 0.5 minutes before adding the wash load. The remaining wash cycle was 8.5 minutes. The washing machine was equipped with a permanent press cycle which allowed for the partial draining and refilling of the tub with cold water to decrease the temperature prior to spinning and rinsing. The cool down cycles were 123.8 to 127.4 F and 114.8 to 118.4 F with each followed by 2.0 minutes of agitation. A complete rinse followed at 102.2 to 106.7 F with 2.0 minutes of agitation. The agitation rate for both washing and rinsing was 70 cycles per minute with spin at low setting and water levels of 10.0 to 11.0 inches.

Drying was effected using the following settings: regular permanent press, automatic cycle and superspeed. This allowed an average of 25 minutes warm tumbling with five minutes cool down. Shirts and yardage were hung immediately after the dryer shut off with straightening and finger pressing as needed. Shirts were laundered unbuttoned and hung buttoned.

Ironed yardage was steam pressed prior to the first laundering and between subsequent launderings with no ironing following the last laundering. A Hoover model 4460 iron was used with a plate temperature of 325 to 350 F.

Weighing

Specimens for all chemical analyses were weighed to constant weight within 0.4 mg. This followed 2.0 hours for nitrogen determinations and 4.0 hours for percent add-on determinations at 221.0 F to 228.2 F and 1.0 hours in a desiccator.

Nitrogen Determinations

Automated Analysis

Fabric was prepared by cutting each specimen into 0.2 cm or smaller squares prior to weighing. Weighed specimens were transferred quantitatively from weighing cans to 150 ml beakers. Distilled water (10.0 ml) was added to each beaker to wet samples a minimum of 1.0 hours before the addition of 15.0 ml concentrated sulfuric acid (H_2SO_4) (specific gravity 1.84, Dupont, reagent). The H_2SO_4 was added by rapidly dispensing the aliquot from an automatic pipet over the surface area of the fabric-water mixture. The mixture was not agitated then nor after the addition of 35.0 ml of distilled water 30 minutes later. Thirty minutes after the last addition, the mixture was stirred with a rubber policeman and immediately poured into a sampling cup.

Samples were analyzed with a Technicon AutoAnalyzer equipped with a continuous digestor. The procedure was that of Technicon (46) Industrial Method 30-69A with the following modifications: 1:2 sample to wash ratio and sodium hypochlorite in the form of Purex (six percent hypochlorite). A flow diagram is shown in Figure 1.

The alkaline phenol solution was purchased from Technicon Corporation (Tech No. T01-0115). The digestion mixture consisted of selenium dioxide (Tech No. T-1-0117), 3.0 gm; H_2SO_4, 900 ml; perchloric acid ($HClO_4$) (70 percent, analytical, Mallinckrodt), 20 mls. The sodium hydroxide reagent contained 350 gm sodium hydroxide (NaOH) (Mallinckrodt, analytical) and 50 gm potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 2\ H_2O$) (Mallinckrodt, analytical) dissolved in 700 ml distilled water and brought to 10,000 ml volume after cooling.

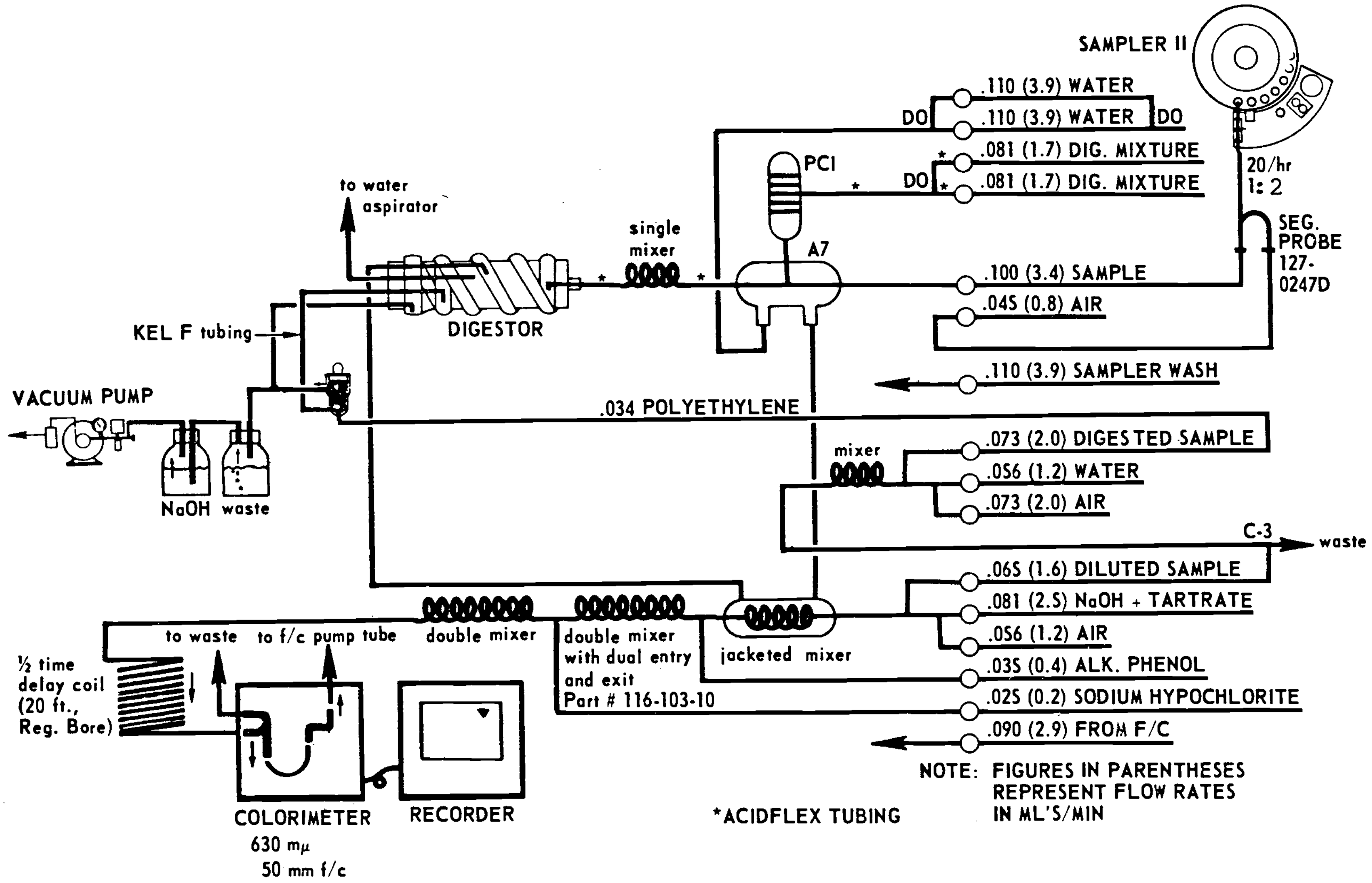


Figure 1. Flow diagram for Kjeldahl nitrogen determination using Technicon AutoAnalyzer.

Technicon Standardization

Yardage fabric of predetermined nitrogen content was run a minimum of every five samples with standard curves being run intermittently over the range tested.

The nitrogen content of these yardage standards had been determined by a modification of the procedure for grain by Snell and Snell (43) using specimens of varying weights up to 0.25 gm. To these in micro-Kjeldahl flasks were added two boiling beads and 5.0 ml of concentrated H_2SO_4. This mixture was heated until the sample blackened, then cooled. Two (2.0) ml of 30 percent hydrogen peroxide (H_2O_2) were added slowly down the side and the flasks allowed to sit 10 to 15 minutes. Heat was applied until white fumes appeared. Then the flasks were cooled and 3.0 ml 30 percent H_2O_2 added. The flasks were then heated at least two hours after white fumes appeared.

After digestion, the samples were cooled and quantitatively transferred with distilled water to 100 ml volumetric flasks and brought to volume after cooling.

The Nessler's reagent was composed of 4.0 gm potassium iodide (KI) (Mallinckrodt), 5.5 gm mercuric iodide (HgI_2) (Mallinckrodt) and 1.5 gm powdered gumghatti in 1000 ml distilled water. Nesslerization was effected by mixing 20.0 ml distilled water with 10.0 ml Nessler's reagent and 5.0 ml of diluted sample. Five (5.0) ml of 10 N NaOH was then added with swirling. After 15 minutes the optical density (O.D.) was read at 450 mμ on a Bausch and Lomb Spectronic 20 spectrophotometer using 1.0 cm cuvettes.

The O.D. was converted to nitrogen using a standard curve similarly prepared using known dilutions of ammonium sulfate and urea. Slopes of the O.D. vs. mg nitrogen (Figure 2) and mg standard fabric were determined using the sum of the least squares method. The nitrogen content was found to be 9.47 mg/gm of standard fabric.

Observations were made on the Technicon on seven different days. A different standard curve was computed for each day by first fitting the O.D. as a function of weight (W) in gm and position (t) in the experimental sequence for that day as follows,

$$\text{O.D.} = \hat{\beta}_0 + \hat{\beta}_1 W + \hat{\beta}_2 t + \hat{\beta}_3 t^2 .$$

The values of the intercept $(\hat{\beta}_0)$ and partial regression coefficients $(\hat{\beta}_1, \hat{\beta}_2, \hat{\beta}_3)$ were determined for each of the seven days.

The nitrogen content per gm of fabric specimen for a specific observation on a given day could then be calculated as

$$\frac{9.47(\text{O.D.} - \hat{\beta}_0 - \hat{\beta}_2 t - \hat{\beta}_3 t^2)}{\hat{\beta}_1 \text{ (gm of specimen)}} .$$

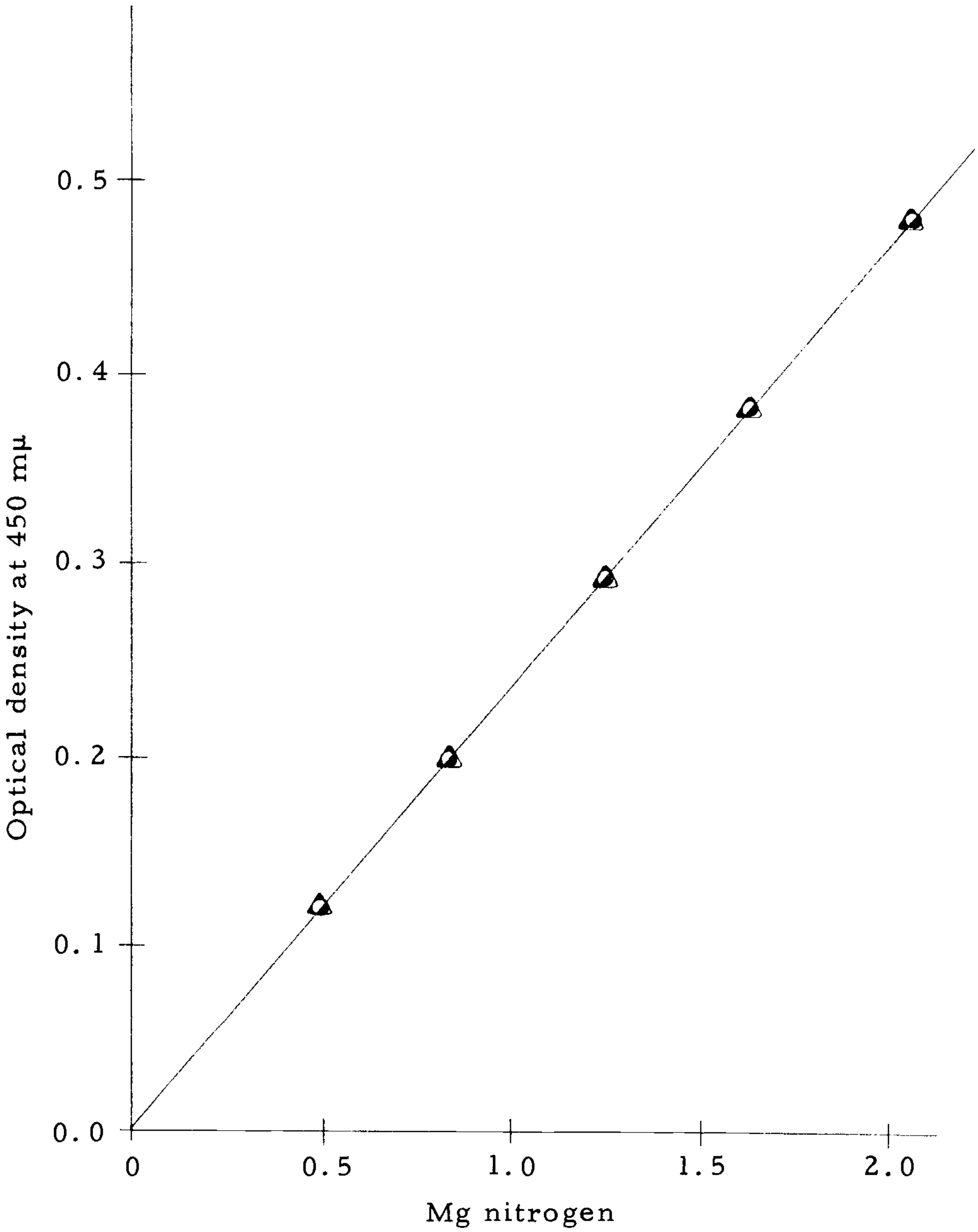


Figure 2. Micro-Kjeldahl standard curve.

Extractions

Finishes on the fabrics were extracted following AATCC (1) Test Method 94-1969 using approximately 5.0 gm samples. For nitrogen determinations, approximately 5.0 gm (ten, 2.5 inch squares) were extracted simultaneously, then subjected to nitrogen analysis independently.

Evaluation of Physical Properties

Standard conditions (65 ± 2 percent relative humidity and 70 ± 2 F) were used for testing.

The durable press appearance ratings of the yardage and shirts were judged by AATCC Test Method 124-1967 (ASTM D1295-67) with the following modifications. Shirts were hung so that the center back area lay in the same plane as the replicas, with judging limited to this relative area. Yardage was folded in thirds and hung so that the center area was in the same plane as the replicas and the filling running crosswise. An intermediate rating of 2.5 was allowed if judges could not rate a sample 2.0 or 3.0.

AATCC Test Method 66-1968 was employed for measuring the wrinkle recovery angles. Bursting strength was measured by ASTM D231(11)-62 on a constant rate of traverse machine equipped with a bursting attachment. Tear resistance was determined on the Elmendorf apparatus using ASTM D1424-63 (reapproved 1970) and the improved model for specimen cutting.

RESULTS AND DISCUSSION

Methodology for Nitrogen Analysis

Standards for Technicon

The nitrogen standards used in the Technicon AutoAnalyzer equipped with a continuous digestor must be similar to the unknowns being analyzed (46, 47, 53). The same amount of nitrogen in a different form or in a different matrix may produce different optical densities.

Unlaundered yardage fabric from the same source as the fabric tested was used for standards in this study. The nitrogen content of these standards was determined by micro-Kjeldahl analysis. The fabric standard contained 9.47 mg nitrogen per gm.

The Nessler's reagent was not the same as described by Snell and Snell (43). The reagent described in the preceeding section allowed the digested fabric solution to be utilized in a higher concentration without interference by precipitating mercuric iodide during spectrophotometric assay.

Preparation of Specimens for Technicon

Up to 0.6 gm of 100 percent cotton fabric could be used in the procedure described in the preceding section. Specimens could be prepared by cutting into approximately 0.2 cm squares or by raveling and cutting the ravelings into approximately 4.0 cm lengths. Cutting was considerably faster than raveling. The same values were obtained by both methods. Milled specimens dispersed easily in the air and were not used.

Polyester/cotton broadcloth had to be raveled and chopped into very short lengths. Even then partially dispersed fibers would clog the sampling device and build up at the tubing joints. The method described was not suitable for polyester/cotton broadcloth unless digestion was effected prior to introducing the sample into the apparatus.

No apparent differences were noted between specimens wetted overnight and those wetted at least one hour prior to addition of H_2SO_4. Specimens wetted less than one hour tended to retain some fibrous matter and give more varied results.

It was essential to add H_2SO_4 to the wetted samples very rapidly and in the same manner to each beaker. Swirling or agitating the beaker produced irregular results. Cotton fabric formed much finer particles which remained more uniformly suspended in solution for longer periods of time than plant material under study in the laboratory where the Technicon was located. Duplicate pours from the same suspension of cotton fabric analyzed in sequence would duplicate each other within 0.3 percent transmittance.

Statistical Analysis of Methods

The analysis of variance (Table 2) for each run used in this study indicates that greater deviations occurred on days 1, 2 and 6. On days preceding these runs or on the same day, plant materials with higher nitrogen content than the cotton fabric were analyzed. These caused some visible accumulation near the beginning of the digestion helix. Although this residue was present to a degree in every run, it is possible that new accumulations may have contributed to observed variations.

Table 2. Summary of variance of fabric standards for each day.

Day	Standard Deviation O.D.	Standard Deviation mg Nitrogen	C.V. Percent	R-square
1	0.0118	0.24	6.87	0.9563
2	0.0094	0.18	6.09	0.9596
3	0.0039	0.08	2.74	0.9932
4	0.0026	0.08	1.48	0.9981
5	0.0062	0.04	4.29	0.9730
6	0.0083	0.17	5.22	0.9410
7	0.0034	0.07	2.16	0.9957

In preliminary studies with the AutoAnalyzer, slight changes were noted in the slope of the standard curves during a run and especially from day to day. Sharp rises in room temperature, sometimes 15 F or more around noon, were also reflected in standard curves.

On days 2, 5 and 6 the Technicon apparatus was in operation continuously for over seven hours, at least two hours longer than on the other four days.

When the tubing was not changed for other analyses or for repairs, the slopes of standard curves were similar from day to day (day 2 and day 3).

The initial treatment with H_2SO_4 during predigestion was done by the same person throughout the study to maintain the process as consistent as possible.

Due to the factors mentioned above, it was necessary to prepare standard curves by regression analysis for each day (Appendix C) with different regression coefficients.

A standard of approximately the same concentration as the specimens being analyzed was run every five samples at the request of the statistician. Standards consisting of three levels of nitrogen covering the range of specimens being tested were run periodically. Running three standard levels of nitrogen after every seven to ten specimens would allow more accurate estimation of the intercept and give a continuous check on slope.

Statistical analysis of samples treated alike and analyzed on days 1, 2, 3 and 4 showed an R-square of 0.973 and a coefficient of variation (C.V.) of 4.51 percent. The micro-Kjeldahl method utilized in this study had a R-square of 0.956 and a C.V. of 4.29 percent on the same fabric. These results compare with similar values reported for plants (47) and soils (41).

The preceding discussion and Table 2 indicate that if material with high nitrogen content is not allowed to accumulate within the apparatus, the automated technique can be better than the micro-Kjeldahl as a precision method for nitrogen determinations on textile products such as durable press finished cotton fabrics.

Other Considerations

Nitrogen determinations are an important tool in research dealing with durable press finishes. Although the equipment represents a major investment, the automated method requires less space, less glassware, less time and is potentially less dangerous than the non-automated Kjeldahl techniques. The procedure described analyzed 20 samples per hour. A maximum of 24 samples could be analyzed in one day using a six unit digestion rack and direct nesslerization for micro-Kjeldahls.

Selection of Test Fabric

Nitrogen analysis of 100 percent cotton shirts from the Oregon portion of Western Regional Project W103 indicated that worn shirts differed from unworn shirts after 12 and 24 launderings (Figure 3). However, variation among shirts treated alike was significantly

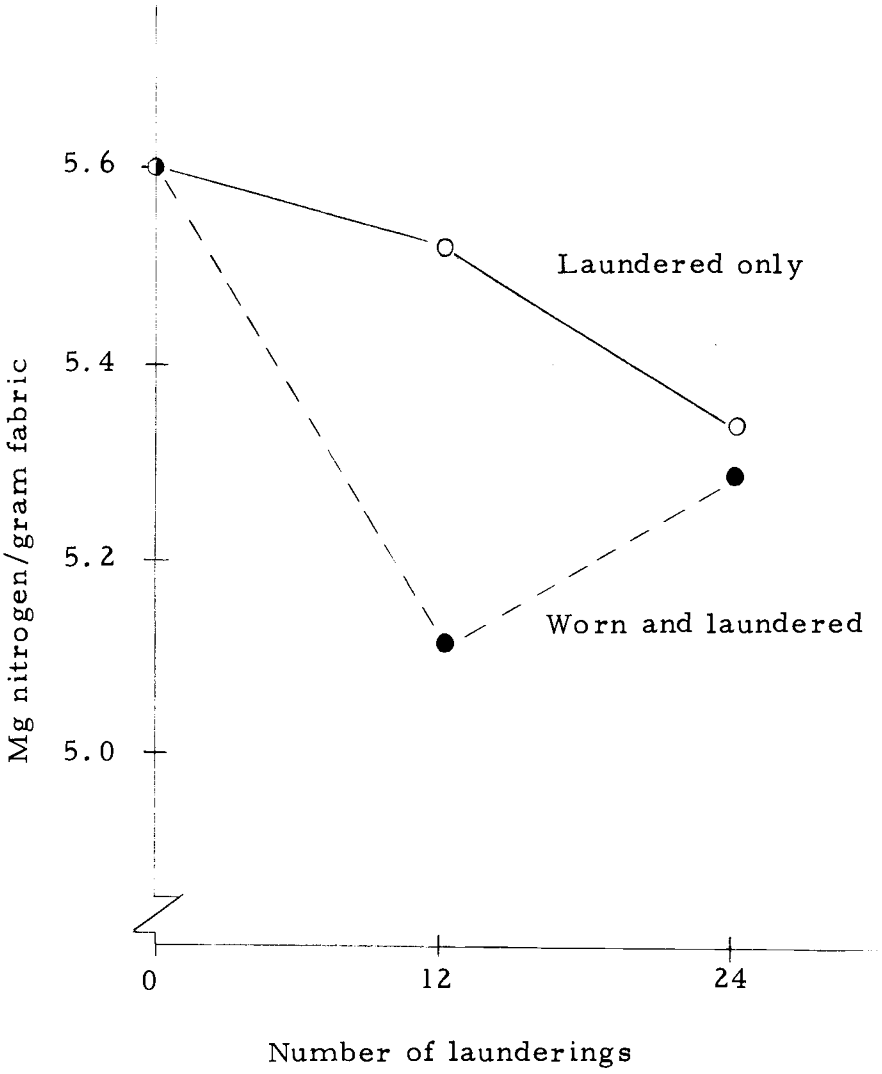


Figure 3. Nitrogen content of W103 shirts before and after laundering.

($\alpha = .025$) greater than variation among specimens from the same shirt (Table 3). This variation was due to initial differences in the nitrogen content of the shirt fabric. The magnitude of difference observed after laundering or between worn and unworn shirts would depend on the proportion of shirts manufactured from different fabric lots. The shirts did not appear to have been randomly selected with regard to nitrogen content.

To eliminate this source of variation, yardage was selected for further study. The yardage was purchased at the same time as the shirts were purchased and was reported by the manufacturer to be the same used in constructing the shirts.

Total percent add-on of the yardage was similar to that of the control shirts used in the Oregon portion of the W103 study. However, the yardage fabric had a higher proportion of nitrogen containing finishes than the shirts (Figure 4). The ethanol extractable nitrogen fraction was much greater in the yardage fabric. This indicated the presence of a greater proportion of unreacted durable press precursors (1) than was present in the shirts.

Additional launderings were included in the study of yardage fabric. These launderings were done to determine the initial effects of laundering and effects of laundering over a greater portion of the actual life of men's shirts.

Table 3. Analysis of variance of total nitrogen content of W103 shirts.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Worn vs. unworn	1	0.9012	0.9012	2.71*
Unlaundered vs. laundered for unworn shirts	1	0.1426	0.1426	0.43
Laundered 12 vs. 24 times for unworn shirts	1	0.0952	0.0952	0.29
Shirts worn by different men	9	5.1767	0.5752	1.73*
Worn and laundered 12 vs. 24 times	1	0.4059	0.4059	1.22
Residual error	15	4.9862	0.3324	7.15**
Sampling (specimen) error	29	1.34766	0.0465	
Total	57	13.0555		

* 25 percent level of significance.
** 2.5 percent level of significance.

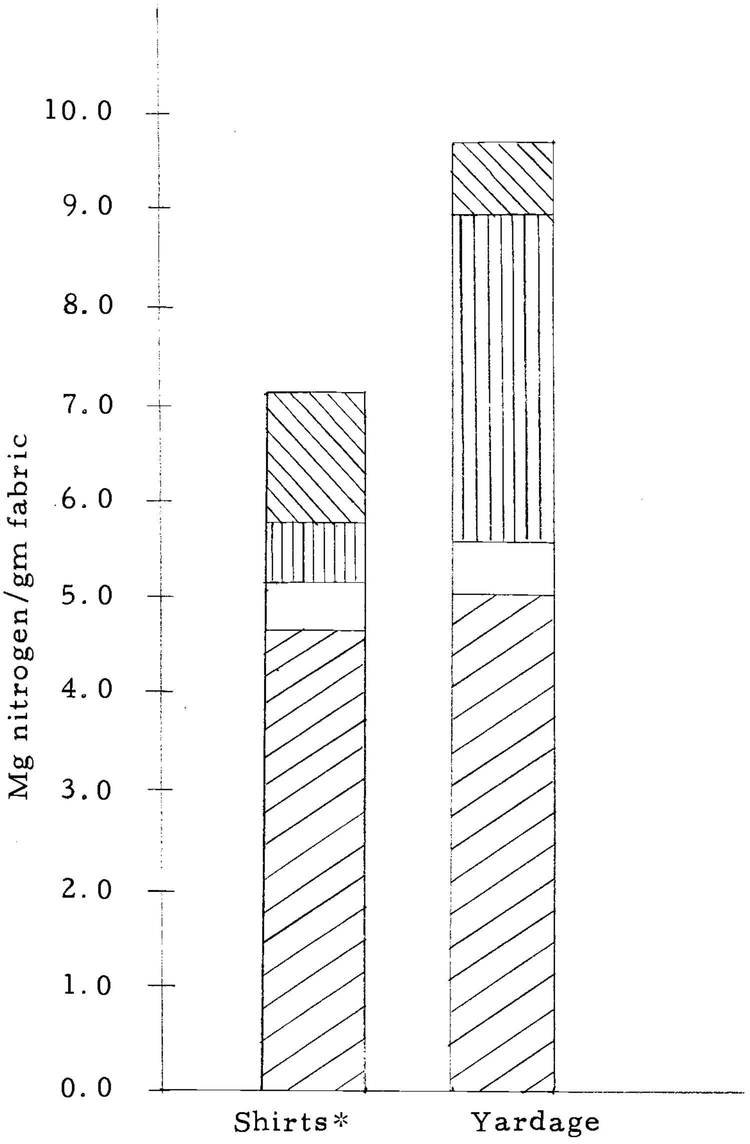


Figure 4. Comparison of shirt and yardage fabric nitrogen content.

* Average of three shirts before laundering
Extractable with perchloroethylene
Extractable with ethanol
Extractable with water
Extractable with 0.1 N HCl

Analysis of Yardage Fabric

Durable press finishes, such as DMDHEU, influence the strength, smooth appearance and wrinkle recovery abilities of cotton fabrics during use. Ball burst and Elmendorf tear tests were used to evaluate strength. Durable press ratings and conditioned wrinkle recovery angles were used to evaluate smoothness of appearance and ability to recover from wrinkling.

Percent add-on was measured to determine the effect of laundering on finishes in general. The contribution of nitrogen containing finishes to changes that might occur during laundering in the physical properties of the yardage fabric was determined by statistical analysis.

Percent add-on, bursting strength, warp Elmendorf tear resistance, wrinkle recovery angles and durable press rating did not vary significantly (α = .05) along the length of the yardage (Table 4) after removing the effects of ironing, laundering and nitrogen content. Filling tear resistance was a possible exception.

Percent Add-On

The apparent difference in percent add-on among blocks was due to non-random sampling of ironed and laundered samples.

Ironing had no additional effect (Table 5) on percent add-on and

Table 4. Summary of analysis of variance of percent add-on, bursting strength, Elmendorf tear resistance, wrinkle recovery angles and durable press rating with blocks after removing the effects of ironing, laundering and nitrogen content.

Variable	d.f.	Sum of Squares	Mean Square	F Value
Percent add-on	2	0.2131	0.1065	1.02
Bursting strength	2	34.7643	17.3822	1.91
Elmendorf tear resistance (warp)	2	514.1201	257.0600	2.80
Elmendorf tear resistance (filling)	2	3463.0427	1731.5213	4.38*
Wrinkle recovery angle (warp)	2	13.9401	6.9700	2.18
Wrinkle recovery angle (filling)	2	5.2290	2.6145	1.62
Durable press rating	2	0.1186	0.0593	1.65

* $F_{2,10}(.05) = 4.10$.

Table 5. Analysis of variance of total percent add-on with blocks, ironing, laundering and nitrogen content of yardage fabric.

Source of Variation	d. f.	Sequential Sume of Squares	Mean Square	F Value
Blocks	2	1.0732	0.5366	5.14*
Ironing	1	0.0193	0.0193	0.19
Unlaundered vs. laundered	1	25.8483	25.8483	248****
Laundering once vs. 12, 24, 36 and 48 times	1	3.2447	3.2447	31.14***
Laundering 12, 24, 36 and 48 times	3	0.4331	0.1444	1.39
Nitrogen content	1	0.0909	0.0909	0.87
$(\text{Nitrogen content})^2$	1	0.0004	0.0004	0.00
Error	13	1.3544	0.1042	
Total	23	32.0644		

* 5 percent level of significance.
*** .1 percent level of significance.
****.01 percent level of significance.

therefore Hypothesis 4b has been accepted.

The total add-on decreased significantly (Table 5) during the first laundering ($\alpha = .0001$) and between the first and twelfth laundering ($\alpha = .0001$) indicating the presence of finishes that were not chemically reacted with the cotton. Such finishes are usually removed by washing. Hypothesis 2 has been rejected since changes in percent add-on were observed after laundering one and 12 times.

Percent add-on extractable with water and HCl accounted for less of the decrease after laundering than did the perchloroethylene and ethanol extractable fractions (Table 6). Major decreases in perchloroethylene and ethanol extractable fractions occurred during the first laundering (Figure 5 and Figure 6). Most of the perchloroethylene extractable finishes had been removed by 12 launderings. Approximately half of the ethanol extractable finishes remained after the first laundering and on throughout 48 launderings.

Percent add-on includes both nitrogen containing and non-nitrogen containing finishes. In order to relate to the compounds added in the durable press finishing process, it is necessary to examine the nitrogen content. The weight of nitrogen represents only a very small portion of the total weight of a finish such as DMDHEU.

Table 6. Average percent add-on of unironed yardage fabric. *

Number of Launderings	Before Extraction	Extractable with Perchloroethylene	Extractable with Ethanol	Extractable with Water	Extractable with 0.1 N HCl
0	9.78	1.42	1.90	0.76	5.60
1	7.93	0.46	0.92	0.50	6.05
12	7.05	0.06	0.85	0.57	5.57
24	6.88	0.05	0.84	0.48	5.48
36	6.45	0.09	0.77	0.51	5.12
48	6.81	0.02	0.83	0.53	5.48

* Average of three determinations of one sample from each of the three blocks.

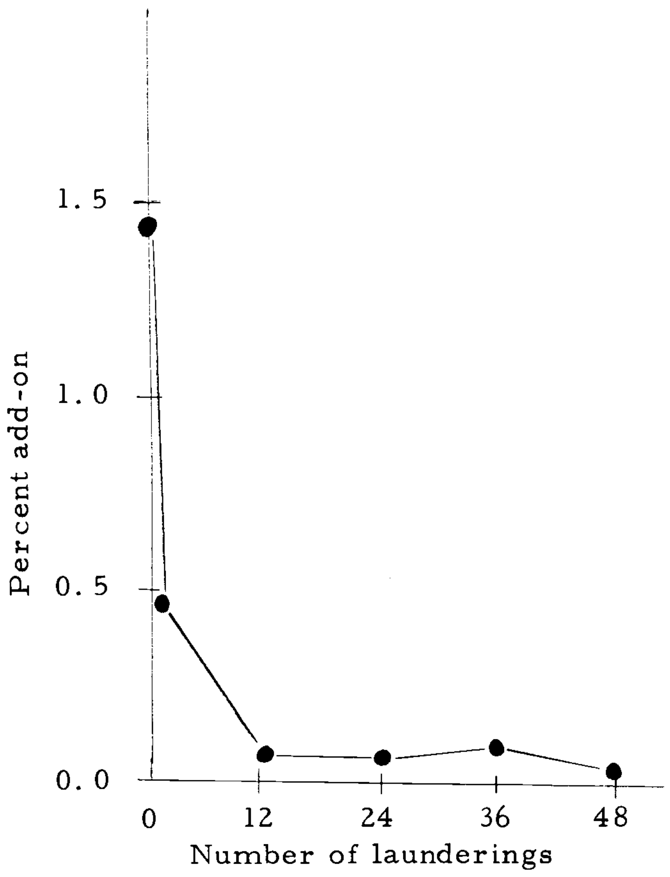


Figure 5. Percent add-on extractable with perchloroethylene from unironed yardage fabric.

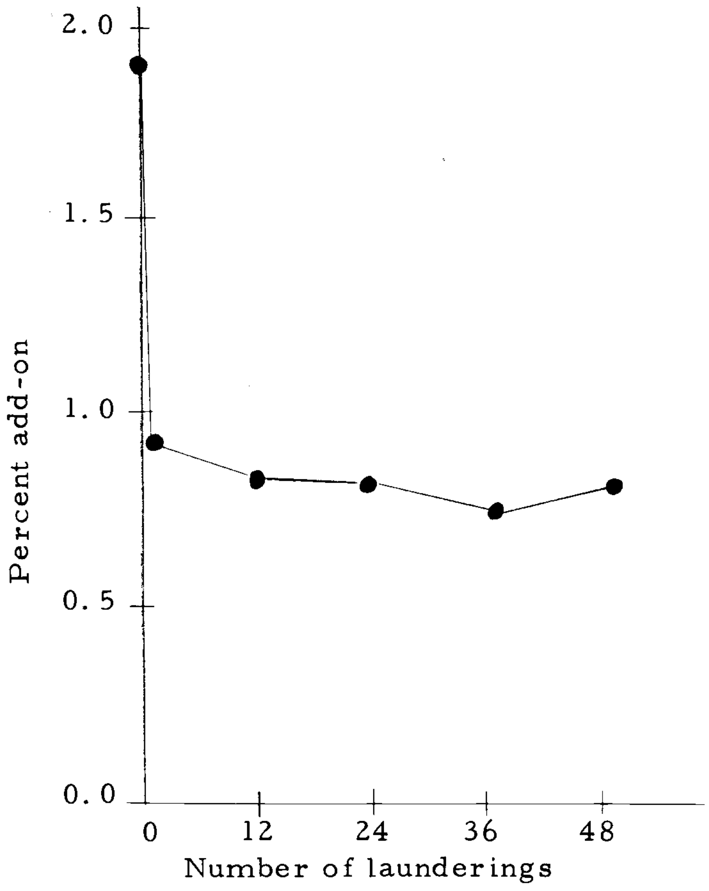


Figure 6. Percent add-on extractable with ethanol from unironed yardage fabric.

Nitrogen Content

There was no significant difference in nitrogen content among blocks (Table 7) after removing the effects of ironing and laundering. Therefore, Hypothesis 1 has been accepted.

Error due to variation among samples treated alike was not significantly greater than error among specimens from the same sample (Table 7). This was further indication that no significant difference in nitrogen content occurred among blocks, since the samples at each laundry level came from different blocks.

There appeared to be a significant ($\alpha = .05$) difference in nitrogen content caused by ironing (Table 7). Figure 7 shows that the nitrogen content of ironed and laundered samples was consistantly lower than for unironed samples. At this level of significance and with fewer ironed and laundered samples than unironed samples, it is possible that there is no real difference due to ironing.

Total nitrogen, like total percent add-on decreased markedly during the first laundering (Figure 7). As with total percent add-on, this was highly significant ($\alpha = .0001$) (Table 7). There was no significant decrease in nitrogen content after the first laundering, indicating that most of the unreacted nitrogenous compounds had been removed. Hypothesis 3 has been rejected on the basis of these results.

Table 7. Analysis of variance of total nitrogen content of yardage fabric.

Source of Variation	d.f.	Partial Sum of Squares	Mean Square	Value
Blocks	2	0.1880	0.0940	1.51
Ironing	1	0.4899	0.4899	7.86*
Unlaundered vs. laundered	1	19.5594	19.5594	314****
Laundering 1, 12, 24, 36 and 48 times	4	0.2198	0.0549	0.88
Interaction of not ironing and laundering with ironing and laundering	1	0.3914	0.3914	6.30*
Interaction of ironing and laundering 1, 12, 24, 36 and 48 times	4	0.3104	0.0776	1.25
Residual error	10	0.6225	0.0623	0.74
Sampling (specimen) error	74	6.2351	0.0843	
Total	96	28.0165		

* 5 percent level of significance.
**** 0.01 percent level of significance.

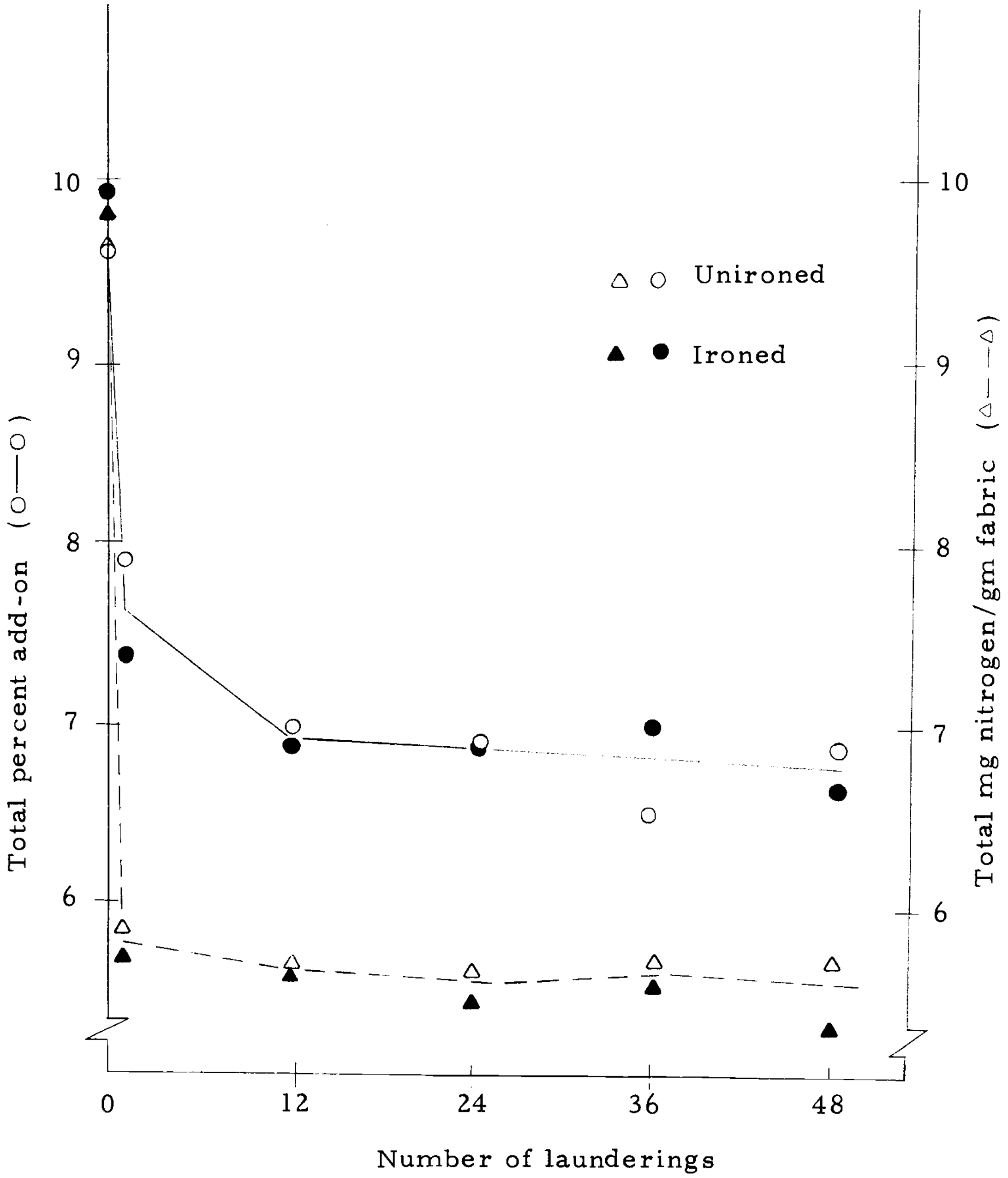


Figure 7. Total percent add-on and total nitrogen content of yardage fabric.

It should be noted at this point, that percent add-on was calculated using the weight of the specimen after extraction with all four solvents. This was not possible for nitrogen, since nitrogen analysis destroys the specimen so further extractions on the same specimen are impossible. Therefore, total nitrogen content was expressed as the weight of nitrogen per gm of fabric before extractions. For a particular solvent, the nitrogen is expressed as change in nitrogen content effected by extraction with that solvent relative to a nitrogen content prior to extraction with that solvent.

The decreases in nitrogen content associated with perchloroethylene and ethanol extraction occurred primarily during the first laundering (Figure 9). Only the HCl extractable portion (Figure 8) continued to decrease slightly after more than one laundering. The water extractable nitrogen fraction (Table 8) showed no definite trend with increasing numbers of launderings. Once the fabric had been laundered, little change occurred in nitrogen concentration.

Vail, et al. (49) reported that although partial hydrolysis of the crosslinks may occur and may affect wrinkle properties, little if any nitrogen is removed from the fabric during use. Any hydrolysis that does occur is probably at the bonding site between DMDHEU and cellulose, since DMDHEU is resistant to ring cleavage (36).

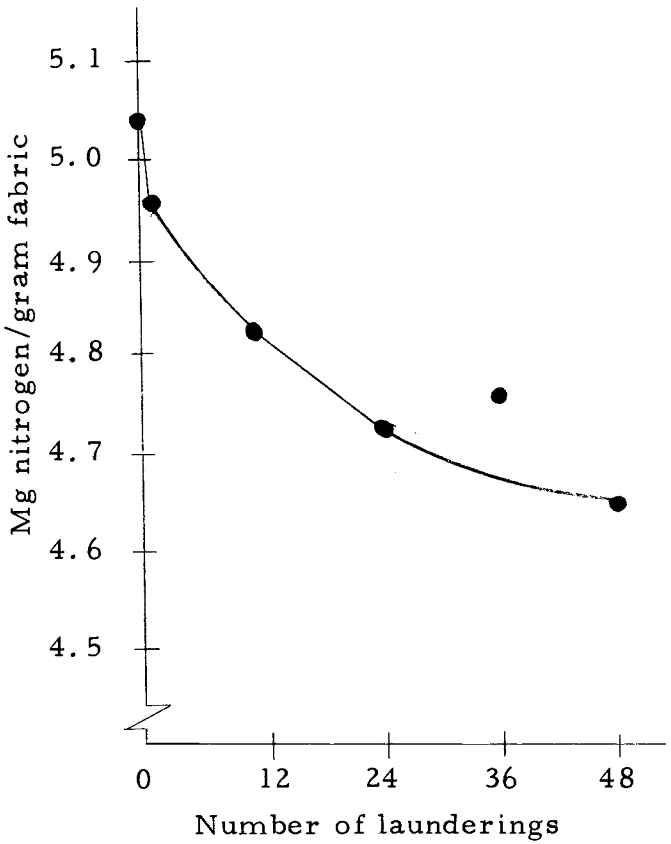


Figure 8. Decrease in nitrogen content of unironed fabric by extraction with 0.1 N HCl.

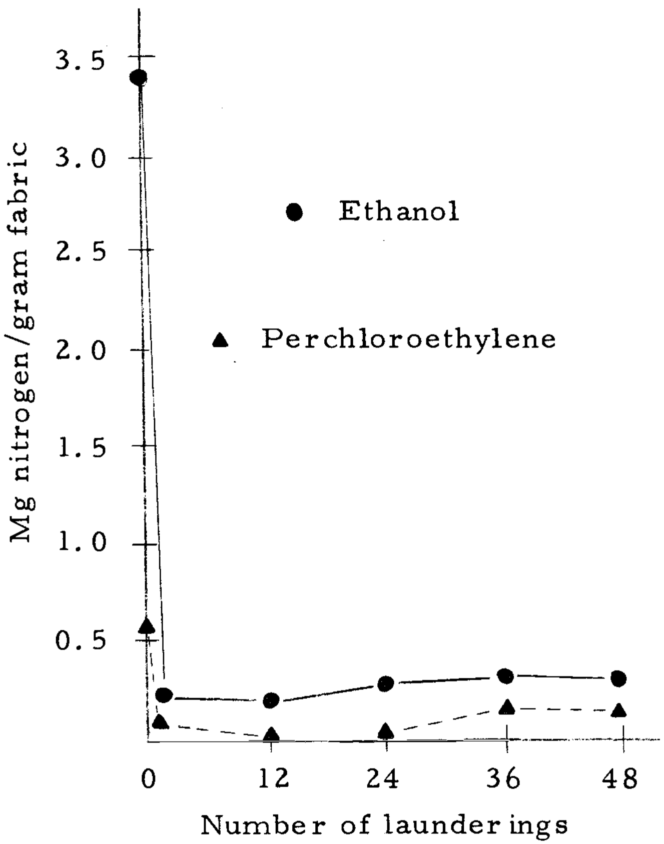


Figure 9. Decrease in nitrogen content of unironed fabric by extraction with ethanol and perchloroethylene.

Table 8. Average nitrogen content of unironed yardage fabric. *

Number of Launderings	Before Extraction	Extractable with Perchloroethylene	Extractable with Ethanol	Extractable with Water	Extractable with 0.1 N HCl
0	9.73	0.64	3.43	0.69	5.04
1	5.84	0.10	0.24	0.54	4.96
12	5.68	-0.03	0.23	0.65	4.82
24	5.57	-0.07	0.30	0.61	4.72
36	5.66	0.17	0.24	0.50	4.75
48	5.68	0.18	0.27	0.58	4.64

* Average of three determinations on one sample from each of the three blocks in mg nitrogen/gm fabric.

Bursting Strength

Although cotton yardage fabric differed from cotton shirt fabric used in the W103 study, the bursting strength results for the yardage (Figure 10) were about the same as the mean for the laundered only and worn and laundered shirts reported by Wylie and Erickson (57) for 0, 12 and 24 launderings.

The yardage fabric that had been ironed and laundered and that had been laundered 36 and 48 times did not react to the ball burst test the same as unironed samples laundered fewer times. A separation of threads and fibers occurred in the fabric area between the pressure from the ball and the ring clamp. This made it difficult to determine exactly when the break occurred and contributed to more variable results among specimens treated alike.

The increase in bursting strength during the first laundering (Figure 10) was not significant at the five percent level (Table 9). This increase could have been due to the effect of laundering or to loss of finish. The possibility of shrinkage contributing to the increase was examined. However, thread counts did not indicate that shrinkage had occurred.

Hypothesis 4c, Hypothesis 5 and Hypothesis 6 were accepted because significant differences in bursting strength associated with ironing, laundering and nitrogen content were not observed in this study.

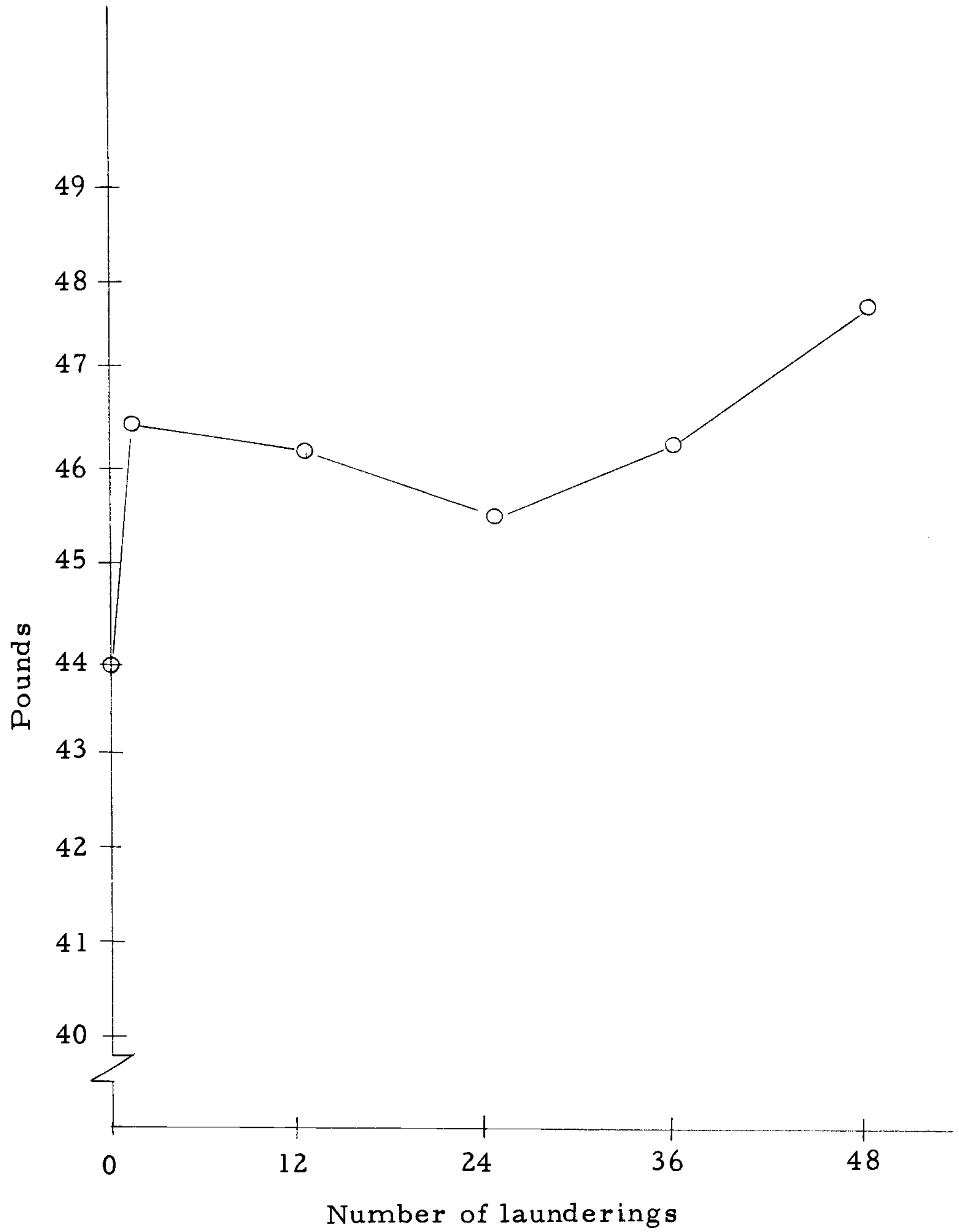


Figure 10. Bursting strength of unironed yardage fabric.

Table 9. Analysis of variance of bursting strength with blocks, ironing, laundering and nitrogen content of yardage fabric.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	35.4900	17.7450	1.93
Ironing	1	14.7606	14.7606	1.61
Unlaundered vs. laundered	1	30.6156	30.6156	3.34*
Laundering 1, 12, 24, 36 and 48 times	4	19.1158	4.7790	0.52
Nitrogen content	1	0.5531	0.5531	0.06
$(\text{Nitrogen content})^2$	1	1.8707	1.8707	0.20
Error	13	119.2191	9.1707	
Total	23	221.6250		

* 9 percent level of significance.

Elmendorf Tear Resistance

The tear resistance of the yardage fabric (Figure 11) was slightly higher than Wylie and Erickson (57) reported for the cotton shirt fabric after laundering 12 and 24 times. The difference between warp and filling tear resistance was probably related to the ribbed construction of broadcloth, where warp yarns predominate on the fabric surface or possibly to the finer warp yarns.

Tear strength decreased with increasing numbers of launderings (Figure 11) and Hypothesis 7 was rejected. Except for the decreases occurring between the 36th and 48th launderings, all strength losses were significant ($\alpha = .01$) in both the warp and filling directions (Table 10 and Table 11). This was related only to the effect of laundering and not to the nitrogen containing finishes, which did not change significantly (Table 7) after the first laundering. Hypothesis 8 was accepted because analysis of variance indicated that there was no linear or quadratic relationship of Elmendorf tear resistance with nitrogen content (Table 10 and Table 11).

Ironing did not alter significantly the effects of laundering on tear resistance (Table 10 and Table 11) confirming Hypothesis 4d.

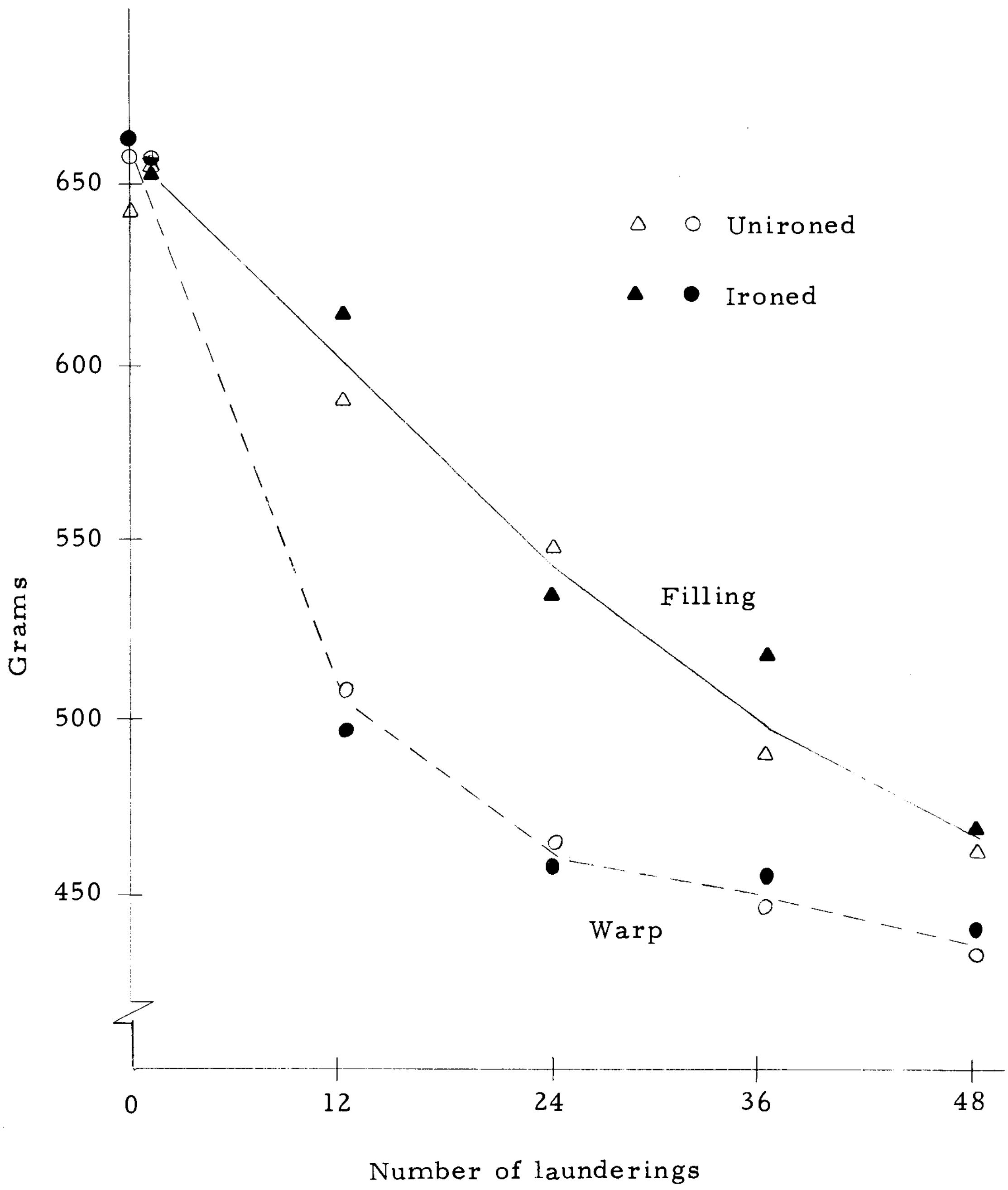


Figure 11. Elmendorf tear resistance of yardage fabric.

Table 10. Analysis of variance of warp Elmendorf tear resistance with blocks, ironing, laundering and nitrogen content.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	4508.3333	2254.1666	24.60
Ironing	1	46.7222	46.7222	0.51
Unlaundered vs. laundered	1	83921.5577	83921.5577	915****
Laundering once vs. 12, 24, 36 and 48 times	1	114136.2779	114136.2779	1245****
Laundering 12 vs. 24, 36 and 48 times	1	11003.2450	11003.2450	120****
Laundering 24 vs. 36 and 48 times	1	1047.8000	1047.8000	11.43**
Laundering 36 vs. 48 times	1	245.6860	246.6860	2.68
Nitrogen content	1	61.7274	61.7274	0.67
$(\text{Nitrogen content})^2$	1	137.0712	137.0712	1.50
Error	13	1191.4125	91.6471	
Total	23	216299.8333		

** 1 percent level of significance.
*** 0.1 percent level of significance.
*** 0.01 percent level of significance.

Table 11. Analysis of variance of filling Elmendorf tear resistance with blocks, ironing, laundering and nitrogen content of yardage fabric.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	3246.3330	1623.1665	2.04
Ironing	1	709.3888	709.3888	0.90
Unlaundered vs. laundered	1	36676.1731	36676.1731	46.42****
Laundering once vs. 12, 24, 36 and 48 times	1	54602.3292	54602.3292	69.10****
Laundering 12 vs. 24, 36 and 48 times	1	27236.5783	27236.5783	34.47***
Laundering 24 vs. 36 and 48 times	1	10397.6145	10397.6145	13.16**
Laundering 36 vs. 48 times	1	1854.0048	1854.0048	2.35
Nitrogen content	1	42.6815	42.6815	0.05
(Nitrogen content)^2	1	282.6675	282.6675	0.36
Error	13	10272.0621	790.1586	
Total	23	145319.8333		

** 1 percent level of significance.
*** .1 percent level of significance.
**** .01 percent level of significance.

<u>Wrinkle Recovery Angles</u>

Warp or filling wrinkle recovery angles of laundered yardage fabric (Figure 12) were the minimum 135° (average of warp and filling) found necessary for consumer satisfaction in Stover's (45) study. This was lower than the 140° minimum for satisfactory performance cited by Franklin, <u>et</u> <u>al</u>.(17).

Hypothesis 4e was accepted because there does not appear to be a real difference in wrinkle recovery angles after laundering caused by ironing (Table 12 and Table 13). The apparent difference among blocks was again ascribed to non-random sampling among blocks for ironed and laundered samples.

Highly significant ($\alpha = .0001$) decreases in wrinkle recovery angles occurred during the first laundering and prior to the twelfth laundering (Table 12 and Table 13). These results caused rejection of Hypothesis 9, that laundering does not affect wrinkle recovery angles. No significant changes were observed after the twelfth laundering.

The decrease in wrinkle recovery angles with laundering could not be accounted for on the basis of differences observed in nitrogen content. When wrinkle recovery angles were analyzed with laundering and nitrogen content as covariants (Table 12 and Table 13) there was no significant relationship with nitrogen and Hypothesis 10 was accepted.

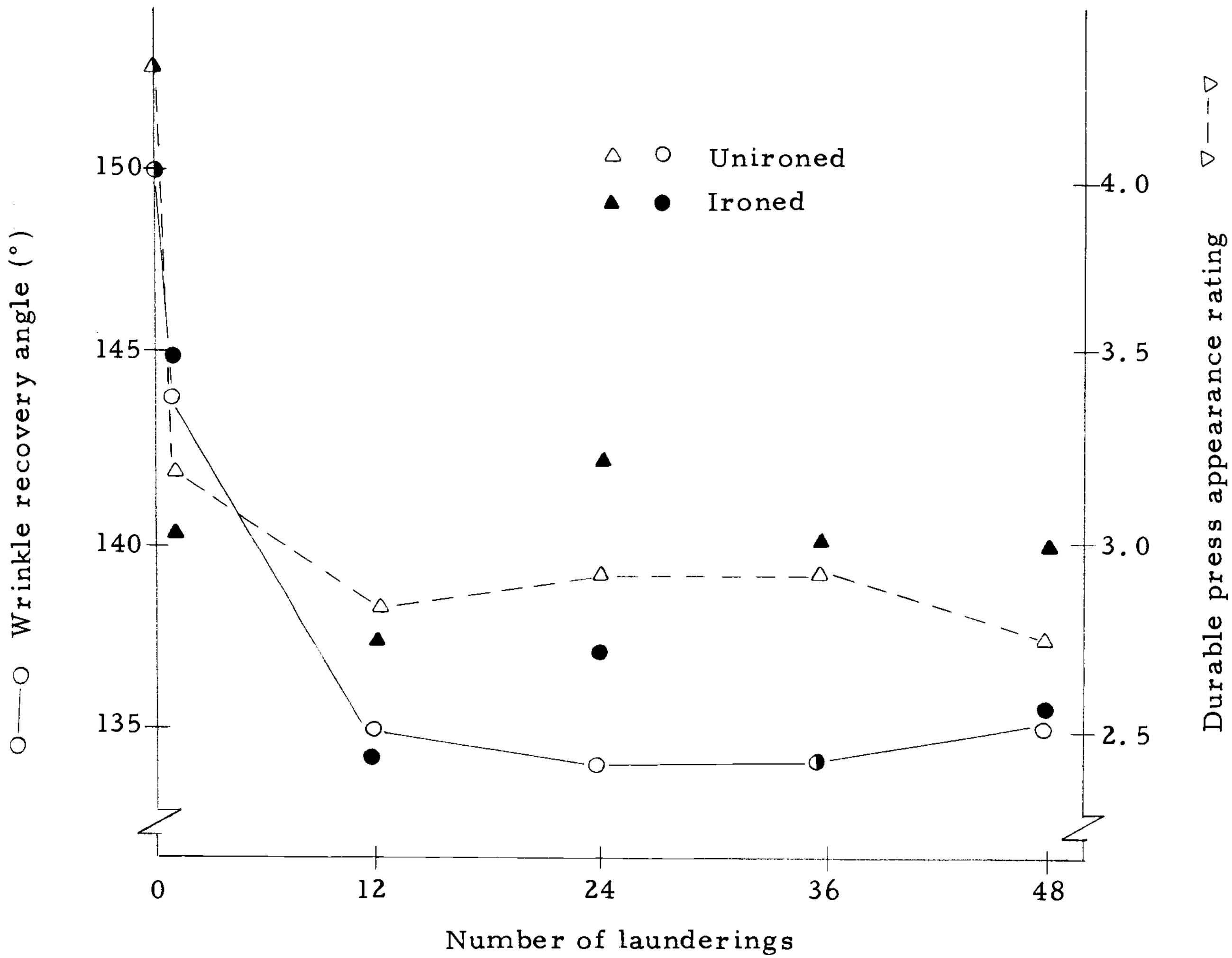


Figure 12. Wrinkle recovery angle (mean of warp and filling) and durable press appearance rating of yardage fabric.

Table 12. Analysis of variance of wrinkle recovery angles (filling) on blocks, ironing, laundering and nitrogen content of yardage fabric.

Source of Variation	d. f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	14.2500	7.1250	4.60
Ironing	1	0.5000	0.5000	0.32
Unlaundered vs. laundered	1	592.3125	592.3125	382****
Laundering once vs. 12, 24, 36 and 48 times	1	279.2316	279.2316	180****
Laundering 12, 24, 36 and 48 times	3	5.7725	1.9241	1.24
Nitrogen content	1	0.2528	0.2528	0.16
(Nitrogen content)^2	1	0.0655	0.0655	0.04
Error	13	20.1150	1.5473	
Total	23	912.5000		

**** .01 percent level of significance.

Table 13. Analysis of variance of wrinkle recovery angles (warp) on blocks, ironing, laundering and nitrogen content of yardage fabric.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	37.7500	18.8750	5.95*
Ironing	1	12.5000	12.5000	3.94
Unlaundered vs. laundered	1	633.5048	633.5048	199****
Laundering once vs. 12, 24, 36 and 48 times	1	193.3688	193.3688	61****
Laundering 12, 24, 36 and 48 times	3	2.6852	0.8951	0.28
Nitrogen content	1	1.3842	1.3842	0.44
$(\text{Nitrogen content})^2$	1	2.0965	2.0965	0.66
Error	13	41.2026	3.1694	
Total	23	924.5000		

* 5 percent level of significance.

**** .01 percent level of significance.

Durable Press Appearance Ratings

The yardage fabric had lower durable press appearance ratings than was reported for the cotton shirts (31) after 12 and 24 launderings. Shirts laundered with the yardage had the same rating as the cotton shirts in the W103 study, indicating some difference between shirt and yardage fabrics. The unpressed yardage controls were 0.2 rating units lower than the steam pressed controls in the W103 study. Durable press appearance ratings were 1.0 rating units lower than those of Stover (45) for cotton shirts after one laundering. The laundering conditions were not described in Stover's report.

Durable press ratings of the yardage fabric decreased in a manner similar to the wrinkle recovery angle (Figure 13). Both wrinkle recovery angle and durable press rating are related to fabric resiliency.

Highly significant decreases in durable press ratings (Table 14) occurred during the first laundering ($\alpha = .0001$) and between the first and twelfth laundering ($\alpha = .01$). No significant changes occurred after the twelfth laundering. Hypothesis 11 that laundering does not affect the durable press appearance rating was rejected on the basis of these results.

Hypothesis 4f was confirmed because there were no significant changes in durable press ratings caused by ironing (Table 14).

Table 14. Analysis of variance of durable press rating with blocks, ironing, laundering and nitrogen content.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	0.0758	0.0379	1.17
Ironing	1	0.0235	0.0235	0.72
Unlaundered vs. laundered	1	6.6174	6.6174	203****
Laundering once vs. 12, 24, 36 and 48 times	1	0.2834	0.2834	8.72**
Laundering 12, 24, 36 and 48 times	3	0.2091	0.0697	2.14
Nitrogen content	1	0.0972	0.0972	2.99
$(\text{Nitrogen content})^2$	1	0.2100	0.2100	6.46*
Error	13	0.4224	0.0325	
Total	23	7.9196		

* 5 percent level of significance.

** 1 percent level of significance.

**** .01 percent level of significance.

Hypothesis 12a was rejected since there appeared to be a significant ($\alpha = .05$) quadratic relationship of durable press rating with nitrogen content (Table 14).

The nitrogen extracted with each of the four solvents was then analyzed as covariants with laundering (Table 15, Table 16, Table 17 and Table 18) to determine if any one of these fractions accounted for the apparent relationship with total nitrogen and durable press rating. Perchloroethylene, ethanol and water extractable nitrogen fractions (Figure 9) decreased during the first laundering and the second through twelfth launderings. The HCl extractable nitrogen (Figure 8) decreased slightly with increased laundering. Hypothesis 12b, Hypothesis 12c and Hypothesis 12d were accepted because perchloroethylene, ethanol and water extractable nitrogen fractions were not linearly or quadratically related to nitrogen content.

The HCl extractable nitrogen (Table 18) was the only nitrogen fraction having a significant ($\alpha = .01$) quadratic relationship with the durable press appearance rating during laundering. Therefore, Hypothesis 12e was rejected.

Table 15. Analysis of variance of durable press rating on blocks, ironing, laundering and decrease in nitrogen content by perchloroethylene extraction.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	0.0758	0.0379	0.68
Ironing	1	0.0235	0.0235	0.42
Unlaundered vs. laundered	1	6.6174	6.6174	119****
Laundering once vs. 12, 24, 36 and 48 times	1	0.2834	0.2834	5.10*
Laundering 12, 24, 36 and 48 times	3	0.1900	0.0633	1.14
Perchloroethylene extractable nitrogen	1	0.0020	0.0020	0.04
(Perchloroethylene extractable nitrogen)^2	1	0.0053	0.0053	0.10
Error	13	0.7221	0.0555	
Total	23	7.9196		

* 5 percent level of significance.
**** .01 percent level of significance.

Table 16. Analysis of variance of durable press rating on blocks, ironing, laundering and decrease in nitrogen content by ethanol extraction.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	0.0758	0.0379	0.75
Ironing	1	0.0235	0.0235	0.46
Unlaundered vs. laundered	1	6.6174	6.6174	131****
Laundering once vs. 12, 24, 36 and 48 times	1	0.2834	0.2834	5.61*
Laundering 12, 24, 36 and 48 times	3	0.1900	0.0633	1.25
Ethanol extractable nitrogen	1	0.0727	0.0727	1.44
$(\text{Ethanol extractable nitrogen})^2$	1	0.0002	0.0002	0.00
Error	13	0.6566	0.0505	
Total	23	7.9196		

* 5 percent level of significance.
**** .01 percent level of significance.

Table 17. Analysis of variance of durable press rating on blocks, ironing, laundering and decrease in nitrogen content by water extraction.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	0.0758	0.0379	0.69
Ironing	1	0.0235	0.0235	0.43
Unlaundered vs. laundered	1	6.6174	6.6174	120****
Laundering once vs. 12, 24, 36 and 48 times	1	0.2834	0.2834	5.14*
Laundering 12, 24, 36 and 48 times	3	0.1900	0.0633	1.15
Water extractable nitrogen	1	0.0030	0.0030	0.06
(Water extractable nitrogen)^2	1	0.0100	0.0100	0.18
Error	13	0.7165	0.0551	
Total	23	7.9196		

* 5 percent level of significance.
**** .01 percent level of significance.

Table 18. Analysis of variance of durable press rating with blocks, ironing, laundering and decrease in nitrogen content by 0.1 N HCl extraction.

Source of Variation	d.f.	Sequential Sum of Squares	Mean Square	F Value
Blocks	2	0.0758	0.0379	1.16
Ironing	1	0.0235	0.0235	0.72
Unlaundered vs. laundered	1	6.6174	6.6174	204****
Laundering once vs. 12, 24, 36 and 48 times	1	0.2834	0.2834	8.72**
Laundering 12, 24, 36 and 48 times	1	0.1900	0.0633	1.95
HCl extractable nitrogen	1	0.0012	0.0012	0.04
(HCl extractable nitrogen)^2	1	0.3060	0.3060	9.42**
Error	13	0.4224	0.0325	
Total	23	7.9196		

* 5 percent level of significance.
** 1 percent level of significance.
**** .01 percent level of significance.

SUMMARY

The objectives of this study were

1. to establish a procedure for using the Technicon Kjeldahl AutoAnalyzer on 100 percent cotton DMDHEU durable press finished shirt fabric used in Western Regional Project W103 or a similar fabric,
2. to study the nitrogen content (total and extractable) in this fabric after increased numbers of launderings and
3. to determine if a relationship exists between nitrogen content (total and extractable) and observed performance (appearance and durability) characteristics of the 100 percent cotton shirt fabric or a similar fabric.

The Technicon AutoAnalyzer equipped with continuous digestion apparatus can be used to analyze the small amounts of nitrogen present on durable press cotton fabrics. A method is described which permits the analysis of 20 cotton samples per hour. The automated technique also requires less space and less glassware than the conventional micro- and macro-Kjeldahl techniques. Nitrogen is measured with the same or better precision than by conventional micro-Kjeldahl methods.

DMDHEU durable pressed cotton broadcloth shirt fabric was examined for bursting strength, Elmendorf tear resistance, wrinkle

recovery angle, durable press rating, percent add-on and nitrogen content. The fabric was laundered only or ironed and laundered 0, 1, 12, 24, 36 and 48 times.

Ironing did not significantly change any of the physical properties studied.

A significant decrease in total nitrogen content occurred only during the first laundering. Perchloroethylene, ethanol and water extractable nitrogen containing fractions decreased during the first laundering, but not during subsequent launderings. There was a gradual decrease in the 0.1 N HCl extractable nitrogen fraction with increased laundering.

Significant tear strength losses occurred with increasing numbers of launderings through 36 launderings. Changes in tear resistance were not related to changes in nitrogen content. An increase in bursting strength occurred during the first laundering, however this was not significant.

Total percent add-on, wrinkle recovery angles and durable press appearance ratings decreased significantly during the first laundering and between the first and twelfth laundering. No significant changes occurred after the twelfth laundering.

When nitrogen and laundering were analyzed as covariants with durable press rating, there was a quadratic effect of nitrogen content on the durable press rating. Further analysis indicated that this was due to the 0.1 N HCl extractable nitrogen fraction. A similar relationship was not observed with wrinkle recovery angle.

RECOMMENDATIONS FOR FURTHER STUDY

The Technicon AutoAnalyzer equipped with continuous digestor could not be used on polyester cotton blends unless they were first digested. The digestion block described by Schuman, Staley and Knudsen (41) and now available from Technicon Corporation would eliminate the digestion helix and the problem of passing partially digested polyester fibers through the sampling device. It might reduce the error occurring during partial acid hydrolysis of specimens prior to being sampled. The disadvantage is that digestion and colormetric analysis are no longer continuous processes.

The digestion block should be investigated, since many durable press items are blends of cotton or rayon and polyester.

In studying durable press fabrics, it is important to examine them after one or two launderings. Laundering removes residual unreacted finish. Laundering once or twice establishes the initial effect of laundering on the properties being investigated.

Although the amount of finish along the length of the yardage involved in this study did not vary significantly, the finish on the considerable length of fabric involved in manufacturing a number of garments may vary. Quantitative analysis of finishes on garments prior to a wear study would allow random sampling if differences did exist, even though determination of changes in finish might not be the chief objective of the study. This would reduce the chance of drawing conclusions about durable press characteristics or strength that were probably associated with variations in finish among fabrics throught to be the same.

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APPENDICES

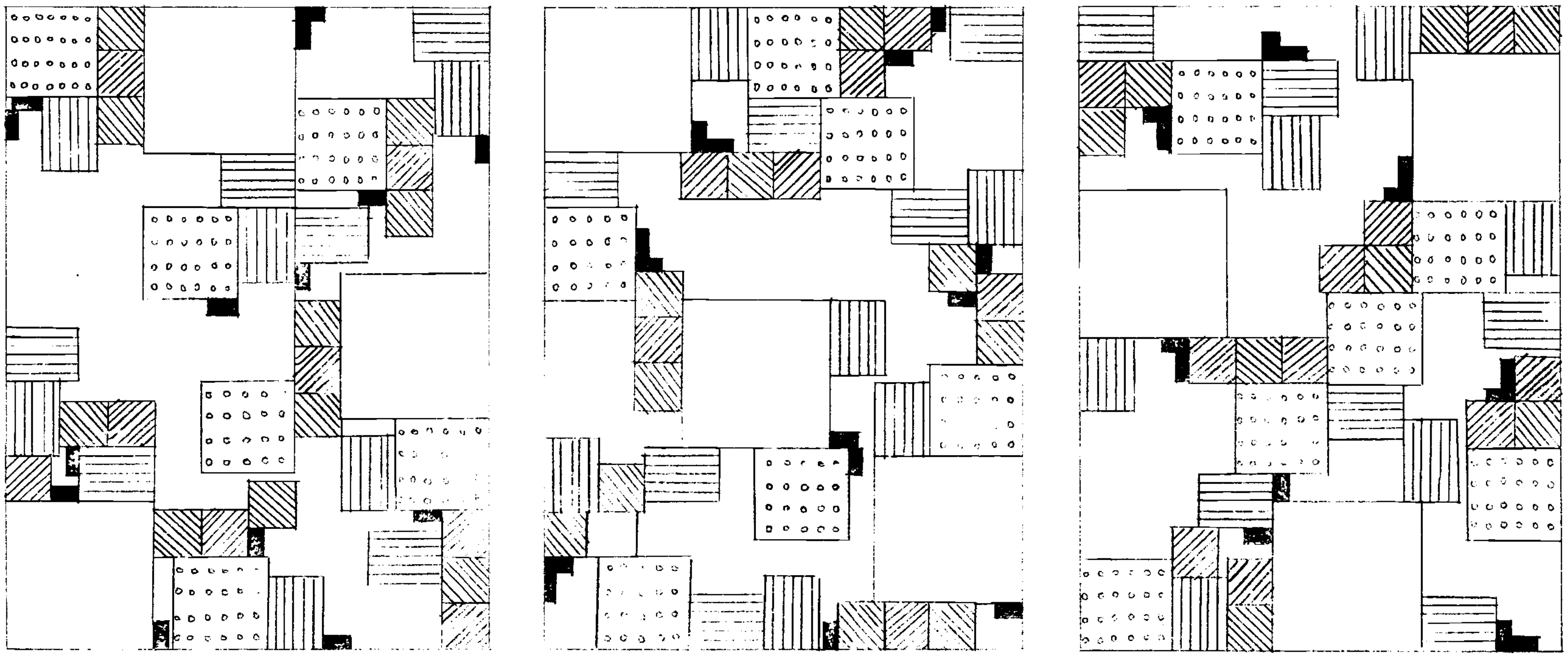
APPENDIX A

Sampling Plan

Number of Launderings or Launderings and Ironings	Sample Number	Yards From End of Bolt	Cutting Diagram
Unlaundered	1	45	Y
	2	24	X
	3	7	Z
Laundered 1x	4	42	X
	5	27	Z
	6	10	Y
Laundered 12x	7	44	X
	8	23	Y
	9	11	Z
Laundered 24x	10	41	Y
	11	25	Z
	12	6	X
Laundered 36x	13	43	Z
	14	28	X
	15	8	Y
Laundered 48x	16	40	Z
	17	26	Y
	18	9	X
Ironed 1x	22	22	X
Ironed and Laundered 1x	23	12	X
Ironed and Laundered 12s	20	39	Y
Ironed and Laundered 24x	24	5	Y
Ironed and Laundered 36x	21	29	Z
Ironed and Laundered 48x	19	46	Z

APPENDIX B

Specimen Cutting Diagrams



X Y Z

Elmendorf tear resistance

Nitrogen before and after extractions

Wrinkle recovery angle

Bursting strength

Percent add-on

Scale: 1.0 cm equals 2.5 inches

APPENDIX C

Estimated Values of β_0, β_1, β_2 and β_3 by Regression for Each Day's Standard Curve

Day	$\hat{\beta}_0$	$\hat{\beta}_1$	$\hat{\beta}_2$	$\hat{\beta}_3$
1	-0.0007	0.4577****	0.00017	-0.0000022
2	-0.0267***	0.4906****	0.00046*	-0.0000037
3	-0.0165****	0.4910****	0.00010	0.0000001
4	-0.0183*	0.5318****	-0.00063	0.0000123
5	0.0010	0.4883****	0.00016	-0.0000019
6	-0.0108	0.5000****	-0.00018	0.0000021
7	-0.0087**	0.4747****	0.00067****	-0.0000106****

* 5 percent level of significance.
** 1 percent level of significance.
*** 0.5 percent level of significance.
**** 0.01 percent level of significance.

APPENDIX D

Summary of Physical Properties Before and After Laundering Unironed Yardage Fabric

Number of Launderings	Durable Press Rating*	Wrinkle Recovery Angle (°)**	Ball Burst*** Strength (lbs)	Elmendorf Tear Resistance (gm)***	
				Warp	Filling
0	4.3	150	44.0	659	645
1	3.2	144	46.5	657	654
12	2.8	134	46.3	513	589
24	2.9	134	45.6	465	549
36	2.9	134	46.3	447	487
48	2.7	135	47.9	434	462

* Average of three judges ratings of one sample from each of three blocks.

** Average of six warp and six filling specimens from one sample from each of three blocks.

*** Average of five specimens from one sample from each of three blocks.

APPENDIX E

Summary of Physical Properties Before and After Ironing and Laundering Yardage Fabric

Number of Ironings and Launderings	Durable Press Rating*	Wrinkle Recovery Angle (°)**	Ball Burst Strength (lbs)***	Elmendorf Tear Resistance (gm)***	
				Warp	Filling
Ironed only	4.3	150	45.3	678	696
1	3.0	145	48.1	654	648
12	2.7	135	53.1	498	612
24	3.2	138	48.0	460	506
36	3.0	134	44.5	460	532
48	3.0	135	51.0	444	468

* Average of three judges ratings of one sample two times.
** Average of six warp and six filling specimens from one sample.
*** Average of five specimens from one sample.