EFFECTS OF LAUNDERING VARIABLES ON FLAME RETARDANT PROPERTIES OF TREATED POLYESTER FLANNELETTE

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES AND PLATES

FIGURES

PLATES

CHAPTER I

INTRODUCTION

Each year approximately 2,000,000 people suffer significant burn injuries in the U. S. The public Health Service reported that fire and explosion kill about 8,000 people each year and rank third (after vehicles and falls) as a cause of accidental death (1). It has been estimated that 6,200 Americans die from fires in their homes, and 1100 of those are children (7).

Clothing, rather than bedding or upholstery, is the type of textile material most often ignited. Burn injuries involving clothing can be severe and are expensive to treat. Treatment costs and earning losses are estimated at more than $250 million a year (1).

In burns involving children under ten, 40% of the garments involved are nightwear, 35% are blouses and shirts, and 25% are other types of clothing (7). Some 44% of all sleepwear burn cases involve children between the ages of 0 and 12 years of age. Of those, 55% are under six years of age (32).

Congress passed the first Federal Flammable Fabrics Act (FFA) in 1953 to eliminate unusually dangerous clothing such as the brushed rayon 'torch' sweaters. In 1967, the FFA was amended and strengthened. The most important feature added was to give the Commerce Department power to issue new flammability standards covering a variety of fabrics without the need of any additional legislation,

providing certain steps are followed. Those steps are: (1) a 'finding of need' must be published, (2) a proposed standard must be published, and (3) after all those interested have had their say, a new standard is issued (1).

A 'finding of need' has been published for sleepwear, underwear, and dresses for the young. One standard has been issued (DOC FF 3-71): Standard for the Flammability of Children's Sleepwear, Sizes 0-6X) (31). A proposed standard has been published for larger sizes (DOC FF 5-73): Proposed Standard for the Flammability of Children's Sleepwear, Sizes 7-14) (32). The proposed standard is essentially the same as DOC FF 3-71, but modified to recognize the ability of older children to take some protective measures. The final standards are expected later this year and would take effect in mid-1974.

Because of the standards for children's sleepwear, a great deal of research is being done to provide fabrics that will satisfy the requirements of the standard. To make a fabric that is suitable, use can be made of fibers that are inherently flame retardant, or the fabric can be treated with a finish to provide flame retardancy. Both of those approaches are being pursued, but efforts to find suitable answers are further complicated by another part of the ruling. The garments must maintain their flame retardant qualities through 50 washings and dryings.

Some washing variables (e. g. detergent, water hardness, and bleach) are detrimental to flame retardant finishes. Perkins reported that tetrakis(hydroxymethyl)phosphonium chloride (THPC) flame

retardant finishes for cotton fabrics became ineffective when laundered with soap in hard water (26). Reeves found that during laundering in hard water, calcium and magnesium were picked up by cation exchange from the wash water by the flame retardant finishes. The deposits that were formed from the calcium and magnesium reduced or inhibited the effectiveness of phosphorus-containing flame retardants. Those deposits were visible in photomicrographs of the fabric (28). Pacheco and Carfagno reported that in laundering a cotton fabric topically treated with an organo-phosphorus finish with a carbonate detergent in hard water, the effect of the flame retardant finish was destroyed in 25 launderings or less (25).

Because recent legislation in parts of Illinois, Florida, New York, and Indiana banned the use of phosphate-built detergents, the effect of carbonate-built and citrate-built detergents is important because those detergents are the two most effective replacements for phosphate-built detergents now known (30). Although carbonate-built detergents have shown a detrimental effect on an organo-phosphorus treated cotton flannelette, the effect of that detergent is unknown for other fibers or finishes. The effect of citrate-built detergents is unknown for any fiber or finish.

In unpublished work done at Kansas State University (17) and in a published study by Daigle (3), it was found that chlorine bleach had a detrimental effect on flame retardant finishes. Daigle (3) found that a THPC treated cotton flannelette failed after 10 launderings with bleach. Organo-phosphorus cotton flannelette failed after 25 launderings with chlorine bleach in the unpublished study (17).

The cost of flame retardant finishes for cellulosics is relatively high, and the finishes may give a less-than-desirable hand to the fabrics (27). For those reasons, producers are turning to man-made fibers for sleepers to produce garments that will pass the standard for sizes 0 through 6X. One of the newest fabric/fiber/finish combinations to be released is a tris (2,3-dibromopropyl) phosphate (DBP) polyester flannelette. This study was planned to study the effect of various laundry factors (detergent, water hardness, and bleach) on that material.

The objectives were:

(1) To investigate the effects of detergent, water hardness, and chlorine bleach on the flame retardant properties of a DBP polyester flannelette;

(2) To investigate the amount of calcium salts deposited on the treated flannelette; and

(3) To observe the microscopic appearance of the calcium deposit on the fabric after laundering under selected conditions.

CHAPTER II

DEFINITION OF TERMS

Char length - The distance from the edge of the specimen exposed to the flame to the upper edge of the burned, charred, or void area. It is the measured length the fabric tears when a weight is suspended from one corner after the fabric has been tested for flammability.

Hard water - Water that has calcium and magnesium ions dissolved in it. Hardness is measured in parts per million (ppm) or grains per gallon (gpg) (17.1 gpg = 1 ppm). Medium hard water is 90 to 170 ppm. Very hard water is more than 170 ppm hard.

Residual flame time - The amount of time a fabric continues to support flame after the source of ignition has been removed. It is measured in 0.1 seconds.

Sample - A piece of fabric used for laundering that later was cut into specimens for testing flammability.

Sequestering agents - Chemicals that form bonds with minerals in the water. These chemicals keep the minerals from depositing on fabrics.

Specimen - Each unit (8.9 cm by 25.4 cm) for which residual flame time and char length were determined.

CHAPTER III

REVIEW OF LITERATURE

To obtain background information for this study, literature in relation to the following was reviewed: (1) flame retardancy and phosphorus-bromine compounds; (2) laundering variables; (3) DOC FF 3-71 and the vertical flame test; and (4) tris(2,3-dibromopropyl) phosphate and treated polyester.

Flame Retardancy and Phosphorus-Bromine Compounds

Virtually all materials are flammable when using one or more identifiable atmospheres or conditions. Hence, flammability becomes a relative rather than an absolute matter (10). The manner in which flame retardant finishes work becomes an important factor of flame retardancy.

There are three theories of flame retardancy: (1) the gas theory, (2) the thermal theory, and (3) the chemical theory. In the gas theory, the flame retardant decomposes at the burning temperature to produce noncombustible gases or foams that dilute the flammable gases from the burning fabric to a concentration below the flaming limit, or by blanketing the material with an inert atmosphere, thus smothering the flame. In either case, the oxygen level of the atmosphere is either reduced or eliminated, thus causing a major change in the fuel-to-air ratio, which, in turn requires an appreciably higher ignition temperature than in the absence of the flame retardant (11) (16).

The thermal theory hypothesizes that affective flame retardants are capable of maintaining the fabric temperature below the minimum flaming limit. The flame retardant is able to either dissipate large quantities of energy internally or to conduct the energy away from the flame front at a rate equal to or greater than that at which it is supplied (10). The formation of Lewis acids (acceptors of electrons) at flaming temperatures catalyze the dehydration of the fabric to carbon and water and enable maintenance of the lowered temperature. The dehydration forms large carbonaceous aggregates that do not oxidize as easily so that flaming is inhibited (11) (16).

The chemical theory hypothesizes that the flame retardant acts as a catalyst in promoting degradation of the fabric in a manner other than that of the untreated fabrics. Non-flammable volatiles may be produced, or barriers may be formed at the surface of the fabric and in the neighboring space that interferes with the oxidation reactions. Oxidation is a free radical process involving hydrogen, oxygen, hydroxide, and other radicals. Addition of substances to achieve flame suppression often is attributed to the ability of the added substance to trap those radicals. Bromine compounds are a good example of this ability: $RBr + H^{\bullet} \rightarrow HBr + R^{\bullet}$. For flame inhibition to result the generated hydrocarbon radical must be less active than the hydrogen radical that is removed. In general, the previously mentioned radicals will be the most active species, and their removal snuffs out the flame. Bromine is superior to chlorine in the above reaction by a factor of two because of their respective molecular weights (21).

Phosphorus is more effective at low levels than any other

element taken alone. Phosphorus chemicals generally are recognized as the most suitable agents to suppress afterglow. The efficiency of phosphorus can be improved by other elements such as bromine and chlorine. Phosphorus-bromine compounds are perhaps the most efficient in the fire suppression sense of all fire retardants (21). Bromine acts independently of the phosphorus, and it acts almost completely in the vapor phase (5).

Washing Variables

Many organo-phosphorus compounds are effective flame retardants. A pick-up of the finish of approximately one percent is enough to reduce flammability significantly for fabrics treated with THPC (27). However, the absence of cation exchange properties is essential to a finish if it must continue to provide flame retardancy after repeated washings in hard water (27).

Fabrics with organo-phosphorus flame retardant finishes have been found to lose their flame retardancy after several washes in hard water. This has been attributed to deposition of calcium and magnesium through cation exchange. The calcium and magnesium ions interfer with esterification of the fiber constituents by the organo-phosphorus compounds that promotes dehydration during pyrolysis of the treated fabric and, consequently, prevents ignition by competing with oxidation reactions (21).

Soaps, carbonate-built detergents, or silicate-built detergents in solutions of moderately hard water leave deposits on fibers that block the flame retardancy of the finish (29). Cotton flannelette

treated with an organo-phosphorus flame retardant may be impaired by 25 washings or less in non-phosphate detergents or soaps. The cause for that impairment is that the use of soap, carbonate-built, or silicate-built detergents in solutions of moderately hard water leave deposits on fibers, which effects the flame retardancy of the finish. Under the same conditions with phosphate-built detergents, there is no detrimental effect, because no deposit is formed (25). Synthetic detergents (rather than soap) and soft water have been recommended to prevent lime soap deposits that impair performance (26). However, more than half of the households in the U. S., use hard water and do not have water softeners (18).

The sequestering action of an adequate level of phosphate detergents prevents solid residue from forming and depositing on fabric surfaces in typical home washing environments in hard water areas. Those phosphate detergents can restore the flame retardancy impaired by previous washings in non-phosphate detergents and soaps by dissolving the deposits (25).

Results of a soap and detergent survey by the Household and Personal Products Industry indicated that anti-phosphate legislation is staying about the same or waning. At present, there is no best substitute for phosphates as builders in detergents. If legal, nitrilo triactic acid (NTA) would be the best substitute followed by carbonate-built, citrate-built, silicate-built, and ethylenediaminetetraacetic acid (EDTA) built detergents (30).

Some flame retardant finishes also are affected when washed with chlorine bleach (3). In unpublished research done at Kansas

State University, washing with chlorine bleach produced detrimental effects on a treated cotton flannelette and a Nomex nylon (17).

Wash water temperature also may affect the amount of deposit on the fabric. Calcium and magnesium carbonate have a low solubility in cold water. Hence, it is important to keep the temperature of the wash water around 60°C; otherwise more of those precipitates will be available for deposit when a fabric is washed in cold water (6).

DOC FF 3-71 and the Vertical Flame Test

It has been stated that "Textile flammability is an illusive, inconsistent phenomenon that does not lend itself readily to laboratory measurement" (34).

The standard (DOC FF 3-71) for children's sleepwear is essentially a modification of AATCC test method 34-1969 Fire Resistance of Textile Fabrics. Until the children's sleepwear standard became law, the only test method recognized by public law was the 45° angle test. The vertical flame test of the standard and the 45° angle test usually are sufficient to indicate that increased amount of the flame retardant finish cause ignition to become more difficult. However, the reproducibility of test results for either test is not good because of the numerous variables involved (10).

The severity of the vertical flame test is at a maximum when the burner is applied for only the interval necessary for ignition of the sample. The usual interval is three seconds, which is the ignition time stipulated in DOC FF 3-71. With a longer application of the burner to fabrics of marginal flammability, the burning

of the fabric may be extinguished by less-than-ambient oxygen content of the burner plume (22). Burning experiments in enclosed spaces showed that oxygen depletion leading to flame extinction occurs even in relatively large volumes of air because convection is only partially effective in supplying air to the burning flame and in removing products of combustion and pyrolysis (24).

Sleepwear must pass the vertical flame test after 50 home washings and dryings. The criteria for passing are: (1) average char length no more than 17.8 cm for five replicate samples; (2) no specimen with a char length greater than 25.4 cm; and (3) no specimen with residual flame time over 10 seconds. The washings and dryings are done according to the AATCC test method 124-1969 "Appearance of Durable Press Fabrics After Repeated Home Launderings."

The standard does not specify water hardness even though the National Bureau of Standards recognizes the failure of flame retardant fabrics when washed in certain hard water areas. Water hardnesses of 0 to 150 ppm usually have no effect on flame retardancy performance of a finish when washed with AATCC detergent (12% phosphate).

However, LeBlanc and LeBlanc (20) demonstrated that water hardness should be specified when laundry studies are done. A water hardness of 150 ppm was added to the wash water. The fabrics were tested after 5, 10, 15, 25, and 50 washings in both high and low phosphate detergents (20). None of the fabrics failed yet Pacheco and Carfagno (25) and others reported that failure of finishes is related to water hardness. No explanation has been offered for this discrepancy.

The standard (DOC FF 3-71) also stipulates a laundry load weight of 1.8 kg. If there is an insufficient amount of fabric being tested, a filler or dummy cloth is to be used to bring the load weight up to 1.8 kg. There is no stipulation in DOC FF 3-71 about the kind of filler cloth to be used. Terry cloth, which is sometimes used as the filler cloth, scavenges deposits preferentially and could result in misleading results for the test fabric (12).

Pressing decreases the effectiveness of some flame retardant finishes, yet, the standard (DOC FF 4-71) allows pressing to obtain flat samples. The ester groups of the alkyl phosphonates are hydrolyzed at pressing temperatures (27). Line drying in sunlight is detrimental to the finishes because ultraviolet light degrades the finish. Machine drying did not have any deleterious effects because the temperature was not high enough to hydrolyze the ester groups (27).

Tris(2,3-dibromopropyl) Phosphate and Treated Polyester

Because it was the one studied and because of the vast numbers of flame retardant finishes, the only finish that will be discussed is tris(2,3-dibromopropyl) phosphate (DBP).

The chemical formula for DBP is: $(Br\text{-}CH_2\text{-}CHBr\text{-}CH_2O)_3\text{-}P{=}O$ (13). It is a pale viscous yellow liquid with a formula weight of 697.69 g/mole with 68.7% bromine and 4.4% phosphorus by weight. DBP is a nonreactive, water insoluable monomeric ester that requires a polymeric bonder for best adhesion to fabrics (11). The finish penetrates both cotton and polyester and produces durable finishes for blend fabrics (4) (5).

A DBP treated polyester and untreated polyester were compared. The DBP polyester had a lower oxygen index (amount of oxygen necessary to support combustion) with an increase in preignition temperature of the specimen than the untreated polyester. Both fabrics increased remarkably in smoke density after ignition, and reached a maximum smoke density in 30 to 60 seconds; after 60 seconds the smoke density decreased. Flame retardant polyester generated less smoke when preheated than when tested at room temperature when compared to regular untreated polyester (4).

The first DBP polyester was released by Lowenstein in 1968. The finish was under the tradename, Fireguard. Washing with a low-phosphate detergent did not affect flame retardancy. However, the type of low-phosphate detergent or water hardness involved were not mentioned.

The finish was not damaged by bleaching or dry cleaning, but it was concluded that it should not be laundered with soap in hard water, or by a commercial laundry. In hard water, a lime soap build-up forms on the fabrics. Acid sours used in commercial laundering destroys the flame retardancy (9).

No information was found concerning the effect of a combination of three laundering variables (detergent, hardness, and chlorine bleach) on a DBP polyester flannelette.

CHAPTER IV

METHOD OF PROCEDURE

This study was done with the support of the Kansas Agricultural Experiment Station.

Fabric

The fabric studied was a 100% polyester flannelette that had been treated with tris(2,3-dibromopropyl) phosphate (DBP) for flame retardancy. The following information about the woven fabric was supplied (15): fabric weight 5.3 oz./sq. yd., 69 warp yarns/inch (16 denier, single yarns), 47 filling yarns/inch (8 denier, single yarns), 115 lbs. tensile strength in warp direction, 83 lbs. tensile strength in filling direction, and 10.5 lbs. tear strength in warp direction.

Approximately half of the 23 meters of the fabric was cut into 25 samples that were 28 cm wide and 137 cm long from which 15 specimens were cut after washing either 0, 25, or 50 times. Fifteen samples were evaluated at 0, 25, and 50 washing cycles at the request of the J. C. Penney Company, who donated the fabric. The remaining piece of the fabric was cut into 36 samples that were 28 cm wide and 91 cm long from which 10 specimens were cut after washing either 3, 6, or 12 times. The specimens measured 8.9 cm wide and 25.4 cm long. From each group of five specimens, three were cut with the warp as the longest direction, and two were cut with the filling as the longest direction. (Figure 1, p. 15) Each sample was stitched around its

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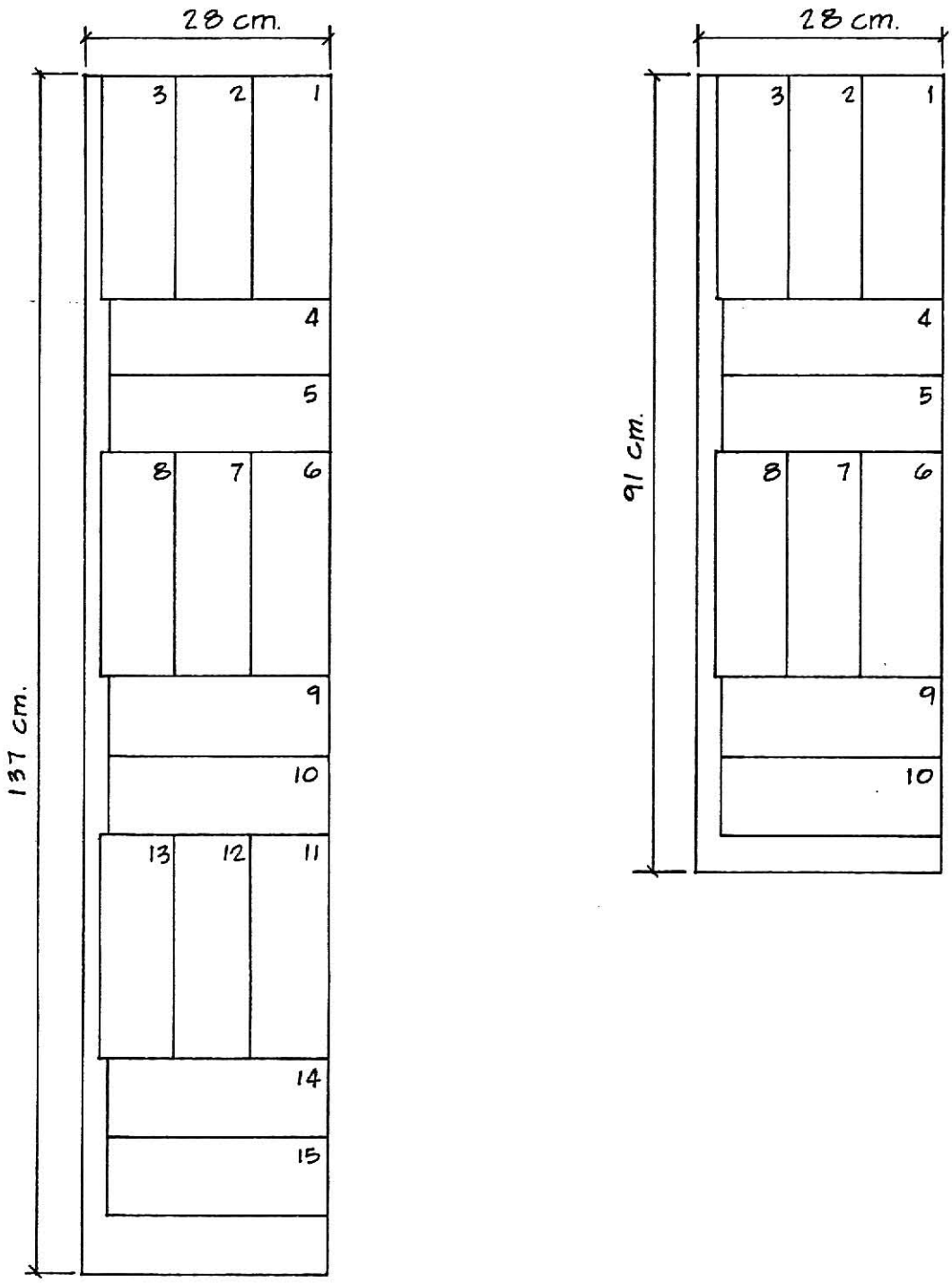

Figure 1

Sampling Plan

edge with a zig-zag stitch to prevent raveling during washing.

Each specimen was coded to designate the washing condition, the number of wash cycle, and the number of the specimen. The code was put in the upper left hand corner of the specimen using a non-washable felt-tipped pen. The following symbols were used in coding the specimens:

phosphate-built detergent, 150 ppm, no bleach = A

phosphate-built detergent, 150 ppm, bleach = B

phosphate-built detergent, 300 ppm, no bleach = C

phosphate-built detergent, 300 ppm, bleach = D

citrate-built detergent, 150 ppm, no bleach = E

citrate-built detergent, 150 ppm, bleach = F

citrate-built detergent, 300 ppm, no bleach = G

citrate-built detergent, 300 ppm, bleach = H

carbonate-built detergent, 150 ppm, no bleach = I

carbonate-built detergent, 150 ppm, bleach = J

carbonate-built detergent, 300 ppm, no bleach = K

carbonate-built detergent, 300 ppm, bleach = L

For example, A-3-1 was specimen number 1 that had been laundered three times with a phosphate-built detergent, 150 ppm, and no bleach.

Calcium deposit was measured on edges from samples laundered 0, 25, and 50 times; the edges also were used for the photomicrographs for observation of the calcium deposits.

Washing of the Samples

An automatic washing machine that provided the following

condition was used: normal agitation of 70 ± 5 cycles per minute, washing time of 10 minutes, spin speed of 500 - 510 rpm, final spin speed cycle of four minutes, wash water temperature of 60 ± 3° C, and a rinse water temperature of 41 ± 3° C. Those conditions are the same as specified in the standard AATCC test method, except that the washing time for the AATCC test method is 12 minutes instead of 10 minutes. When the tub is full of water, it holds about 60 liters.

A no-vent dryer that meets the conditions specified in AATCC test method 124-1969 was used to dry laundered samples. Those conditions are: a controlled exhaust temperature that cycles from 60 to 71° C and a cooling period while tumbling five minutes at the end of the drying cycle.

A hardness concentrate was added to the wash water to attain the desired hardness because the water in the laundry laboratory was 0 ppm as it came from the tap. The concentrate (4000 ppm) was made by dissolving 203 g $MgCl_2 \cdot 6H_2O$ and 441 g $CaCl_2 \cdot 2H_2O$ in one liter of distilled water. For a hardness of 150 ppm, 25 ml of the concentrate were added to the water at the start of the wash cycle. For a hardness of 300 ppm, 50 ml of the concentrate were added.

A phosphate-built detergent, a citrate-built detergent, and a carbonate-built detergent were used. The citrate-built detergent was a liquid; the other two were granular detergents. As specified in AATCC test method 124-1969, 90 g of the granular detergent were used. Since there was no specification for the liquid detergent, Dr. St. John suggested that 79 ml would be an appropriate amount.

The filler load or dummy load of 50/50 cotton/polyester

percale was selected, because it resembled that specified in AATCC test method 124-1969. The test method specified 100% cotton sheeting.

A liquid hypochlorite (chlorine) bleach (237 ml, recommended by the manufacturer) was used.

The procedure was the same for all samples. The washer was started, the hardness concentrate was added to the incoming water, and the detergent, bleach (if stipulated in that load), and fabric to be laundered were added to the washer in that order. The fabric consisted of the samples (two large and three small) and filler cloth to bring the load to the 1.8 kg specified in the test method. The same procedure was followed for each of the 50 loads of the 12 conditions with a different set of randomly selected samples for evaluation at each condition.

Flammability Testing

The test chamber was a steel cabinet with outside dimensions of 30 x 30 x 76.2 cm. The chamber had a frame which permitted the suspension of the specimen holder over the center of the base of the cabinet at such a height that the bottom of the specimen holder was 1.7 cm above the highest point of the barrel of the gas burner, and parallel to the front of the cabinet. The front of the cabinet was a close fitting door with a glass insert (20 x 40 cm) to permit observation. A 15 cm hole with a baffle over it was located at the top of the chamber for ventilation. The test chamber met the specifications of AATCC test method 34-1969 rather than those of DOC FF 3-71.

The specimen holder permitted suspension of the specimen

to be tested. The holders consisted of two U-shaped steel plates 42.2 x 8.9 cm with aligning pins. The openings in the plates were 35.6 x 5.1 cm. The specimens were fixed between the plates, which were held together with side clamps.

The burner was a Bunsen burner that was connected to the gas source by a rubber tube that had been stiffened with wire. Correct positioning of the burner was assured by a device on the floor of the chamber against which the burner was pushed. The burner met the requirements of AATCC test method 34-1969 rather than that of DOC FF 3-71.

Since the fabric weighed 172 g/m^2, the weight used to determine the char length was 113.4 g as specified by DOC FF 3-71. A weight of 110 g was placed in a sack of cheesecloth with a hook attached; the total weight was 113.4 g. A linear scale, graduated in millimeters, was used to determine char length. A stopwatch was used to measure the residual flame time to the nearest 0.1 seconds.

Specimens were dried in a forced circulation air oven set to provide 105° C $\pm$ 2.8° C. After drying, the mounted specimens were cooled in a desiccator with anhydrous silica gel as the desiccant.

A hood provided a draft-free environment around the test chamber. After each test, a fan enclosed in the hood exhausted the smoke and/or toxic gasses produced.

After the designated number of washings, a sample was randomly selected (a small sample if the number of washings were 3, 6, or 12, and a large sample if the number of washings were 25 or 50). The selected sample was removed from the washer, and placed in the

dryer until the sample felt dry to the hand. The sample was removed from the dryer, and marked into specimens, coded, and cut. The coded specimens were placed in holders, and clamped in place. Five specimens were placed in the over for 30 minutes, removed when that time had expired, and cooled in the desiccator for 30 minutes. The same procedure was followed for the remaining specimens (in groups of five each) from that sample.

The desiccator was next to the hood in which the test chamber was placed. A specimen was removed from the desiccator and placed in the chamber, and the door of the chamber closed. The burner plume was placed in contact with the specimen for 3 seconds. When the specimen ceased burning, the residual flame time (time on the stop-watch minus the 3.0 seconds ignition time) was recorded, the fan was started, and the specimen was removed from the test chamber.

The specimen was removed from the holder, folded in half lengthwise through the highest point of the charred area, and creased by hand. Then, the specimen was unfolded, and the weighted hook was placed through the lower corner of the specimen one-fourth inch from a lower corner. The other lower corner was lifted slowly from the surface of the work bench until the weight was suspended in the air. The distance, in centimeters, from the bottom of the specimen to the top of the tear was recorded as the char length. The same procedure was followed for each specimen at each level of washing for each of the 12 conditions.

Calcium Determination

Two calcium determinations were done for each of the 12 conditions at 0, 25, and 50 washing cycles following the procedure outlined by Wasserman and Bausch (32). Determinations were done only at those cycles because the fabric did not fail the standard for any of the conditions, and there was no desire for the intermediate information. Calcium carbonate as a percentage of the fabric's weight was determined by an EDTA back-titration (Appendix A, p. 46).

All samples were dried one hour in the oven and placed in a desiccator. For each of the two replications, a sample weighing between 100 and 200 mg was cut. The weighed sample was cut into small pieces and placed in a conical flask. To the fabric, EDTA solution (10 ml) was pipetted into the flask; several drops of ammonia buffer (pH = 10) and 15 to 20 ml of distilled water were added. The solution was boiled for 10 to 15 minutes, and filtered through a sintered glass funnel (medium). The fabric was washed three times with small amounts of distilled hot water. The solution was transferred quantitatively into another flask, and buffer of pH = 10 was added until the pH of the solution was brought to 9.8. Several drops of the indicator were added, and the solution was titrated with the calcium solution from a 10 ml microburet until the color changed from blue to red.

The percentage of calcium carbonate of the fabric's weight was determined by the following calculations: $\frac{[(B - A) \times f] \times 40}{W}$, where A is the milliliters of the calcium chloride solution used, B is the milliliters of the EDTA solution used, f is the molarity of

the EDTA solution, and w is the weight of the fabric in milligrams.

Photomicrographs

The specimens were observed with an ETECH autoscan electron scanning microscope (SEM) with a working voltage of 20 kilovolts. The electron beam impinged on the sample with 45° to its surface.

Photomicrographs were taken for each condition of the samples laundered 0 and 50 times. For two conditions (carbonate-built detergent, 300 ppm, bleach and carbonate-built detergent, 300 ppm, no bleach) photomicrographs were taken at 25 laundering cycles because of the high calcium deposits found by chemical analysis.

To prepare samples for photomicrographs, specimens (approximately 1 x 1.5 cm) were glued to the stub, which serves the same purpose as the glass slide for an optical microscope, by a silver paint. Each set of four stubs was placed in a drying oven to dry the samples and the paint. The set of four stubs were placed in a vacuum chamber and coated with approximately 200 $\mathring{A}$ of 60% gold and 40% palladium to allow observation and to prevent charging. Charging occurs when a particle becomes electrically charged which prevents its viewing with the SEM. The prepared samples were placed in the chamber of the SEM, and the photomicrographs were taken for all samples at 960X magnification.

Experimental Design and Statistical Analysis

The statistical design of the study was a split-split-split plot. An analysis of variance was done to determine differences

attributable to the washing conditions and cycles for residual flame time, char length, and calcium deposit. When F- values were significant, least significant differences (LSD) were calculated at the five percent level of probability. Residual flame time and char length were analyzed for each of the 12 conditions at each of the six washing cycles. From the 15 specimens at 0, 25, and 50 washings, 10 specimens were selected randomly for the analysis, because only 10 specimens were laundered at each of the 3, 6, and 12 cycles. Calcium carbonate as percentage of the fabric weight was determined for each of the 12 conditions at 0, 25, and 50 washing cycles.

CHAPTER V

DISCUSSION OF RESULTS

The effect of washing variables (detergent, water hardness, and bleach) on flame retardant properties of DBP polyester flannelette was studied. The fabric was selected because it is one of the newest fiber/fabric/finish combinations available.

Fabric Flammability

None of the specimens failed to meet the criteria of DOC FF 3-71 after 50 washings. Those criteria are: (1) average char length no more than 17.8 cm for five replicate samples; (2) no specimen with a char length greater than 25.4 cm; and (3) no specimen with residual flame time over 10 seconds.

Two specimens (out of 15) failed 25 washings under condition D (phosphate-built detergent, 300 ppm, and bleach); but, all specimens for that condition passed after 50 washings. Those two specimens had residual flame times of greater than 20.0 seconds. The char lengths were no greater than the rest of the specimens because the two specimens that failed burned out rather than up. The reason for their failure is unknown. The two specimens were adjacent before they were cut. It is possible that the finish had not been applied uniformly (so that the fabric from which those two specimens were cut had an inadequate amount), but, it seems certain that calcium deposition was not responsible. The amount of calcium deposited on the fabrics (with a mean of 0.08%) was an insignificant amount of the

fabric's weight. Furthermore, condition L (carbonate-built detergent, 300 ppm, and bleach) produced the most calcium deposit (with a mean of 0.80%), but all specimens of that condition passed the standard.

Residual Flame Time

Significant differences occurred between the phosphate-built detergent and the citrate-built and carbonate-built detergents (Table 1). The phosphate-built detergent produced a significantly longer residual flame time than either the carbonate-built or the citrate-built detergents. The significant difference could be due to the specimens of condition D that failed. There was no significant difference between the carbonate-built and the citrate-built detergents.

Table 1

Means of Residual Flame Time for Detergents

Detergent	Mean in seconds'
Phosphate	1.032
Carbonate	0.716a
Citrate	0.637a

' Ranked in descending order
a Differences between means with the same superscript are not significant

There was no significant difference in residual flame time between bleach and no bleach (Table 8, Appendix B, p. 47).

Residual flame time for specimens washed in 300 ppm water was significantly longer than for specimens washed in 150 ppm water (Table 2).

Table 2

Means of Residual Flame Time for Water Hardness	
Water Hardness	Mean in seconds'
300	0.914
150	0.676

' Ranked in descending order

Significant difference in residual flame time occurred between the number of times the specimens were washed before testing for flame retardancy. There is no significant difference between samples laundered 0, 3, or 6 times. Samples washed 25 times have a significantly longer residual flame time than those washed 50 times. That discrepancy also may be due to the failure of those two specimens from condition D at 25 cycles (Table 3). The relationship of residual flame time to washing level is plotted in Figure 2 (p. 27).

Table 3

Means of Residual Flame Time for Washing Levels	
Washing Levels	Mean in seconds'
25	1.170a
12	0.897ab
50	0.815 b
6	0.706 bc
3	0.702 bc
0	0.480 c

' Ranked in descending order
a Differences between means with the same superscript are not significant

Neither two-way interactions (bleach-hardness, washings-bleach, or hardness-washings) nor three-way interaction (bleach-

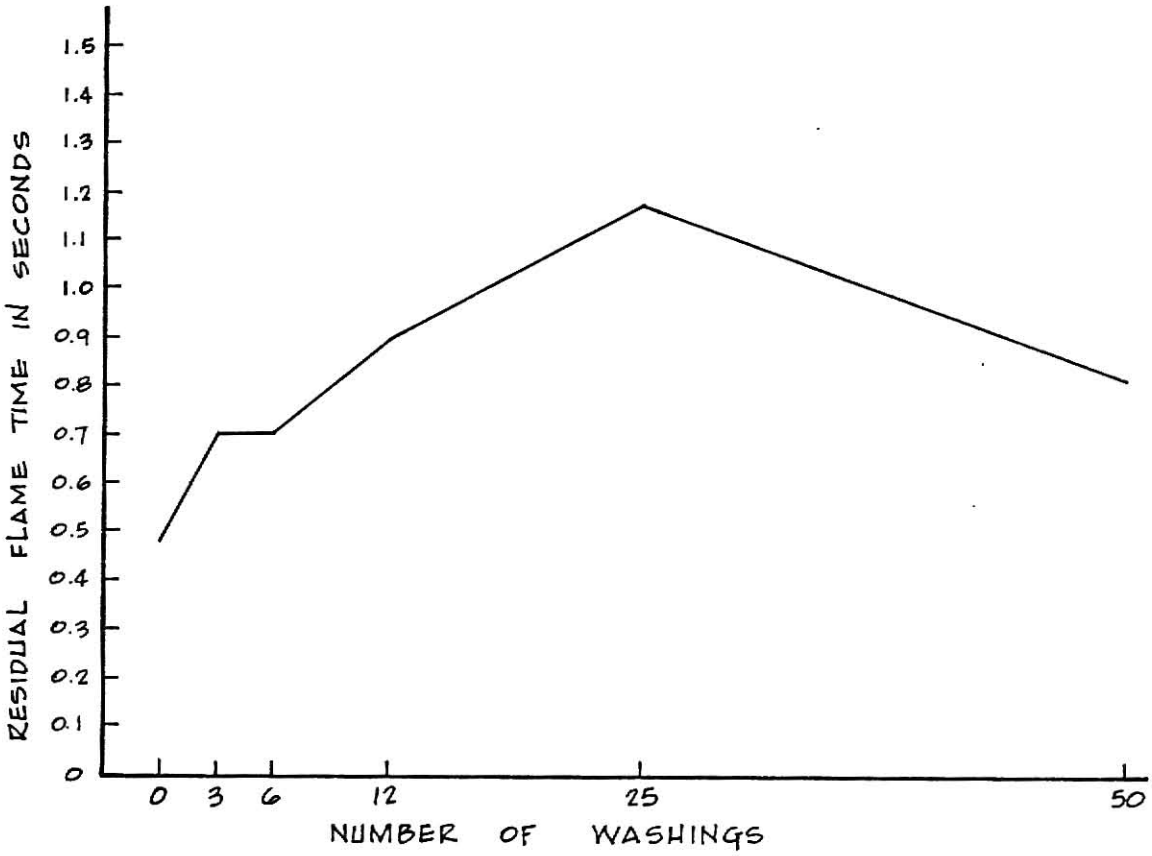

Figure 2

Relationship of Residual Flame Time

to Washing Levels

hardness-washings) were significant.

Char Length

There was no significant difference in char length for detergents (Table 9, Appendix B, p. 47), bleach (Table 10, Appendix B, p. 48), or hardness level (Table 11, Appendix B, p.48); neither was there any significant interaction among those variables. However, there were significant differences among number of laundering cycles (Table 4). Specimens washed 12 times had a significantly greater char length than those tested at any other cycle. There was no significant difference between samples washed 3, 6, 25, or 50 times. Specimens tested at zero washings had a significantly smaller char length than those tested at any other level. The relationship of char length to washing level is plotted in Figure 3 (p. 29).

Table 4

Means of Char Length for Washing Levels

Washing Levels	Means in cm'
12	7.916
50	7.654a
6	7.649a
25	7.599a
3	7.495a
0	6.752

' Ranked in descending order
a Differences between means with the same superscript are not significant

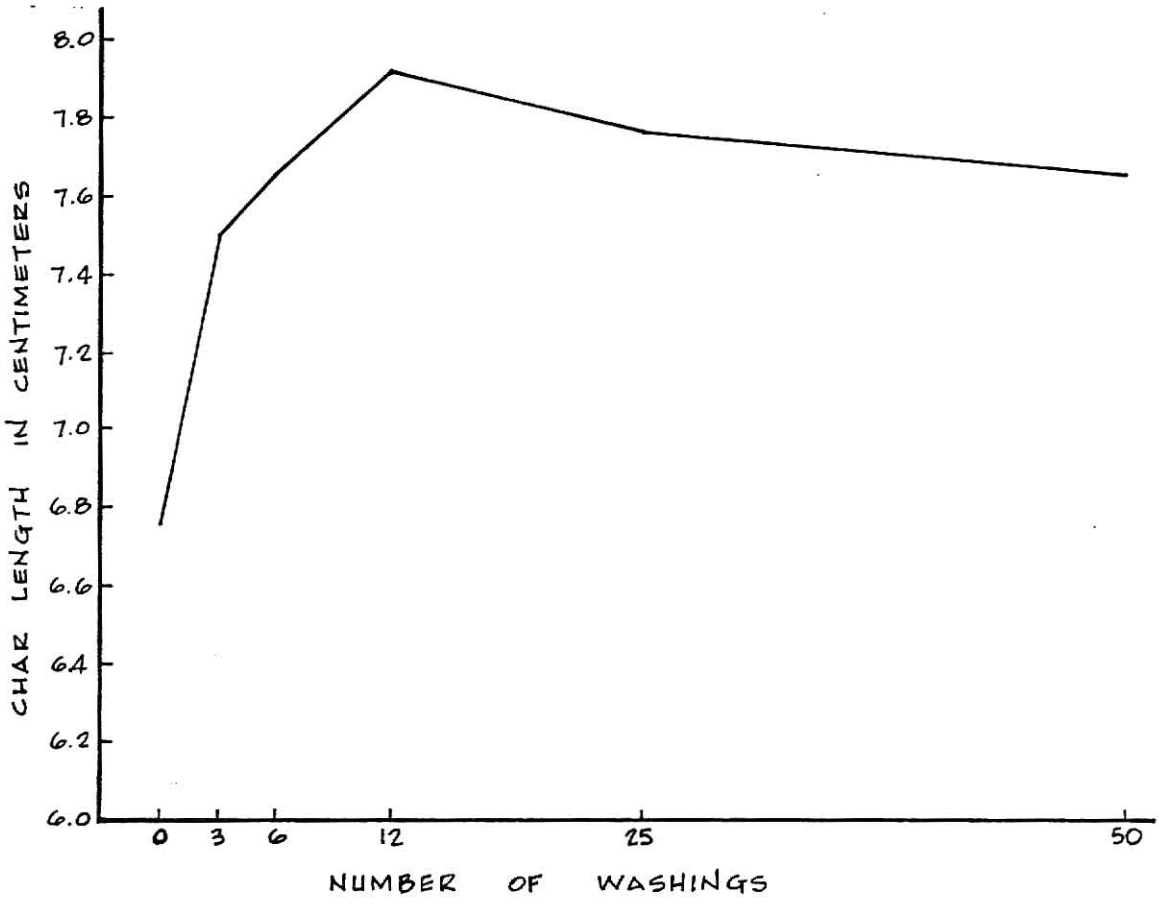

Figure 3

Relationship of Char Length

Levels to Washing Levels

Calcium as Percentage of Fabric Weight

Specimens washed in the carbonate-built detergent had a significantly larger amount of calcium deposited on them than the specimens washed in either the citrate-built or phosphate-built detergents (Table 5).

Table 5

Means of Calcium Percentage by Detergents	
Detergent	Mean in percent'
Carbonate	0.222
Citrate	0.078a
Phosphate	0.062a

' Ranked in descending order
a Differences between means with the same superscript are not significant

There was no significant difference in calcium deposit between bleach and no bleach treatments (Table 12, Appendix B, p. 48), but the deposit was significantly greater at a water hardness level of 300 ppm than at 150 ppm (Table 6).

Table 6

Means of Calcium Percentage for Water Hardness	
Water Hardness	Mean in percent'
300	0.162
150	0.080

' Ranked in descending order

There was a significantly greater amount of calcium carbonate deposited on specimens laundered 50 times than on those

laundered 25 times, and a significantly greater deposit of calcium on specimens laundered 25 times than those laundered 0 times (Table 7).

Table 7

Means of Calcium Percentage for Washing Levels

Washing Levels	Mean in percent'
50	0.242
25	0.121
0	0.000

' Ranked in descending order

There was not a significant difference in calcium deposit attributable to two-way interaction between bleach and water hardness, between bleach and number of washings, and between water hardness and number of washings. There was significant difference in calcium deposit attributable to a three way interaction between bleach, water hardness, and number of washings. Specimens washed 50 times with 300 ppm water and bleach had significantly more calcium than the others.

The graph of Figure 4 (p. 32) plots the build-up of calcium for the detergents. The phosphate and citrate-built detergents are depicted with one line because their graphs were not significantly different. The carbonate-built detergent is plotted for each of the conditions because there were significant differences. As can be seen, the two conditions with bleach are higher than the two without bleach. The two conditions with 300 ppm water are higher than the similar conditions with 150 ppm water.

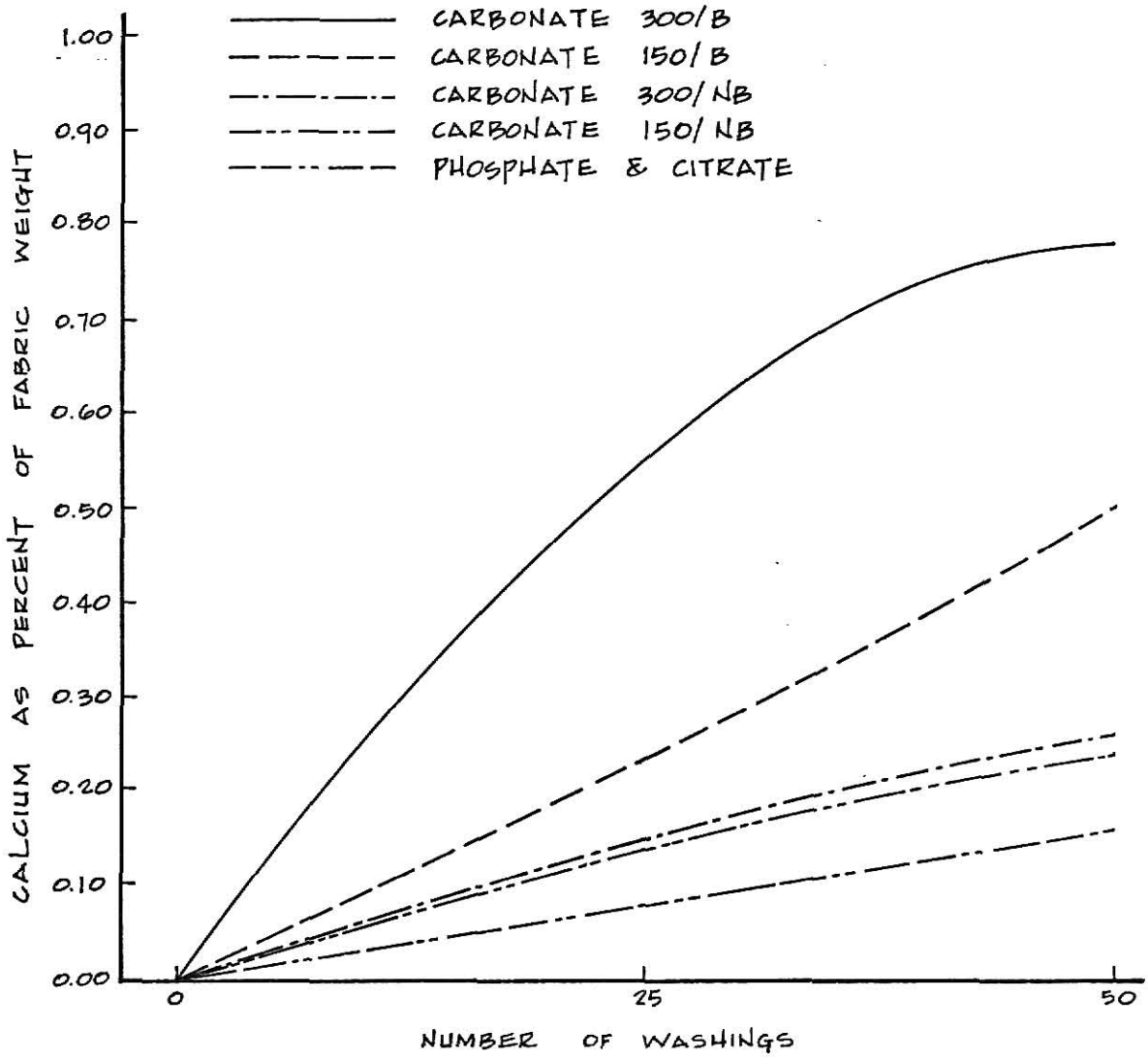

Figure 4

Relationship of Calcium Deposit to Number of Washings with Detergents

Photomicrographs

The photomicrograph (Plate I, Fig. 1) illustrates the appearance of the fibers of the DBP polyester flannelette before washing. Deposits seen in the photomicrograph were removed during laundering. After laundering three times under condition A (phosphate-built detergent, no bleach, and 150 ppm), the majority of the deposits were removed during washing (Plate I, Figure 2). Because the deposit is removed during laundering, it was assumed that the deposits were residue from processing.

Because no significant difference was observed between the amount of calcium deposit attributable to the phosphate-built or the citrate-built detergents, a representative photomicrograph was chosen (Plate II, Fig. 1) to illustrate the effect of both of those detergents. That photomicrograph was taken of a specimen that had been washed 50 times in citrate-built detergent, 300 ppm, no bleach. In the photomicrograph, there is little evidence of calcium deposit which agrees with the data for calcium deposit measured by the EDTA back-titration.

Significant differences in calcium were observed between the carbonate built detergent and the citrate-built detergent (Plate II, Fig. 2). That specimen was washed 25 times in the carbonate-built detergent with a water hardness of 300 ppm, and no bleach. The amount of calcium deposit was approximately midway between that observed in Plate II, Fig. 1 and that of Plate III, Fig. 1. The specimen of Plate III, Fig. 1 had been washed 50 times in condition L (carbonate-built

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EXPLANATION OF PLATE I

Photomicrographs of DBP Polyester Flannelette

(magnification, 960X)

Fig. 1 Zero launderings

Fig. 2 Three launderings, phosphate-built detergent, no bleach, 150 ppm

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PLATE I

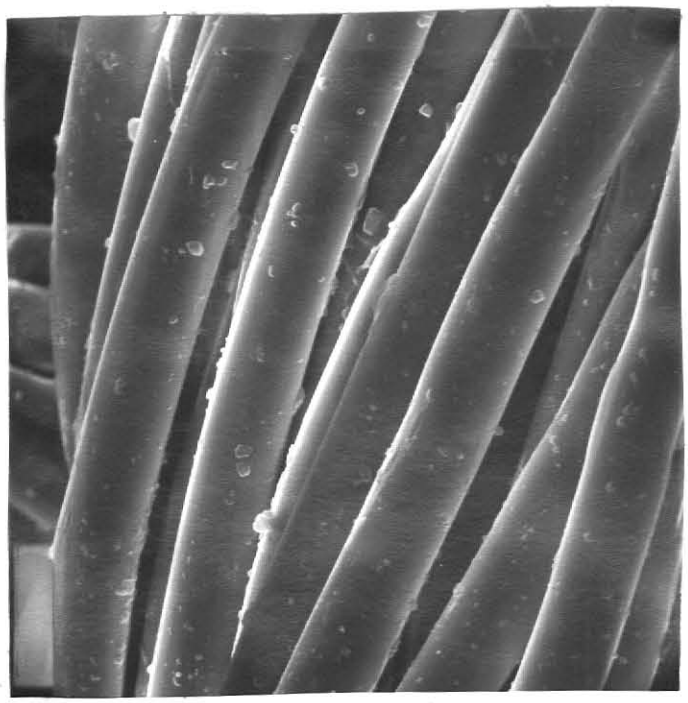

Fig. 1

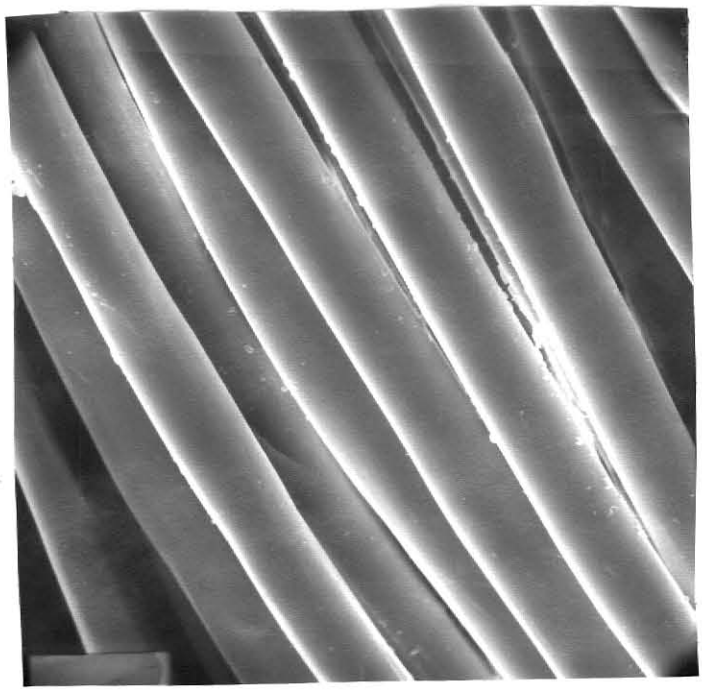

Fig. 2

EXPLANATION OF PLATE II

Photomicrographs of DBP Polyester Flannelette

(magnification, 960X)

Fig. 1 Representative of specimens from phosphate-built and citrate-built detergents

Fig. 2 25 launderings, carbonate-built detergent, no bleach, 300 ppm

PLATE II

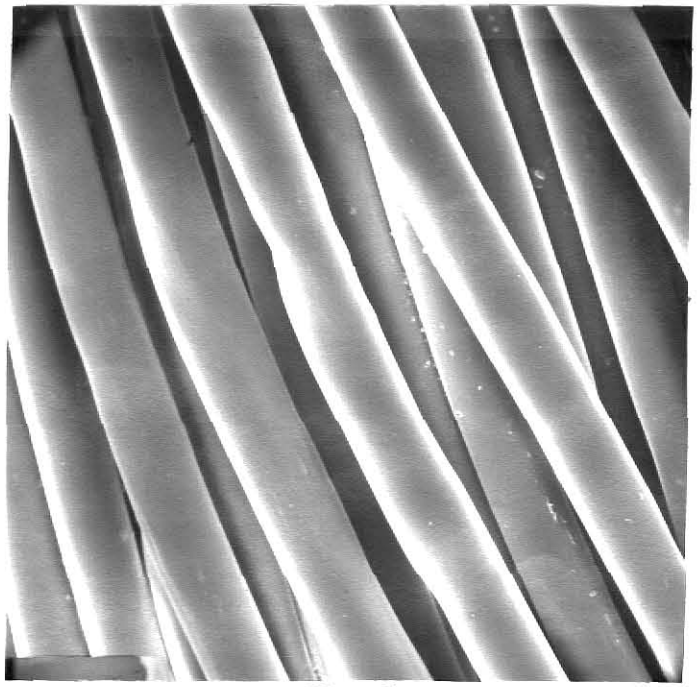

Fig. 1

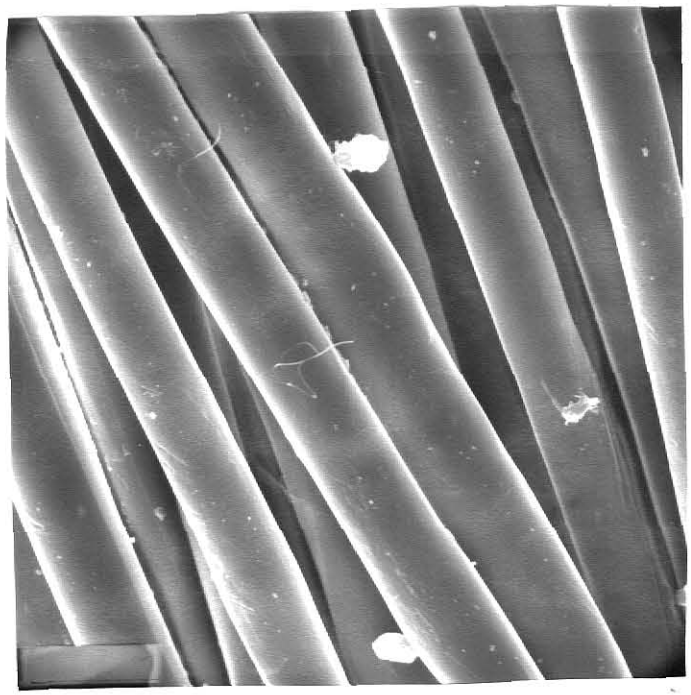

Fig. 2

EXPLANATION OF PLATE III

Photomicrographs of DBP Polyester Flannelette

(magnification, 960X)

Fig. 50 launderings, carbonate-built detergent, bleach, 300 ppm

PLATE III

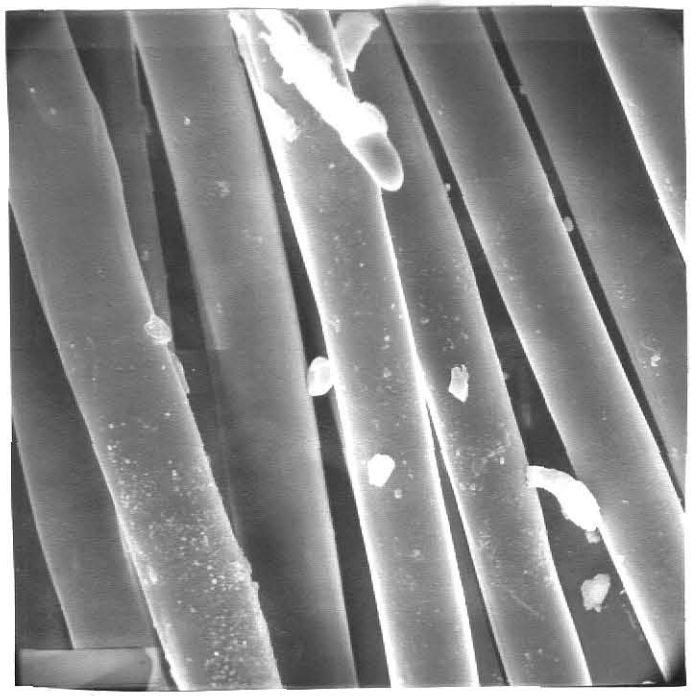

Fig. 1

detergent, 300 ppm, and bleach). The deposit was found to be 0.80% of the fabric's weight, which was the greatest amount of deposit found. However, that amount of calcium did not cause a detrimental effect, and the fabric continued to pass the standard.

CHAPTER VI

SUMMARY AND RECOMMENDATIONS

This study was designed to evaluate the effect of washing variables (detergent, water hardness, and bleach) on the flame retardant properties of a DBP polyester flannelette. The specimens were laundered following the procedure of AATCC test method 124-1969. Fifteen specimens were evaluated after 0, 25, and 50 washings; 10 specimens were evaluated after 3, 6, and 12 washings. Each group of five specimens had three cut in the warp direction and two in the filling direction. DOC FF 3-71 was used as the test method for testing flame retardancy. Residual flame time and char length were the two observations recorded.

The percent of fabric weight that was calcium deposit was determined by an EDTA back-titration. The sample was boiled in an EDTA solution and titrated with a calcium chloride solution until the end point was reached.

Photomicrographs were taken of selected specimens with a SEM. The photomicrographs were taken at 960X magnification to determine the visual appearance of the calcium deposits.

The design of the study was a split-split-split plot. If the F-values were significant, LSD's were determined. There was significant difference between the carbonate-built detergent and the other two detergents for residual flame time. There was no difference between bleach and no bleach for residual flame time. There was significant difference between levels of water hardness for residual

flame time. There was significant difference between the number of times the specimens had been washed before testing residual flame time.

There was no significant difference for detergent, bleach, and water hardness for char length. There was significant difference for level of washing.

There was significant difference for the carbonate-built detergent when compared with the other detergents for calcium deposit. There was significant difference for laundering level for calcium deposit. There was no significant difference for hardness and bleach.

The fabric passed the specifications of DOC FF 3-71 at all 12 conditions. Hence, the fabric is acceptable for children's sleepwear. However, significant differences occurred in the flame retardant properties due to washing variables. Those washing variables that produce significant changes in one or more of the flame retardant properties are: water hardness, phosphate-built detergent, carbonate-built detergent, and number of times the fabric has been washed. The flannelette would give the best performance if laundered in citrate-built detergent, without bleach, and with water 150 ppm hard.

Other studies could be based on the results of this study. The effect of line drying versus machine drying on the flame retardant properties of the DBP polyester flannelette is an area that needs further investigation. Other areas of investigation for possible research are: effect of stains and stain removal techniques on the flannelette, the abrasion resistance of the fabric, the wearability of the fabric, and the effect of other washing variables on the flame retardant properties of the fabric.

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APPENDIXES

APPENDIX A

Preparation and Standardization of EDTA Solution

To make the EDTA solution, 37.244 g of Na-EDTA and 4.0 g of NaOH were dissolved in one liter of distilled water. The solution was standardized by comparison with a standard calcium solution, which was made by dissolving 15.703 g $CaCl_2 \cdot 2H_2O$ in one liter of distilled water. To standardize the EDTA solution, a 25 ml sample of the calcium chloride solution was pipetted into a conical flask. Ten to fifteen ml of an ammonia buffer of pH = 10 and several drops of indicator were added. The EDTA solution was titrated with the calcium solution until the color change from wine red to clear blue was noted. The EDTA solution was standardized to .109 M.

APPENDIX B

NON-SIGNIFICANT DATA

Table 8

Means of Residual Flame Time for Bleach	
Bleach	Mean in seconds'
Without	0.860a
With	0.730a

' Ranked in descending order
a Differences between means with the same superscript are not significant

Table 9

Means of Char Length for Detergents	
Detergent	Mean in cm'
Carbonate	7.556a
Citrate	7.547a
Phosphate	7.430a

' Ranked in descending order
a Differences between means with the same superscript are not significant

Table 10

Means of Char Length for Bleach	
Bleach	Mean in cm'
Without	7.550a
With	7.471a

' Ranked in descending order
a Differences between means with the same superscript are not significant

Table 11

Means of Char Length for Water Hardness	
Water Hardness	Mean in cm'
300	7.558a
150	7.464a

' Ranked in descending order
a Differences between means with the same superscript are not significant

Table 12

Means of Calcium Percentage for Bleach	
Bleach	Mean in percent'
With	0.140a
Without	0.101a

' Ranked in descending order
a Differences between means with the same superscript are not significant

EFFECTS OF LAUNDERING VARIABLES ON FLAME RETARDANT PROPERTIES OF TREATED POLYESTER FLANNELETTE

by

SARA JEAN KADOLPH

B. S., Iowa State University, 1972

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Clothing, Textiles, and Interior Design

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

This study was designed to evaluate the effect of washing variables (detergent, water hardness, and bleach) on the flame retardate properties of a DBP polyester flannelette. The specimens were washed following the procedure of AATCC test method 124-1969. Fifteen specimens were evaluated after 0, 25, and 50 washings; 10 specimens were evaluated after 3, 6, and 12 launderings. Each group of five specimens had three cut in the warp direction and two in the filling direction. DOC FF 3-71 was used to test for flame retardancy. Residual flame time and char length were measured for each specimen.

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