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The Effect of Laundering Variables on the Flame Retardancy of Cotton Fabrics[1]

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ABSTRACT

Some durable flame retardant finishes for cotton fabrics can become ineffective if improper laundering procedures are used. For example, one flame resistant fabric will lose a significant amount of its flame resistance after 5, 10 or 20 soap launderings (yet show no reduction in phosphorus content) while another fabric treated with a different formulation will remain flame resistant. Synthetic detergents, rather than soap chips, and soft water have been recommended for some tetrakis (hydroxymethyl) phosphorium chloride-based flame retardant fabrics to prevent a "lime soap" deposit which impairs performance. The effect of these laundering variables has been studied in relation to a variety of different types of durable flame resistant fabrics.

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INTRODUCTION

Both scientists and legislators have been actively trying to prevent the devastating results of fire to property and people. Recent statistics from the Department of Health, Education and Welfare estimate about 150,000 persons injured as a result of the ignition of clothing, and a death toll of 2000 to 3000 from fire each year (1). This exists despite efforts by scientists to make clothing flame resistant and by legislators to make it illegal to sell or offer for sale any textile product intended for use in apparel which do not meet certain requirements. The Flammable Fabrics Act of 1953 was amended in 1967; the new law strengthens the old and extends the covering to interior furnishing and certain apparel fabrics which had originally been excluded.

Anticipating new requirements, the government and the textile industry have accelerated their research and development efforts to supply flame retardant materials for varied and numerous end uses. Old processes are being evaluated further and new processes are being developed.

Cotton in its most natural state, i.e., in the boll, is flammable. By contrast, a very tightly woven, heavy cotton fabric, such as an 18 oz/yd^2 duck, will resist flaming when a match is applied to it; however, it will glow, smoke and slowly be completely consumed. The task of developing an effective, durable flame retardant finish for cotton is difficult because of the many requirements the finish must meet. To be satisfactory for most uses, a flame retardant must be easy to apply, principally with existing finishing equipment from a water solution; be effective with low increases in weight; leave the fabric permeable to air; be physiologically inactive; render the fabric resistant to afterglow; cause little or no loss in strength; not appreciably stiffen the fabric nor adversely alter the aethetic properties of the fabric; be reasonable in cost; and produce a finish durable to laundering and drycleaning.

It is the object of this paper to discuss some of the problems involved in laundering cotton fabrics that have

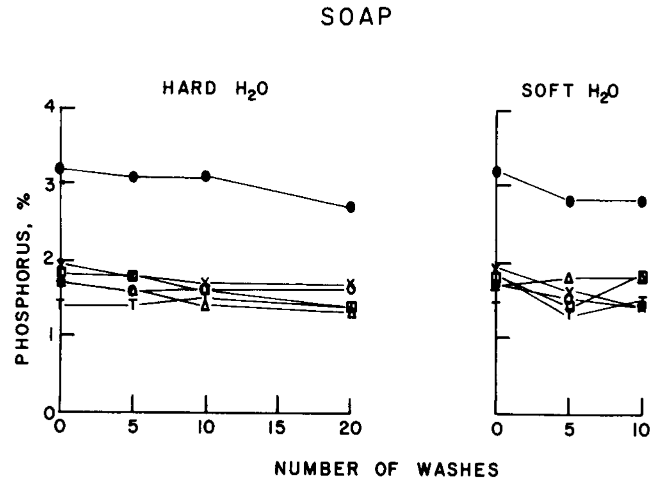

FIG. 1. The phosphorus content of flame-resistant cotton fabrics laundered with soap in either hard or soft water. •, THPC-APO; X, THPC-NH_3; ○, THPC-amide; □, THPOH-amide; △, THPC-cyanamide; T, Commercial Prod.

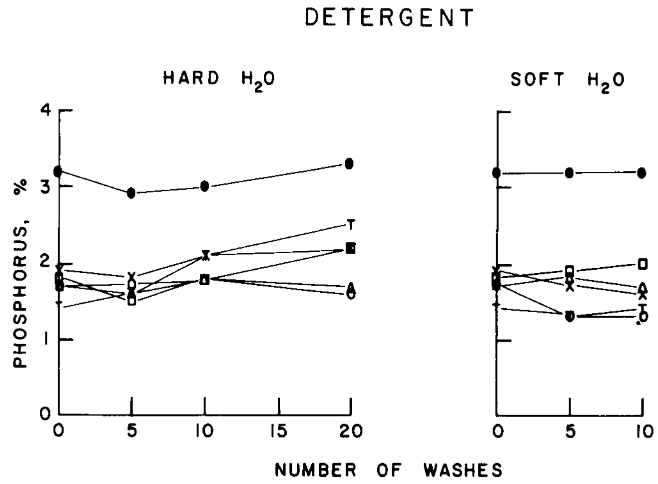

FIG. 2. The phosphorus content of flame resistant cotton fabrics laundered with a detergent in either hard or soft water. •, THPC-APO; X, THPC-NH_3; ○, THPC-amide; □, THPOH-amide; △, THPC-cyanamide; T, Commercial Prod.

been made flame resistant by a variety of processes.

PROCEDURES

The most widely used durable flame retardants for apparel and household goods and for certain military items, such as tent liner fabrics, are based upon tetrakis (hydroxymethyl) phosphonium chloride (THPC). This is a water soluble, crystalline compound produced in high yield from formaldehyde, phosphine and hydrochloric acid. In the U.S., THPC is sold by Hooker Chemical Company and Aceto Chemical Company and, in Europe, by Albright and Wilson Co. Ltd., England. The methylol groups of the THPC react readily with amines and amides (2). A flame retardant based upon THPC and an amide was reported by Reeves and Guthrie in 1954 (3,4). The formulation consists of THPC, urea and trimethylolmelamine (TMM) (2:4:1 mole ratio) plus various auxiliaries (5). Normally a solution of about 35% is applied (70% wet pickup) to an 8 oz cotton fabric to impart durable flame resistance. Variations of this process have been developed by the Hooker Chemical Co. and they have licensed these processes to various textile finishing plants (6).

THPC has been used in a formulation with tris(1-aziridinyl)phosphine oxide (APO) (7,8). The aziridine rings in APO are extremely reactive, especially in acid medium. Both THPC and APO react for form polymers inside the cotton, producing a very durable flame resistant fabric with relatively low add ons. A typical formulation for treating 8 oz cotton contains 14% THPC and 13% APO, plus about 1.5% NaOH and wetting and softening agents. This finish provides a number of additional desirable properties; however, it is not now being used commercially.

A third THPC-based finish utilizes a chemical fixation of the polymer (rather than a heat cure). THPC and urea (1:0.8 mole ratio) are made into a water soluble precondensate (9-11). After impregnation, the fabric is dried, exposed to ammonia vapor and then passed through ammonium hydroxide. The initial ammonia reaction immobilizes the polymer in the fiber; the subsequent aqueous ammonium hydroxide treatment insures complete penetration of the ammonia and the production of a highly insoluble polymer. This process has been used in Europe for about 10 years and is sold under the Proban label.

A new experimental process substitutes THPOH for THPC in the THPC-amide formulation (12). When one mole of THPC is reacted with 0.8 to 1 mole of NaOH, to a pH of about 7, a mixture of products results and the major product is referred to as "THPOH." The THPOH flame retardant imparts significantly different properties to fabrics; fabrics retain 80-90% of their original breaking strength and, because of reduced stiffness, this retardant is applicable to a wider variety of fabrics.

Recently, Ciba introduced Pyrovatex CP, which is a fiber reactive "phosphone alkyl amide," for treatment of cotton (13,14). Effective treatment requires an add on of 25-35%. Children's night clothing having this finish is marketed in the U.S. by several large retail outlets.

Finally, another experimental finish utilizes THPC with cyanamide and phosphoric acid (15). A flame retardant finish based on cyanamide and phosphoric acid has been known (16,17), and it was theorized that the incorporation of THPC in the formulation would provide a new finish that would improve the strength and reduce ion exchange properties, thereby improving the durability of the cyanamide-treated fabrics. The padding solution contains a 2:1 molar ratio of cyanamide to THPC and a concentration of 25-36% total solids plus about 2.0-2.5% phosphoric acid.

The effect of laundering fabrics finished by the six above-described processes was measured by changes in phosphorus content and in flame resistance, as measured by the Angular Match Test and by the Vertical Flame Test as described below. The phosphorus content was determined by an x-ray fluorescence method using a General Electric XRD-5 diffractometer modified for fluorescence analysis (18). The Vertical Flame Test is usually considered one of the most difficult to pass. The lower edge of a 2 3/4 x 10 in. fabric sample suspended vertically hangs 3/4 in. into a 1 1/2 in. high yellow luminous flame from a Bunsen or Tirell burner (19). After 12 sec the flame is removed. The duration of afterflame and afterglow, and the char length are measured. The other test used, the Angular Match Test, is much simpler and has been found to be extremely useful as a research tool (3,20). In this test, a match is applied to a 1 cm strip of fabric and the angle at which it fails to support combustion is recorded. Fabrics passing the 180° angle have very good flame resistance, fabrics passing the 90° angle have modest flame resistance, and those passing the 0° angle have very little flame resistance. Fabrics passing the 135° angle or more usually pass the Vertical Flame Test.

Laundering was done in a home, agitator type washer and tumble dryer. Standard soap chips or a detergent (Tide XK) was used. In the soft water series (0-10 ppm total hardness), about 50 cc of the soap or detergent was used for each washing; in the hard water series (about 100 ppm

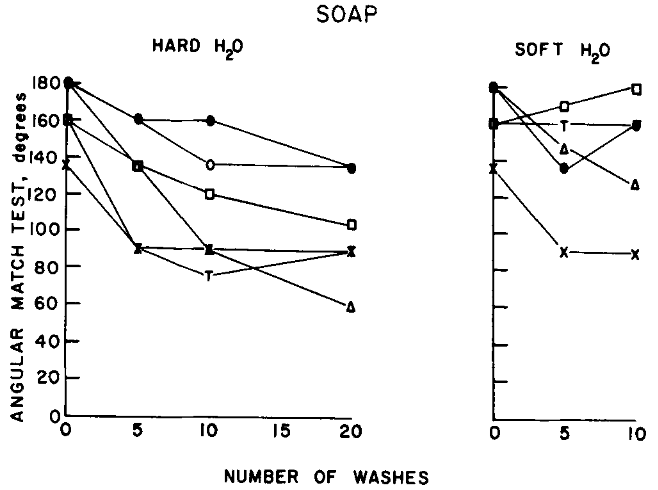

FIG. 3. The degree of flame resistance of cotton fabrics after laundering with soap in either hard or soft water. •, THPC-APO; X, THPC-NH_3; ○, THPC-amide; □, THPOH-amide; △, THPC-cyanamide; T, Commercial Prod.

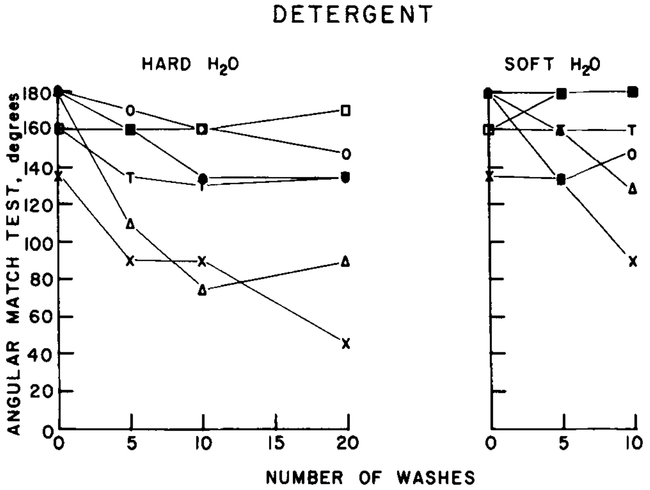

FIG. 4. The degree of flame resistance of cotton fabrics after laundering with a detergent in either hard or soft water. •, THPC-APO; X, THPC-NH_3; ○, THPC-amide; □, THPOH-amide; △, THPC-cyanamide; T, Commercial Prod.

total hardness), 100 cc of soap or detergent was needed. The laundry cycle for cotton was used. Samples were tumble dried for 30 min or line dried.

RESULTS AND DISCUSSION

The phosphorus content of the fabrics was measured before and after launderings. The results after washing with a soap are shown in Figure 1. In general, treated fabrics washed with soap in hard water retained 80% or more of the phosphorus after 10 or 20 washes. About the same amount of phosphorus was retained when soft water was used. The phosphorus content of the THPC-APO samples was higher than for fabrics treated by the other processes because this polymer has a higher phosphorus concentration. The per cent of phosphorus retention of the THPC-APO samples was essentially the same after 10 washings, whether the initial content was 3.2% or 1.2% phosphorus.

When a detergent was used to wash the fabrics in soft water, little or not phosphorus was lost; in hard water, there was some increase in phosphorus, as shown in Figure 2.

This apparent pickup of phosphorus occurred in the untreated samples as well as the treated, and was rather high for the fabrics treated with the commercial phosphonate type product. After 10 detergent washings in hard water, these commercial product-treated fabrics had about a 40% increase in phosphorus content, compared to the original control.

Flame resistance as measured by the Angular Match Test and the number of washings under varying conditions are plotted in Figures 3 and 4. The THPC-precondensate-NH_3 samples failed the Angular Match Test rather rapidly under all conditions. However, these samples had only a 135° angle initially, thus the failures were not surprising. This finish (upon which the Proban treatment is based) is more durable with a higher initial add on.

The THPC-cyanamide fabrics had fairly good flame resistance after 10 washings in soft water with either soap or detergent, but in hard water, adequate flame resistance was lost after about five washings. When treated fabrics were washed with soap in hard water, only the THPC-amide and the THPC-APO samples had good durability. With detergent in hard water, the THPC-amide, THPOH-amide, THPC-APO and commercial product samples had good durability after 20 washings.

After 10 launderings in hard water with soap or a detergent, the samples were subjected to the Vertical Flame Test. After soap washings, the THPC-APO and the THPC-amide or THPOH-amide samples passed the test. When a detergent was used, the THPC, cyanamide and the THPC-precondensate-NH_3 samples, failed the vertical flame test; the other passed. These results are shown in Table I.

TABLE I

Flame Resistance of Some Treated Fabrics After Laundering 10 Times in Hard Water (100 ppm) With Either Soap or a Detergent

Treatment	Vertical flame test, char length after 10 launderings, in.		
	Control	Soap	Detergent
THPC-APO	4.0	3.4	3.8
THPC-amide	3.8	3.6	3.1
THPOH-amide	2.5	2.1	2.4
Commercial product	3.8	BEL[a]	3.4
THPC-cyanamide	4.6	BEL	BEL
THPC-NH_3	3.7	BEL	7.9

[a]BEL, burned entire length.

Thus, the soap and hard water combination can cause problems with a number of finishes, but detergent and hard water, or either laundering agent in soft water causes no serious loss in flame resistance after 10 to 20 launderings. Reports in British trade journals cautioned against the "soap-lime" buildup and resulting loss of flame resistance of Proban treated fabrics washed with soap in hard water (17-19). The water reported had a 250 ppm hardness, which is considerably harder than in our study. However, in the U.S., it was found that municipalities, even in very small towns, soften the water before pumping it for use by the town.

During our experiments with hard water and soap, it was noticed that a white film formed on the agitator of the washer and also in a nonuniform manner on the fabric. After tumble drying, however, much of this white film was gone. It was theorized that the action of the tumble dryer may have caused the film to powder and fall off. Some samples were washed with soap and then line dried in an effort to accumulate this white deposit. Specimens were then selected for the match test where there appeared to be little or no film and also where there was a maximum. Although the results are inconclusive, it appeared that the film did not minimize flame resistance and that the area without a deposit had less flame resistance than the area with some deposit. Some samples that had been washed 20 times with soap in hard water were extracted with acetic acid. Flame resistance was regained by the fabrics because the acetic acid removed the calcium and magnesium deposits. The phosphonate-treated fabric was the exception; the finish was removed by the extraction.

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