

Treatment for Improving Flame Retardancy of Wool and Minimizing Toxic Gas Evolution in Burning

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Synopsis

A treatment involving formaldehyde, a reducing agent, and a boron-containing compound of a wool shag carpet imparted to it a flame-retardancy effect that was effective after the seventh but not the eighth shampoo. This treatment also decreased the concentration of carbon monoxide and hydrocyanic acid generated in the products of combustion by at least a factor of 2. Analogous treatment of a wool flannel fabric produced a 15-22% sample area shrinkage and imparted a flame-retardancy effect that was still effective after a 2-hr cold water rinse.

INTRODUCTION

The presently practiced approaches to the flame retarding of wool fabric and carpet involve the use of polymeric phosphorous-containing compounds.¹⁻³ One of the processes involves the use of a precondensate of tetrakis-hydroxymethylphosphonium chloride (THPC), urea, and melamine resin in a relatively long and costly procedure requiring careful control of a number of variables. In the other process, a cyanamide-phosphoric acid combination is used which demands rather careful control of temperature in the handling of the cyanamide-phosphoric acid solutions as well as of the flame-retardant-treated wet fabric but can apparently be easily controlled.

Incorporation of additives, however, is only one approach to flameproofing. Physical structural modification of the fiber or at least of its surface layer may be an alternative to incorporation of phosphorus and/or halogen additives. We would like to report our initial efforts in this direction. The approach has consisted of reducing wool in the presence of formaldehyde and a water-soluble boron compound which results in approximately 10% shrinkage of the pile yarn and incorporation of only a small amount (0.5%) of boron in the yarns. Comparable shrinkage data for the Pyroset® CP and Proban® processes was not available.

Our main work has involved a wool shag carpet, and only preliminary investigations have been done on a wool flannel fabric. In the evaluation

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of carpets for flammability, a federal standard, DOC FFI-70, has been established which took effect on April 15, 1971.^{4,5} Unfortunately, the requirement in this standard that the carpet undergo ten washings according to the washing and drying procedure prescribed in Method 124-1967, Part 6.2 (III) and Part 6.32 B, of the American Association of Textile Chemists and Colorists⁶ prior to testing was entirely too drastic to leave the face yarn of the carpet undamaged and, hence, could not be followed. Thus, our experience was similar to that of O'Brien and Weyker¹ with regard to the proposed washing procedure, and another wet cleaning method had to be sought. We adopted with minor modifications the shampoo procedure of O'Brien and Weyker in our work. Using this shampoo procedure, our flame-retardancy treatment was effective after the seventh but not after the eighth shampoo.

EXPERIMENTAL

Materials

The untreated wool shag carpet samples (35 oz/sq yd pile weight and 2 in. pile height) were obtained by courtesy of Mr. David Hall of the Wool Bureau, Inc., Woodbury, L. I., N. Y. The various chemicals were used as received from the following sources: sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$), sodium hydrogen sulfite (NaHSO_3), sodium sulfite (Na_2SO_3), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium lauryl sulfate, and trichloroethylene from Fisher Scientific Company; formaldehyde solution (37%) and boric acid from Mallinckrodt; methyl polyborate ($2(\text{CH}_3\text{O})_3\text{B} \cdot 3\text{B}_2\text{O}_3$) from Aldrich Chemical Co., Inc.; zinc borate ($\text{Zn}_2\text{B}_6\text{O}_{11}$) from Alfa; and du Pont Fiber Identification Stain No. 4 and staining chart courtesy of the Dyes and Chemicals Division of Organic Chemicals Department, E. I. du Pont de Nemours and Company.

Treatment Procedure

The carpet sample (6 × 6 in.), shag side down, was submerged as far as the backing in the treatment solution. A typical solution composition was: 7.7% formaldehyde (CH_2O), 7.7% borax, 1.5% sodium hydrosulfite; usually a 500-ml treating bath was used. The temperature of the treatment solution was maintained at 90°C for 20 min, then increased to 100°C for an additional 20 min. This schedule was chosen for convenience as comparable results could be also obtained at 90°C, however requiring a longer than the 40-min treatment time. The wet pickups by the entire carpet (pile yarns and backing material) were always more than 300%. At the start of this work, to determine the initial pickup of boron by the pile yarns, the carpet was passed through a hand wringer after the treatment and then dried in a forced-air oven at 100°C for 2 hr. In the subsequent work, the treatment was always followed by a running tap water rinse (15 min) and a trichloroethylene rinse (3 min) before drying the carpet

at 100°C for 2 hr in a forced-air oven. The trichloroethylene rinse was used to ensure the removal of any water-insoluble materials. No cure is used in this treatment.

The Pyroset® CP and the Proban® treatments contrast with our treatment as follows. In the Pyroset® CP process, the flame retardant is in contact with the carpet at room temperature preferably for a period of 8 hr or more. This is followed by a 240°F cure for about 40 min. The Proban® process requires two or more dips in the application of the flame retardant, followed by drying at 210–240°F and curing at 285–310°F for 4–6 min. An after-finishing sequence is recommended which involves afterwash, oxidizing scour, rinse, extraction, and drying.

Flame-Retardance Evaluation

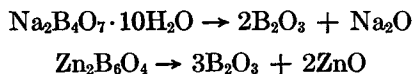
The standard pill test (Federal Specification DDD-C-95¹⁵) was used in this evaluation. Both the carpet sample to be tested and the methenamine tablets (No. 1588, Eli Lilly and Co.) were dried in a vacuum desiccator over silica gel for at least 16 hr prior to testing. The pill was ignited with a match immediately after removal from the desiccator and placed in the center of the 6 × 6-in. carpet sample. The test was performed after the treatment of the carpet and after each subsequent shampoo.

Shampoo Procedure

The shampoo procedure was essentially that of O'Brien and Weyker¹ which consisted of: (1) leaching carpet sample 3 min in 0.5% sodium lauryl sulfate solution at 49°C, (2) removing excess water in a hand wringer, (3) rinsing in water for 3 min, (4) removing excess water in a hand wringer, and (5) drying at 100°C for 2 hr in a forced-air oven. The differences in our procedure were the trichloroethylene rinse before the shampoo procedure, the use of a hand wringer instead of a centrifuge to remove excess water, and drying at 100°C for 2 hr in a forced-air oven.

Analysis for Boron

As a result of some of our work with organoboron compounds on cotton fabric, a simple and fast technique involving radiofrequency-discharged oxygen was developed for determining boron in cotton fabric.⁷ We find now that this technique is equally applicable to determining boron in wool materials. The validity of this technique was established by comparing the discharge results with those of Galbraith Lab., Inc., on duplicate samples. Their procedure consisted of digesting the sample with nitric acid in a sealed tube at 300°C and then determining the boron content volumetrically using the mannitol procedure. In those formulations in which borax and zinc borate were used in calculating for the % boron, a correction for the % sodium and zinc oxides formed was used assuming the following stoichiometry:



Thus, in the case of borax formulations, the weight of the residue multiplied by $2B_2O_3/(2B_2O_3 + Na_2O)$ was used in the calculation for the %B, and a corresponding procedure was used in the zinc borate case. In the case of the carpet samples, only the pile material was analyzed.

Gas Analysis

The gases evolved during the burning of both control and treated samples were tested for carbon monoxide, hydrocyanic acid, and phosgene concentrations. For the purpose of this analysis, the test was conducted in the standard vertical char test method (AATCC Test Method 34-1966) chamber (12 in. \times 12 in. \times 30 in.) and thus represents the evolving gas composition in the chamber during the time of the measurement. A carpet sample of 6 in. \times 6 in. was always used. The gases were analyzed at the top of the chamber above the center of the carpet sample with the Multi Gas Detector, Model 21/31, manufactured by the Drägerwerk Lübeck, West Germany. Briefly, the technique consisted of passing a specified volume of gas through a glass tubing containing indicating layers of granulated carrier material impregnated with color reagents. The measuring scale was imprinted upon the glass tube, and the concentration of the desired gas component was read off the scale directly in relation to the length of the discolored zone. The tubes contained also precleansing layers to remove interfering gases. No comparable data are available on treated or untreated carpets in the literature.

RESULTS AND DISCUSSION

A common approach to the modification of wool has involved the replacement of the disulfide groups by some other linkages. Thus, for example, wool has been made insect resistant,⁸ chemically resistant,^{9,10} and flame resistant¹¹ by reacting the sulfhydryl groups of the reduced wool. We find that by reducing wool in the presence of formaldehyde and a water-soluble boron compound, it was not only shrink-proofed but also flame-retarded to undergo eight shampoo treatments before the flame-retardance effort was lost. It should be emphasized that this treatment introduced only a minor amount (up to 0.5%) of boron in the wool, and the shampoo procedure that we used did little damage to the pile yarns that could be noticed.

Treatment Variables

Several treatment temperatures and reaction times were investigated; however, those given in the experimental part were the most successful in achieving pile yarn add-ons up to 10%, estimated from a treatment of only the pile yarn material. Of the three reducing agents (sodium hydrosulfite, sodium hydrogen sulfite, and sodium sulfite) investigated, sodium hydrosulfite gave the most consistently good flame retardance and the highest boron content (0.5%).

Four materials (borax, boric acid, methyl polyborate, and zinc borate) were investigated as sources of boron. Borax and boric acid gave the most consistently good flame-retardancy results and methyl polyborate, the poorest. After the treatment and before the trichloroethylene and water rinses, the boron content in the pile yarns was in the 2–3% range. However, the trichloroethylene and water rinses reduced it to 0.3–0.5% which remained constant through the seven shampoo procedures. The flame-retardancy results of the best treatment are summarized in Table I.

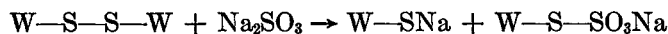
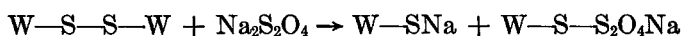
TABLE I
Flame-Retardancy Results in the "Standard Pill" Test^a

Treatment	Char diameter, in.
None	6
Borax/Na ₂ S ₂ O ₄ /CH ₂ O ^b	3/4
Borax/Na ₂ S ₂ O ₄ /CH ₂ O, after 1st shampoo	1
" " " , after 2nd shampoo	1
" " " , after 3rd shampoo	1 1/2
" " " , after 4th shampoo	1 1/2
" " " , after 5th shampoo	1 1/2
" " " , after 6th shampoo	1 1/4
" " " , after 7th shampoo	1 1/4
" " " , after 8th shampoo	6
" " " , after one machine wash ^b	6

^a Determined on 6 × 6 in. samples.

^b 10% add-on.

The form in which the boron compound has been incorporated into the reduced wool has not been investigated. However, the inorganic reducing agents have been shown to react with the disulfide bonds as follows¹⁰:



The sulfhydryl groups produced directly and from the unstable reducing agent portion of the cleaved disulfide bond can conceivably form thioborates with the boron compounds which may become stabilized as a result of N → B dative bonds between the amine and borate ester groups. This type of stabilizing effect has been shown to be responsible for the high hydrolytic stability of boron esters of amino alcohols.¹² Although the amount of boron incorporated is small, it is essential for the enhanced flame retardancy, as the treatment in absence of boron compounds results in only a small improvement. Likewise, the treatment with only the boron compounds to a boron level of 0.5% produced only a marginal improvement in flame retardancy which was not stable to one shampoo procedure. Thus, both a physical modification of the substrate and the presence of a small amount of boron are responsible for the enhanced flame retardancy.

Gas Analysis

It has been stated that smoke and the toxic products of combustion are often more dangerous than the fire itself.¹³ Previous work has shown that wool is superior to most common fibers with regard to evolution of smoke and toxic gases.¹⁴ We have evaluated the treated and untreated carpets for three gases under a number of different testing conditions. The results are recorded in Table II. Initially, the standard pill test conditions

TABLE II
Gas Analysis

Sample	CO, ppm	HCN, ppm	Phosgene, ppm
Metheneamine pill	<1	<1	—
Untreated carpet, pill test	8	2	<1
Treated carpet, pill test ^a	3	2	<1
Treated carpet, after three shampoo procedures, pill test	3	1	—
Untreated carpet, ASTM C 209 test ^b	8	2	<1
Untreated carpet, ASTM C 209 test modified ^c	152	4	<1
Treated carpet, ASTM C 209 test, modified	70	2	<1
Gas burner	4	—	—
Untreated carpet, gas burner ^d	800	55 ^e	<1
Treated carpet, gas burner	190	20	—
Treated carpet, after three shampoo procedures, gas burner	110	13	—

^a Performed on formaldehyde, sodium hydrosulfite, and borax-treated samples (add-on, 9%; boron content, 0.45%).

^b We used a 6-in.² sample instead of the 12-in.² as specified in the test.

^c The cup of 1 ml of alcohol was placed next to the surface of the sample.

^d A Busen burner with a 1¹/₂-in. flame (Matheson Gas B) was used next to the surface of the sample.

^e Estimated from 1/₆th of the volume as specified in the test.

were used to analyze the toxic products of combustion; however, under these conditions little toxic gas was formed. We then used the ASTM C 209 test conditions,¹⁶ which gave results identical to those of the pill test. By lowering the sample to the edge of the cup, more vigorous burning was induced with consequent increase in CO generation. Finally, the samples were tested by bringing the surface of the sample at a 45° angle to the tip of a gas flame from a Busen burner and keeping it there for the duration of the test. The untreated carpet burned vigorously under these conditions while the treated carpet burned only slowly and was self-extinguishing once the flame was removed. As we had no information about the composition of the backing material, we also tested the gases evolved for phosgene; however, none was detected. The lower CO and HCN concentrations after the carpet had undergone three shampoo procedures could have been due to a slower rate of burning caused by a higher moisture

content in the sample. In summary, the treatment decreased the flammability of the carpet and, as a consequence, the concentration of CO and HCN generated in the products of combustion by at least a factor of 2.

Some Wool Flannel Fabric Data

It was of interest to investigate the extent to which the treatment would be applicable to a wool flannel fabric. A 5.35 oz/sq yd undyed worsted woolen flannel (Test Fabrics, Inc., New York, N. Y.) was first extracted with diethyl ether (8 hr) followed by 95% ethyl alcohol (8 hr) and then rinsed with tap water for about 2 hr. The fabric was heated in a water solution of formaldehyde (7.7%), borax (7.7%), and sodium hydrosulfide (1.5%) at 100°C for 1 hr, followed by a running tap water (15 min) rinse and trichloroethylene extraction for at least 1 hr and drying at 100°C for 2 hr in a forced-air oven. This resulted in a 5% sample weight increase and a 0.5% boron content. The treatment typically produced only a 15–22% area shrinkage of the sample as compared to at least a 50% shrinkage when no formaldehyde was used in the treatment bath. The treatment produced a flame-retardancy effect (2 in. char in the vertical char test method, AATCC Test Method 34-1966) that was still effective after a 2-hr cold water rinse. The flame-retardancy results of the various treatments are summarized in Table III. No change in the melting point

TABLE III
Flame-Retardancy Results in the Vertical Char Test

Treatment ^a	Char length, in.
None	burned entire length
Borax/Na ₂ S ₂ O ₄ /CH ₂ O	2
Boric acid/Na ₂ S ₂ O ₄ /CH ₂ O	1 ³ / ₄
Borax/NaHSO ₃ /CH ₂ O	2
Borax/Na ₂ SO ₃ /CH ₂ O	2 ¹ / ₂
Zn ₂ B ₆ O ₁₁ /Na ₂ S ₂ O ₄ /CH ₂ O	3
Methyl polyborate/Na ₂ S ₂ O ₄ /CH ₂ O	8 ¹ / ₂

^a Add-ons 5–8%; for boric acid and zinc borate treatments, add-ons 22%. Boron content, 0.3–0.5%.

(130°C) of the fibers (performed as described in ref. 17) was induced by this treatment, and the sample gave a deep purple color response to du Pont Fiber Identification Stain No. 4, which is typical of fibroin (silk). Thus, the treatment has either eliminated the sulfur from the fiber surface or masked it in such a manner that the typical keratin response is lost and the fiber responds to the dye as a fibroin material. In summary, the treatment flame-retarded the fabric and caused diminished shrinkage, however, without the introduction of the additional covalent crosslinks associated with the α -helices¹⁷ and modified the chemical surface of the fibers to give a typical fibroin response to the du Pont Identification Stain No. 4.

CONCLUSION

In conclusion, the reduction of the pile yarn in a wool shag carpet in the presence of formaldehyde and water-soluble boron compounds imparted to the carpet flame-retardancy properties that were durable to seven but not eight shampoo treatments. Furthermore, the treatment decreased the concentration of carbon monoxide and hydrocyanic acid generated in the products of combustion by at least a factor of 2. The main advantages of this approach lie in the simplicity and inexpensiveness of the treatment for both wool shag carpet and flannel fabric.

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