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APPLICATION OF THE APO-THPC FLAME RETARDANT TO COTTON FABRIC

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A typical laboratory and commercial procedure for the application of the APO-THPC flame-retardant to cotton fabric is given. The finish can be readily applied to cotton using commercial equipment, the resulting fabric properties being comparable to those of fabrics processed in the pilot plant. Commercial processing by various finishers necessitated some modification in the laboratory technique to adapt it to existing equipment.

The functions of the various components of the treating solution and the necessary precautions to be observed during fabric processing are discussed.

INTRODUCTION

THE fire hazards associated with the use of combustible fabrics for decorative or utilitarian purposes have caused intensification of research to develop improved durable flame-retardant finishes for use by the textile industry. In modern warfare the use of incendiary weapons, such as napalm bombs, phosphorus grenades, flame throwers and high-energy radiating explosives makes it mandatory for our military forces to be equipped with flame-retardant textiles. Interest by civilian and industrial groups in flame-retardant textiles is increasing as shown by Public Law 88 of the 83rd Congress which bars dangerously flammable fabrics from interstate commerce.

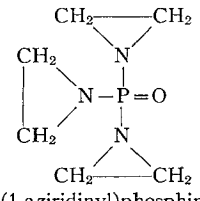
Many of the existing flame-retardant processes have one defect or another, which renders them unsuitable for general application to textile products. The defects may be objectionable changes in hand, appearance, texture, flexibility, inadequate fastness to repeated launderings, possible irritating action on the skin, lowered air or water permeability, excessive add-ons, lowered breaking or tearing strengths, technical difficulties or expense in applying the processes, poor resistance to dusting or stickiness at elevated atmospheric temperatures.

The task of developing a satisfactory flame retardant for cotton is important and difficult because of the many requirements a generally satisfactory flame retardant must meet simultaneously. To meet the requirements, the finish must be:

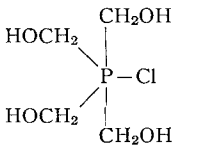
1) Applicable from water solution, preferably.
2) Easily applied, preferably on existing finishing equipment.
3) Capable of being processed without objectionable odor and toxic fume development when applied with conventional ventilation.
4) Durable to laundering and drycleaning.
5) Resistant to strength damage from chlorine bleach.
6) Able to form a tough char when exposed to high-energy irradiation.
7) Efficient and preserve the natural fiber character after application; and at the same time render it glow and flame resistant.
8) Void of adverse physiological reactions to persons handling or exposed to the treated fabric.
9) Suitable for further finishing such as dyeing or application of a water repellent.
10) Reasonable in cost, particularly when put into large-scale use.

This paper covers development of pilot plant and commercial application of our most recent flame retardant which meets the above requirements.

This flame retardant is based upon a new thermosetting resin made by reacting a rather unusual compound, tris-(1-aziridinyl)phosphine oxide abbreviated "APO" (*1*) with tetrakis(hydroxymethyl)-phosphonium chloride, abbreviated "THPC" (*2*). The structures are shown in Figure 1.



Tris(1-aziridinyl)phosphine oxide



Tetrakis(hydroxymethyl)phosphonium chloride

Figure 1

APO is prepared in good yield by reacting ethyleneimine with $POCl_3$. The reaction may be represented as follows:

$$POCl_3 + 3HN\overline{CH_2-CH_2} + 3R_3N \rightarrow [\overline{CH_2-CH_2-N}]_3P=O + 3R_3NHCl$$

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Chemical companies have recognized the potentialities of APO. Six of these companies have already developed satisfactory pilot-plant methods for its production and made it available. THPC is already available commercially. It has been indicated that the cost of APO based on a large-scale production will be acceptable to the industry.

The treating solution is easily prepared by mixing the chemical components APO, THPC, triethanolamine, and a suitable wetting agent with water. The flame-retardant solution is then applied to the fabric with a high-pressure padder, usually with two dips and two nips. After padding, the fabric is dried at a relatively low temperature, cured at an elevated temperature, washed, dried in the open width, and softened.

TYPICAL APPLICATION———The following description of a laboratory pilot-plant application to several hundred yards of 8.5-oz OD sateen fabric illustrates a typical application procedure. [See Section A of Discussion.]

COMPOSITION AND PREPARATION OF TREATING SOLUTION———A treating solution was composed of the following:

15.7% APO
17.3% THPC
4.3% Triethanolamine
0.2% Triton X-100[2], an alkylarylpolyether alcohol
62.5% water.

The solution was prepared by adding the measured quantity of THPC to one-half of the total amount of cold water with rapid stirring until completely dissolved. To this solution the triethanolamine was added with continued stirring. This combination is designated as solution A. The APO was then added, with rapid stirring, to the remainder of the cold water and designated as solution B. Just prior to treatment of the fabrics, the two solutions A and B were thoroughly mixed and the wetting agent Triton X-100 was added. This gave a solution of 33% solids, based on APO and THPC in an equimolar ratio, of pH 6.6. [See Section B of Discussion.]

Padding. The 40-inch-wide, 8.5-oz OD sateen was padded through the above solution using two dips and two nips with a squeeze-roll pressure of ten tons and batched with a minimum amount of tension. A wet pickup of 70% was obtained. [See Section C of Discussion.]

Drying. The fabric was dried in a forced-air, roller-type drying oven for 5.5 minutes at a temperature of 185°F. [See Section D of Discussion.]

Curing. The fabric was cured for five minutes at 290°F in the same oven used for drying. [See Section E of Discussion.]

Washing and Drying. The fabric was washed in a winch for a total of 30 minutes, with the water being changed every five minutes. Initial and final cycles were made in cold water, the other cycles being hot water washes at 140°F. The first hot-water wash cycle contained 0.1% Duponol LS Paste, a long-chain alcohol sulfate. Following the final wash, the wet fabric was passed through squeeze rolls and then dried on a tenter frame. [See Section F of Discussion.]

Softening. The dry fabric was softened with a 4% solution of a cationic softener by padding to a 50% wet pickup using one dip and one nip and redried on the tenter frame. The softener used in the processing of this fabric was Triton X-400, a tetraalkylammonium halide. [See Sections G and H of Discussion.]

In addition to the above fabric, 100 yards of the same 8.5-oz OD sateen was processed through a solution containing 26% APO-THPC solids using the same processing conditions and procedure.

PROPERTIES OF TREATED FABRIC———The fabric, processed with 33% total solids APO-THPC, contained approximately 15% resin add-on, and withstood repeated launderings and drycleanings. Char length in the standard vertical flame test was 2.7 inches with no after flame (Fed Spec CCC-T-1916, No. 5902), and was 2.9 inches after 15 launderings using a fluoride sour (Fed Spec CCC-T-1916, No. 5556). The samples would also pass the 180° strip angle flame test (3) before and after washing. The treated fabric, after softening, retained about 90% of its original warp breaking strength. After 15 launderings the tearing strength of the treated fabric containing 10% resin add-on was better than that of the untreated control. The fabric strength was not harmed by a chlorine bleach. Some crease resistance was imparted by the treatment. The flex abrasion of the treated fabric, after washing, was better than that of the untreated fabric. Comparable properties were obtained with a 10% resin add-on from processing with the 26% solution. Properties of the fabric are presented in Table I.

FUNCTIONS OF THE VARIOUS COMPONENTS OF THE SOLUTION———

APO. This compound furnishes phosphorus and nitrogen for imparting flame resistance by reacting with THPC to form an insoluble highly cross-linked, thermosetting resin. It also combines chemically with the cellulosic fiber, which probably accounts for the exceptional durability of the finish to acid and alkali washings. APO is usually shipped as an 85% solution containing a stabilizer. Various stabilizers such as ethyl alcohol, dehydrating substances such as phosphorus pentoxide, anhydrous sodium sulfate and others have been reported recently (4, 5).

THPC. This compound also serves a two-fold purpose. It furnishes some of the necessary phosphorus for imparting flame resistance to the fabric by forming an insoluble highly crosslinked condensation polymer with the APO. It also acts as a latent acid catalyst, liberating HCl along with formaldehyde, and tris(hydroxymethyl)phosphine oxide during the polymerization. THPC is a hygroscopic compound, but is stable at room temperature.

Triethanolamine (TEA). This is used to stabilize the resin-forming solution, acts as an acid acceptor during the curing process, and reduces any acid tendering. At room temperature, treating solutions from which triethanolamine is omitted will polymerize to a viscous liquid in several hours. Use of this viscous solution results in surface deposition of the polymer and imparts stiffness to the fabric. A preferred range of triethanolamine concentration is equivalent to about ¼ of the THPC concentration by weight.

Wetting Agents. A wetting agent is used to aid in uniform penetration and wetting of the fabric with the treating solution.

[2]The mention of trade products and firms does not imply their endorsement by the U S Department of Agriculture over similar products of firms not mentioned.

TABLE I

Properties of APO-THPC-treated 8.5-oz OD sateen

Test		Untreated control* Number of launderings 0	5	15	APO-THPC-treated fabric — 10% Add-on Number of launderings 0	5	15	15% Add-on Number of launderings 0	5	15
Thread count	W	87.0	86.6	87.1	86.4	88.4	88.4	86.2	88.4	89.6
	F	56.0	57.0	58.6	54.6	57.2	59.0	54.4	56.2	59.6
Width (in)		39.3	—	40.0	40.1	—	39.3	40.1	—	38.8
Weight (oz/yd²)		9.0	—	8.8	9.65	—	10.42	9.96	—	11.2
Thickness (in)		0.0248	0.0212	0.0211	0.0190	0.0211	0.0232	0.0190	0.0227	0.0250
Stiffness (bending moment × 10^4 in lbs)	W	13.5	6.8	13.8	14.2	11.6	14.2	36.6	9.0	15.5
	F	12.0	6.7	13.4	18.8	7.4	11.9	16.3	7.0	15.0
Char length (in)		—	—	—	2.97	3.68	4.12	2.65	2.77	2.87
% N		—	—	—	1.63	1.50	1.31	2.12	2.04	1.95
% P		—	—	—	1.40	1.20	0.91	1.76	1.87	1.39
Strip breaking strength (lbs)	W	134.0	120.8	125.5	123.2	115.0	107.4	113.6	96.2	92.6
	F	118.6	100.0	115.2	97.0	86.2	96.6	88.6	97.2	99.0
Elongation (%)	W	11.6	13.2	13.5	7.9	11.3	13.5	6.3	7.8	19.9
	F	21.8	19.3	20.0	20.7	19.7	21.7	20.9	19.3	12.2
Abrasion resistance (flex)	W	1856	443	228	1109	1263	1027	482	654	704
	F	2267	752	393	2252	1513	1416	1062	928	1048
Elmendorf tear (lbs)	W	14.8	8.3	6.2	10.6	8.4	8.6	8.8	7.1	6.9
	F	20.9	10.1	7.9	11.7	9.5	10.2	9.1	7.5	6.8
Tongue tear (lbs)	W	15.0	7.4	6.2	8.2	7.1	7.6	7.7	6.1	6.2
	F	15.9	9.5	8.6	10.8	8.1	8.9	8.8	7.8	8.4
Crease resistance (Monsanto W+F)		229	210	225	270	237	243	275	250	246
Breaking Strength† (lbs) after chlorine bleach	W	118.5	134.5	—	102.4	123.4	—	97.4	100.6	—
Chlorine bleach + scorch	W	127.0	127.9	—	101.8	112.4	—	101.2	105.8	—

*Fabric rinsed one time in hot water and frame dried.
†AATCC Tentative Test Method 92-1958.

Softeners. Softeners usually improve the hand and tearing strength of the fabrics. There are a large number which are commercially available and can be used with good results.

COMMERCIAL APPLICATION———Very often a new finish can be applied successfully to a fabric under strictly controlled laboratory conditions, but for various reasons, the exact laboratory procedures cannot be duplicated when the processing procedures are scaled up to plant size. Therefore, it is necessary for the finisher to make changes in the process in order to find the optimum procedure and conditions suitable for producing a fabric with the desired properties by use of existing equipment. The APO-THPC flame-retardant treatment is very flexible in this respect.

Cooperation has been very close with industry in the application of the APO-THPC finish to fabrics and plant runs at various mills have been very successful in duplicating pilot-plant results, athough in most cases modifications had to be made in the processing procedures. Details for one of these mill runs are described below.

Fabric Description. Approximately 220 yards of 10-oz/yd² 32 inches wide, 54 × 54 army duck were finished with the APO-THPC flame retardant.

Procedure. The pad formulation was based on 50 gallons of treating solution using a one to one mole ratio of APO to THPC and containing a 33% total solids content, total solids being based on the APO and THPC only. The formulation contained the chemicals listed below:

18.5% Imine IP, an 85% commercial solution of APO.
17.3% THPC
4.3% TEA
0.5% Triton X-100
59.4% water[3]

[3]15 lbs of the total amount of water was cracked ice. The solution formed was pH 6.0.

The THPC was dissolved in about one-half of the required amount of water, the TEA added and thoroughly mixed. The remaining water and ice was added to the above solution then the Imine IP was added, with stirring. All mixing was done in a large mixing tank. To this solution was added the Triton X-100 wetting agent and the solution allowed to flow, by gravity, to the pad box. The temperature of the treating solution at this stage was below 70°F. The above solution was mixed just prior to use.

Padding was accomplished by using two padders. One, which contained the treating solution in the pad box, was a lever-set, gravity-fed padder with two rubber rolls, 50 inches wide, one hard and one soft. A five-ton pressure was maintained between rolls. The second padder was a microset pad with one hard rubber roll and one metal roll, each 50 inches wide. A 15-ton squeeze roll pressure was maintained.

The fabrics were padded through the solution with one dip and one nip with the first padder and one nip with second padder, at a rate of 42 yds per minute. Wet pickup of the duck fabric was determined prior to the actual run by passing a weighed piece of fabric through the bath and pad rolls. Wet pickup was 58%. The fabric was skied, passed between two pairs of opposed gas-fired infrared burners for preheating, then passed to an enclosed 70-foot tenter frame with an inlet temperature of about 195-198°F and an exit temperature of about 210°F. Elapsed time on the frame was one minute and 40 seconds. After passing through the frame, the fabric was cured in a gas-fired, roller-type curing oven (80 yds capacity) for three minutes at 345°F. These operations were carried out with a minimum amount of tension on the fabric.

After curing, the flame-resistant fabric was washed in an open, six-compartment continuous washing range. The number one compartment contained 0.25% soda ash in the water and the other compartments contained only hot water. The water temperature was maintained at approximately 140°F. Washing time was approximately one minute.

After washing, the fabric was dried over steam cans

TABLE II
Properties of army duck fabric commercially treated with APO-THPC

Test	Untreated	APO-THPC-treated — Commercially	SURDD
Width (in)	32¼	31¼	—
Thread count	53 × 43	56 × 40	—
Weight, oz/yd²	10.1	10.9	—
Elmendorf tear* (w) lb	9.3	6.3	6.4
After-flame (sec)	—	0	0
Afterglow (sec)	—	1	0
Char length (in)	—	3.2	2.8
Char length (in) after three-hour soap-soda boil		3.3	2.7
Breaking strength (in break) lbs (w)	124.6	102.4	117.0

*Application of a softener to the treated sample would increase the tearing strength making it about comparable to the untreated fabric.

(25 psig steam). Drying time was approximately two minutes.

Test results of this run are shown in Table II, along with some results obtained on the identical fabric processed with APO-THPC at the Southern Utilization Research and Development Division.

It is apparent from analyses shown in Table II that the APO-THPC process is adaptable for use in finishing fabric on commercial equipment. Without the addition of a softener, the tearing strength loss was approximately 30%. Tearing strength values would have been about comparable to the control fabric if a softener had been applied to the treated fabric. There was a loss of approximately 17% in the breaking strength of the commercially treated fabrics compared with approximately 7% for the pilot-plant sample. The flame resistance, durability of the finish, hand and other properties of the commercially finished fabric were similar to those of the sample prepared in the laboratory.

Other mills have successfully applied this APO-THPC flame-retardant finish to other fabrics and have found this flame retardant to be outstanding (*6*, *7*).

Treatment of 8.5-oz OD sateen fabric with APO-THPC to a resin add-on of about 10%, which is needed to impart the required degree of flame resistance, has been estimated to cost about 28.6 cents per pound of product, based on a projected price of 70 cents per pound for THPC and $2.25 per pound for APO. Using a projected APO price of $1.00 per pound, the finishing cost would be 16.9 cents per pound of product (*8*).

DISCUSSION

A) FABRIC PREPARATION———The fabric to be treated must be clean and preferably absorbent. It should be essentially free of any of the ordinary sizing materials, also alkalies which may have been used during wet processing of the fabric (such as in scouring, mercerizing, bleaching, dyeing, etc) must be thoroughly neutralized and rinsed out.

Starches, which are left in the fabric from improper desizing, interfere with the penetration of the reactant into the cellulose fiber. This causes increased stiffness and could possibly decrease the washfastness of the finish. Excellent results are always obtained when the fabrics are thoroughly desized before application of the APO-THPC flame retardant. Grey fabrics can be processed with the use of a good wetting agent, such as Triton X-100, to assist penetration.

Whenever possible, fabrics should be dried on a tenter frame before resin treatment. This makes the fabric more absorbent and produces a balanced crimp distribution. Fabrics should also be allowed to condition between drying and resin treatment. It has been found that dry fabrics which are still warm when stored in boxes or in tight rolls on padding can exhibit non-uniform absorbing tendencies and increase the temperature of the flame-retardant solution.

B) APO-THPC TREATING SOLUTIONS———The APO-THPC flameproofing solution will gradually become warm upon standing due to the heat of solution and to heat from some polymerization initiated by the rise in temperature. It is therefore necessary to keep the solution cool. This can be done in various ways. Substitution of ice for a portion of the required water has been found very satisfactory for small quantities of solution. Once the solution has been prepared, ice cannot be added since it will dilute the solution to a lower solids content. For obvious reasons, at no time must any heat be applied to aid solution of the chemicals.

C) PADDING———Fabric can be processed on either a continuous or batch-wise basis. In either case the fabric is padded through the resin-forming solution, dried, cured, washed, softened, and dried.

A commerical padder in good repair, equipped with a constant level control pad box and a combination of metal to rubber squeeze rolls, and adjustable in pressure up to 10 tons is recommended. The constant level control pad box insures that all portions of the fabric have the same immersion time. The high-pressure squeeze rolls provide a deep uniform penetration of the solution into the fibers and eliminate surplus treating liquor from the fiber interstices. If the resin-forming solution does not penetrate to the interior of the fiber and an excessive amount of material remains between the fibers, the treated fabric will be inferior because of the greater stiffness and losses in tearing strength and abrasion resistance. In general the fabric will receive a more uniform application if it is padded through the resin-forming solution twice using about a 10-ton squeeze-roll pressure on the rolls each time. (Hard rubber rolls can be substituted for the rubber to metal rolls providing a squeeze-roll pressure of ten tons or greater is used). Incorporation of a wetting agent is highly desirable.

The wet pickup obtained will depend on the squeeze roll pressure, hardness of the rolls, and the fabric weight and structure. It is suggested that mill trials be preceded by laboratory application to the particular fabric to be processed so that the necessary resin add-on required to impart adequate flame resistance can be determined. The finisher may find from these laboratory experiments that adequate flame resistance can be obtained with lower resin add-ons on fabrics designed for a particular end use. Use of lower resin add-ons will also lower the cost of the finish. Preliminary laboratory examination may also make the difference in the success or failure of the treatment. Once the solution concentration has been established for any particular fabric, this laboratory work will not have to be repeated. When the solution concentration has been established it is essential that a correlation be made between the wet pickup obtained on the laboratory versus the wet pickup obtained on the mill padder so that a corresponding adjustment can be made in the solids content. Very often this correlation is forgotten and such an omission may be the cause for an otherwise successful run to result in failure if there is a large difference in the wet pickups obtained with the two padders.

If after processing a given fabric with APO-THPC it is found that an additional resin add-on is required,

ric with the readily available phosphorus-containing chemicals APO and THPC. The treatment consists of padding fabric through an aqueous solution of APO-THPC, then drying at a relatively low temperature, curing at an elevated temperature, to form a highly crosslinked resin inside the fiber, followed by washing, drying, and softening.

The APO-THPC flame-retardant process can be readily applied to cotton using commerical equipment to obtain properties equivalent to those obtained when fabrics are processed in the pilot plant. Commercial processing by various finishers necessitated some modifications in the laboratory technique in order to be applicable on existing equipment.

Important processing points are:

1) Keep APO-THPC treating solution cool and mix just prior to treatment of fabric.

2) Treat fabric in tandem operation with minimum amount of tension.

3) Pad fabric through the treating solution using two dips and two nips with high squeeze-roll pressure.

4) Dry the fabric in a forced-air roller-type oven at a temperature of approximately 185°F until dry.

5) Cure the fabric at or above 285°F for times sufficient for adequate cure.

6) Wash using standard procedures.

7) Apply softener as an aftertreatment.

This new flame retardant appears to meet all of the many requirements for a generally satisfactory flame retardant.

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