

TECHNICAL BULLETIN



COTTON INCORPORATED

6399 Weston Parkway, Cary, North Carolina, 27513 • Telephone (919) 678-2220

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FABRIC FLAME RETARDANT TREATMENT "PRECONDENSATE"/NH₃ PROCESS

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INTRODUCTION

The "precondensate"/NH₃ process¹ is designed to impart durable flame retardance to 100% cotton fabrics when applied under proper application procedures. This process provides fabrics with good fabric handle and strength retention.

Proper application of precondensates to cotton fabrics requires:

- Adequate fabric preparation.
- Proper padding to ensure homogeneous application.
- Proper phosphorus add-on relative to fabric properties.
- Appropriate moisture control prior to ammoniation.
- Control of the ammoniation step to ensure adequate polymer formation.
- Effective oxidation and process washing of the treated fabric.

This bulletin provides operational guidelines relating to each requirement, and these data can be used for laboratory applications as well as for mill-scale operations.

FABRIC PREPARATION

Proper fabric preparation is essential for uniform treatment with the ammonia cure process; therefore, particular care should be taken in this step. Fabrics should be scoured, bleached and dyed before application of the flame retardant. Printing usually follows application of the flame retardant.

The fabric should be neutral or slightly acidic, free of alkali and other extraneous matter, and absorbent. Absorbency is easily determined visually by applying a few drops of the pad bath formulation. Testing wettability with water alone, or water plus wetting agent, may lead to an erroneous conclusion. Fabrics showing inadequate absorbency should be treated so that they wet instantaneously with a drop of pad solution.

PRECONDENSATE FORMULATION

A generalized precondensate² formulation, applicable to a range of fabric weights and constructions, is the following:

	<u>% By Weight</u>
<i>Precondensate</i>	20.0 to 50.0
<i>Sodium acetate (anhydrous)</i>	0.8 to 2.0 ³
<i>Nonionic surfactant</i> ⁴	0.2 0.2
<i>Water</i>	79.0 to 47.8

¹The "precondensate"/NH₃ process refers to an application of one of several commercial phosphonium "precondensates," after which the fabric is cured with ammonia, then oxidized with hydrogen peroxide. (See text for full details.)

²Precondensate is the designation for a tetrakis-hydroxymethyl phosphonium salt pre-reacted with urea or another nitrogenous material. The reaction products are complex oligomers; exact compositions are proprietary information of chemical suppliers.

³The amount of anhydrous sodium acetate is 4% of the amount of precondensate used. Some precondensates are available with the sodium acetate already combined.

⁴Our experience has been with Tergitol TMN-6 (Dow Chemical); other products that are compatible with the formulation and provide adequate wetting can be substituted at the user's discretion.

Since the precondensates and sodium acetate are miscible with water in the proportions used, the order of addition for bath preparation is not critical. Some softener-modified precondensates, when diluted with water, form a milky emulsion; therefore, it is advisable to dissolve the sodium acetate in the water and follow this by adding the precondensate. The wetting agent diluted with water is added last to the mix. The pH of the pad bath should be approximately 5.0. Pad baths of precondensates usually are stable for at least eight hours.

APPLICATION

The amount of flame retardant required depends primarily on fabric type, application conditions, and test criteria to be met. Screening experiments should be conducted to determine the minimum application level for a fabric. Figure 1 shows guideline application levels for treatments designed to pass 16 CFR Part 1615 Standard for the Flammability of Children's Sleepwear: Sizes 0 through 6x (FF3-71). Generally, fabrics can be classified into weight groups, and the amount of applied phosphorus⁵ needed to pass 16 CFR Part 1615, will be similar within each weight group. Applications of different phosphorus levels should be made by changing the pad bath formulation rather than adjusting pad roll pressure.

Application of the formulation to fabric can be accomplished with conventional mill pads, but for optimum performance, it is essential that the bath be distributed homogeneously within the fibers. Experience shows that padding with multiple dips and nips, followed by 30 to 60 seconds dwell, is good for this purpose.

MOISTURE CONTROL PRIOR TO AMMONIATION OF TREATED FABRIC

A critical factor in the successful application of precondensate/NH₃ flame retardant is control of fabric moisture before ammoniation. Generally, moisture levels between 10% and 20% give successful treatment, although the optimum level should always be determined for a specific fabric.

An experimental padded fabric sample is dried to a desired level and weighed. The sample is then dried completely (e.g., 10 min. @ 225°F, maximum) and reweighed to provide the two figures for calculation.

⁵ $\frac{\% \text{ WPU}}{100}$

$$\% P_d = \% P_b \times 100$$

% P_d = percent phosphorus deposited on the fabric.

% P_b = percent phosphorus in bath (calculated from product data and concentration, or determined by assay as described in Appendix A).

The following method of moisture determination has been used:

$$\% M = \frac{W_m - W_d}{W_m} (100)$$

M = Moisture in fabric

W_m = Weight moist fabric

W_d = Weight dried fabric (including solids add-on)

Optionally, experience has shown that the Mahlo moisture meter (Type DMB-6 with roller electrode No. 215) gives results that correlate predictably with the calculated values. Since the correlation coefficient may vary with different precondensates, laboratory comparison of the measured and calculated moistures is advised.

Drying may be accomplished in any convenient fashion so long as care is exercised to obtain homogeneous drying (side to side, end to end, and back to face) and to avoid undue surface migration of chemicals. Our experience has shown that to accomplish this, oven temperatures should not exceed 250°F. Overdrying fabric tends to retard reaction with ammonia, while underdrying tends to form a less durable flame retardant polymer.

AMMONIATION

Chemical curing is accomplished by exposing the moist, precondensate-padded fabric to anhydrous, gaseous ammonia. The ammonia cure can be accomplished in laboratory equipment as basic as a simple box, contained in a hood, in which fabric samples are suspended and to which anhydrous ammonia gas is delivered, or in a mechanized, continuous laboratory unit with ammonia flow controls. For commercial application, a continuous ammonia delivery and exposure unit is used. Generally, the best results are obtained when the delivery system forces ammonia through the fabric. The objective is to ensure adequate and thorough ammoniation to form an insoluble polymer with the cotton fibers. Theoretically, one mole of ammonia per mole of phosphorus on the fabric should be required for fixation, but in practice, an excess of ammonia ensures more complete reaction.

The amount of ammonia required for a given treatment is calculated readily considering the following factors:

- Weight of fabric (lbs./lin. yd.)
- Desired running rate (yd./min.)
- Percent of phosphorus applied to fabric
- Desired excess

Thus, for an 8 oz./lin. yd. fabric, at 50 yds./min., containing 5% P (on the weight of the fabric):

$$8 (1/16 \times (50) \times (0.05) \times (1/31) \times 17 =$$

$$0.69 \text{ lbs. NH}_3/\text{min.}$$

where

1/16 = conversion from oz. to lbs.

1/31 = conversion to moles of phosphorus

17 = molecular weight of NH_3

In theory, a calculated amount of 0.69 lb. of NH_3 is required per minute of operation to react stoichiometrically with the phosphorus; some excess (probably 2 to 10 times as much) should be employed to obtain best results. The rate of ammonia delivery should be controlled by a flow meter.

The amount of ammonia delivered at a given flow rate can be determined from the ammonia supplier's flow conversion tables or determined by measuring the rate of neutralization of hydrochloric acid solution, as described in Appendix B.

OXIDATION AND PROCESS WASHING

The final steps in achieving a high quality precondensate/ NH_3 finish are oxidation of the phosphorus polymer, process washing of the fabric to remove unreacted chemicals, and adjustment of the fabric pH. Oxidation can be accomplished by either a batch or a continuous process, employing commercial hydrogen peroxide.

For the batch process, 10% H_2O_2 (50% concentration) based on the weight of the treated fabric is added to sufficient water at 120°F to 140°F to provide a 20:1 liquor-to-fabric ratio. The fabric is immersed in the dilute peroxide solution to avoid any concentrated peroxide contact with the fabric.

Oxidation for 10 minutes in a rope washer in the mill or in a home washing machine in the laboratory is normally sufficient to complete conversion of the phosphorus to the pentavalent, or durable, state and to remove traces of odor. Rinsing with warm water or dilute (2% to 5%) Na_2CO_3 solution finishes the process wash. Fabric pH should be 5 to 8 following the wash.

For open-width, continuous oxidation, 10% H_2O_2 (50%) is padded at room temperature onto the fabric from a bath containing the appropriate amounts of H_2O_2 . Sufficient "sky-time" to allow 30 to 60 seconds exposure of fabric to this solution is required before rinsing and pH adjustment. If the wet pick-up of the treated fabric is significantly below 100%, the peroxide bath should be adjusted to an appropriate higher concentration.

Continuous washing requirements after oxidation are dependent upon fabric weight and construction and on the amount of unfixed polymer to be removed. Wash equipment that will produce a clean, neutral fabric should be available. After oxidation, the fabric normally is acidic and may require chemical neutralization in addition to water washing to neutralize the acidity.

After washing, the fabric is framed to width and dried.

MISCELLANEOUS FABRIC AFTER-TREATMENTS

Ammonia cure flame retardant fabrics lend themselves to further chemical treatments, such as top softening, durable press, and water repellency treatments. Normal procedures for these applications should be followed. Top treating should be done after the fabric has been oxidized, process washed and dried.

Aftertreatment with crosslinking resins decreases the shrinkage of the flame retardance treated fabrics and confers a modest level of easy-care properties. Strength losses experienced in resin treatment of the fire retardant fabric are considerably less than those expected for untreated cotton.

Flame retardant treated cotton fabrics can be compressively shrunk by common commercial techniques to obtain reasonable shrinkage control.

FLAMMABILITY EVALUATION

Fabrics treated adequately with precondensate/ NH₃ pass standard flammability tests both initially and after multiple washings, with short average char lengths. The short char lengths obtained after multiple washings attest to the durability of the polymer finish.

For research purposes, the oxygen index technique is often a useful guide.

Depending on the level of treatment, fabrics can meet either the rigorous 16 CFR Part 1615, the children's sleepwear standard, or at somewhat reduced add-ons, Federal Test Method Standard No. 191A, Method 5903, for safety apparel.

TREATMENT OF FABRIC BLENDS OF COTTON WITH MAN-MADE FIBERS

The precondensate/NH₃ polymeric flame retardant finish is specific in its protective mechanism for cotton fibers. The finish is readily insolubilized within the cotton fiber. Blends of cotton with other fibers, when cotton is the predominant fiber in the blend, can sometimes be successfully treated with this finish. Often, higher chemical add-ons are required to impart adequate fire retardance to such blends than would be required for 100% cotton fabrics of similar construction. While deposits of precondensate/ NH₃ may form on the surface of hydrophobic fibers, such as polyester, such surface applications have limited durability and cannot impart long-term fire retardance. Specific formulations applicable to blends must be determined empirically from laboratory experiments related to the level and identity of the synthetic fiber in the blend.

FUME HANDLING AND DISPOSAL

At certain stages of the precondensate/NH₃ process, discharge of fumes could prove offensive if precautions are not taken. Formaldehyde and ammonia, both of which can be detected in low concentrations, are the chemicals most often involved. Trace amounts of phosphorus chemicals with their characteristic odor can be handled readily in any system designed to exhaust formaldehyde and ammonia. Adequate ventilation is essential in the bath preparation area, over the pad and throughout the drying frame (including exit and entrance ends). If facilities do not adequately handle fume removal, modifications or extensions of in-place facilities may suffice to correct the problem. Disposal of exhausts into the atmosphere may not be permissible; scrubbing to remove excessive amounts of chemicals may be required.

Some ammonia delivery units have self-contained fume evacuation systems. Normally, ammonia fumes from these units can be discharged into the drying frame exhaust system so that disposal and scrubbing problems can be handled simultaneously. Residual ammonia on fabric as it exits the unit is usually minor and should permit handling with only normal ventilation facilities in that area.

While traces of odor may be observed during oxidation, no significant quantities of formaldehyde, ammonia, or other volatile material are present; thus, specific ventilation and disposal considerations may not be necessary.

CHEMICAL SOURCES			
Product	Chemical Name	Source	Product Information
A. Nonionic Surfactant	Tergitol TMN-6	Dow Chemical	Trimethylnonyl ether of polyethylene glycol
B. Flame Retardant Chemicals	Proban [®] CC	Rhodia	Phosphonium salt precondensate (chloride)
	Pyrosan [®] S-FRC	Noveon	Phosphonium salt precondensate (sulfate)
	Pyroset [®] TPO	Noveon	Phosphonium salt precondensate (sulfate)

APPENDIX A

ASSAY PROCEDURE FOR ACTIVE PHOSPHORUS

Standard Solutions

1. N/10 iodine (iodine/iodide)

2. Buffer pH-5

136g NaOAc · 3H₂O

30 ml HOAc (glac.)

Dilute to one liter total volume

3. Starch indicator

Method

1. Weigh about 0.2 g of product to be assayed into a 125 ml. Erlenmeyer flask. (Weigh to 3 significant figures.)

2. Add 10 ml. buffer (pH 5).

3. Add 25 ml H₂O.

4. Titrate with N/10 iodine to end point.

a. If starch indicator is used, add 10 drops just prior to reaching end point (color change is from colorless to blue).

b. If no indicator is used, color change is to pale yellow (slight excess of iodine).

Calculation

$$\begin{array}{l} \% \text{ P} \\ \text{(active phos.)} \end{array} = \frac{\text{ml. I}_3^- \times 0.1549}{\text{wt. of sample}}$$

Application

Determine P content in phosphonium flame retardants, either in product form or in prepared pad baths.

APPENDIX B

DETERMINATION OF AMMONIA FLOW BY HCl TITRATION

Equipment

- ammonia delivery system (tank, tubing, flow-meter)
- balance
- magnetic stirrer
- 250 ml. Erlenmeyer flask
- rubber tubing
- pipette
- graduated cylinder (100 ml.)
- stop watch

Reagents

- hydrochloric acid
- methyl orange indicator
- anhydrous ammonia

1. Make up a stock solution of 1 normal HCl (100 grams 37% HCl in one liter).
2. Add an aliquot of 100 ml. of stock solution to 100 ml. of water in a 250 ml. Erlenmeyer flask.
3. Add a few drops of methyl orange to the solution.
4. Pass anhydrous ammonia into the rapidly stirred solution, using the delivery system at a specific setting on the flow meter. Record the time required for neutralization (color change).
5. Repeat steps 2-4 at different flow meter settings. Because 0.1 mole of HCl is used in all cases, the ammonia time/flow relationship can be converted directly to the time required to deliver 0.1 mole of NH₃.

EXAMPLE:

It takes 4.8 seconds to neutralize 0.1 mole of HCl. Since 0.1 mole of NH₃ is required to neutralize 0.1 mole of HCl, 4.8 seconds were required to deliver 0.1 mole of NH₃, or 48 seconds to deliver one mole. The reciprocal of 48 is the moles per second of ammonia delivered; therefore, 0.0208 moles of NH₃ were delivered in one second.

$$\frac{0.1 \text{ mole NH}_3}{4.8 \text{ seconds}} = 0.0208 \text{ moles NH}_3/\text{second}$$

APPLICATION GUIDELINES

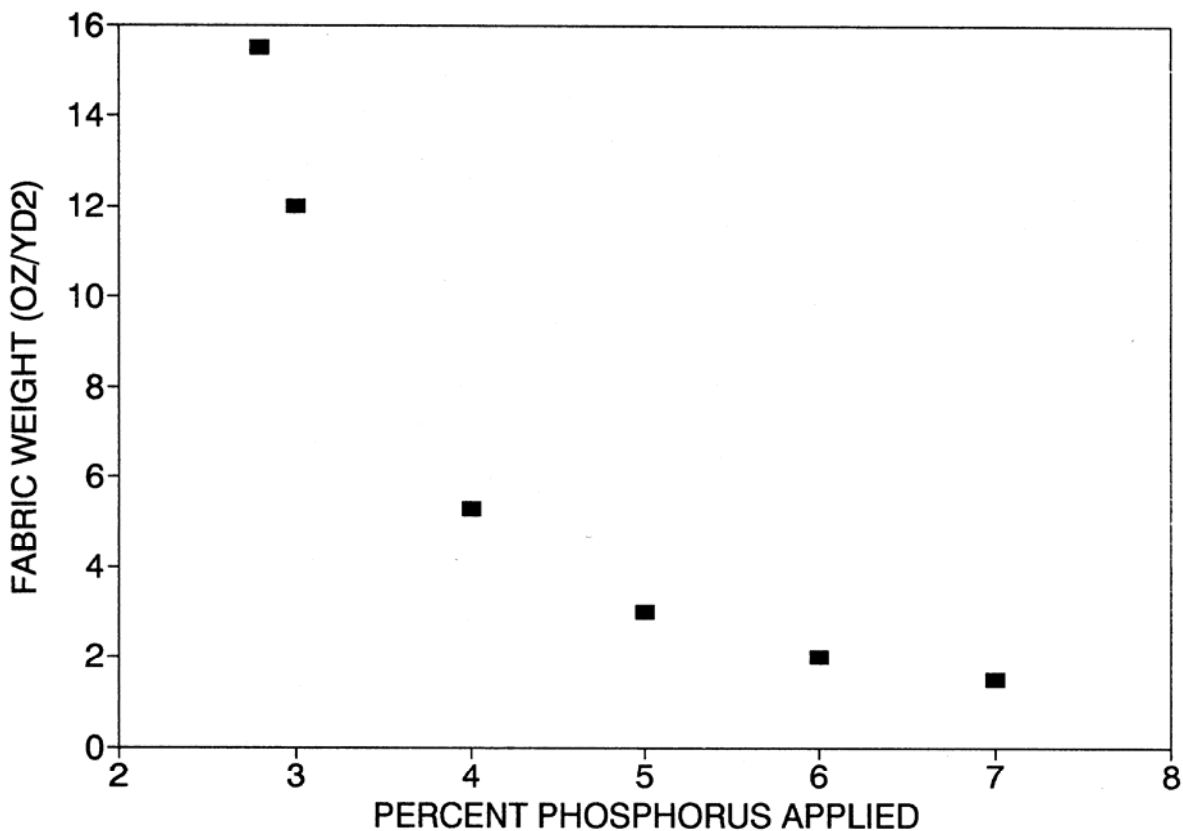


Figure 1

The statements, recommendations and suggestions contained herein are based on experiments and information believed to be reliable only with regard to the products and/or processes involved at the time. No guarantee is made of their accuracy, however, and the information is given without warranty as to its accuracy or reproducibility either express or implied, and does not authorize use of the information for purposes of advertisement or product endorsement or certification. Likewise, no statement contained herein shall be construed as a permission or recommendation for the use of any information, product or process that may infringe any existing patents. The use of trade names does not constitute endorsement of any product mentioned, nor is permission granted to use the name Cotton Incorporated or any of its trademarks in conjunction with the products involved.

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Cotton Incorporated is a research and promotion company representing cotton worldwide. Through research and technical services, our company has the capability to develop, evaluate, and then commercialize the latest technology to benefit cotton.

- Agricultural research leads to improved agronomic practices, pest control, and fiber variants with properties required by the most modern textile processes and consumer preferences. Ginning development provides efficient and effective machines for preservation of fiber characteristics. Cottonseed value is enhanced with biotechnology research to improve nutritional qualities and expand the animal food market.
- Research in fiber quality leads to improved fiber testing methodology and seasonal fiber analyses to bring better value both to growers and then mill customers.
- Computerized fiber management techniques result from in-depth fiber processing research.
- Product Development and Implementation operates programs leading to the commercialization of new finishes and improved energy and water conserving dyeing and finishing systems. New cotton fabrics are engineered -- wovens, circular knits, warp knits, and nonwovens -- that meet today's standards for performance.
- Technology Implementation provides comprehensive and customized professional assistance to the cotton industry and its customers -- textile mills and manufacturers.
- A fiber-to-yarn pilot spinning center allows full exploration of alternative methods of producing yarn for various products from cotton with specific fiber profiles.
- The Company operates its own dyeing and finishing laboratory, knitting laboratory, and a laboratory for physical testing of yarn, fabric, and fiber properties including High Volume Instrument testing capable of measuring micronaire, staple length, strength, uniformity, color, and trash content.

For further information contact:

COTTON INCORPORATED
WORLD HEADQUARTERS
6399 WESTON PARKWAY
CARY, NC 27513
PHONE: 919-678-2220
FAX: 919-678-2230

COTTON INCORPORATED
CONSUMER MARKETING HEADQUARTERS
488 MADISON AVENUE
NEW YORK, NY 10022-5702
PHONE: 212-413-8300
FAX: 212-413-8377

Other Locations

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