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DEVELOPMENT OF THERMALLY STABLE POLYBENZIMIDAZOLE (PBI) FIBER

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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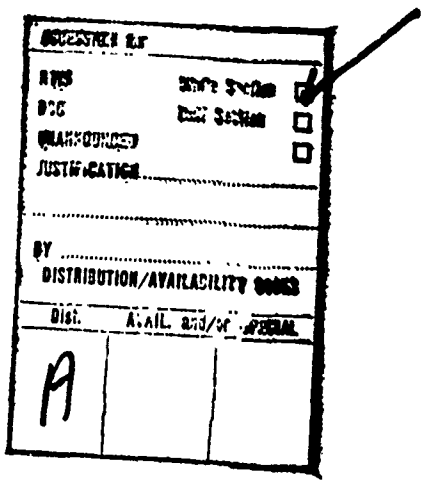

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FOREWORD

This report was prepared by Dynatech R/D Company under Contract No. F33657-70-C-1156 to the Aeronautical Systems Division, Life Support System Program Office, Endeavor Number AO117, Wright-Patterson Air Force Base, Ohio. The work was administered by the Nonmetallic Materials Division, Air Force Materials Laboratory, Directorate of Laboratories. Mr. Robert M. Stanton and Mr. Stanley Schulman were project engineers.

This report covers work conducted from June 8, 1970 to November 16, 1971. Dynatech Report Number: 1022.

The program was directed by Mr. Ralph L. Wentworth. Technical supervisor of the program was Mr. Kenneth R. Sidman. Physical testing and polymer evaluation was supervised by Mr. John B. Gregory. Assisting in the evaluation of candidate reagent systems and the set-up of the fabric treatment facility were Mr. Glenn K. Armstrong, Dr. Shafik E. Sadek, and Mr. William H. Crandell. Consultants to the project team were Prof. P. L. T. Brian and Prof. J. Baldwin.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and simulation of ideas.

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13. ABSTRACT

Textiles composed of polybenzimidazole (PBI) fibers combine superior qualities of non-flammability and comfort with functional utility. A further improvement desired in the qualities of PBI fabric is reduction of its tendency to shrink when exposed to flame and high temperature. Such shrinkage on exposure of an individual to a fire may bring the fabric of a garment in more intimate contact with the wearer. Elimination of the tendency to shrink would reduce the rate of heat transfer to a wearer, prolonging the period of protection in a fire exposure situation. The work reported here was undertaken to develop a treatment for PBI which stabilizes it with respect to thermal shrinkage.

Chemical treatment of PBI fiber or fabric which introduces chemical bonds between the basic polymer chains of PBI was found to stabilize PBI against thermal shrinkage. Among such treating agents examined a treatment involving immersion of PBI in a liquid mixture of 5% chlorosulfonic acid in phosphorous oxychloride followed by heating and neutralization was found to be satisfactory. Fabric so treated is resistant to thermal shrinkage yet unchanged in strength and nonflammability. The treatment is stable to laundering.

Woven PBI fabric was treated by the process developed. Following demonstration of the adequacy of this fabric, a pilot processing line for treating PBI tow was constructed. PBI tow treated on this pilot line was converted into fabric for evaluation.

As a result of this work, a functionally acceptable process for reducing the thermal shrinkage of PBI fiber has been developed. It is recommended that further investigation of the tow treatment process be conducted in order to attain improved balance of the color and fabric properties of treated material.

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Flammability						
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Polybenzimidazole						
Chlorosulfonic Acid						
Phosphorous Oxychloride						

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ABSTRACT

Textiles composed of polybenzimidazole (PBI) fibers combine superior qualities of nonflammability and comfort with functional utility. These characteristics qualify PBI fabric especially well for service in Air Force garments such as flyer's suits and coveralls. A further improvement desired in the qualities of PBI fabric is reduction of its tendency to shrink when exposed to flame and high temperature. Such shrinkage may bring the fabric of a garment in more intimate contact with the wearer, thus increasing the rate of heat transfer to the individual from a flame source. Elimination of the tendency to shrink would reduce the rate of heat transfer to a wearer, prolonging the period of protection in a fire exposure situation. The work reported here was undertaken to develop a treatment for PBI which stabilizes it with respect to thermal shrinkage.

Chemical treatment of PBI fiber or fabric which introduces chemical bonds between the basic polymer chains of PBI was found to stabilize PBI against thermal shrinkage. The effectiveness of a number of such treating agents and the coincident effects on other fiber properties were determined. A treatment involving immersion of PBI in a liquid mixture of 5% chlorosulfonic acid in phosphorous oxychloride followed by heating and neutralization was found to be satisfactory. Fabric so treated is resistant to thermal shrinkage yet unchanged in strength and nonflammability. The treatment is stable to laundering.

Woven PBI fabric was treated by the process developed. Following demonstration of the adequacy of this fabric, a pilot processing line for treating PBI tow was constructed. PBI tow treated on this pilot line was converted into fabric for evaluation.

A functionally acceptable process for reducing the thermal shrinkage of PBI fiber has been developed. It is recommended that further investigation of the tow treatment process be conducted in order to attain improved balance of the color and fabric properties of treated material.

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Section 1

SUMMARY

Polybenzimidazole (PBI) fibrous structures exhibit stability to high temperature oxidation, excellent textile physical properties, and high moisture regain. However, when subjected to flames PBI fabrics tend to shrink. Work at Dynatech R/D Company under contract for NASA-MSC improved both the thermal and oxidative resistance and dimensional stability of PBI fabric. An optimization of the vapor treatment was undertaken for the Aeronautical Systems Division, Life Support System Program Office ASWL, Wright-Patterson Air Force Base.

Reagent systems other than the vapor phase treatment of PBI with phosphoryl chloride proved to be superior, and treatment of fabric with 5% chlorosulfonic acid in phosphorus oxychloride proved to be outstanding. Seven yards of fabric were treated by this process and submitted to the Air Force Material Laboratory for evaluation. This fabric met the target requirements: exhibiting less than 10% thermal shrinkage in a test of exposure for seven seconds to a controlled Meker burner flame, less than 10% shrinkage on treatment, no reduction in tensile strength, and flammability essentially the same as the untreated fabric. The treatment was stable to prolonged rinsing in alkaline solutions and washing in alkaline soap solutions.

In Phase II of the program the chlorosulfonic acid treatment was converted to a continuous process to treat PBI tow. A pilot processing line capable of treating approximately one pound per hour of PBI tow was constructed. Process variables were adjusted on this line until a combination of tow properties including low thermal shrinkage, good color, and high tensile strength was achieved. Thirty pounds of treated tow were prepared and converted into fabric for evaluation.

It is recommended that development work on the treatment of tow by this process be extended to include the investigation of other parameters which could not be examined under the scope of this program. It is anticipated that the material and specifications developed in such an investigation will enable the attainment of the balance of color and fabric properties necessary for Air Force textile material.

Section 2

INTRODUCTION

2.1 Background

As a result of the interest of the Department of the Air Force in developing a chemical treatment of polybenzimidazole (PBI - specifically, 2,2' (m-phenylene) -5, - (6,6' -bibenzimidazole)) fibrous structures to effect a superior nonflammable, thermally stable, and nonshrinking material, Contract No. F33657-70-C-1156 was awarded to Dynatech R/D Company. The primary emphasis of this work was to be the optimization of vapor phase treatment of PBI with phosphoryl chloride to effect a thermal stabilization of the fiber. A two phase investigation was proposed - the first phase consisting of the research and development of the treatment method and the second concerned with scale-up of the process to treat quantities of material.

2.1.1 Scope

As the investigation progressed, it became apparent that the phosphoryl chloride treatment was not exceptionally effective in stabilizing fibrous structures of the polymer. Consequently, the study was broadened to include the investigation and optimization of other reagent systems that provide thermally stable crosslinks between polymer chains. The crosslinks were intended to restrict the polymer chain mobility so that the highly strained, anisotropic chain configuration produced by the fiber drawing would not relax when heated.

2.1.2 Technical Discussion

Polybenzimidazole fibers have tremendous potential value in the manufacture of nonflammable clothing - they exhibit the flexibility, drape, surface characteristics, moisture regain and physical properties known to determine comfort. In addition, they are self-extinguishing in environments containing less than 35% by volume oxygen (for fabric conditioned at 70° F and 65% relative humidity). The present PBI fibers, however, exhibit thermal shrinkage in the brief exposure, high intensity heat of the open pit flame test. This shrinkage is apparently due to a relaxation of the polymer chains.

Two methods present themselves for minimizing thermal shrinkage. One involves preshrinking the fabric through chemical or heat treatment so that the resultant cloth exhibits a very low thermal shrinkage. The other involves reducing the mobility of the polymer chains.

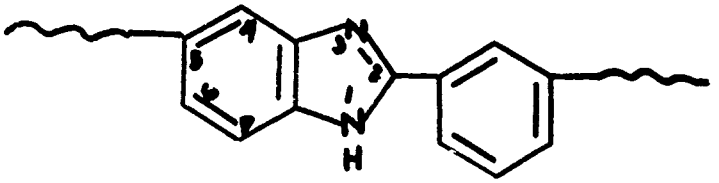
The PBI fibers may be preshrunk through the use of chemical agents able to swell and plasticize the polymer. In this case the swelling agent enhances chain mobility and permits the polymer molecules to reorient themselves to relieve the strain. The same relaxation may be achieved by heating the fibers. In either case, a decrease in tensile strength occurs because the anisotropic, strained configuration contributing to the fiber strength is lost.

To reduce chain mobility, crosslinks may be introduced along the polymer chain in sufficient number so that these bonds will connect the individual polymer molecules into a three-dimensional network. Such a network greatly restricts the fiber shrinkage. In this approach the tensile strength of the fiber is retained.

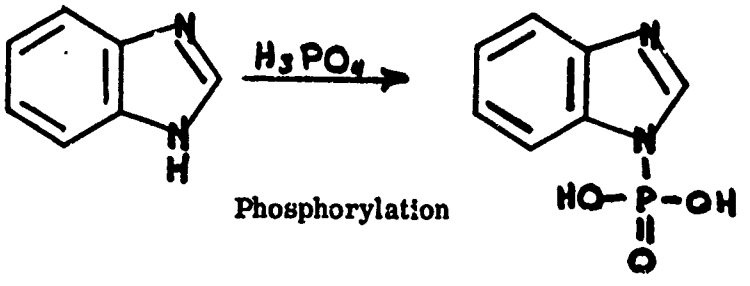
Crosslinks may be introduced into the fiber thermally or chemically. Thermal crosslinking of certain polybenzimidazoles was described by Plummer and Marvel (Ref. 1). They found that heating the polymers under vacuum at temperatures exceeding 300° C tended to change the yellowish compounds to a brownish-black form that was insoluble in all solvents. The conversion of the aromatic rings to diphenyl groups was discussed as a possible crosslinking mechanism. In oxygen-containing atmospheres, temperature above 350° C have been reported to induce crosslinking. In these cases also, a reduction in polymer solubility was taken as evidence of crosslinking behavior. Shulman and Lochte reported (Ref. 2) that at pyrolysis temperatures between 450° C and 500° C crosslinking of PBI occurs via amide interchange or bisphenyl coupling.

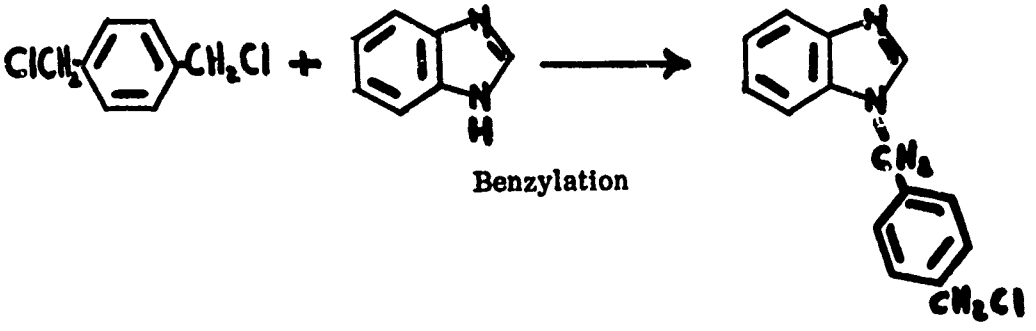
Chemically, crosslinks may be introduced through the incorporation of any moiety on the polymer chain that will bridge across chains. The 1- and 3-positions of the benzimidazole ring and the aromatic moieties are particularly susceptible to attack. Consequently, multifunctional agents selected on the basis of their reactivity with these sites, offer promise as potential crosslinking agents.

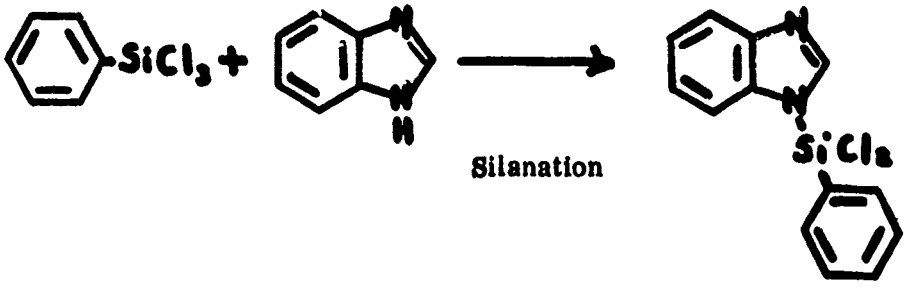
The site-numbering system is as follows:

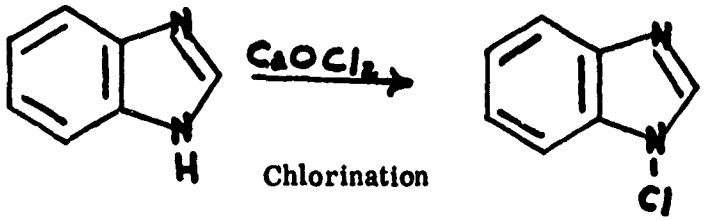


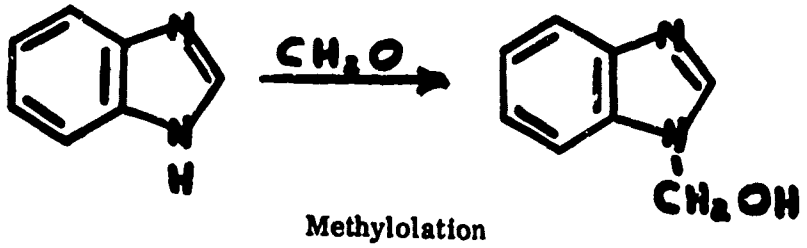
From a review of the chemistry of benzimidazoles (Ref. 3), it is possible to identify a number of candidate reactions. The imidazole ring, for example, may be attacked by phosphorylating, silanating, chlorinating, and methylolating agents.





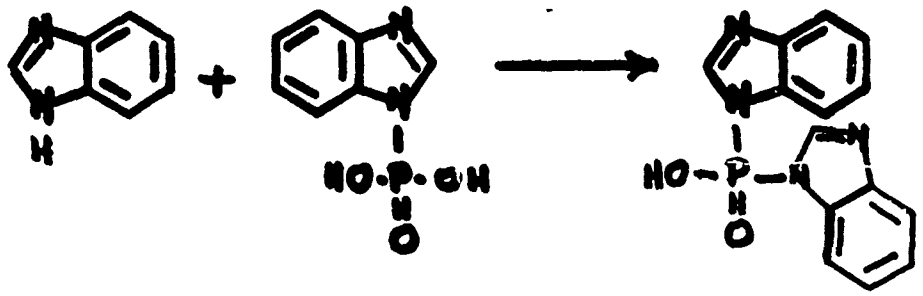




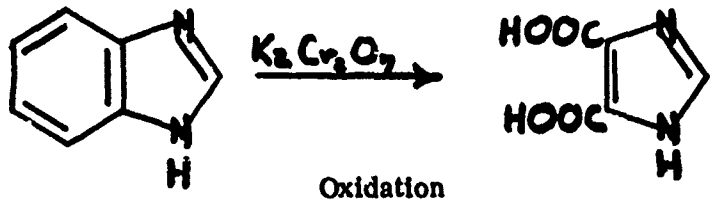


Methylolation

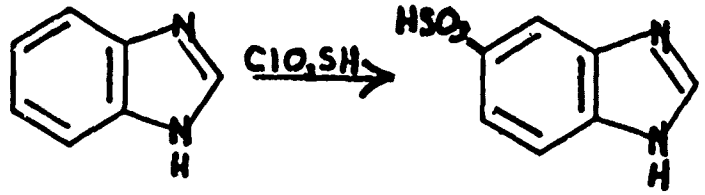
These agents may crosslink through imidazole rings. For example,



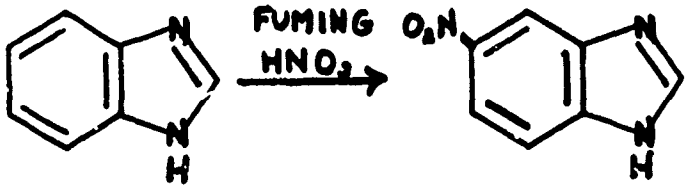
Oxidizing, sulfonating, nitrating, acylating, and free-radical generating agents have been shown to attack aromatic nuclei. For example,



Oxidation

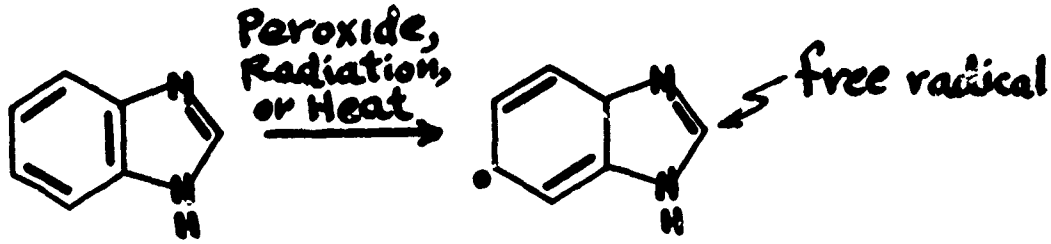


Sulfonation



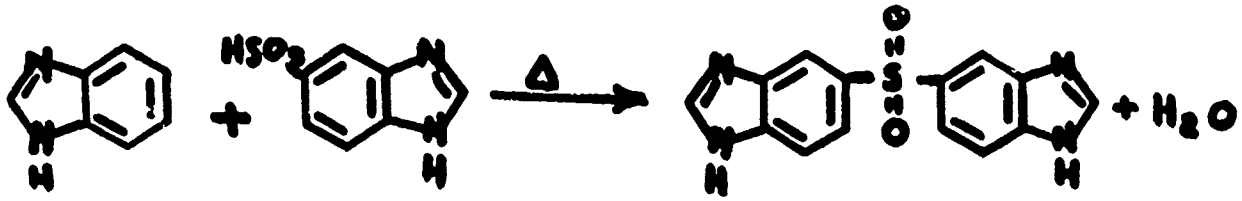
Nitration

Acylation



Free-Radical Generation

Crosslinking may then occur either between aromatic rings



or between an aromatic and an imidazole ring.

The effectiveness of the crosslinking is measured with respect to improvements in fabric dimensional stability while at the same time maintaining desirable textile properties.

2.2 Method of Approach

In Phase I of the program two experimental approaches were undertaken. The first involved an extension of the $POCl_3$-oxygen, vapor-phase treatment developed for NASA-MSC under Contract NAS 9-8179. The second approach consisted of a search for and optimization of crosslinking agents which dimensionally stabilize PBI fibrous structures.

Treatments were evaluated first for effectiveness in reducing the thermal shrinkage of fabric samples. If shrinkage behavior was found to be improved then the durability of the treatments to laundering was evaluated. If they passed these two examinations, the treated fabrics were examined for color, hand and drape, flammability, and moisture regain.

The goal of this first phase of the contract was to produce a treated fabric with less than 20% thermal shrinkage by the end-use application test of the Air Force Materials Laboratory, less than 30% fabric shrinkage on treatment, less than 25% reduction in tensile strength, and flammability essentially the same as the untreated fabric.

In Phase II of the program the feasibility of the process developed in Phase I was evaluated for treating PBI in the form of fabric, yarn, staple, fiber, and spinning dope. The advantages and disadvantages of treatment in the various forms are summarized in Table I. On the basis of this analysis, it was decided to treat PBI tow.

A tow treatment facility was established on which the process variables were adjusted to give the best combination of low thermal shrinkage, good color, and high tensile strength.

Thirty pounds of PBI were then processed to provide a sufficient quantity of treated cloth for end-item tests in full scale open-pit flame trials.

Table I

The Advantages and Disadvantages of Treating PBI in Various Forms

PBI Form Treated	Advantages	Disadvantages
	- Uniform treatment of PBI ensured regardless of form of end item and end item precursors.	- Changes in PBI reaction conditions, spinning conditions, and drawing conditions would be required
Spun and drawn fiber	- Uniform treatment of PBI ensured-independent of end item. - No change required in present PBI processing techniques. - Applicable to proposed 1-2 million lb/yr facility producing fiber and tow.	- Changes in fiber handling and processing equipment may be required to adjust for changes in surface characteristics and denier of fiber
Staple	- Fiber may be processed through to staple with no change in equipment settings or equipment. Batch processing possible.	- Not applicable to continuous filament processing. - Changes in staple handling and processing equipment may be required.
Yarn	- PBI may be processed through to staple with no change in equipment setting or equipment.	- Changes in present yarn handling and processing equipment may be required. - Changes in chlorosulfonic acid process reaction conditions will be required depending on weight of yarn.
Fabric	- Fiber may be processed into end-item-no dislocation of any PBI processing step is necessary.	- Chlorosulfonic acid process would have to be modified for various weaves, weights, and widths of fabric.

Section 3

PROCEDURES AND RESULTS

3.1 Phase I - Experimental

The experimental fabric treatments discussed in this report were conducted in four types of reactors - one constructed of stainless steel, two of glass, and one of stainless steel and glass. The 316 stainless steel reactor, a Benco Model 150-E equipped with a gas sparge tube, dual heating mantles, condenser, and pressure gauge, is shown in Figures 1 and 2. The Benco stainless steel reactor was used to evaluate phosphorus oxychloride vapor phase reactions at elevated temperatures and pressures. Glass Reactor #1, consisting of a 4000 mℓ beaker heated by a hot plate and covered by a 2000mℓ round flask to serve as an air condenser, was used to evaluate treatments involving fabric immersion. Glass Reaction #2, consisting of a 2000mℓ resin reaction kettle, Scientific Glass Company Catalogue Number J4401, equipped with an electric heating mantle, oxygen sparge tube, and a condenser, was used to conduct reactions in the vapor phase under reflux conditions. A reactor constructed from 310 stainless steel and Pyrex glass was used to process continuously the seven square yards of fabric submitted to the Air Force Materials Laboratory in fulfillment of one of the contract requirements of Phase I. This continuous fabric treatment reactor, which was the prototype for the tow treatment facility in Phase II, described in detail below.

3.1.1 Continuous Reactor

A pilot scale treatment facility was constructed to evaluate the critical elements in the continuous process. A seven inch 316 stainless steel pipe was used as the reactor. Heat lamps were set up before and after the reactor to dry the fabric and vaporize excess phosphorus oxychloride, respectively. A motorized take-up roll with variable speed control was used to vary the residence time of the fabric in the reactor. A Schematic diagram of the pilot facility is given on page 13. Following treatment of a web of fabric in the pilot facility, the roll of fabric was unwound and draped in an air circulating oven at 300° C for varying periods in order to complete the treatment.

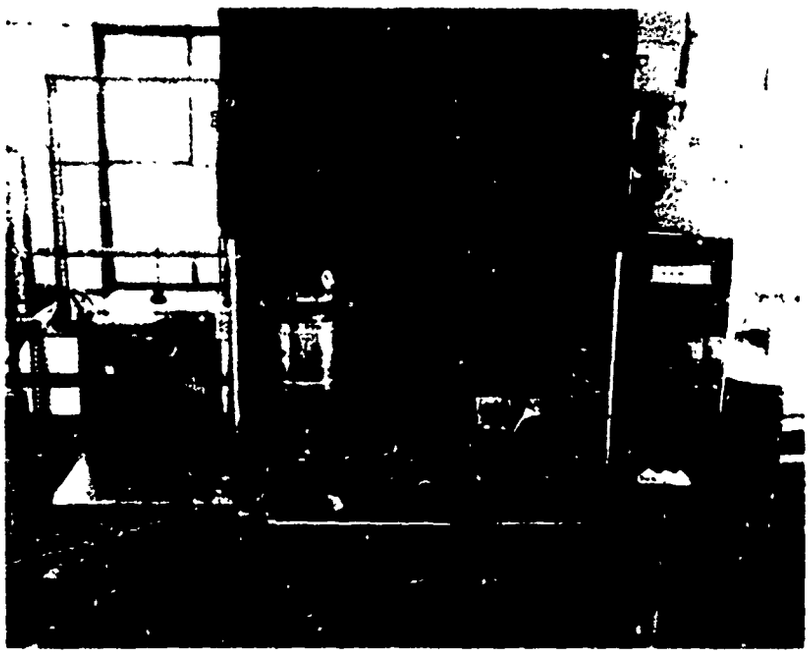


Figure 1. Photograph of $POCl_3$ Treatment Apparatus

From left to right:
Gas Cylinders
Control Panel
Constant Temperature Oil Bath
Bubblers (removed from bath for photograph)
Reactor
Oven
Scrubber (not shown)

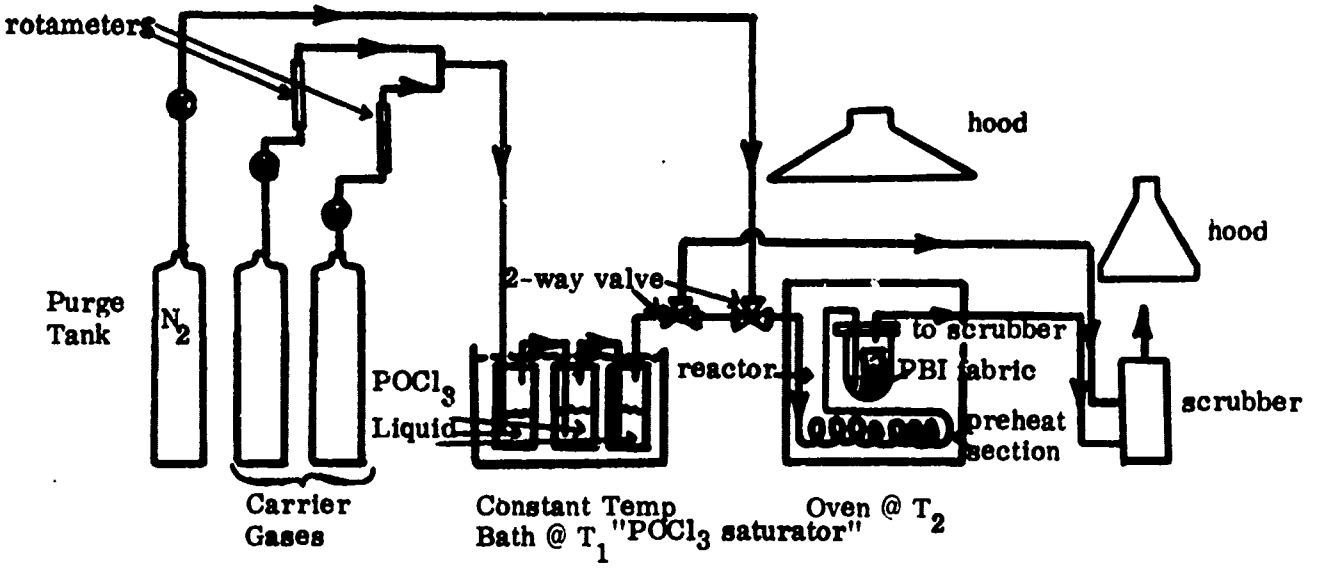


FIGURE 2

Schematic Arrangement of $POCl_3$ Treatment Apparatus

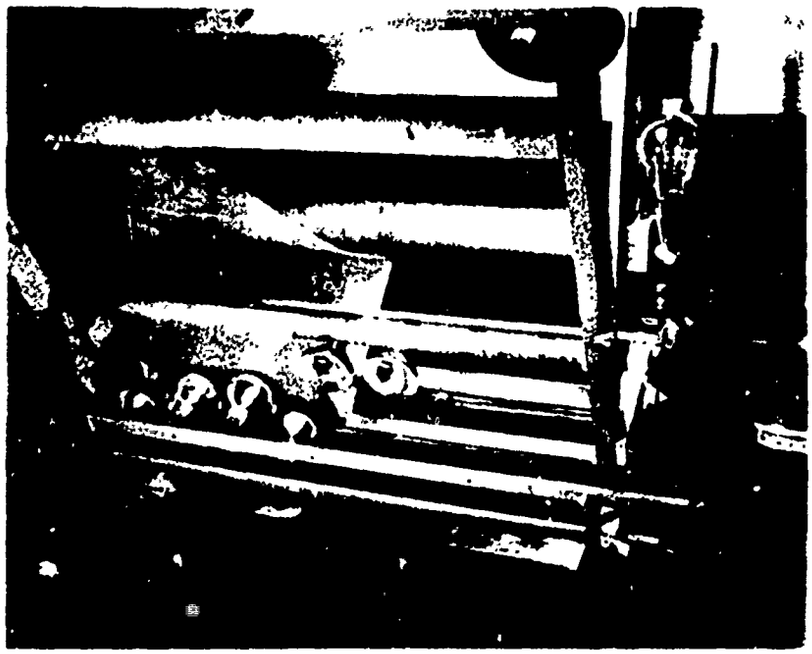


FIGURE 3

Continuous Process Line Set Up to Show

Path of Fabric

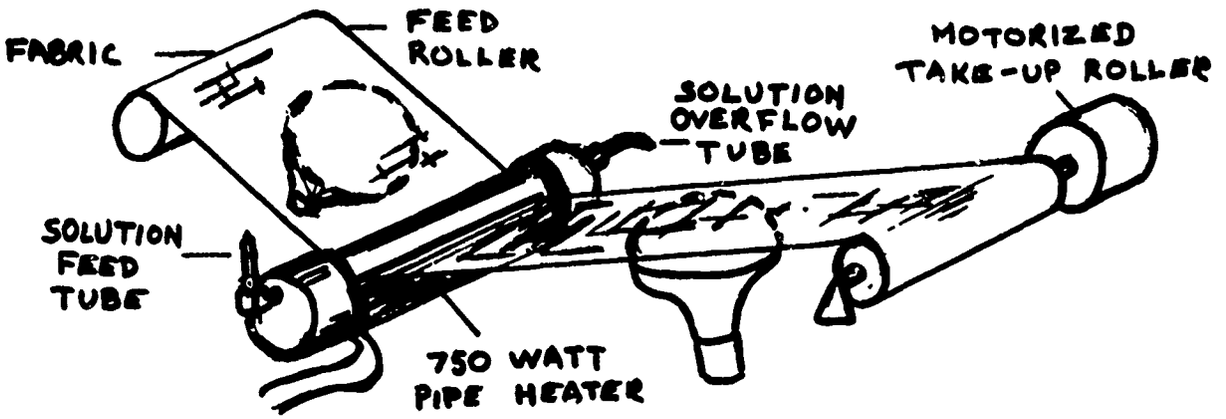


Figure 4. Schematic Diagram of Pilot Scale Treatment Facility

The pilot reactor was scaled up to treat a 46 inch wide fabric swatch. From the pilot work it was found that contact between layers of the fabric on the take-up roll caused discolorations and stiffening in the contact areas. To remedy this, polyethylene film was inserted between each layer. The full scale unit is shown schematically below and is pictured in Figure 3.

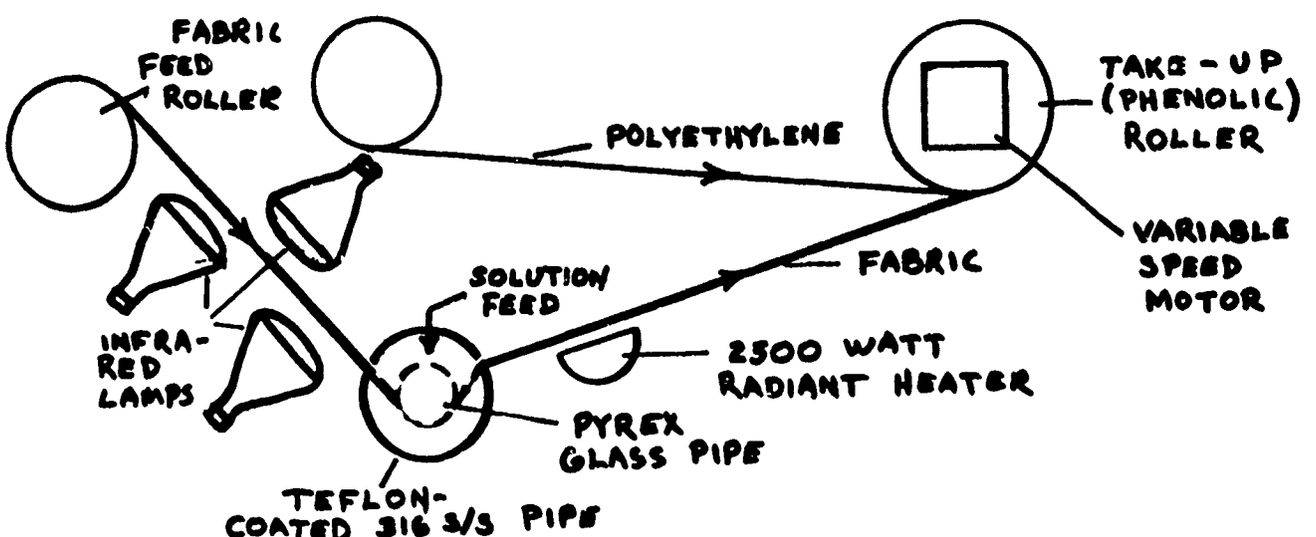


Figure 5. Schematic Diagram of 46-Inch Wide Treatment Facility

3.1.2 Chemicals

Reagent grade chemicals were used in the experiments except where otherwise noted.

3.1.3 Polybenzimidazole Fabric

The physical properties of the fabrics used in Phase I are given in Table II. The method for testing for fabric shrinkage during flame impingement is given in Appendix A.

3.1.4 Study of Effectiveness of Various Treatments

The study of treatments of the reduction of thermal shrinkage of polybenzimidazole fabric is summarized in Tables IV and XI.

3.1.5 Preparation of 7 Yards of Fabric Using Optimum Conditions

Table XII gives the details of the fabric treatment procedure and the physical properties of the fabric before and after treatment.

3.2 Phase II - Experimental

3.2.1 Apparatus

The pilot facility for the treatment of PBI tow is shown in Figure 4.

3.2.2 PBI Tow

In the process evaluation experiments 550 fil (1.5 denier/fil) fiber was plied to 16,500 fil tow. To prevent the tow from expanding as it passed over rollers in the process line, a twist of 1.5 turns/inch was incorporated into the tow.

In the production of 30 lbs of treated fiber, 5000 fil tow, plied to 15,000 fil and twisted 1.5 turns/inch was utilized.

The tow was treated in the as received condition - the lubricating oils were not removed prior to processing.

The physical properties or the fiber used in the process evaluation experiments are given in Table III.

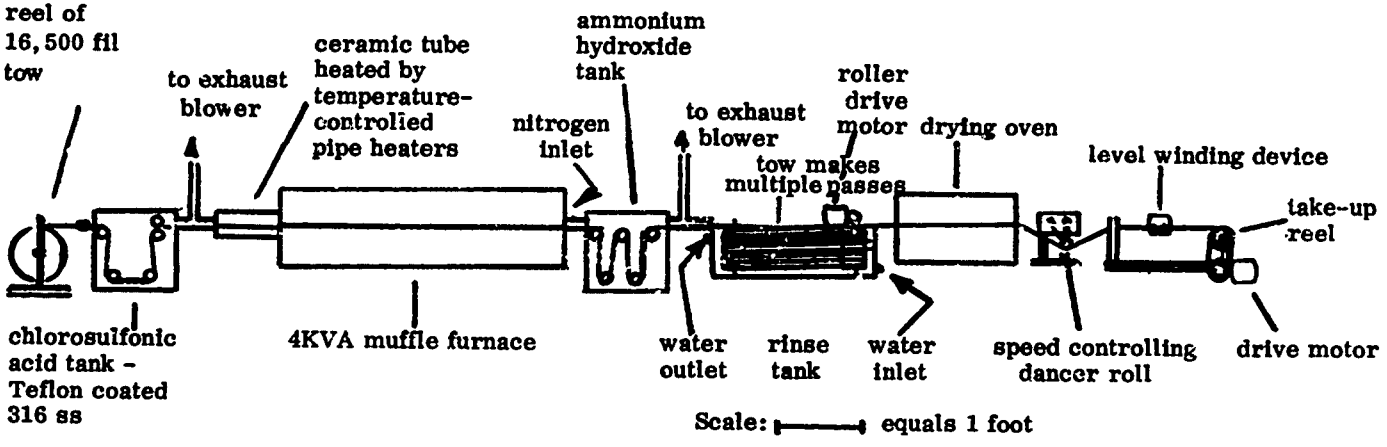


Figure 6. Processing Facility for the Application of the Chlorosulfonic Acid Stabilization Treatment to PBI Tow

3.2.3 Chemicals

Technical grades of chlorosulfonic acid (duPont) and phosphorus oxychloride (Hooker) were used in Phase II processing.

Table II
Physical Properties of Polybenzimidazole Fabric

Sample Number	6-1[1]	6-2[1]	73-1[7]	118-1[8]
Thread Count - threads/in.	68 x 68	90 x 90	-	-
Weave	2/1 Twill	3/3 Twill	2/1 Twill	2/1 Twill
Weight - oz/yd^2				
As received	4.49	4.77	-	-
After Dry Cleaning [3]	4.51	4.88	-	-
After Dry Cleaning [3] and Washing[4]	4.64	4.77	-	-
Tensile Strength[5] - lbs/in.				
As received	98	97	94	-
After Dry Cleaning	95	95	-	-
After Dry Cleaning and Washing	91	93	98	100
Elongation at Break[5] - %				
As received	25	20	23	-
After Dry Cleaning	21	10	-	-
Af After Dry Cleaning and Washing	20	13	22	17
Shrinkage Druing Flame Impingement[6] - %	57.5	61.9	62	65
LOI[9]	-	-	0.36	0.34

Notes

(1) Samples received from Air Force Materials Lab (AFML) on 6 July 1970, approx. 3 yds^2 of 6-1 and 4 yds^2 of 6-2.
(2) Fed. Test Method Std. 191, Method 5040, full width short specimen method.
(3) Dry cleaned for 45 minute cycle in a coin operated dry cleaning machine.
(4) Washed in 8 lb. commercial coin operated washer with reciprocating agitator for full cycle through spin dry, using hot water and 38 grams of standard neutral soap chips obtained from AATCC Research, Triangle Park, N.C. 27709, and 38 grams of technical sodium meta silicate, Will Scientific Co., Cambridge, Mass., and dried for 30 minutes in a commercial coin operated dryer.
(5) Fed. Test Method Std. 191, Method 5104 - three specimens warp direction only. Test performed on fabric after washing and dry cleaning.

Notes continued on next page.

(6) The shrinkage test used consisted of exposure of fabric to 1300° F temperature for 1 minute (see Appendix A). This thermal exposure greatly exceeds the thermal input anticipated in personnel-survivable fires. This test was used as a research tool to screen candidate stabilization treatments and the shrinkage results obtained greatly exceed the shrinkages obtained in end-item application tests such as the open-pit flame test.
(7) Approx. 20 yds^2 received from AFML on 21 August 1970.
(8) 3 yds^2 received from AFML on 11 January 1971.
(9) LOI (limiting oxygen index) is the minimum percent oxygen by volume in a mixture of oxygen and nitrogen in which the sample will burn.

Table III
Physical Properties of PBI Fiber (550 fil)[1]

Denier	1.5
Tensile Strength[2]	-
Shrinkage on Thermal Exposure[3]	60-70%

Notes

(1) Received from the Air Force Materials Laboratory March 1971
(2) See Appendix B
(3) See Appendix C

TABLE IV

Study of Treatments for Reduction of Thermal Shrinkage of Polybenzimidazole Fabric*

Run No.	Fabric Type	Reagent	Reagent Concentration	Reaction Temp. °F	Carrier Gas	Special Conditions	Reactor Type	Reaction Time min.	Neutralization Procedure	Wt. % Addition	% Shrinkage	Tensile Strength lbs/in
0	6-2	---	----	---	---	---	--	---	----	----	61.9	97
1a	6-2	$POCl_3$	gas, 104 mm	225	N_2, 1.9SCFH	before laundering	steel	140	washed with H_2O	----	55.3	---
						after laundering	steel		washed with H_2O	----	58.1	---
1b	6-2	$POCl_3$	gas, 220 mm	225	N_2, 1.9SCFH	before laundering	steel	150	washed with H_2O	----	41.5	---
						after laundering	steel		washed with H_2O	----	57.0	---
2	6-1	$POCl_3$	gas, 220 mm	240	O_2, 1.2SCFH	anhydrous	steel	140	soda ash + H_2O	----	56.5	---
3	6-2	$POCl_3$	gas, 440 mm	253 - 250	O_2, 0.8SCFH	anhydrous	steel	90	water wash	27.4	58.8	91 ± 2
4	6-2	$POCl_3$	gas, 440 mm	240	O_2, 4.4SCFH	anhydrous	steel	30	water wash	5.2	54.2	91 ± 15
5	6-2	$POCl_3$	gas, 440 mm	240	O_2, 4.4SCFH	anhydrous	steel	240	water wash	3.2	61.3	100 ± 3
6	6-2	$POCl_3$	gas, 440 mm	245	N_2, 1.9SCFH	anhydrous bubbler	steel	60	water wash	5.7	50.9	89 ± 4
7	6-2	$POCl_3$	gas, 440 mm	240	O_2, 1.9SCFH	anhydrous	steel	60	water wash	2.4	57.1	91 ± 10
8	6-2	$POCl_3$	gas, 440 mm	300	O_2, 0.8SCFH	anhydrous	steel	165	water wash	12.1	----	---
9	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 0.4SCFH	under reflux	glass	30	NaOH + H_2O	9	~50	---
10	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 0.4SCFH	under reflux wet with 10% H_3PO_4	glass	30	NaOH + H_2O	----	Insufficient Sample	---
11	6-2	$POCl_3$	gas, 440 mm	225 - 235	O_2, 1.9SCFH	fabric wet with 10% H_3PO_4	steel	120	Na_2CO_3 + H_2O	----	47.8	---
12a	6-2	$POCl_3$ - pyridine	40% $POCl_3$	240	---	---	glass	30	Na_2CO_3 + H_2O	----	49.4	---
12b	6-2	"	40% $POCl_3$	240	---	---	glass	180	Na_2CO_3 + H_2O	----	63.9	---
12c	6-2	"	40% $POCl_3$	240	---	---	glass	1440	Na_2CO_3 + H_2O	----	57.7	---
13	6-2	$POCl_3$	gas, 440 mm	240 - 280	O_2, 1.9SCFH	20% H_3PO_4 painted on	glass	35	$NaHCO_3$ + H_2O	----	49.6	---
14a	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	wet with $POCl_3$, no reflux	glass	60	$NaHCO_3$ + H_2O	----	50.0	---
14b	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	reflux, no $POCl_3$	glass	60	$NaHCO_3$ + H_2O	----	49.0	---
14c	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	no reflux, no $POCl_3$	glass	60	$NaHCO_3$ + H_2O	----	50.6	---
14d	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	reflux sample heated 700°F, 3-1/2 hrs.	glass	60	$NaHCO_3$ + H_2O	----	26.0	---
14e	6-2	----	----	---	---	heated 700°F, 3-1/2 hrs.	----	---	----	----	40.0	---
15a	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	$POCl_3$ wet out	glass	240 - 300	Na_2CO_3 + H_2O	----	41.3	---
15b	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	$POCl_3$ wet out/heated 700°F, 3 hrs.	glass	240 - 300	Na_2CO_3 + H_2O	----	32.5	---
15c	6-2	$POCl_3$	liq/gas, 760 mm	218 - 228	O_2, 1.9SCFH	20% H_3PO_4 wet out	glass	240 - 300	Na_2CO_3 + H_2O	----	28.0	---
16	6-2	$POCl_3$	liquid	80	---	---	glass	300	water rinse	----	50.8	---

CONTINUED

See Table II for Fabric Identity

TABLE IV (Continued)

Run No.	Fabric Type	Reagent	Reagent Concentration	Reaction Temp. F	Carrier Gas	Special Conditions	Reactor Type	Reaction Time min.	Neutralization Procedure	Wt. % Addition	% Shrinkage	Tensile Strength lbs/in
17	6-2	$POCl_3$	liquid	230	---	---	glass	60	water rinse	----	45.1	---
18	6-2	$POCl_3$	liquid	150	---	---	glass	30	water rinse	11.7	44.7	---
19	6-2	$POCl_3$	liquid	150	---	---	glass	30	water rinse	10.4	43.5	---
20	6-2	$POCl_3$	liquid	150	---	---	glass	5	water rinse	10.4	53.5	---
21	6-2	$POCl_3$	liquid	70	---	---	glass	30	water rinse	9.0	53.2	
22	6-2	$POCl_3$	liquid	70	---	---	glass	30	$Na_2CO_3 + H_2O$	10.3	54.8	---
23	6-2	$POCl_3$	liquid	70	---	---	glass	2	Na_2CO_3	----	58.1	---
24	6-2	$POCl_3$	liquid	70	---	---	glass	5	water rinse	4.9	58.1	---
25	6-2	$POCl_3$	liquid	70	---	---	glass	30	water rinse	9.6	58.1	---
26	6-2	$POCl_3$	liquid	70	---	---	glass	2	water rinse	6.0	61.9	---
27	6-2	$POCl_3$	liquid	39	---	---	glass	5	water rinse	2.5	61.6	---
28	6-2	$POCl_3$	liquid	39	---	---	glass	30	water rinse	3.1	59.4	
29	6-2	$POCl_3$	liquid	39	---	---	glass	2	water rinse	1.9	58.0	
30	6-2	$POCl_3$	liquid	70	---	---	glass	30	water rinse	4.2	54.7	---
31	6-2	$POCl_3$	liquid	70	---	---	glass	6	$Na_2CO_3 + H_2O$	1.8	59.0	---
32	6-2	$POCl_3$	liquid	150	---	---	glass	30	$Na_2CO_3 + H_2O$	10.3	46.4	---
33	6-2	$POCl_3$	liquid	150	---	---	glass	30	$Na_2CO_3 + H_2O$	9.0	50.1	---
34	6-2	$POCl_3$	liquid	150	---	---	glass	5	$Na_2CO_3 + H_2O$	9.9	53.1	---
35	6-2	$POCl_3$	liq gas, 750 mm	218 - 228	O_2, 1.9 SCFH	H_3PO_4 spread on fabric waste $POCl_3$ used	steel	90	$Na_2CO_3 + H_2O$	----	23.0	---
36a	6-2	H_3PO_4	liquid	260	---	---	glass	30	$Na_2CO_3 + H_2O$	----	30.3	---
36b	6-2	H_3PO_4	liquid	268	---	---	glass	30	$Na_2CO_3 + H_2O$	----	23.0	---
36c	6-2	H_3PO_4	liquid	268	---	---	glass	60	$Na_2CO_3 + H_2O$	----	30.8	---
36d	6-2	H_3PO_4	liquid	288	---	---	glass	15	$Na_2CO_3 + H_2O$	----	30.3	---
36e	6-2	H_3PO_4	liquid	288	---	---	glass	30	$Na_2CO_3 + H_2O$	----	31.2	---

TABLE V-1

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing Temp °F	Rinsing Time Mins	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	By Treatment Only	% Shrinkage Over-all Shrinkage	By Thermal Exposure(2)
37	6-2	200 ml $POCl_3$ + 10 ml Br_2	RT to 193	15	-	-	-	-	-	Fabric smells of Br_2	-	-	-	36
81	6-2	10g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	380	5	Color unchanged	non-burning	-	-	62
82	6-2	10g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	380	15	Color unchanged	non-burning	-	-	62
83	6-2	10g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	380	5	Color unchanged	-	-	-	56
84	6-2	100g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	380	15	Color unchanged	-	-	-	54
85	6-2	Sat Soln $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	390	15	Color unchanged	-	-	-	54
86_1	6-2	10g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	390	5	-	-	-	-	55
86_2	6-2	10g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	390	15	-	-	-	-	50
82_1	6-2	100g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	212	5	H_2O	RT	1	390	45	-	-	-	-	42
83_2	←	←	same as above →					390	330	-	-	-	-	42
83_3	←	←	same as above →					390	120	-	Darker after heating	-	-	44
Control	6-2	←	omitted →					400	210	-	-	-	-	67
8K	6-2	85g/L $K_2Cr_2O_7$ to pH of 1 @ HCl	RT + 212	10 60	H_2O	RT		390	10 10	leach in $(NaPO_4)6$ + HCl 5 min rinse; leach $(NaPO_4)6$ + NaOH, 4 rinses NaOH at 212 dry	Color br-black after 1st day very slight green at end	slight tendency to burn	-	-	42

See last page of Table for notes.
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TABLE V-2

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing	Rinsing Temp °F	Rinsing Time Mins.	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure (3)
$S8_1$	6-2	10g/L $K_2Cr_2O_7$ + 20 ml glacial acetic acid	212	5	H_2O	RT	1	-	-	-	Darkened slightly	Slight burning	-	-	44
$S8_2$	← same as above →							390	15		Soft darkened	burns	-	-	39
$S8_3$	← same as above →							390	105	-	Less soft than $S8_1$ and darker	-	-	-	23
38A	6-2	10g/L $KMnO_4$	212	5	H_2O	RT	1	-	-	-	-	-	-	-	36
38B	6-2	10g/L $KMnO_4$ + 10ml glacial acetic acid	212	5	H_2O	RT	1	-	-	-	Very dark	-	-	-	48
38C	6-2	10g/L $KMnO_4$ + 100 ml glacial acetic acid	212	5	H_2O	RT	1	-	-	-	Very dark	-	-	-	47
38D	6-2	10g/L $KMnO_4$ + 10gm/L NaOH	212	5	H_2O	RT	1	390	5	-	-	-	-	-	42
39	6-2	3 MEV electrons various doses up to 12 Mrads	500	-	-	-	-	-	-	-	-	-	-	-	60
Control 73-1		← omitted →								-	Soluble in boiling NMP	LOI=0.36(2)	-	-	-
N1	6-2	4 ml /L 70% HNO_3	212	5	running H_2O			410	5	-	Insoluble in boiling NMP (purple color)	LOI=0.35(2)	-	-	22
N3	← same as above →							160	1	-	Color unchanged	LOI=0.35(2)	-	-	38
N4	6-2	4ml /L 70% HNO_3	212	5	running H_2O			160+	1	-	Some brown spots	-	-	-	37
								410	5	-	-	-	-	-	
N4A	← same as above →							160 + 410	1 60	-	-	-	-	-	37
$N4_1$	← same as above →							410	5	Sample dyed with Maxilon Blue before drying	Did not turn purple	-	-	-	-

See last page of Table for Notes.

TABLE V-3

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Conditions: Reagent	Conditions: Temp °F	Conditions: Time Mins.	Rinsing	Drying: Temp °F	Drying: Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage: By Treatment Only	% Shrinkage: Over-all Shrinkage	% Shrinkage: By Thermal Exposure(3)
40A	6-2	40 ml /L formic acid	RT	5	running H_2O	390	10	-	-		0		-
40B	6-2	200 ml /L formic acid	RT	5	running H_2O	390	10	-	-		22		-
40C	6-2	400 ml /L formic acid	RT	5	running H_2O	390	10	-			42		-
40D	6-2	600 ml /L formic acid	RT	5	running H_2O	390	10	-	-		53		-
40E	6-2	800 ml/ L formic acid	RT	5	running H_2O	390	10	-	-		61		
N5	6-2	20g/L 70% HNO_3	212	5	running H_2O	410	3	-	deep purple color		-		17
N6	6-2	20g/L 70% HNO_3	212	5	running H_2O plus 1g/L NaOH room temp 10 min & running water	-	-	-	-		-		
41	6-2	80% H_3PO_4	220	5	NaOH pH 12, 212°F, 15 min running water	400	15	-	soluble in boiling NMP		32		-
CL1	6-2	400 ml /L 5.25% Chlorox	212	15	none	410	5	-	cloth stiff and color slightly darker		-		34
CL1*	6-2	400 ml /L 5.25% Chlorox	212	15	running hot water	410	5	-	-		-		53
CL2	6-2	400 ml /L 5.25% Chlorox plus 4 gm/L NaOH	212	5	none	410	5	-	cloth stiff and color slightly darker		-		25
CL2*	6-2	same as above	212	5	running hot water	410	5	-	-		-		37
42	6-2	70% HNO_3	-32	30	rinse and immerse in $SnCl_2$ sol'n & HCl	390	15	*Rinsed and immersed in* KNO_2 & HCl after $SnCl_2$ treatment and before drying	deep purple color insoluble in boiling NMP non-dyeable at boil at 5% formic acid containing 1.5% of various dyes		-		20
42A	6-2	70% HNO_3	-32 to -12	15	rinse and immerse in $SnCl_2$ sol'n & HCl	390		Rinsed and immersed in $POCl_3$ at 76°F, after $SnCl_2$ treatment then rinse in Alconox sol'n, rinsed in H_2O before drying	purple color		-		25

See last page of table for notes.

TABLE V-4

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(3)
43B	6-2	-			rinse and immerse in $SnCl_2$ sol'n & HCl	-	-	same as above except dyed with Maxilon blue GRC before final rinse - color green	color green	-	-	-	25
N73	6-2	4 ml L 70% HNO_3	80	5	running water	300	15	-	color unchanged	-	-	-	53
N74	←	←	same as above		→	410	15	-	purple stains	-	-	-	53
N83	←	←	same as above		→	300	15	-	color unchanged very brittle after shrinkage test	-	-	-	58
N84	←	←	same as above		→	410	15	-	purple stain		-	-	58
N91	6-2	24 ml/L 70% HNO_3	90	5	running water	240	15	-	color unchanged	-	-	34	34
N92	←	←	same as above		→			-	color unchanged	-	-	-	34
N93	←	←	same as above		→	300	8	-	slightly purple	-	-	-	34
N94	←	←	same as above		→			-	slightly purple	-	-	-	34
N95	←	←	same as above		→	410	5'	-	dark purple	-	-	-	23
N96	←	←	same as above		→			-	dark purple	-	-	-	30
N10	6-2	143 ml/L 70% HNO_3	90	5	running water	240	16	-	brittle after shrinkage test	-	-	-	30
$N10_2$	←	←	same as above		→			-	brittle after shrinkage test	-	-	-	30
$N10_4$	←	←	same as above		→	300	6	-	very brittle after shrinkage test	-	-	-	30
$N10_5$	←	←	same as above		→	410	6	-	purple color	-	-	-	34
$N10_6$								-	-	-	-	-	22
$N11_1$	6-2	40° Be conc HNO_3	93	5	running water	300	5	-	slightly purple (edges)	-	-	-	19

See last page of table for notes.

TABLE V-5

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Conditions: Reagent	Conditions: Temp °F	Conditions: Time Mins.	Rinsing	Drying: Temp °F	Drying: Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage: By Treatment Only	% Shrinkage: Over-all Shrinkage	By Thermal Exposure(3)
$N11_2$	← same as above →					100	5	-	Dark purple streaks	-	-	-	13
$N11_3$	← same as above →					210	15	-	Very slight darkening	-	-	-	23
N12	6-2	40° Be conc HNO_3	90	5	running water	310	15	-	Color brown	-	-	-	30
$N12_1$	← same as above →							neutralized in $NaHCO_3$ solution before drying	Color brown	-	-	-	23
$N13_1$	← same as above →					210	90		Color unchanged	-	-	-	13
$N13_2$	← same as above →							neutralized in $NaHCO_3$ solution before drying	-	-	-	-	39
$N13_3$	← same as above →					310	15	neutralized in NH_4OH before drying	Turned purple	-	-	-	19
44A	6-2 ←	omitted									0	65	65
44B	6-2	water	212	5		-	-	-	-	-	0	65	65
44C	6-2	6.7 ml /L 40° Be HNO_3	212	5	running water	-	-		-	-	15	42	31
44D	6-2	13.4 ml /L 40° Be HNO_3	212	5	running water	-	-	neutralized in NH_4OH	-	-	15	56	48
44E	6-2	40 °Be conc HNO_3 plus 98% H_2SO_4 1ith 1 1 by vol	~40	5	running water	280	10	neutralized in NH_4OH before drying	-	-	25	63	50
44F	6-2	40° Be conc HNO_3	~10	5	running water	280+ 410	10 60	neutralized in NH_4OH before drying	-	-	27	54	51
45A	73-1	40° Be conc HNO_3 plus 98% H_2SO_4 1 1 by vol	~12	3	NH_4OH PH12 plus running water	400	15	rinse in 30% HCl sat with $SnCl_2$ for 5' at RT wash + NH_4OH + wash. Dye in Polyamide Fast Blue FBL 10g/L+10 cc formic acid at 212°F for 5 rinse + NH_4OH +rinse before drying	Deep blue color and not turn purple at 400°F	-	-	-	44

See last page of table for notes.

TABLE V-6

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(3)
45B		same as 45A except after treatment fabric dipped into $POCl_3$ at RT for 2: neutralized with Na_2CO_3 soln rinse and dry							Olive (sage) green Color did not turn Purple in oven at 400°F	-	-	-	44
46A	73-1	40° Be conc HNO_3 plus 98% H_2SO_4 1 1 by vol	-12	3	NH_4OH 12 plus running water	400	15	Rinse in 30 -HO sat with $SnCl_2$ for 5 at RT wash H_2O, rinse NH_4OH_2 wash H_2O immerse in liquid $POCl_3$ neutralize in Na_2CO_3 solu, wash, rinse NH_4OH wash dve as in 45A	Forest blue color - did not turn purple at 400°F	-	-	-	39
46B		same as above				-	-	same as above except repeated $POCl_3$ dip and wash	Same as above	-	-	-	39
47	73-1 dried 15' at 200°C	40° Be conc HNO_3 plus 98% H_2SO_4 1 1 by vol.	-20	5	NH_4OH pH 12 plus running water	400	15	-	Color unchanged before shrinkage test		25	58	44
48	73-1 dried 15' at 200°C	40° Be conc HNO_3	0	5	NH_4OH pH 12 plus running water	400	15	98% H_2SO_4 added to HNO_3 after 5' temp rose to 12°C	Non-uniform purple color developed		52	62	19.5
49A	73-1	$POCl_3$	0 RT	5	NH_4OH pH 12 plus running water	400	15	Dip sample in cold ethylene glycol after immersion in $POCl_3$	-	-	-	40	-
49B		same as above						Dip sample in cold methanol after immersion in $POCl_3$	-	-	-	43	-
49C	73-1	$POCl_3$	212	30	NH_4OH pH 12 plus running water	400	15	Dip sample in boiling ethylene glycol for 20 mins and rinse Dip sample in boiling methanol for 15 mins and rinse	-	-	-	31 39	- 15.7
50	73-1 dried 15' at 200°C	40° Be conc HNO_3	-8	15	NH_4OH pH 12 plus running water	400	15	Purple only in crease	Purpled only in crease but tensile strength 51 lbs/in vs. 87 for control	-	-	-	-

See last page of table for notes.

TABLE V-7

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type(1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing Medium	Rinsing Temp °F	Rinsing Time Mins.	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(3)
50	73-1 dried 15' at 200°C	40° Be conc HNO_3	-5	15	NH_4OH pH12 plus running water			400	15	-	Purpled only in creases, but tensile strength 51 lb/in vs. 87 for control.	-	-		15.7
51A	73-1	70% HNO_3, 98% H_2SO_4 90% HNO_3 75 75 100 by vol	-10	15	NH_4OH pH12 plus running water			100	15	-	Fabric yellowish brown large discolored area appears to have yellow precipitate on fabric.	-	-		-
51B	← same as above →		-10	10 sec	Same as above			500	5	-	-	-	-		
52	73-1	50cc 85% H_3PO_4, 100cc H_2O 50g urea pH 0.3	Soak		-			400	15	-			28	47	26
53	← same as above →				NH_4OH pH12 plus running water			400	15	-	-	-	42	53	19
54	same as above plus heating at 700°F				same as above plus washing cycle(4)			400	15	-	Cloth darkened	-	-	-	42
55	73-1	Dilute HNO_3 pH0.5 for 2 min place on hot plate & add $POCl_3$ with eye dropper			-			400	15	-	Fabric turned yellow when $POCl_3$ added, did not turn purple at 400°F.	-	-	-	50
56A	73-1	conc H_3PO_4 85%	662	5	-			-	-	-	Fabric shrank and turned black & brittle.	-	38	-	-
56B		10% H_2SO_4 at 392°F for 15' plus 85% H_3PO_4 at 230°F for 10'			wash heat at 395°C for 10' rinse in 15% NH_4OH, rinse in water and dry			-	-	-	After H_2SO_4 color yellowish brown, after H_3PO_4 greenish brown	-	48		22

See last page of table for notes.

TABLE V-8

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type (1)	Reagent	Conditions Temp °F	Conditions Time Mins.	Rinsing Temp °F	Rinsing Time Mins.	Drying Temp °F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(3)
57A	73-1	10% H_2SO_4 at 392°F for 5' plus Lupersol 133 (4) at 437°F for 5'	-	-	-	-	-	-	-	Fabric shrank			45	-
57B	73-1	Epichlorohydrin brushed on fabric dried 500°F 5'		-	-	-	-	-	-	No stiffening of fabric	-	-	45	-
57C	73-1	10% H_2SO_4 plus drying at 700°F for 10'	-	-	-	-	-	-	-	Treated areas did did not dye with combination of Geigy Maxilon Blue and Polyamide	-	-	-	-
58A	73-1	Silane Y-4310(5)	392	15	-	-	-	-	-	Fast Blue	-	-	-	61
58B	73-1	Silane A 1100(6)	392	15	-	-	-	-	-	-	-	-	-	64
59	73 1	250 cc $POCl_3$ 10g terephthalic acid, 25 cc PCl_3 10g $AlCl_3$	212	15	-	-	-		-	-	-	-	-	50
60	73-1	Same as above substituting maleic anh. for terephthalic acid	212	10	Water & NH_4OH & water		428	10	-	-	-	-	-	48
61A	Similar to above using chloromaleic anhydride		same as above						-	-	-	-	-	50
61B	same as above		same as above except rinsed after drying						-	-	-	-	-	31
62A	73-1	10% H_2SO_4 tested at 428°F for 10' plus 85% H_3PO_4 at 230°F for 15'			Water and NH_4OH		428	10	-	-	-	-	-	33
62B		same as above except dried before neutralizing in NH_4OH and rinsing							-	-	-	-	-	27

See last page of table for notes.

TABLE V-9

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

Run No.	Fabric Type (1)	Reagent	Conditions Temp F	Conditions Time Mins.	Rinsing Temp F	Rinsing Time Mins.	Drying Temp F	Drying Time Mins.	Additional Treatment	Remarks	Burning Characteristics	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(3)
63A	73-1	30 cc chlorosulfonic acid plus 270 cc $POCl_3$ + 2g $AlCl_3$	212	5	15% NH_4OH		536	5	Repeated treatment	-	-	-	53	-
63B	← same as above except heated 30 mins at 212 →									-	-	-	53	-
63C	73-1	30 cc chlorosulfonic acid plus 270 cc $POCl_3$	212	5	no rinse		536	5	Repeated treatement	-	-	18	31	16
63D	73-1	30 cc chlorosulfonic acid plus 270 cc $POCl_3$	212	5	15% NH_4OH		536	5	Repeated treatment	-	-	18	38	24
63E	← same as 63C plus treatment in 10% H_3PO_4 and drying →									Fabric somewhat stiffer	-	18	33	19
63F	same as 63E except rinsed in 15% NH_4OH and dried →									than before treatment	-	18	34	20
64	73-1	10g I_2 in 400 cc 85% H_3PO_4	300	30	15% NH_4OH and rinse		428	10		Treated fabric lighter than original	-	-	39	-

NOTES:

(1) See Table I for fabric description. All fabric was laundered as specified in Table I before treatement.

(2) LOI (limiting oxygen index) is the minimum percent oxygen by volume in a mixture of oxygen and nitrogen in which the sample will burn.

(3) See Appendix A for procedure.

(4) 90% 2.5 dimethyl 2.5 di (t butylperoxy) hexane Lucidol Div.- Wallace and Tiernan

(5) Alcohol solution of proprietary silane-Union Carbide Co.

(6) gamma aminopropyl triethoxy silane - Union Carbide Co.

TABLE VI-1

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC[1]

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment[2]	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure[3]
58-1	100 ml L 98% H_2SO_4	100	15	running water	10	300	15		Soft, flexible char after shrinkage test	-	-	16
58-2	100 ml/L 98% H_2SO_4	100	15	running water	10	300	15	Washed once in standard soap solution	Soft, flexible char after shrinkage test	-	-	16
58-3	100 ml/L 98% H_2SO_4	100	15	running water	10	500	15		Soft, flexible char after shrinkage test	-	-	13
58-4	100 ml/L 98% H_2SO_4	100	15	running water	10	500	15	Washed once in standard soap solution	Soft, flexible char after shrinkage test	-	-	13
58-5	100 ml/L 98% H_2SO_4	100	15	running water	10	500	15	Washed twice in standard soap solution; pH of solution after wash ~6	Soft, flexible char after shrinkage test	-	-	13
58-6	100 ml/L 98% H_2SO_4	100	15	running water	10	500	15	Washed three times as above; pH of solution after wash ~11	Soft, flexible char after shrinkage test	-	-	23
58-7	100 ml/L 98% H_2SO_4	100	15	running water	10	500	15	After 4th wash as above, pH~11.5	Soft, flexible char after shrinkage test	-	-	42
60-1	50 ml/L 98% H_2SO_4	100	15	running water	10	300	15		Soft, flexible char after shrinkage test	-	-	8
60-2	50 ml/L 98% H_2SO_4	100	15	running water	10	300	15	Washed once in standard soap solution	Soft, flexible char after shrinkage test	-	-	8
60-3	50 ml/L 98% H_2SO_4	100	15	running water	10	500	15		Soft, flexible char after shrinkage test	-	-	12
60-4	50 ml/L 98% H_2SO_4	100	15	running water	10	500	15	Washed once in standard soap solution	Soft, flexible char after shrinkage test	-	-	12
60-5	50 ml/L 98% H_2SO_4	100	15	conc. NH_4OH plus running water	10	500	15		Hard, brittle char after shrinkage test	-	-	44
61-1	20 ml/L 98% H_2SO_4	100	15	running water	10	300	15			-	-	12
61-2	20 ml/L 98% H_2SO_4	100	15	running water	10	500	15			-	-	9

For notes see end of table.

TABLE VI-2

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC[1]

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment[2]	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure[3]
61-3	20 ml/L 98% H_2SO_4	100	15	running water	10	500	15	Washed once in standard soap solution	Soft, flexible char after shrinkage test	-	-	9
61-4	20 ml/L 98% H_2SO_4	100	15	conc. NH_4OH plus running water	10	500	15		Hard, brittle char after shrinkage test	-	-	45
62-1	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Immerse 10 gm/L urea in water after first rinse and rinse again; pH of urea solution after treatment = 2	Soft, flexible char after shrinkage test	-	-	14
62-2	44 ml/L 98% H_2SO_4	RT	5	running water	10	220	10	Immerse 10 gm/L urea in water after first rinse and rinse again; pH of urea solution after treatment = 2	Soft, flexible char after shrinkage test	-	-	20
63-1	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Immerse 10 gm/L urea in water after first rinse and rinse again; pH of urea solution after treatment = 2	Soft, flexible char after shrinkage test	-	-	16
64-1	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Immerse 10 gm/L urea in water after first rinse and rinse again; pH of urea solution after treatment = 2		-	-	9
64-2	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Washed once; pH of wash = 6		-	-	22
64-3	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Washed twice		-	-	31
64-4	44 ml/L 98% H_2SO_4	RT	5	running water	10	400	10	Washed twice; pH of wash = 9.9		-	-	52
65-1	20 ml/L glacial acetic	RT	10	none	-	160	10			-	-	62
65-2	20 ml/L glacial acetic	RT	10	none	-	400	2			-		62
65-3	20 ml/L conc. HCl	RT	2	none	-	160	10			-	-	50
65-4	20 ml/L conc. HCl	RT	2	none	-	400	2			-	-	50
66-1	20 gm urea + 50 ml 40% HCHO + 100 ml water then into 120 ml/L 98% H_2SO_4	RT RT	10 5			 400	 10			 -	 -	 17
66-2	20 gm urea + 50 ml 40% HCHO + 100 ml water then into 120 ml L 98% H_2SO_4	RT	5			400	10	Washed once; pH of soap was 3.8 after washing		-	-	23

For notes see end of tables.

TABLE VI-3

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC[1]

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment[2]	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure[3]
67-1	Into 50% H_3PO_4 5' then 28% NH_4OH for 1' then in 50 gm/L Ca I_2 for 5'			running water	10	400	3			-	-	30 to 40
67-2	Into 50 gm L NaH_2PO_4 then into 50 gm/L $CaCl_2$			running water	10	400	5			-	-	55
68-1	None					700	45		Fabric turned brown	-	-	44
68-2	None					700	960		Fabric very dark brown., flexible, strong char after shrinkage	-	-	20
68-3	None					700	960	Rinse conc. NH_4OH 5 mins., dried at 400° F	Flexible, strong char after after shrinkage	-	-	28
69-1	20 ml/L conc. HNO_3	RT	5	running water	10	240	15	Washed once; pH of soap = 9 after washing	Brittle char after shrinkage	-	-	34
69-2	20 ml/L conc. HNO_3	RT	5	running water	10	240	15	Washed twice; pH of soap = 10 after washing	Brittle char after shrinkage	-	-	61
69-3	20 ml/L conc. HNO_3	RT	5	running water	10	400	5	Washed once; pH of soap = 9 after washing	Fabric turned purple after drying	-	-	25
69-4								Washed twice; pH of soap = 10		-	-	28
69-5								Washed thrice;pH of soap = 10		-	-	31
69-6								Washed four times; pH of soap = 10		-	-	31
69-7								Washed 69-5 in conc. NH_4OH for 5' at RT; dried at 400° F		-	-	23
70-1	30 gm/L $K_2Cr_2O_7$ plus 20 ml/L 98% H_2SO_4	RT	5	running water	10	400	3	Washed once		-	-	58
71-1	None					700	120		Fabric brown - will not dye	6	-	50
71-2	None					700	240		Fabric brown - will not dye	-	-	36
71-3	None					610	1400		Fabric brown - will not dye	6	-	28
72-1	30 gm/L $K_2Cr_2O_7$ plus 20 ml/L 98% H_2SO_4	RT	350					Washed once	Fabric very dark		-	23

For notes see end of table.

TABLE VI-4

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC[1]

NOTES:

(1) See Table I in the second status report on this project dated July 16, 1970 for a description of fabric 6-2 used in these tests.

(2) The washing procedure used was to boil the fabric for 15 minutes in 800 ml of soap solution containing 1 gram of neutral chip soap and 1 gram of sodium metasilicate.

(3) See Appendix A for shrinkage test procedure. The % shrinkage is based on the area of the treated sample.

TABLE VII-1

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions Temp °F	Conditions Time (Mins.)	Rinsing Medium	Rinsing Time (Mins.)	Drying Temp °F	Drying Time (Mins.)	Additional Treatment	Remarks	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure (2)
63-1	40°Bé HNO_3	50	5	Hot H_2O	3	280	90		-	-	-	15
63-2	←	same as above		→				Dip in $POCl_3$ 5' wash hot H_2O 5' rinse in conc NH_4OH and dry	-	-	-	14
63-3	←	same as above		→				Sat with $SnCl_2$ 5' at RT, wash hot H_2O, neutralize in NH_4OH and dry	-	-	-	14
63-4	←	same as above		→				Same as above plus dip again in $POCl_3$, rinse hot H_2O, 3' dip conc NH_4OH, wash 2' and dry 10' at 200°F	-	-	-	14
64-1	40°Bé HNO_3 plus conc H_2SO_4 50 50 by vol	-	-	Hot H_2O 5' plus NH_4OH rinse		280	15	-	-	-	-	15
64-2	←	same as above		→				Dip in $POCl_3$ 5' wash hot H_2O rinse NH_4OH	-	-	10	33
64-3	←	same as above		→				Dip in conc HCl sat with $SnCl_2$ 5' rinse neutralize in NH_4OH and dry	-	-	-	25
64-4	←	same as 64-1		→				-	-	-	-	33
64-5	←	same as 64-3 plus dip in $POCl_3$ 5' neutralize wash and dry		→				-	-	-	-	33
65-1	same as above	-30	4	Hot H_2O 5 plus NH_4OH rinse		280	15	-	-	-	-	29
65-2	same as above	-10	5	same as above				-	-	-	-	31
65-3	Boiling $POCl_3$ 1' hot plate to drive off $POCl_3$	dip in methanol dry on hot plate - neutralize NH_4OH						-	-	-	22	33
65-4	Dry fabric into $POCl_3$ at boil dry on hot plate	-	-			-	-	-		-	-	44
65-5	Same as above except damp fabric		-			-	-	-	-	-	-	39

See end of table for notes.

TABLE VII-2

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure(2)
65-6	← same as above except for damper fabric							-	-	-	-	38
65-7	ethylene glycol heat to 300°F	-	-	-	-	-	-	-	-	-	-	42
65-8	ethylene glycol dry then $POCl_3$ then dry	-	-	-	-	-	-	-	-	-	-	26
65-9	like 66-8 except neutralized in NH_4OH	-	-	-	-	-	-	-	-	-	-	29
66-1	$POCl_3$ at RT, 16 hrs hot plate dry plus 10' at 356°F	-	-	-	-	-	-	-	-	-	-	16
66-2	same as above except methanol dip plus wash in cold H_2O before drying →							-	-	-	10	9
66-3	Dip in $POCl_3$ plus conc HCl at 150°F, 2'. Pad on methanol, dry, neutralize with NH_4OH, wash with hot H_2O							-	-	-	-	42
66-4	Dip in mixture of $POCl_3$ and methanol at 150°F for 2', dry, wash in methanol							-	-	-	-	39
67-1	1% glycol 85% H_3PO_4	212	5	-	-	-	-	-	-	-	0	65
67-2	← same as above except 5% sol'n →							-	-	-	3-1	53
67-3	← same as above except 10% sol'n →							-	-	-	10	19.5
67-4	Like 67-1 except after treating with 70% urea solution at boil, rinse with dil NH_4OH, wash, and dry							-	-	-	-	44
67-5	Like 67-2 except after treating with 70% urea solution at boil, rinse with dil NH_4OH, wash, and dry							-	-	-	-	40
67-6	Like 67-3 except after treating with 70% urea solution at boil, rinse with dil NH_4OH, wash, and dry							-	-	-	-	35
67-7	5% by vol 85% H_3PO_4 in water	212	5	-	-	392	5 days	-	Sample turned brown	-	-	43
67-8	1% by vol 85% H_3PO	212	5	-	-	392	5 days	Boil in 2% Alconox and dry	-	-	-	56
67-9	same as above using 5% H_3PO_4 sol'n →								-	-	-	44
67-10	same as above using 10% H_3PO_4 sol'n →								-	-	-	34
68-1	PCl_3	212	5	-	-	392	600	-	-	-	-	49
68-2	Equal parts $POCl_3$ and PCl_3	212	5	-	-	392	600	-	-	-	-	53
68-3	PCl_3	212	5	methanol plus H_2O rinse		-	-	-	-	-	-	57
68-4	$AlCl_3$ + PCl_3 then	212	10	methanol plus H_2O rinse		-	-	Hot $POCl_3$ for 1' after treatment with $AlCl_3$ etc. and before dip in methanol and rinse				

See end of table for notes.

TABLE VII-3

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure (2)
69-1	H_2SO_4	140	5	Rinse pH of rinse water 1.5		392	10	-	-	-	-	23
69-2	Repeat of 69-1											
69-3	Repeat of 69-1 except neutralize with NH_4OH to pH 9.5											
69-4	Cold 100% chlorosulphonic acid								Fabric dissolves			
69-5	100% chlorosulphonic acid plus $PCCl_3$ 1 9	230°F	5	Hot H_2O	2	-	-	-	-	-	7	29
69-6	← Same as above except neutralize in case NH_4OH					-	-	-	-	-	-	22
69-7	Same as 69-5 except					-	-	-	-	-	-	22
71-1	20ml L 85% H_3PO_4	185	5	-	-	300	15	-	Brittle char	-	7	44
71-2	50ml/L 85% H_3PO_4	185	5	-	-	300	15	-	Brittle char	-	21	23
71-3	100 ml/L 85% H_3PO_4	185	5	-	-	300	15	-	Flexible char	-	22	17
71-4	same as 71-1 washed after treatment	-	-	-	-	300	15	-	Flexible char	-	-	44
71-5	same as 71-2 washed after treatment	-	-	-	-	300	15	-	-	-	-	44
71-6	same as 71-3 washed after treatment	-	-	-	-	300	15	-	-	-	-	44
71-7	same as 71-4 except heat treated before washing (3)	-	-	-	-	500	15	-	-	-	-	28
71-8	same as 71-5 except heat treated before washing (3)	-	-	-	-	500	15	-	-	-	-	23
71-9	same as 71-6 except heat treated before washing (3)	-	-	-	-	500	15	-	-	-	-	10
71-10	same as 71-4 except two washes (3)	-	-	-	-	-	-	-	-	-	-	44
71-11	same as 71-6 except two washes	-	-	-	-	-	-	-	-	-	-	20

See end of table for notes.

TABLE VII-4

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions Temp °F	Conditions Time (Mins.)	Rinsing Medium	Rinsing Time (Mins.)	Drying Temp °F	Drying Time (Mins.)	Additional Treatment	Remarks	% Shrinkage By Treatment Only	% Shrinkage Over-all Shrinkage	% Shrinkage By Thermal Exposure(2)
71-12	Same as 71-7 except two washes	-	-	-	-		-	-	-	-	-	20
72-1	Soak in 50% urea - 85% H_3PO_4 sol'n	410	10	-	-	410	10	-	-	-	-	53
72-2	Same as above					410	10	-	-	-	-	53
72-3	Sat solution of diammonium phosphate	-	-	-	-	410	25	-	-	-	-	42
72-4	soak in 10% H_2SO_4 $\frac{1}{2}$ hour 70°C wash & then in solution 40 ml H_2O, 10g urea, 10g 37% HCHO	-	-	-	-	-	-	-	-	-	-	44
73-1	85% H_3PO_4	220	15	33% urea solution at 150°F	1	220	120	-	-	-	33	16
73-2	50 ml L 85% H_3PO_4	176	15	33% urea solution at 150°F	1	220	25	-	-	-	20	45
74-1	120ml L 85% H_3PO_4	176	5	-	-	600	7	-	-	-	23	0
74-2	← same as above →							neutralize in NH_4OH at boil	-	-	-	36
74-3	← same as above but washed in NH_4OH a second time →											39
74-4	10% H_2SO_4	176	5	Conc NH_4OH two washes		-	-	-	Flexible char	-	-	19
74-5	← same as above →							dip in $POCl_3$ at 212°F for 2' .	Flexible char	-	-	18
74-6	$POCl_3$ at 212°F for 10' plus 10% H_2SO at 176°F for 5'	-	-	-	-	600	15	-	Flexible char	-	-	23

See end of table for notes.

TABLE VII-5

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions: Temp °F	Conditions: Time (Mins.)	Rinsing: Medium	Rinsing: Time (Mins.)	Drying: Temp °F	Drying: Time (Mins.)	Additional Treatment	Remarks	% Shrinkage: By Treatment Only	% Shrinkage: Over-all Shrinkage	% Shrinkage: By Thermal Exposure(2)
74-7	←	same as 74-6					→	dip in $POCl_3$ for $\frac{1}{2}$ hr	Flexible char	-	-	17
74-8	chlorosulfonic acid in $POCl_3$ 10 parts to 100	140	15	neutralize in H_2O		446	60	-	-	-	-	6
74-9	←	same as above except no neutralization					→					0
75-1	10% H_2SO_4	167	5	25ml. L conc NH_4OH for 15' just before shrinkage test		284	5	10% H_2PO_4 5' at 185°F after drying and then drying repeated	-	-	-	39
75-2	10% H_2SO_4	167	5	same as above		-	-	30' in $POCl_3$ at 212°F after drying and then drying repeated	-	-	-	39
75-3	$POCl_3$	212	30	same as above		284	5	10% H_2SO_4 fluid drying plus $POCl_3$ at 212°F plus drying	-	-	-	39
75-4	←	same as above					→					61
75-5	10% chlorosulphonic acid in $POCl_3$	212	3	same as above		284	5	10% H_2SO_4 plus drying	-	-	-	30
75-6	←	same as above					→	10% H_3PO_4 plus drying	-	-	-	44
75-7	10% H_3PO_4	336	10	same as above		284	5	10% H_3PO_4 plus dip into 50% urea solution & dry	-	-	-	44
75-8	←	same as above					→	$POCl_3$ at 212°F for 15 min plus 10% H_3PO_4 plus dip into 50% urea	-	-	-	49
75-9	$POCl_3$	212	30	same as above		284	5	10% H_3PO_4 plus dry plus H_3PO_4 dry plus 50% urea dry & dip	-	-	-	49
75-10	←	same as above					→					

See end of table for notes.

TABLE VII-6

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure(2)
76-1	10% chlorosulfonic acid in pyridine	113	5	anhyd ethanol	rinse	516	20	-	Moderately flexible char	-	-	31
76-2	same as 76-1 above except NH_4OH wash before shrinkage test				-	-	-	-	-	-	-	45
76-3	10% chlorosulfonic acid in pyridine	200	30	anhyd ethanol	rinse	536	20	-	Moderately flexible char	-	-	30
76-4	same as 76-3 above except NH_4OH wash before shrinkage test							-		-	-	72
76-5	same as 76-1							plus 5' in 10% chlorosulfonic acid in pyridine at 200°F plus 30' heat in at 520°F	Fairly flexible char	-	-	30
76-6	same as76-5 above except NH_4OH wash before shrinkage test							-		-	-	40
76-7	8 ml chlorosulfonic acid 8 ml pyridine 2 ml $POCl_3$	200	5	anhyd ethanol	rinse	536	20	wash in NH_4OH before shrinkage test		-	-	39
76-8	5 ml chlorosulfonic acid in 100 ml $POCl_3$	200	30	NH_4OH wash	after heating	527	90			-	-	44

NOTES

1. See Table I for a description of fabric 6-2 used in these tests.

2. See Appendix A for shrinkage test procedure. The % shrinkage is based on the area of the treated sample.

TABLE VIII-1

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Temp °F	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure
58-1	5% solution of P_2O_5 in 85% H_3PO_4	80	15	water, Na_2CO_3 sol'n, water		500	10	-	-	17	-	53
58-2	same as above	80	30		same as above			-	-	-	-	41
58-3	same as above	80	60		same as above			-	-	30	-	39
60-1	same as above	100	5		same as above			-	-	-	-	42
60-2	same as above	100	15		same as above			-	-	30	-	30
60-3	same as above	100	30		same as above			-	-	30	-	40
61-1	20 ml/L 85% H_3PO_4 plus 20g/L $K_2Cr_2O_7$	80	1/2	cold water	15	-	-	-	fairly resistant to burning	-	-	21
64-1	same as above	200	1/2		-	500	10	treated for 10' in boiling $KHSO_3$ solution and dried again 10' at 500°F	no significant effect on tensile strength	-	-	24
66-1	50g/L $K_2Cr_2O_7$ in 85% H_3PO_4	200	1	Na_2CO_3 plus K_2SO_3	-	500	10	-	tensile strength 87 lbs/in. elongation at break 59%	-	-	51
70-1	85% H_3PO_4	267	30	water, Na_2CO_3 sol'n, water	-	500	10	-	fabric practically destroyed, tensile strength 9 lbs/in.	-	-	
70-2	same as above	210	30	same as above	-	500	10	-	heavily stained	-	-	10
70-3	same as above	210	60	same as above	-	500	10	-	uneven staining	-	-	32
71-4	same as above	225	30	same as above	-	500	10	-	-	-	-	28
72-1	same as above	225	60	same as above	-	500	10	-	fabric not stained	-	-	14
72-2	4g $K_2Cr_2O_7$ in 400 ml 85% H_3PO_4	225	30	same as above	-	500	10	-	fabric did not burn fabric unevenly stained	-	-	28
72-3	same as above	225	60	same as above	-	500	10	-	fabric badly stained, did not burn	-	-	20

TABLE VIII-2

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC (1)

Run No.	Reagent	Conditions		Rinsing		Drying		Additional Treatment	Remarks	% Shrinkage		
		Temp °F	Time (Mins.)	Medium	Time (Mins.)	Medium	Time (Mins.)			By Treatment Only	Over-all Shrinkage	By Thermal Exposure
74-1	85% H_3PO_4	210	60	water Na_2CO_3 sol'n and water	-	500	10	-	tensile strength 50 lbs/in.	-	-	-
74-2	8g $K_2CR_2O_7$ in 400 ml 85% H_3PO_4	75	5	same as above	-	500	10	-	tensile strength 60 lbs/in.	-	-	-
74-3	4g $K_2Cr_2O_7$ in 400 ml 85% H_3PO_4	225	60	same as above	-	500	10	-	tensile strength 20 lbs/in.	-	-	-
74-4	85% H_3PO_4	225	60	same as above	-	500	10	-	tensile strength 75 lbs/in.	-	-	-
74-5	85% H_3PO_4	210	30		-			-	tensile strength 80 lbs/in.	-	-	-
74-6	4g $K_2Cr_2O_7$ in 400 ml 85% H_3PO_4	225	30	same as above	-	500	10	-	tensile strength 60 lbs/in.	-	-	-
86-1	50:50 by volume 40° Be HNO_3 and 98% H_2SO_4	0	15	2-1/2% NH_3 in water	15	500	10	-	-	44	-	61
85-2	90:10 by volume 40° Be HNO_3 and 98% H_2SO_4	0	15	same as above	15	500	10	-	-	50	-	23
92-1	25:75 by volume 40° Be HNO_3 and 98% H_2SO_4	32	15	KOH sol'n pH_7	15	500	10	H_2O rinse 5l	rinse solution acid	44	-	12
92-2	same as above	32	15	buffer sol'n pH_7	15	500	10	same as above	rinse solution acid	44	-	11
92-3	same as above	27	15	KOH sol'n until pH of fabric in water ≈ 6		438	15	H_2O rinse	-	-	-	3
92-4	←	same as above	→					after H_2O rinse boiled in Alkanox for 10 mins.	-	-	-	15
94B-1	25:75 40° Be HNO_3 and 98% H_2SO_4	18	15	NH_4OH sol'n	to pH 1	438	15	rinse in H_2O and test pH of sample	fabric yellow after rinse	-	-	10
	←	same as above	→		to pH 4-1/2	438	15	-	see above	-	-	18
	←	same as above	→		to pH 7-1/2	438	15	-	fabric turns brown when pH over 7	-	-	12
	←	same as above	→		to pH 8-1/2	438	15	-	see above	-	-	25
	←	same as above	→		to pH 9-1/2	438	15	-	see above	-	-	35

TABLE VIII-3

STUDY OF TREATMENTS FOR REDUCTION OF THERMAL SHRINKAGE OF POLYBENZIMIDAZOLE FABRIC

NOTES:

(1) See Table I for a description of 6-2 the fabric used in these tests. The thermal shrinkage test procedure is given in Appendix A. The % thermal shrinkage is calculated on the area of the treated sample.

TABLE IX-1

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT[1]

Run No.	1st Treatment Solution	1st Treatment Temp °C	1st Treatment Time Mins	Drying Temp °C	Drying Time Mins	Shrinkage %	2nd Treatment Solution	2nd Treatment Temp °C	2nd Treatment Time Mins.	Drying Temp °C	Drying Time Mins	Shrinkage %	3rd Treatment Solution	3rd Treatment Temp °C	3rd Treatment Time Mins.	Shrinkage %	Drying Temp °C	Drying Time Mins	Shrinkage %	Rinsing in 5% of NH_4OH: pH of NH_4OH After Rinse	Rinsing in 5% of NH_4OH: pH of Rinsed Fabric	Drying Temp °C	Drying Time Mins	Tensile Strength lbs/in.	% Thermal Shrinkage[3]	Flexibility of Cloth
1	5% ClO_3SH in $POCl_3$	108	5	150	5	6.7	5% ClO_3SH in $POCl_3$	111	5	150	5	13.6	42.5% H_3PO_4	110	10	28.1	220	10	44.4	11.4	9.5	RT	48 hrs	-	37.4	Brittle
2		112				1.9		112				7.4				30.0			41.3	11.5	9.4	RT	48 hrs	-	31.6	
3		110				9.0						21.8				27.2			37.9	11.5	9.5	RT	48 hrs	-	37.5	
4	Same but fresh sol'n	112				9.1						17.6				27.2			29.3	11.4	9.3	220	5	82	40.0	
5						5.1						15.9				25.9			31.0	11.45	9.4			-	44.6	
6		112				1.3						2.5				18.2			22.3	11.49	9.4			-	41.2	
7	Same but fresh sol'n	111			10	11.4										21.8			25.0	11.40	9.2			103	42.6	
8	Same but fresh sol'n	112				12.3										23.1			36.3	11.45	9.3			89	41.3	
9		112				11.0									30	22.1			29.0	11.40	9.0			98	38.1	
10		112				7.9									30	16.8			25.3	11.42	9.0			85	41.8	
11	Same but fresh sol'n	112	10			9.5									10	21.8			22.5	11.45	9.4			94	40.0	

O M I T T E D

TABLE IX-2

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT[1]

Run No.	1st Treatment Solution	1st Treatment Temp °C	1st Treatment Time Mins.	Drying Temp °C	Drying Time Mins.	Shrinkage %	3rd Treatment Solution	3rd Treatment Temp °C	3rd Treatment Time Mins.	Shrinkage %	Drying Temp °C	Drying Time Mins	Shrinkage %	Rinsing in % of NH_4OH pH of NH_4OH After Rinse	Rinsing in % of NH_4OH pH of Rinsed Fabric	Drying Temp °C	Drying Time Mins	Tensile Strength lbs/in	% Thermal Shrinkage[3]	Flexibility of Char	Observations
12	Same but fresh sol'n	112	10	150	10	11.9	4% 85% H_3PO_4 fresh sol'n	110	10	22.4	220	10	22.4	11.49	9.4	220	5	93	47.5	Brittle	Fabric darker than any of above except no spots 1 to 3
13	↓	112	20	180	20	19.3	↓	↓	20	20.1	↓	20	22.8	11.4	9.3	180	10	76	40.0	↓	Spots pattern of alum. shelf
14		112				13.9				14.1			21.3	11.3	9.4			70	42.6		
15		112				18.2				-			22.2	11.4	9.4			78	42.3		
16		112				9.2				-			15.4	11.5	9.4			69	40.0		
17		112				9.3				16.1	240		17.6	11.4	9.5			58	32.6		Some black deposit on fabric after treatment in $POCl_3$ ClO_3SH. Fabric somewhat brittle after treatment, also quite dark
18		112				15.2				18.5	240		20.07	11.45	9.5			-	40.0		Considerable black deposit on fabric after $POCl_3$ ClO_3SH treatment. Fabric brittle after treatment and quite dark.
19	Fresh sol'n	112	10	150	20	5.05				21.8	220		25.8	11.4	9.4	150		-	37.5		
20		112				5.05				21.0			25.4	11.4	9.3			-	35.9		
21		112				5.4				23.2			27.9	———	omitted			-	20.0	Soft	
22		112				3.8				21.5			26.7	———	omitted			-	16.5	Soft	

TABLE IX-3

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT (1)

Run No.	1st Treatment: Solution	1st Treatment: Temp °C	1st Treatment: Time Mins.	Drying: Temp °C	Drying: Time Mins.	Shrinkage %	3rd Treatment: Solution	3rd Treatment: Temp °C	3rd Treatment: Time Mins.	Shrinkage %	Drying: Temp °C	Drying: Time Mins.	Shrinkage %	Rinsing in 5% of NH_4OH: pH of NH_4OH After Rinse	Rinsing in 5% of NH_4OH: pH of Rinsed Fabric	Drying: Temp °C	Drying: Time Mins.	% Thermal Shrinkage(3)	Flexibility of Char	Observations
23(2)	Fresh sol'n	112	10	150	20	4.11	43.5% H_3PO_4 fresh sol'n	110	20	22.5	220	20	26.9	11.4	9.35	150	10	36.0	Brittle	
24(2)						5.9				22.2			28.9	11.5	9.4			38.4		These samples were dipped in 0.1 NHCl after washing in NH_4OH rinsed again and pH tested again and then dried at 150° C as before.
25						9.2				27.1			27.1	11.5	9.3			36.0		pH of solution 2.2, of fabric 4.2.
26						16.0				22.9			22.9	11.4	9.5			43.7		
27			5	150 plus 200		10				12.2			-	11.5	9.4			22.2		After a 2nd rinsing in NH_4OH and redrying the thermal shrinkage was 23%.

NOTES:

(1) Cloth sample 73 (see Table I) used for all runs. Except for samples 1, 2, and 3, before drying the samples after treatment in H_3PO_4 they were sandwiched between two 4" square pieces of 40 mesh stainless steel screen and covered by a 6" square of .032" thick copper plate and placed on the aluminum oven shelf with a 2070 gm lead weight on top. For #13 and after the screen and plate were kept in the oven at all times. Before that they were removed with the sample and were allowed to cool. For #13 a 6" square aluminum plate .032" thick was substituted for the copper plate and for #14 and after, the screens were sandwiched between two 8" square aluminum plates .032" thick. Except for the % heat shrinkage all % shrinkage values are based on the original sample area.

(2) The cloth for these runs was dried for 10 mins. at 150°C before treating.

(3) See Appendix A for test procedure. The % thermal shrinkage is based on the area of the treated sample.

TABLE X-1

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT[1]

Run No.	Fabric dried @ 150°C	1st Treatment Solution	1st Treatment Temp °C	1st Treatment Time (Mins.)	1st Drying Temp °C	1st Drying Time (Mins.)	Shrinkage %	Heating Temp °C	Heating Time (Mins.)	Shrinkage %	2nd Treatment Solution	2nd Treatment Temp °C	2nd Treatment Time (Mins.)	Shrinkage %	2nd Drying Temp °C	2nd Drying Time (Mins.)	Shrinkage %	Rinsing in 5% NH_4OH pH of rinsed fabric	3rd Drying Temp °C	3rd Drying Time (Mins.)	Heat Shrinkage[2] %	Flexibility	Observations
28	yes	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	5.1	280	2	7.56	42.5% H_3PO_4	110	10	12.5	200	10	25.5	9.2	150	10	10.0	soft	Temperature of oven used to heat fabric " minutes @ 280°C may have been considerably higher than 280°
29	yes	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	7.90	280	2	9.07	42.5% H_3PO_4	110	10	20.4	200	10	36.10	9.2	150	10	27.5	brittle	
30	no	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	20.00	280	2	34.30	42.5% H_3PO_4	110	10	34.3	200	10	34.30	9.2	150	10	31.3	brittle	Looked dark ed had some black spots
31	no	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	15.25	280	2	18.40	42.5 H_3PO_4	110	10	20.0	200	10	23.90	9.3	150	10	34.4	brittle	Looked dark had some black spots
32	yes	10% $ClHSO_3$ in $POCl_3$	112	10	150	10	7.70	280	2	10.10	42.5% H_3PO_4	110	10	12.4	200	10	19.25	9.2	150	10	40.0	brittle	
33	yes	10% $ClHSO_3$ in $POCl_3$	112	10	150	10	6.00	280	2	7.10	42.5% H_3PO_4	110	10	15.5	200	10	18.65	9.3	150	10	40.0	brittle	
34	300°-400°	-	-	-	-	-	-	300°-400°	2	-	-	-	-	-	-	-	-	-	-	-	60.0	-	
35	yes	5%$ClHSO_3$ in $POCl_3$	112	10	150	10	4.50	280	2	4.50	42.5% H_2PO_4	110	10	19.3	200	10	26.50	9.2	150	10	36.0	brittle	Some dark brittle areas there appear after H_3PO_4 treatment and oven dry
36	yes	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	4.90	280	2	5.80	42.5% H_2PO_4	110	10	21.9	200	10	28.40	9.2	150	10	37.6	brittle	see above
37	yes	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	3.50	300	2	8.40	42.5% H_2PO_4	110	10	24.1	200	10	26.20	9.3	150	10	37.5	brittle	see above
38	yes	5% $ClHSO_3$ in $POCl_3$	112	10	150	10	3.50	300	2	6.20	42.5% H_2PO_4	110	10	17.6	200	10	22.00	9.2	150	10	36.1	brittle	Somewhat darker than 35, 36, 37, 40, 41, 42 after muffle furnace treatment at 287°- 340°

TABLE X-2

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT (1)

Run No.	Fabric dried @ 150°C	1st Treatment Solution	1st Treatment Temp °C	1st Treatment Time (Mins.)	1st Drying Temp °C	1st Drying Time (Mins.)	1st Drying Shrinkage %	Heating Temp °C	Heating Time (Mins.)	Heating Shrinkage %	2nd Treatment Solution	2nd Treatment Temp °C	2nd Treatment Time (Mins.)	2nd Treatment Shrinkage %	2nd Drying Temp °C	2nd Drying Time (Mins.)	Rinsing in 5% NH_4OH Shrinkage %	Rinsing in 5% NH_4OH pH of rinsed fabric	3rd Drying Temp °C	3rd Drying Time (Mins.)	Heat Shrinkage (2) %	Flexibility	Observations
39	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	7.6	320	2	5.60	42.5% H_2PO_4	110	10	17.2	200	10	25.2	9.3	150	10	37.6	brittle	see comment on 35
40	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	3.5	320	2	3.50	42.5% H_2PO_4	110	10	19.8	200	10	24.2	9.4	150	10	35.9	brittle	see above
41	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	3.8	340	2	6.20	42.5% H_2PO_4	110	10	22.2	200	10	26.0	9.4	150	10	29.9	brittle	see above
42	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	3.7	340	2	3.70	42.5% H_2PO_4	110	10	20.1	200	10	26.5	9.4	150	10	35.9	brittle	This was heated less than 10 minutes in H_3PO_4
43	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	4.7	400	2	7.30	42.5% H_2PO_4	110	10	21.0	200	10	23.2	9.4	150	10	10.0	soft	Some dark brittle spots which appeared after H_2PO_4 treatment and oven dry. Both fabrics were slightly brown and stiff after heating at 400°C but otherwise looked okay. Both samples were rinsed a second time in 5% NH_4OH and redried and again the thermal shrinking was 10%.
44	yes	5% Cl HSO_3 in $POCl_3$	112	10	150	10	9.1	400	2	10.30	42.5% H_2PO_4	110	10	18.6	200	10	25.8	9.4	150	10	10.0	soft	
45	yes	5% Cl HSO_3 in $POCl_3$	112	5	150	5	-	340	2	neutralized with NH_4OH dried and retreated	42.5% H_2PO_4	110	5	Rinsed in H_2O	200	10	-	10.6(5)	150	10	21.3	-	After a second NH_4OH rinse and redrying the thermal shrinkage was 33%
46	#28 after immersion in maxilon blue and polyamid fast blue 5% dye on weight of fabric in 200 cc water at boiling for 5 minutes, rinsed and dried.																-	8.9	150	10	19.0	soft	
47	yes	5% Cl HSO_3 in $POCl_3$	112	5	150	5	2.4	280	2	11.90	42.5% H_2PO_4	110	10	23.2	200	10	30.5	9.3	150	10	40.5	brittle	The weight change of the two samples after 1st treatment +31% +27%
48	yes	5% Cl HSO_3 in $POCl_3$	112	5	150	5	1.8	280	2	16.10	42.5% H_2PO_4	110	10	24.3	200	10	26.3	9.3	150	10	40.5	brittle	after 2nd treatment +127% +124%

TABLE X-3

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT (1)

NOTES:

(1) The samples of cloth 78-1 (see Table I) were heated in the oven after H_3PO_4 treatment sandwiched between sheets of 40 mesh stainless steel screen and 6" x 6" x 1/32" aluminum plates under a 2070 gram lead weight. The sheets and weights were in the oven at all times. % shrinkages, except for the heat shrink test, are based on the original area of the fabric.

(2) Samples in brackets were all treated in the same batch of $C\ell HSO_3$. $POC\ell_3$ solution.

(3) See Appendix A for test procedure. The % shrinkage is based on the area of the treated sample.

(4) Same solution as that used for samples 35 to 42.

(5) pH of rinse solution. This is lower than normal. See Table VII.

TABLE XI-1

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT[1]

Run No.	Dried at 220°F (Mins.)	Treatment: % ClO_3SH in $POCl_3$ solution	Treatment: Temp °C	Treatment: Time (Mins.)	Drying: Temp °C	Drying: Time (Mins.)	% weight add-on	Color	Stiffness	L.O.I.(2)	Observations	Shrinkage[3]	Flexibility of yarn
1	5	5	RT	5	340	30	-	-	-	-	Fabric slightly darkened	38.7	brittle
2	5	5	RT	20	340	30	-	-	-	-	Fabric darkened more than 1	37.5	brittle
3	5	5	RT	5	400	30	-	-	-	-	Fabric black, flexible	7.5	flexible
4	5	5	RT	20	400	30	-	-	-	-	Fabric black, flexible	3.5	flexible
5	5	5	RT	5	320	20	-	-	-	-	Fabric light	51.3	
6	5	5	RT	5	320	40	-	-	-	-	Fabric light	54.5	
7	5	5	RT	5	320	90	-	-	-	-	Fabric darkened about like 1	47.5	
8	5	5	RT	5	360	5	-	-	-	-	Fabric light similar to 5	54.5	
9	5	5	110	5	360	5	-	-	-	-	Fabric light similar to 5	25.8	
10	5	5	RT	5	320	80	2.04	OK	OK	0.36	Fabric light brown same as 6	57.0	very brittle
11	5	5	RT	5	340	20	3.10	OK	OK	-	Fabric light brown about same as 10	54.0	very brittle
12	5	5	RT	5	340	80	2.40	Slightly darker	Slightly stiff	-	Fabric dark brown about same as 7	52.0	brittle
13	5	5	65	5	320	80	6.95	OK	OK	0.35	Fabric light brown but darker than 10	32.0	brittle
14	5	5	65	5	340	20	6.40	OK	OK	-	Fabric light brown same as 13	27.7	brittle
15	5	5	65	5	340	80	10.00	Slightly darker	Stiffened	-	Fabric dark brown about same as 2	18.8	semi-brittle
16	5	5	110	5	320	20	11.50	OK	Slightly stiff	-	Fabric medium brown about same as 13	30.0	brittle
17	5	5	110	5	340	20	10.50	Slightly darker	Stiffened		Fabric a little bit darker	23.3	brittle

TABLE XI-2

STUDY OF CHLOROSULFONIC ACID $POCl_3$ TREATMENT[1]

Run No.	Dried at 230% mmo	Treatment: %Cl O$_2$SH in $POCl_3$ solution	Treatment: Temp°C	Treatment: Time (Mins.)	Drying: Temp°C	Drying: Time (Mins.)	% weight add-on	Color	Stiffness	L.O.I.(2)	Observations	Shrinkage(3)	Flexibility of char
18	5	5	110	5	340	80	-	Darkened	Stiffened	-	Dark because of spent $POCl_3$	17.5	brittle
19	5	10	65	5	320	20	6.50	OK	OK	0.35	Light brown good texture	30.0	brittle
20	5	10	65	5	340	20	4.00	OK	OK	0.33	Light brown good cloth-like texture	34.7	brittle
21	5	10	65	5	340	80	9.20	Darkened	Slightly stiff	0.34	Dark brown good cloth-like texture	26.0	semi-brittle
22	5	10	110	5	320	20	16.50	Slightly dark	Stiffened	0.39	Medium-brown texture somewhat coarse	12.5	semi-brittle
23	5	10	110	5	340	20	17.00	Slightly dark	Stiffened	0.36	Medium-brown texture somewhat coarse	14.5	semi-brittle
24	5	10	110	5	340	80	20.50	Darkened	Stiffened	-	Dark brown texture somewhat coarse	14.5	semi-brittle

NOTES.

(1) Cloth 73-1 (see Table I) used after drying 5 minutes at 220°C before treatment. Temperature in drying oven questionable for runs 1 to 9 and ± 5°C thereafter.

(2) LOI (limiting oxygen index) is minimum percent oxygen by volume in a nitrogen oxygen mixture in which the sample will burn.

(3) See Appendix A for procedure. Percent shrinkage is based on the area of the treated material.

It was noted that when preforming the flame shrinkage test on the 2 X 2 squares that a lesser amount of visible fumes were emitted from the fabric when the shrinkage was low, i.e. the more the fabric shrinkage the greater the fumes emitted.

TABLE XII

Properties of 7 Yards of Fabric Submitted to Air Force for Further Evaluation Treated for Evaluation by Technical Monitor Using Optimum Process(1)

Sample Description(2)	Tensile Strength(3) lbs/in.	Elongation at Break(3) %	% Shrinkage Due to Processing	Weight Add-on(4)	% Moisture Regain 50% RH	% Moisture Regain 65% RH	Thermal Shrinkage(6) %	L. O. I.(7)
Untreated control	88	13	-	-	7	12	64	36
Sample #1	99	27	-	-	-	-	33	29
Sample #2	95	26	-	-	-	-	31	-
Sample #3	89	27	14	5	8	14	27	29
Sample #4	92	26	-	-	-	-	29	-
Sample #5	89	27	-	-	-	-	27	28

NOTES:

(1) Two pieces of cloth 118-1 described in Table I, one 2 yards long and one 5 yards long, were sewn together and treated in the full scale apparatus shown in Section 3.2. The fabric drying section had 3 banks of 250 watt infrared lamps, 5 lamps per bank, setting of 2500 watt radiant heater 5 (with this setting one end of the heater was hotter than the other), solution 5% chlorosulfonic acid in $POCl_3$ at room temperature, residence time 40 seconds per 2" length, solution feed rate 33 cc/min. The leader section broke at the beginning of the run, therefore, the first 3 feet of fabric was pulled through the reactor by hand. The temperature of the heating solution increased during the run to about 80° C. After treatment, the cloth was heated for 1 1/4 hours at 300°C. The oven temperature dropped to 285°C when the fabric was introduced.

(2) The sample locations were as follows:
1 - initial 3-foot section pulled through by hand
2 - end of first 2-yard section

TABLE XII (Continued)

NOTES: (Cont.)

3 - beginning of second 5-yard section taken from side where radiant heater was at a lower temperature
4 - same as 3 except taken from the opposite side of the section where the radiant heater was the hottest
5 - end of 5-yard section at the same side as 4

(3) Fed. Test Method Std. 191 Method 5104, three specimens warp direction only.

(4) Based on original area.

(5) Dry weight determined as in Fed. Test Method Std. 191, Method 2600 and moisture regain determined by periodic weighings until sample reaches a constant weight when exposed in a constant temperature room at 73 $\pm$ 2° F and 50 $\pm$ 5% relative humidity. Figures 3 and 4 show the plots of 5 moisture regain and the fluctuations in relative humidity during the period the samples were exposed. The relative humidity was measured each morning.

(6) See Appendix A for procedure. % shrinkage is based on the area of the treated sample.

(7) LOI (limiting oxygen index) is the minimum percent oxygen in a mixture of oxygen and nitrogen in which the sample will burn.

(8) Same as note (5) except after drying cloth was conditioned for 20 hours in a dessicator at 78.5° F over a solution of sulfuric acid having a density of 1.27.

Section 4
DISCUSSION OF RESULTS

4.1 Phosphorylation

Initial work was conducted with phosphorus oxychloride (Table XIII). This reagent gave non-uniform treatments resulting in thermal shrinkages generally greater than 40%. Moisture present on the fabric appeared to enhance weight gain and aid in the stabilization of the material. Since water decomposes $POCl_3$ to phosphoric and hydrochloric acids, these acids were examined individually and in combination with $POCl_3$. Treatments of the fabric with hydrochloric acid were ineffective in reducing thermal shrinkage; but treatments with phosphoric acid were successful. A summary of the effects of various combinations of $POCl_3$ and phosphoric acid has been selected from Table II and given in Table XI.

Of all these treatments, direct reaction with 85% phosphoric acid at 210° - 300° F appeared to provide a treated fabric with the best resistance to thermal shrinkage. In addition, an increase in the oxidation resistance of the fabric was noted - an untreated sample had a Limiting Oxygen Index of 0.36 while the treated sample had one of 0.47. However, significant fabric shrinkage occurred during the treatment process itself. For example, a sample treated 30 minutes in 85% H_3PO_4 at 218° F shrank another 23%. While the combined shrinkages of this sample was still lower than the shrinkage of an untreated sample on thermal exposure along (60-65%), the shrinkage on immersion in phosphoric acid was considered too large to be acceptable.

4.2 Candidate Crosslinking Agents

Of all the candidate crosslinking agents evaluated when the study was broadened, chlorosulfonic acid produced the greatest improvement in the dimensional stability of the fabric at the least expense to the desired fabric physical properties. This treatment appears to be completely resistant to laundering or washing in alkaline solutions. Table XIV summarizes the thermal shrinkage results of fabrics treated by the candidate systems.

Table XIII

SUMMARY OF EFFECTIVENESS OF $POCl_3$ - PHOSPHORIC ACID TREATMENTS

	Treatment	Thermal Shrinkage
1a.	$POCl_3$ (vapor) + PBI $\xrightarrow[225 - 245°F]{\text{nitrogen}}$	42
b.	$POCl_3$ (vapor) + PBI $\xrightarrow[235 - 300°F]{\text{oxygen}}$	54
c.	$POCl_3$ (vapor) + PBI $\xrightarrow[225 - 235°F,\ H_3PO_4]{\text{oxygen}}$	48
2a.	$POCl_3$ (reflux) + PBI $\xrightarrow[218 - 228°F]{\text{oxygen}}$	50
b.	$POCl_3$ (reflux) + PBI $\xrightarrow[218 - 228°F,\ H_3PO_4]{\text{oxygen}}$	23
c.	$POCl_3$ (reflux) + PBI $\xrightarrow[218 - 228°F,\ POCl_3\ (liq)]{\text{oxygen}}$	41
	$\xrightarrow[3\ hrs.\ in\ air]{heat\ 700°F}$	28
3.	$POCl_3$ (liquid) + PBI $\xrightarrow[70 - 230°F]{}$	45
4.	$POCl_3$ (liquid) + PBI $\xrightarrow[240°F]{\text{pyridine}}$	49
5.	H_3PO_4 (85%) + PBI $\xrightarrow[210 - 300°F]{}$	23

Table XIV-1

Results of Treatments Utilizing Candidate Reagents (1)

Reagent	Conditions	Thermal Shrinkage**	Comments
10% Potassium Dichromate Sol'n	pH = 1, 212° F 5 min*	42%	Fabric burns in air due to residual dichromate
1% $KMnO_4$ Sol'n	pH ≅ 12, 212° F 1 min*	42%	Fabric turns very dark - burns in air
0.7% Nitric Acid	212° F, 5 min*	56%	Fabric neutralized with NH_4OH prior to oven heating - no fabric color change
0.7% Nitric Acid	212° F, 5 min*	22%	Fabric turned deep purple color in oven
30% Hydrogen Peroxide	400° F, 15 min	64%	
5% Chlorosulfonic Acid in Phosphorus Oxychloride	230° F, 5 min followed by oven treatment at 360° C for 10 min	15%	Sl. darkening of fabric
10% H_2SO_4	400° F, 5 min	45%	Fabric shrinks
250 cc Phosphorus Oxychloride 10 g Terephthalic Acid 25 cc $POCl_3$ 10 g Aluminum Chloride	230° F, 10 min	55%	
Same as above except Maleic Anhydride substituted for Terephthalic Acid	230° F, 10 min 220° C, 10 min	48%	
Het Anhydride substituted for Maleic Anhydride	230° F, 10 min 220° C, 10 min	31%	
100% Lupersol 130	200° C, 10 min	65%	

Table XIV-2

Reagent	Conditions	Thermal Shrinkage	Comments
Radiation, 12 Mrads, 3 MeV electrons	500° F	60%	
Phosphorus Oxychloride	230° F, O_2 gas	48%	
Phosphoric Acid	260° F, 30 min	23%	32% shrinkage occurred on treatment
Hydroquinone	200° C, 10 min	65%	
Silane Y-4310	200° C, 15 min	60%	
Silane A-1100	200° C, 15 min	60%	
37% Formaldehyde Solution	boiled, 5 min 210° C, 10 min	61%	
2.1% Sodium Hypochlorite solution - 0.4% Sodium Hydroxide	boiled, 5 min 210° C, 5 min	37%	

(1) Data selected from Tables III to VII.

*Following immersions in reagent solution, fabric was heated in oven to 390-400° F for about 15 min.

**Determined by exposing 2" x 2" fabric swatch between metal gauze restraints to ~ 1300° F for 1 min. Shrinkage quoted as $\frac{\text{initial area - final area}}{\text{initial area}} \times 100\%$.

Except for nitric acid, the oxidizing agents were largely ineffectual. Of particular note in the case of dichromate and permanganate solutions is the tenacious pick-up of these agents by the fiber. Even after extensive washing with soaps and reducing agents (oxalic acid, stannous chloride - hydrochloric acid, sodium thiosulfate), a substantial percentage of the dichromate and permanganate remained in the fiber. Since benzimidazoles are known to form a wide variety of complexes with metals (Ref. 4), it is conceivable that the chromium and manganese are chelated by PBI. If these metals are in fact chelated, they may be used as mordants to permit the uniform dyeing of the fiber - which is a prime requisite for the development of commercial interest in the fiber.

Treatment of PBI with nitric acid and heat produced a purplish tinge to the fabric. Concomitant with the purpling was a reduction in the thermal shrinkage to 22%. The coloration and thermal stabilization could be prevented by neutralizing the acid treatment with ammonium hydroxide solution before heating the fabric in the oven. It was found that fabric that had been turned purple could not be dyed with the dyes normally used with PBI. On the other hand, fabric, first dyed, could not be turned purple or stabilized through treatment with nitric acid and heat. A hypothesis consistent with these observations is that both the acid and the dye react with the same site on PBI - probably the amido nitrogen.

4.3 Chlorosulfonic Acid Treatment

In the batch chlorosulfonic acid treatment, PBI fabric*, dried at 300° F for ten minutes, is immersed in a solution of 5% by volume chlorosulfonic acid (Eastman) in phosphorus oxychloride (Matheson Coleman and Bell) for 5 minutes. The fabric is removed and padded with absorbent towels to approximately a 50% wet weight addition. The fabric is then placed in a 340° C muffle furnace for 30 minutes. Following the heat treatment, the fabric is neutralized with a 10% ammonium hydroxide solution, rinsed, and dried.

An optimization of the chlorosulfonic acid process was undertaken to determine the reaction conditions that would give maximum dimensional stability to a minimum change in PBI fabric flammability, color, and tensile strength.

*Fabric dry cleaned and then washed with 1% neutral chip soap, 1% sodium silicate solution in commercial laundering equipment.

Table XV which gives data selected from Tables X and XI shows the effect of the temperature of the chlorosulfonic solution on the thermal shrinkage of 2/1 twill fabric.

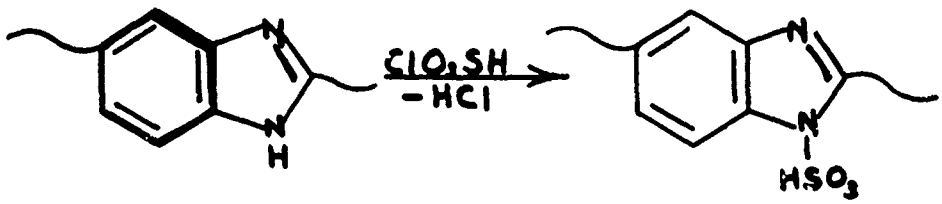
As the solution temperature is increased, so is the permanent weight addition to the fabric. In addition, the oven temperature has a decided effect on the weight gain. Figure 7 shows the correlation between the per cent shrinkage (in the thermal shrinkage test) and the per cent weight gain. Of particular note is the effect of oven temperature. In fact, a trade-off between oven temperature and time was found. For example, identical thermal shrinkage results are obtained for fabric heated at

$400^{\circ}C$ for 2 min
$360^{\circ}C$ for 10 min
$340^{\circ}C$ for 25 min

This implies that the reaction rate increases 1.5 times for every $10^{\circ}C$ increase in temperature.

The graphic presentation of Figure 8 shows how different conditions of time and temperature of treatment may be selected to obtain equivalent levels of stabilization of PBI through treatment with chlorosulfonic acid. Of course, stabilization is not the only result of exposure to the treatment. Other changes resulting in darkening and reduction in physical strength occur at the same time. Indeed, changes of this kind may occur as a result of treatments which do not yield optimum stabilization. This combination of behavior may be represented as shown in Figure 9, where the influence of time and temperature on the coexisting properties of stabilization and physical attributes are shown. Over-all optimization of treatment requires selection of a desired field within such a chart.

A theory of reaction consistent with the above information is that two reactions occur. The first takes place on immersion of the fabric in the chlorosulfonic acid solution.



If the fabric at this stage is neutralized with 10% NH_4OH solution, the fabric shows no weight gain.

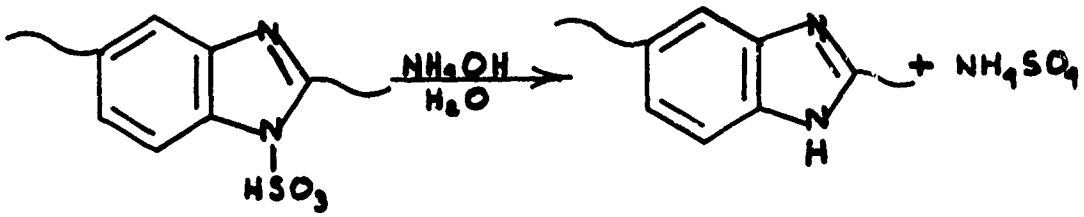


Table XV

Effect of Temperature of 5% Chlorosulfonic Acid in Phosphorus Oxychloride on Fabric Thermal Shrinkage

Run No.	Solution Temperature °C	Time of Immersion (Min.)	Oven Temp/Time °C (Mins.)		Percent Weight Gain %	Thermal Shrinkage (1) %
10	room temp.	5	320	20	2.04	57
11	room temp.	5	340	20	3.10	54
12	room temp.	5	340	80	2.40	52
13	65	5	320	80	6.95	32
14	65	5	340	20	6.40	27.7
15	65	5	340	80	10.0	19.8
16	110	5	320	20	11.50	30.0
17	110	5	340	20	10.50	23.3
25	110	5	340	20	26.2	10.5
26	110	5	340	20	11.0	14.7
27	110	5	340	20	8.6	19.0
28	110	5	340	20	8.4	19.0

NOTES:

(1) See Appendix A for Test Procedure.

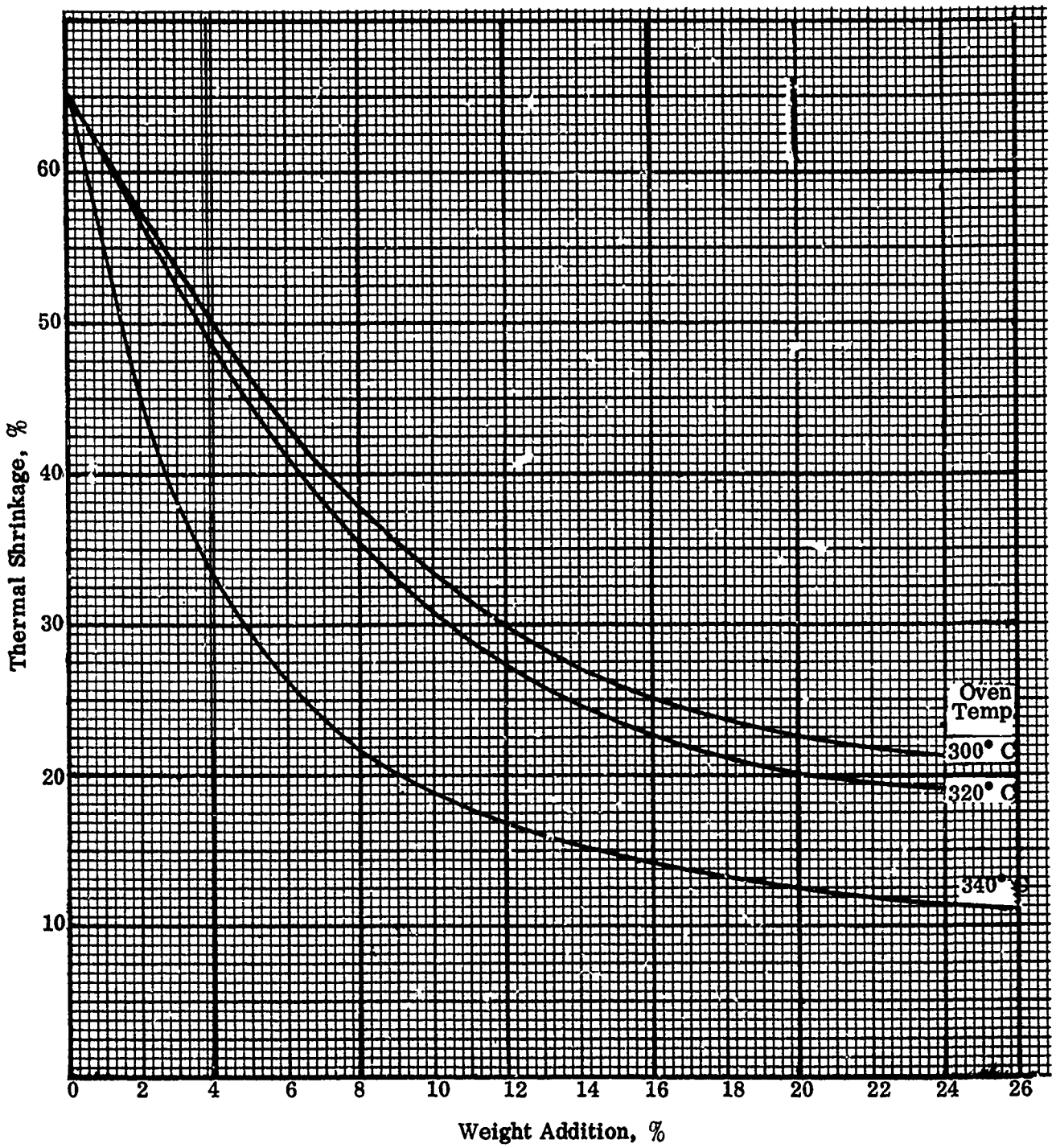


FIGURE 7

Fabric Thermal Shrinkage Versus Weight Addition

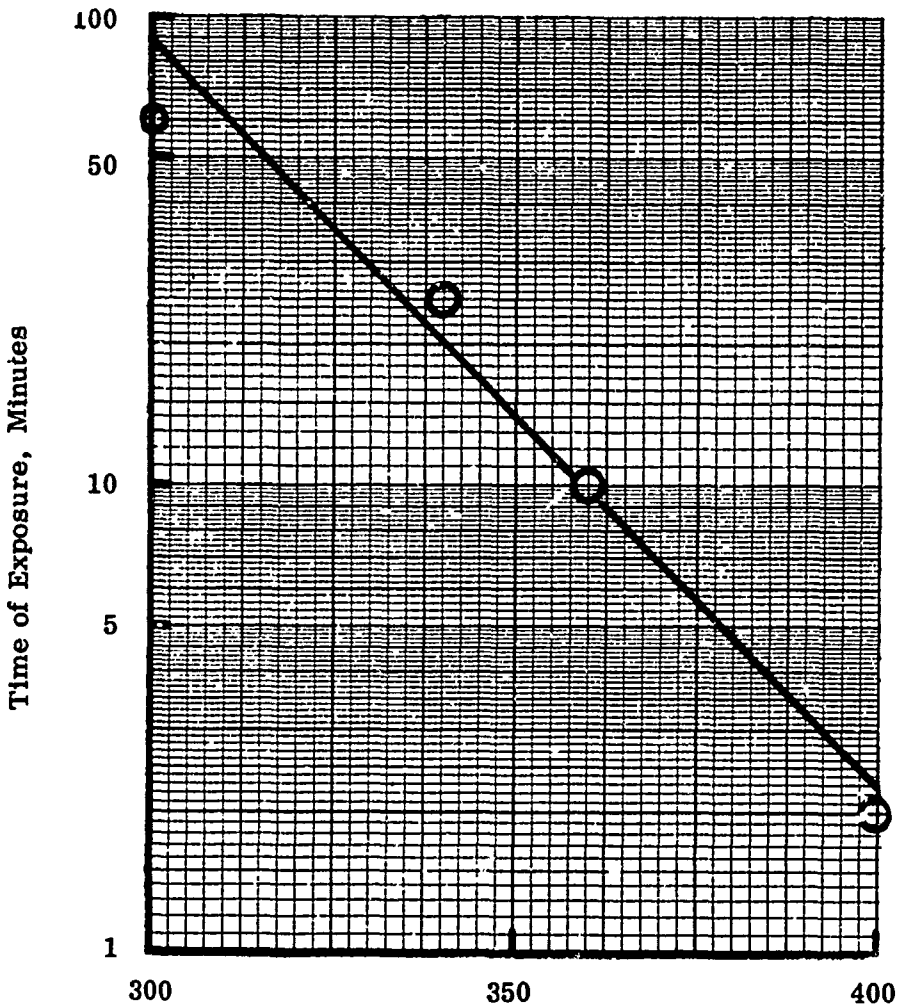


Figure 8

Conditions of Time and Temperature of Treatment Producing Equivalent Stabilization of PBI with Chlorosulfonic Acid

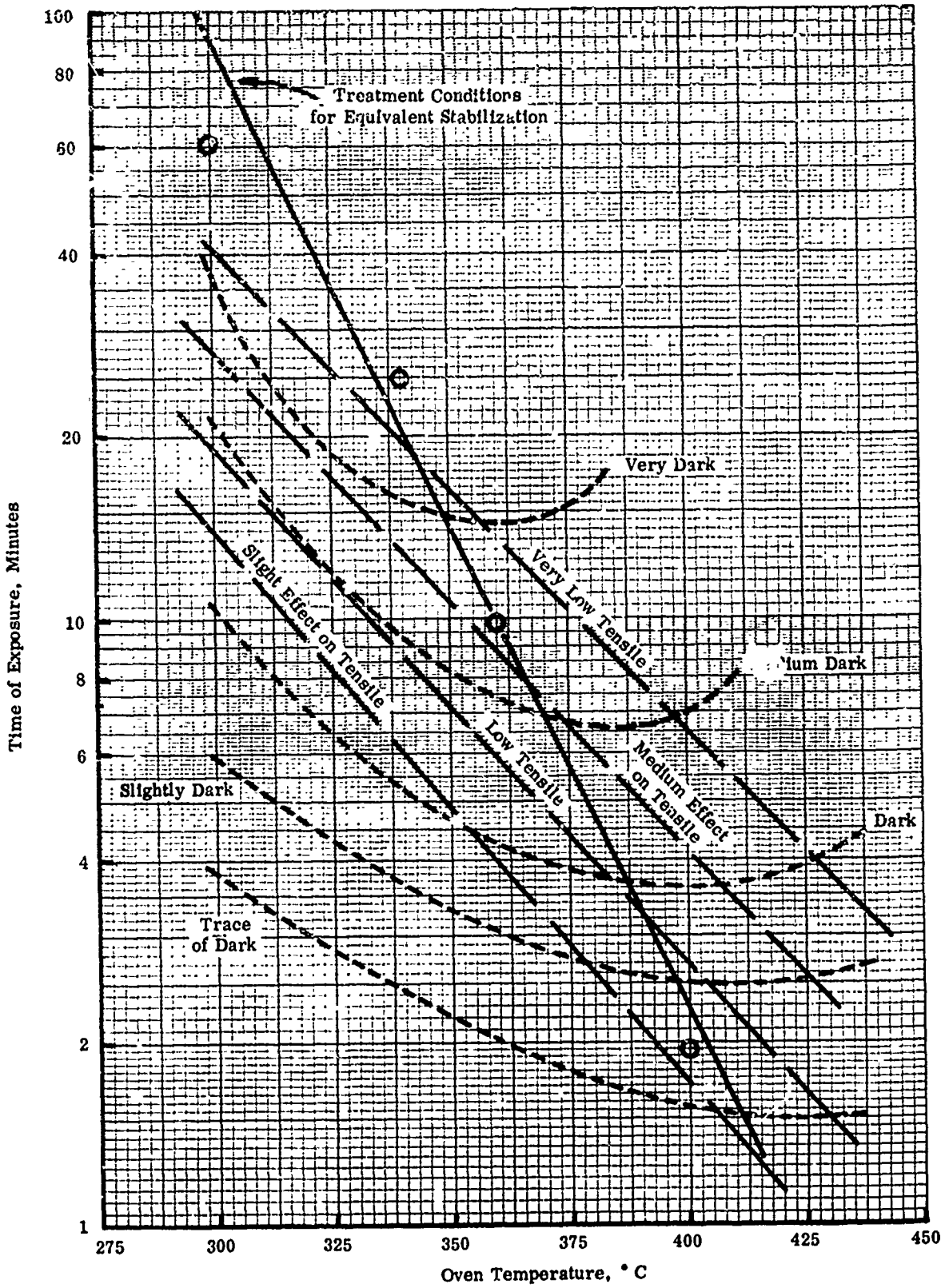
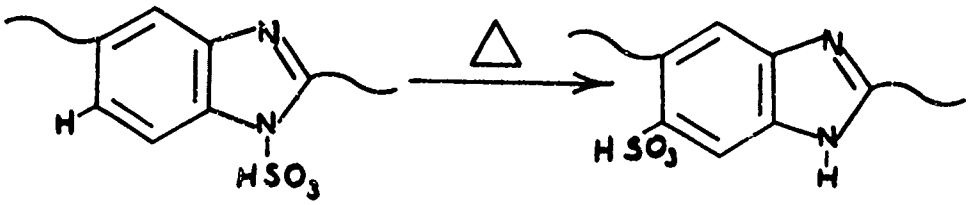


Figure 9

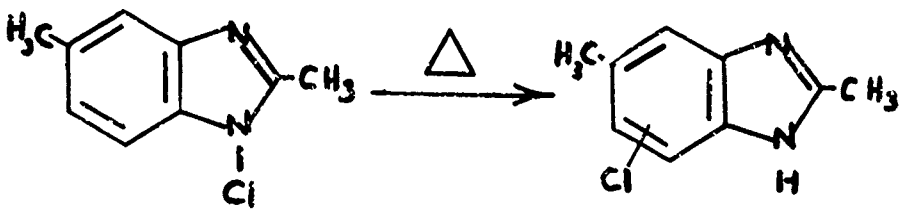
Representation of Effects on Physical Properties in Stabilization Treatment of PBI

If, however, the material is heated, the following rearrangement may occur:

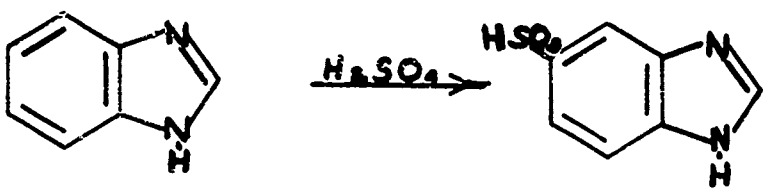


A sulfonate group on the ring is not susceptible to hydrolysis with ammonium hydroxide – thus, a permanent weight gain, durable to laundering, is obtained after the heat treatment.

Lending credence to the proposed theory is the fact that nitrogen-substituted benzimidazoles are known to rearrange under the influence of heat (Ref. 5). For example,



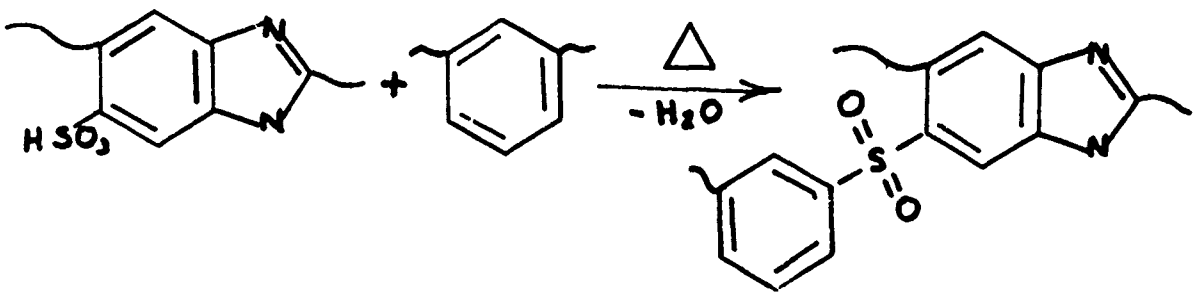
Also well documented is the sulfonation of benzimidazoles with sulfuric acid and chlorosulfonic acid (Ref. 6).



In the patent literature these sulfonations generally involve dissolving the benzimidazoles in the sulfonating reagents. Since both sulfuric and chlorosulfonic acids are excellent solvents for the polymer, direct treatment with these reagents causes the fabric to be reduced to a jellied mass. To minimize the dissolution, solutions of

chlorosulfonic acid in various non-solvents for the fabric were evaluated. Phosphorus oxychloride proved to be the best because it was non-protonating, completely miscible with chlorcsulfonic acid, and effective in rapidly penetrating the PBI.

The cross-linking of the fabric appears to occur simultaneously with the rearrangement of the sulfonate group. Cross-linking through sulfonate groups probably occurs as shown below.



4.4 Seven Yards of Fabric Treated for Evaluation by Technical Monitor

As shown by the test results in Table XII, the seven yards of fabric treated by the chlorosulfonic acid in $POCl_3$ meets all the goals for Phase I. It has tensile and elongation properties equal or better than the control, essentially the same flammability, and the treatment shrank the fabric only 14%. The color of the fabric was affected only very slightly, the fabric is still dyeable and the hand and moisture regain properties are excellent. The fabric has 27% thermal shrinkage by our very severe thermal shrinkage test, however, our test produced about three times higher shrinkages than the open pit flame test. Consequently, shrinkages of the order of 8-10% are anticipated in the pit test. In fact, another lot of PBI fabric treated in this way under contract F33615-71-C-0342 and fabricated into flight suits performed outstandingly in pit test exposures at Maynard, Mass., August, 1971.

As shown in Tables X and XI it is possible, using this chlorosulfonic acid treatment, to produce fabric having much better resistance to thermal shrinkage than 27%, but problems are encountered with fabric darkening and stiffening. It is probable, however, that with commercial equipment and careful choice of reaction conditions it will be possible to produce light colored fabric with a good hand having less than 20% thermal shrinkage even by our test.

4.5 Tow Treatment Facility

The tow processing line was constructed using the fabric treatment facility as a model; however, provisions were made on the tow line so than precise control could be maintained of processing times, temperatures, and the gas environment to which the tow was exposed.

Initial trial runs on the equipment demonstrated the effectiveness and uniformity of the treatment. Twisted PBI tow, 30 plies of 550 fil fiber with about 1 1/2 twists per inch, was run through the continuous process at three speeds, 1.18 in/sec, 1.27 in/sec, and 1.88 in/sec. An oven temperature of 475° C and a nitrogen gas purge was employed. Thermal shrinkage results were obtained on tow sections by placing individual fibers in glass tubes, and then heating the tubes until the fiber became a blackened char (about 400° C for 1 hour).

Table XVI summarizes the thermal shrinkage results, obtained at two processing speeds, of fibers selected from the cross-section of the tow.

Table XVI. Thermal Shrinkage of 30 Ply Tow

Processing Speed	Residence Time in Oven	Oven Temp.	Fiber No.	Thermal Shrinkage
1.18 in/sec	35.7 sec	475° C	1	22.1%
			2	23%
			3	23%
			4	22.6%
			5	22.9%
			6	23.4%
			7	24.8%
			8	30.6%
			9	25.3%
			10	19.8%
			11	19.7%
			12	19.7%
			13	17%

Table XVI. Thermal Shrinkage of 30 Ply Tow (continued)

Processing Speed	Residence Time in Oven	Oven Temp.	Fiber No.	Thermal Shrinkage
			Average	21.8%
			Control A	62.2%
			Control B	58.3%
1.88 in/sec	22.3 sec	475° C	1	28.6%
			2	27.7%
			3	23.5%
			4	23.6%
			Average	25.9%
			Control A	52%
			Control B	54.5%

The treated fiber produced in these first trials had a chocolate brown appearance: to minimize fiber discoloration, the oven temperature was lowered. Various temperature settings and oven residence times were evaluated to produce low thermal shrinkage fiber with minimum discoloration. During these trials it was found that a nitrogen purge did not appreciably prevent discoloration, and the purge was eliminated as a processing step. The process condition that were finally established are given in Table. XVII.

Table XVII

Final Processing Conditions Established for Tow Line

Fiber:	16,500 filament tow; twisted ~1.5 $\frac{\text{twists}}{\text{inch}}$
Line Speed:	10 ft/min
Chlorosulfonic Acid Make-up:	5% ClO_3SH (Eastman): 95% $POCl_3$ (Ventron)
Residence Time in Acid Saturator:	~2 sec.
Tube Furnace Temperature:	430° C
Nitrogen Purge in Furnace:	No
Residence Time in Furnace:	21 sec.
Ammonium Hydroxide Concentration:	~58% NH_4OH
Residence Time in Ammonium Hydroxide:	~9 sec.
Drying Oven Temperature:*	room temp.

*The final dry step was accomplished by placing the fiber (on a bobbin) in a 300° F oven for 12 hours.

Fibers selected from the cross-section of the treated tow showed the thermal shrinkages and tensile strengths listed in Table XVIII.

Table XVIII

Thermal Shrinkage of Individual Fibers

Control	60.2%
Fiber A	18.6
Fiber B	23.3
Fiber C	21.4
Fiber D	22.0
Average for treated fibers	21.3%

Tensile Strength*

Control 1	52*
Control 2	51
Control 3	59
Fiber D	54
Fiber E	51
Fiber F	51

*arbitrary units

The average shrinkage of 21.3%, the light color, and the maintenance of the tensile strength of the fiber indicated that the process had been developed to the point where a large scale production run could be made with confidence.

One and one-half pounds of tow were processed under these conditions and submitted to the Air Force Materials Laboratory for approval. Approval of the tow and to proceed with the processing of 30 lbs of PBI was received on July 16, 1971.

4.6 Production of Treated Tow

Five-thousand filament tow (1.5 denier/filament) was plied to 15000 filament tow having approximately 1-1/2 turns per inch. This tow was unreeled from 3 inch diameter bobbins into the continuous processing line. The saturator was filled with 5% by weight chlorosulfonic acid in phosphorus oxychloride. At the selected line speed the tow remained immersed in the 6 inch saturator for 3 seconds. The furnace following the saturator was set at 430° C. The period of immersion in the ten-inch neutralization tank was about 5 seconds. The tow was arranged to make seven double passes through the water rinse tank, giving a residence time of about 2 minutes. The drying oven was set at 420° C. The initial bobbin was processed with the above arrangement, and second bobbin was processed similarly, with the exception that the drying oven temperature was raised to 460° C.

The color of the fiber produced on the first and second bobbins was quite light, and it was concluded that a somewhat higher oven temperature could be tolerated. The oven temperature accordingly was raised to 448° C, and 4 additional bobbins were produced with this single change in processing conditions. The first two bobbins were designated Lot 1 and the last four bobbins were designated Lot 2.

4.7 Conversion of Tow into Fabric

The PBI tow, processed as described in 4.6, was supplied as two lots wound on six bobbins to Celanese Research Company to be crimped and cut to 2-inch length. The material could be handled satisfactorily in the crimping and cutting operations, but it was observed that the fiber affected the metal parts of the processing equipment. Following the processing it was found that aluminum parts were pitted and steel parts were heavily rusted. This action suggests that some of the fiber contained a residue of alkali while another part remained acid through incomplete neutralization. Support of this explanation is furnished by the observations of those handling the fiber at Celanese that the smaller lot, which had been processed at 430° C had a slight odor of ammonia. The larger lot, which had been processed at 448° C was characterized as smelling of "nitrates", i.e., gave an impression of acidity. It is evident that the

neutralization and water-washing steps in the continuous processing facility varied in effectiveness. During the processing, pH measurements of the damp tow leaving the rinse tank were made with indicator paper, but indications of neutrality obtained in this way obviously were not totally adequate.

The crimped and cut tow was sent to Textile Research Services, Inc., Raleigh, North Carolina, for weaving into cloth. In preparation for carding the fiber was sprayed with Nopco 2152P antistat. Upon attempting to card and draw the fiber it was found that the card loaded up with fiber after a very short time, preventing continuation. A relatively hard, powdery substance was found to build up on metal parts as it was attempted to process the fiber. This behavior is believed to be a further consequence of the presence of residual alkali or acid on the fiber as noted at Celanese Research Company. It is probable that the antistat material reacted with the acid and alkali to produce a coating on the fibers having adhesive qualities. This adhesiveness probably caused the card loading, and the material observed to build up on metal parts may well have been the reaction product of the antistat.

In order to overcome the behavior just noted the fiber was scoured. The scouring procedure was carried out with Igepon P in water at 190° F. The scouring cycle consisted of 15 minutes washing, two rinses of twenty minute duration, and 5 minutes extraction. After drying and conditioning Nopco 2152P antistat was again sprayed on the fabric. Following this treatment the fiber processed normally. The procedures followed in converting the fiber to cloth at Textile Research Services, Inc., are summarized in Table XIX.

Table XIX

Spinning and Weaving Procedure Applied to Crimped and Cut Tow

Step	Lot 1	Lot 2
1. Card, draw, and rove to spin and ply	Yarn no. 37/2 Twist 3.85 T.M. 'Z' x 14.5 T.P.I. 'S'	Yarn no. 37/2 Twist 3.85 T.M. 'Z' x 14.5 T.P.I. 'S'
2. Number spool	140 spools 380 yards/spool	140 spools 700 yards/spool
3. Make 2 warps via the silk system	140 ends/band 20 bands 3 turns/band	140 ends/band 20 bands 6 turns/band
4. Draw and reed	8 body harness (skip draw) 4 selvage harness 80 total selvage ends (40/side) 26.5/2 Reed 52" Reed width	Same
5. Weave	2 x 2 L.H. Twill 54 x 52 Off Loom Const. 4.4 oz/yd^2 Fitting same as warps	Same

4.8 Performance of Fabric

The fabric produced from the tow processed as described in 4.6 had excellent color and hand, appearing entirely like other samples of fabric examined previously. Measurements were made of the tensile strength, limiting oxygen index and thermal shrinkage of samples taken from the two lots of cloth. These data are presented in Table XX. It will be seen that the two lots differed importantly in their response to thermal exposure.

Table XX

Evaluation of Fabric Woven from Treated Tow

Property	Lot 1	Lot 2	Control
Tensile Strength, lb/inch width	74	73	94-96
LOI	0.40	0.50	0.41
Shrinkage, %	57	32	61

Lot 1 differed very little from an untreated control, whereas Lot 2 showed much improved shrinkage and a significant increase in oxygen index. The shrinkage obtained with Lot 2 was like that obtained earlier in treating already formed fabric. The oxygen index of the Lot 2 fabric prepared from tow was found to be higher than that of fabric treated as such.

Since the essential difference in preparing lots 1 and 2 was the oven temperature, no other reason for the differences in behavior can be advanced. The discussion of PBI behavior has made it clear that the thermal exposure following chemical treatment is important in determining response, but the levels selected in tow processing were within the range found useful. The temperature level of 430 selected initially and utilized in processing Lot 1 was selected on the basis of preliminary work (using single fibers for evaluation) as the lowest effective temperature and therefore a level at which fiber discoloration would be least. Upon observing that the fiber produced as Lot 1 was very little affected in color the decision was made to raise oven temperature 18° C, as reported. The color of the fiber so processed was not affected importantly and it is evident that this change in oven temperature was of profound importance.

It is apparent that the conditions of treatment chosen in processing the tow were too conservative. Referring to Figure 9, it may be appreciated that other conditions, specifically those involving higher oven temperatures, at the fixed residence time chosen, would have given consistently adequate stabilization at the cost of some additional darkening of the fiber. The limited experience in working with tow contributed to the conservative choice of conditions; in subsequent treatment of tow it will be possible to raise the level of stabilization substantially. Further work on tow processing and preparation of fabric from treated tow is recommended in order to achieve the desired level of stabilization in conjunction with acceptable fabric properties.

Section 5

CONCLUSIONS

The shrinkage which occurs when polybenzimidazole (PBI) fabrics are exposed to the high temperatures encountered in flames can be reduced substantially through suitable chemical treatment of the fibers or of finished cloth. A treatment involving immersion in a solution of 5% by weight chlorosulfonic acid in phosphorus oxychloride followed by thermal treatment at 300°- 450° C was found to reduce the area shrinkage of treated fabric by 50% without affecting the hand and drape, color, or physical properties of the fabric to an important degree. The flammability of the treated fabric is essentially unaffected. The treatment is durable, permitting the fabric to be laundered normally.

The process for thermally stabilizing PBI is suited to continuous processing of fiber in the form of tow or fabric. A lot of PBI fabric, treated as described, and fabricated into flying suits performed exceptionally well on exposure in flame pit tests, indicating that the treatment provides additional properties of high value to PBI fabric. PBI tow was processed on a continuous basis with the treatment, the tow being subsequently woven into cloth. The thermal stabilization process developed has been shown to provide the necessary fabric improvement while enabling fabric color and physical properties to be acceptably maintained.

The success achieved in developing a practical stabilization process for PBI supports the recommendation that the parameters involved in satisfactory treatment of PBI tow be subjected to additional investigation. Such further work on tow treatment will enable full-range utilization of this important improvement in manufacturing PBI fabric for all Air Force applications.

Appendix A

TEST FOR FABRIC SHRINKAGE DURING FLAME IMPINGEMENT

Equipment

Meker Burner-Cenco Cat #11043
Two 2 1/4" square pieces of 40 mesh stainless steel screen
300 gram weight-made by melting a 60/30 mixture of lead and 50/50 solder in a 600 ml stainless steel Beaker, Fisher Cat #2-583
4 x 4 Corning Ware Ceramic Dish (P-41 Petite Pan)
2 x 2 Steel die which cuts a sample 4.0 in^2 in area

Procedure

1. Mount the ceramic dish on a ring stand so that it is 3/8" above the Meker burner and adjust gas to give a temperature of 800° F ± 10° F as measured by a copper constantan thermocouple touching the center of the ceramic dish.
2. Warm the weight to 450° F ± 10° F (about the melting point of the lead solder mixture).
3. Place a 2" x 2" cloth sample (A_o = 4.0 in^2) die cut from the sample to be tested between the pieces of wire screen and lay it in the hot ceramic dish and cover with the weight. Remove after 1 min. ± 5 secs.
4. After the cloth is cool, measure area A_1 by tracing an outline on a piece of 10 x 10 per 1/2" rectangular coordinate graph paper and counting the number of squares. Calculate % shrinkage.

$$\% \text{ shrinkage} = \frac{A_o - A_1 \times 100}{A_o}$$

5. Repeat above and report the average shrinkage of the two samples.
6. The data below obtained on untreated fabric shows the precision to be expected from the test.

Fabric	Original Area	Area After Heating	% Change (based on original area)
Continuous Filament	4 in^2	1.50 in^2	-62.5%
Continuous Filament	4 in^2	1.44	-64.0%
2.85 oz/yd^2	4 in^2	1.56	-61.0%
6.17 oz/yd^2	4 in^2	1.62	-59.5%

Appendix B

FIBER TENSILE TEST METHOD

Equipment

Tensile Testing Machine suited for measurements of 0-15 lb at 12 inches/minute.

Sample jaws suited to clamp one end of a loop formed from 6-7 inch fiber and suspend other end of loop.

Procedure

1. Form a loop of a length of fiber. holding the free ends between thumb and forefinger.
2. Clamp end of fiber loop formed at free ends in tester jaw.
3. Hook blind end of loop over suspending rod on other jaw of tester.
4. Check that loop is secure with jaw separation 2-3/4" - 3-1/4".
5. Set tester speed at 12 inches/minute.
6. Record tensile at break.
7. Repeat, determining results for 5 fibers.
8. Calculate and report the average tensile at break for the 5 samples tested.

Appendix C

PROCEDURE FOR DETERMINING SHRINKAGE OF POLYBENZIMIDAZOLE FIBER

Standard Testing Procedure, Number 25 - Dec. 1970

Equipment

3 glass tubes, 1 ft. long, 1.2 mm ID. Circulating Air Oven at 500° C.

Procedure

1. Thread fiber through the glass tube using slight suction, cut the fiber at both ends of the tube; measure its length to the nearest 1/32".
2. Repeat step 1 with two more fibers in two more tubes.
3. Place the tubes in an oven set at 500° C ± 5° C as measured with a calibrated or thermocouple for 10 mins.
4. Remove the tube from the oven and remeasure fiber lengths to the nearest 1/32".
5. Determine linear shrinkage based on 1' initial length and length as measured in tube after shrinkage.

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