

# The Effects of Weathering and Atmospheric Pollutants on Cotton Fabric and Cotton Fabric Treated with Selected Flame Retardants. I. Physical, Chemical, and Flammability Properties

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## Synopsis

The effects of weathering and atmospheric pollutants on the physical, chemical, and flammability properties of cotton fabric treated with Pyrovatex 3805 and with THPOH-NH<sub>3</sub> flame retardant finishes and untreated controls were determined. The fabrics were exposed to SO<sub>2</sub>, NO<sub>2</sub>, and ozone singly and in combination for 50, 100, and 150 hr in a 2500-watt xenon arc Weather-Ometer using gas controls with and without light at a temperature of 35°C and a relative humidity of 90%. Excessive strength losses and large changes in D.P. for the untreated control occurred under all exposure conditions after 150 hr. Changes in the physical and chemical properties of the treated fabrics were moderated by the finishes, with Pyrovatex 3805 providing better protection to the cellulose than THPOH-NH<sub>3</sub>. Elemental analysis and oxygen index measurements indicate that the Pyrovatex 3805 finish was severely degraded under these exposure conditions, with a resultant loss in flammability properties of the treated fabric after weathering. The THPOH-NH<sub>3</sub> finish was not appreciably affected by these exposure conditions and the treated fabric retained most of its flammability properties after weathering.

## INTRODUCTION

The need for flame retardant textile fabrics has existed for centuries, but consumer demand for these fabrics has occurred only in recent years. Numerous flame retardant finishes for cotton fabrics have been proposed and their properties described. Several of these finishes, properly formulated and applied, can withstand 50 home-type launderings and tumble dryings with excellent retention of their flame retardant properties.

In cotton fabrics impregnated with moderate amounts of a durable flame retardant, continuous outdoor exposure has been shown to cause degradation of both the flame retardant and the cotton. In some cases, loss of flame retardant properties is more rapid than loss of fabric strength.<sup>1</sup> The stability of the finish to weathering, which includes exposure to both sunlight and air-borne contaminants, is more dependent on the chemical structure of the resin than on the presence or absence of chemical bonds between the resin and the cotton cellulose.<sup>1,2</sup> The effect of weathering on the laundering durability of flame retardant cotton fabrics indicated that these finishes were generally durable to repeated washings and tumble dryings, but may be degraded or sensitized by exposure to sunlight, ultraviolet light, or heat.<sup>3</sup> Limited information on the effect of line

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drying on THP-amide finished fabrics is available.<sup>4</sup> Cotton yarn exposed to filtered and unfiltered air under the same lighting conditions showed a larger deterioration of samples exposed to unfiltered air.<sup>5</sup> Chemical treatments which reduce the degradation of flame retardants by sunlight, including THPOH-NH<sub>3</sub>, have also been reported.<sup>6</sup>

Reasons for the differing degradation with various weathering conditions may be partially traced to the presence of atmospheric contaminants. Studies<sup>7,8</sup> of the effects of air contaminated with SO<sub>2</sub> on nylon and cellulosic fabrics showed that the breaking strength of cotton and regenerated cellulosic fabrics exposed to 0.1 ppm SO<sub>2</sub> and light was less than the loss when exposed to light and air alone.<sup>8</sup> Long-term exposure of various fabrics to 2 ppm SO<sub>2</sub> under humid conditions indicated breaking strength varied with fiber type.<sup>9-11</sup> Exposure of cellulose to ozone in concentrations which may occur in the environment (up to 6 ppm) indicated that ozone deteriorates cotton textiles when they are wet, but the deterioration is slight in comparison with that caused by other elements of "weathering."<sup>12</sup> From these studies one may conclude that gaseous SO<sub>2</sub>, ozone, and oxides of nitrogen when found in contact with cotton fabrics will have a noticeable effect on the physical properties of those fabrics.

The purpose of this study was to determine the effects of the various weathering components on cotton fabric with and without selected flame retardants. The flame retardants selected were the THPOH-NH<sub>3</sub> finish developed by the Southern Regional Research Center, United States Department of Agriculture, and the Pyrovatex 3805 finish developed by Ciba-Geigy Corporation. The air contaminants selected (NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>) are being monitored nationwide by the Continuous Air Monitoring Program (CAMP) of the Environmental Protection Agency.

A Weather-Ometer was used to simulate the conditions of weathering that occur in the natural environment. The use of simulated conditions is necessary to eliminate uncontrollable variations in outdoor environment conditions and to accelerate the effects of weathering in order to obtain results in a feasible time period.

## EXPERIMENTAL

The fabric used was a scoured, bleached, mercerized 80 × 80 cotton print cloth obtained from Testfabrics, Inc., New York. All reagents, unless otherwise specified, were analytical grade.

### Application of Flame Retardant Finishes

**Pyrovatex 3805.** This is an experimental form of Pyrovatex CP (N-methylol dimethyl phosphonopropionamide) developed by Ciba-Geigy which can be stored as a concentrate, thereby enhancing shelf life and stability at room temperature. Fabric samples 2 m × 0.5 m were finished using a pad-dry-cure process. Solution composition and treating conditions are given in Table I.

**Aerotex 23 Special Resin.** Cotton print cloth was treated with Aerotex 23 Special resin (polymethylolmelamine) developed by American Cyanamid using the same concentrations and conditions as stated in Table I. The Pyrovatex 3805 was left out, and the volume was made up with water.

**THPOH-NH<sub>3</sub>.** A 20-m length of the print cloth was treated with THPOH,

TABLE I  
Finishing of Fabric with Pyrovatex 3805 Flame Retardant

Fabric			
80 × 80 Cotton print cloth			
Padding Solution			
	Pyrovatex 3805, g		1000
	Aerotex Resin 23 Special, g		300
	Triton X100, g		1.5
	H <sub>3</sub> PO <sub>4</sub> , g		90
	H <sub>2</sub> O, g		1610
	2 Dips and 2 Nips 24 in. Padder 60 lb		
Drying			
	5 Min at 215°F		
Curing			
	2 Min at 300°F		
Washing			
	Wash temp., °F	Rinse temp., °F	Soap
1	105	105	2% Na <sub>2</sub> CO <sub>3</sub>
2	175	105	2% Na <sub>2</sub> CO <sub>3</sub>
3	175	175	2% Na <sub>2</sub> CO <sub>3</sub>
4	175	175	none
5	105	105	none
Dried			
	Tumble dried		
	Add-on: 9%		

tetrakis (hydroxymethyl) phosphonium hydroxide, and ammonia cured by George Drake at the Southern Regional Research Center. Treatment was by the pad-dry-cure procedure using a continuous treatment train. Padding solution composition and treatment conditions are given in Table II.

TABLE II  
Finishing of Fabric with THPOH-NH<sub>3</sub> Flame Retardant<sup>a</sup>

Fabric	
80 × 80 Cotton Print Cloth	
Padding Solution	
THPC (80%), %	48.8
NaOH, %	6.5
Triton 770, %	0.2
H <sub>2</sub> O, %	44.5
Processing	
Padded with tight role pressure	
Wet pickup—101%	
Dried—60°C, 1 $\frac{2}{3}$ min	
Moisture content 18%	
Curing	
NH <sub>3</sub> (anhydrous) 5 min	
Oxidized	
1% H <sub>2</sub> O <sub>2</sub> —0.5% Na <sub>2</sub> SiO <sub>3</sub> solution	
Washed and Dried	
Add-on: 19%	

<sup>a</sup> Fabric was treated by George Drake, Jr., S.R.R.C.

### Weathering Studies

An Atlas Model 25-WR123 xenon arc Weather-Ometer equipped with a 2500-watt xenon arc lamp, Type 205 quartz inner and outer filter glasses, and temperature and humidity control was used throughout the study. The Weather-Ometer was coupled with an Atlas gas analyzer and gas controller providing capabilities for individual controls for light, humidity, temperature, sulfur dioxide, nitrogen dioxide, and ozone gases. All fabrics and finishes were exposed at a temperature of  $35 \pm 1^\circ\text{C}$ , a relative humidity of 90%, and a black-body temperature under a light-on condition of  $42^\circ\text{C}$ . Samples were exposed singly and to a combination of the three gases to chamber concentrations of 25 ppm  $\text{SO}_2$ , 50 ppm  $\text{NO}_2$ , and 10 ppm  $\text{O}_3$  for varying times up to 150 to 165 hr with and without light. These concentrations were selected to approximate the highest pollution conditions that would be expected to occur in major cities as indicated by the CAMP data.

### Phosphorus Analysis

Phosphorus was determined quantitatively by a colorimetric technique described by Ciba-Geigy.<sup>13</sup> The method was modified by using a digestion mixture of concentrated nitric, perchloric, and sulfuric acids in a volume ratio of 7:2:7, respectively. Phosphorus was also determined by x-ray fluorescence analysis using a Panalyzer 4000 x-ray fluorescence analyzer made by Panametrics, Inc. Calibration curves were prepared by treating samples of the  $80 \times 80$  print cloth with differing add-ons of phosphoric acid. The phosphorus content of the standard fabrics was determined colorimetrically and by Galbraith Laboratories, Knoxville, Tennessee. The standardization was accomplished with either 2-in. circles of fabric or 1-in. pellets weighing approximately 0.6 g prepared from samples ground in a Wiley mill to pass a 20-mesh screen. It was necessary to prepare the ground sample pellets for analysis of the weathered samples due to a leaching of the finish from the exterior of the fabric resulting in a difference in leaching from front to back.

### Nitrogen Analysis

Finish nitrogen was determined by a semimicro Kjeldahl technique,<sup>14</sup> using samples ground in a Wiley mill to pass a 20-mesh screen. The same procedure with a modified digestion step<sup>15</sup> was used to determine cellulose nitrate nitrogen. All determinations were done in triplicate.

### Determination of Degree of Polymerization (D.P.)

Intrinsic viscosities of nitrated samples<sup>15</sup> were determined using Cannon-Fenske Ubbelohde shear gradient dilution viscometers.<sup>16</sup> Molecular weights and D.P. were calculated from the intrinsic viscosities using the relationship  $[\eta] = KM^\alpha$ , where  $K = 2.60 \times 10^{-4}$  and  $\alpha = 0.83$  as given by Hugue and co-workers.<sup>17</sup>

### Physical Tests

Breaking strengths, breaking extension, and work to rupture were measured on a table-model Instron tensile tester as described in ASTM D 1682-64.<sup>18</sup> The samples were broken in the Instron using a 50 kg/cm<sup>2</sup> clamping pressure on the 5.1-cm rubber-padded jaws and a cross-head speed of 5 cm/min. Work to rupture was expressed in kg-cm and is equivalent to the area under the load-elongation curve. All samples were conditioned overnight at a relative humidity of 65 ± 2% and a temperature of 21 ± 1°C.

### Oxygen Index

Oxygen Index (O.I.) values were obtained using a Michigan Chemical Company Oxygen Index Apparatus.

### Scanning Electron Microscopy

Specimens (1/4 × 1/4 in.) were mounted on standard specimen stubs with an acetate glue and placed in a platform in a vacuum evaporator and coated with gold. Observations were made with a Cambridge Steroscan Mark IIA microscope operating in the secondary mode at 10 kV acceleration voltage.

## RESULTS AND DISCUSSION

The weathering of the flame retardant-treated and untreated cotton fabrics produced dissimilar changes in physical and chemical properties. This was evident when the data showing changes in physical and chemical properties for each of the three fabrics for each simulated weathering condition were analyzed. Since the data showed marked differences in resistance of the fabrics to weathering conditions, the discussion of the effects of the various weathering conditions on each fabric will be presented separately.

Initial breaking strengths of the untreated cotton print cloth, cotton print cloth treated with THPOH-NH<sub>3</sub> finish, and cotton print cloth treated with Pyrovatex 3805 finish were 23.4, 26.2, and 18.3 kg, respectively. The decrease in the breaking strength of the Pyrovatex 3805-finished fabric is caused by the formation of crosslinks between the cellulose and the pentamethylmelamine and/or hydroxymethyl uron present in the padding mixture. Decreases in the breaking strength of fabrics due to crosslinking with finishes have been previously noted.<sup>19-22</sup>

The increase in breaking strength achieved by finishing the fabric with THPOH-NH<sub>3</sub> is possibly due to the formation of a polymeric coating on the exterior of the yarn and fiber which does not change the morphological structure of the treated fibers.<sup>23</sup> This interpretation is supported by scanning electron microscope studies (SEM)<sup>23,24</sup> which show that a layer of polymer was formed on the fiber surface of the THPOH-NH<sub>3</sub>-treated samples.

### Untreated Cotton Fabric

Analysis of the changes in physical and chemical properties of the untreated fabric after weathering showed that extended exposure to light and/or gases caused major degradation of the cotton cellulose.

#### *Photo-oxidation by Light*

The degradation of the untreated fabric by light in the presence of moisture produced a 40% loss in breaking strength (Table III, Fig. 1) and a 54% loss in energy to rupture. The degree of polymerization (D.P.) of the cellulose was reduced from an initial value of 3600 to 1170. This severe loss of strength and D.P. is in agreement with Daruwalla's observations.<sup>25</sup> He studied the effect of moisture regain on cellulose exposed to carbon arc radiation and concluded that degradation was by oxidation processes. This must be the case for the degradation of untreated cellulose fabric by xenon arc radiation in the absence of added gases. At room temperature and in neutral medium, cellulose reacts to a significant extent with molecular oxygen.<sup>26</sup>

It has been established<sup>25</sup> that degradation of cellulose by light under low moisture conditions occurs by photo-oxidation of the alcohol groups to carbonyl and carboxyl groups, thereby weakening the glycosidic linkages of the polymer chain. The energy of the xenon arc radiation at wavelengths which can be absorbed by cellulose is less than the energy necessary to break the glycosidic linkages.<sup>27</sup> Thus, the predominant reaction for xenon arc radiations in the presence of oxygen is that of photo-oxidation of alcohol groups followed by chain scission rather than the direct rupture of glycosidic bonds. The photo-oxidation of alcohol groups in cellulose under these conditions takes place through the primary step of abstraction of hydrogen from the carbon atom with the hydroxyl group. A free radical is formed on the cellulose backbone, providing a site where further reactions can take place.

Considerable degradation of cotton exposed to xenon arc light at high moisture regains was observed (Table III). This may be due to the breakdown of free water present in the system into H and OH radicals, which in turn could form hydrogen peroxide leading to enhanced damage. Although water itself does not

TABLE III  
Physical Properties of Fabrics After Exposure to Xenon Arc Light in a Weather-Ometer

Hours	Breaking strength, kg	Elongation, mm	Energy to rupture, kg-cm	D.P.
Untreated Cotton				
0	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	3600
100	16.4 ± 0.5	7.4 ± 0.1	7.9 ± 0.3	1608
150	14.0 ± 0.2	6.6 ± 0.3	6.2 ± 0.4	1170
Pyrovatex 3805				
0	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	3300
100	—	—	—	2760
150	20.1 ± 0.3	7.2 ± 0.1	9.4 ± 0.5	2383
THPOH-NH <sub>3</sub>				
0	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	3100
100	24.0 ± 1.3	7.3 ± 0.3	10.7 ± 1.1	2560
150	24.3 ± 2.0	7.1 ± 0.4	11.9 ± 1.0	2460

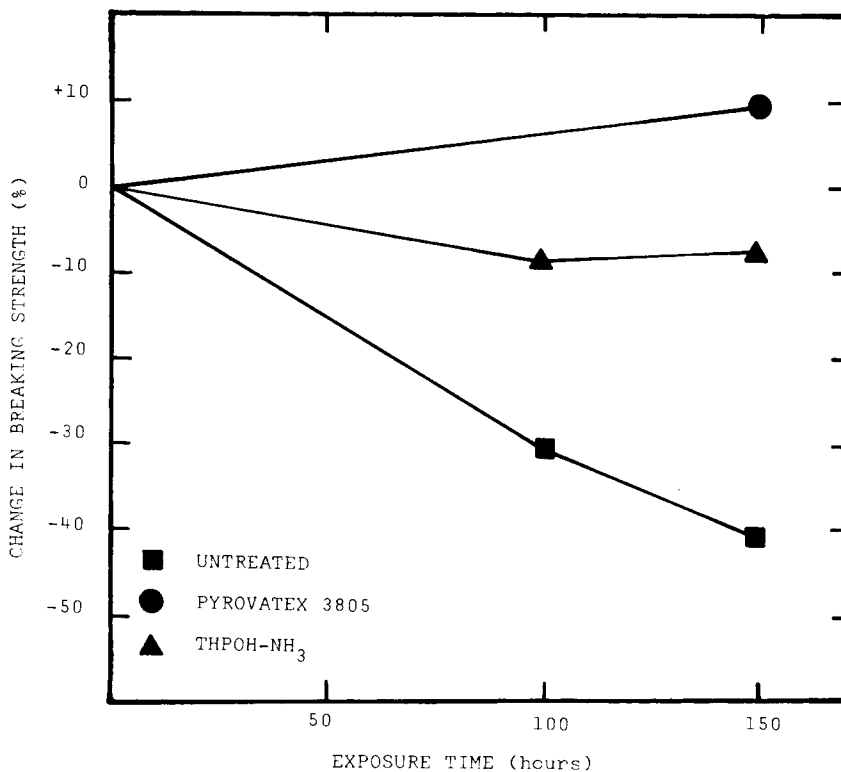


Fig. 1. Weather-Ometer exposure of fabrics to xenon arc light: (■) untreated; (●) Pyrovatex 3805; (▲) THPOH-NH<sub>3</sub>.

absorb an appreciable amount of light above 2000 Å,<sup>28</sup> it is likely that in the presence of cellulose an activated oxygen decomposition of water might take place with xenon arc radiation to form H and OH radicals.

Another scheme for the oxidation of cellulose by molecular oxygen (auto-oxidation) was developed from kinetic studies by Entwistle and coworkers.<sup>29</sup> These workers concluded that the primary auto-oxidation process is a reaction of molecular oxygen with aldehyde groups which initiates a chain reaction resulting in more profound changes and decomposition of the molecule.

The two mechanistic schemes are complementary. Photo-oxidation paths would be predominant during short exposure times producing a limited number of aldehydes and acids. Auto-oxidation is predicted on the initial presence of aldehydes which are formed in the oxidation. This is in agreement with results presented in Table III. After 100 hr of exposure to light only, large losses in D.P. and energy to rupture were observed. Exposures of longer duration caused more severe degradation of the cellulose.

#### *Degradation by Oxides of Nitrogen*

The breaking strength data for the interaction of NO<sub>2</sub> with/without the presence of light are plotted in Figure 2 and given in Table IV. These data indicate that the untreated fabric is severely damaged after 150 hr of exposure, with a greater loss in breaking strength with light (42.5%) than without light (32.5%), as shown in Figure 2.

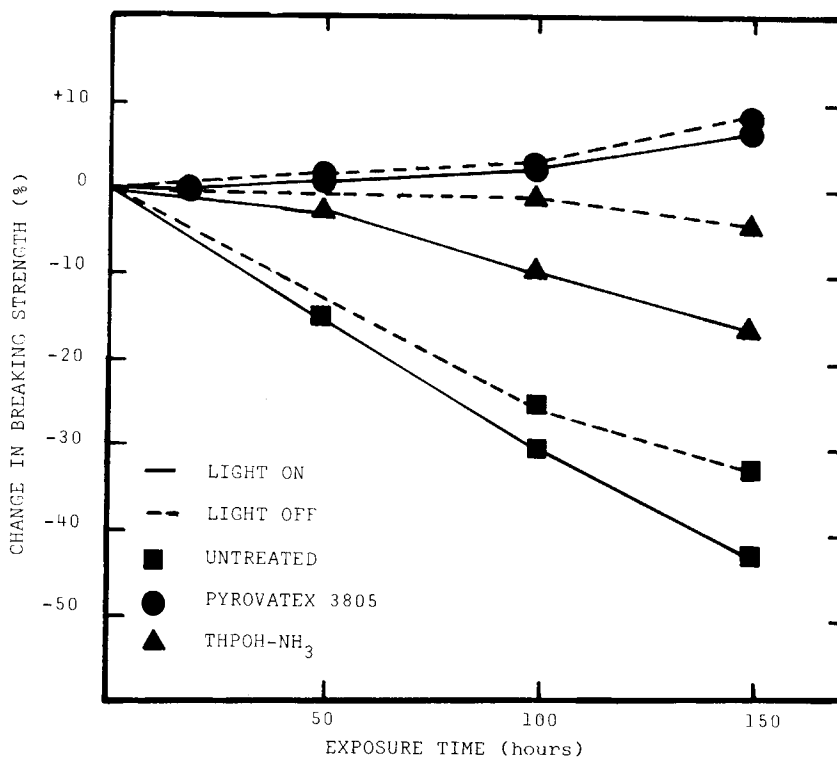


Fig. 2. Weather-Ometer exposure of fabrics to  $\text{NO}_2$  with and without xenon arc light: (■) untreated; (●) Pyrovatex 3805; (▲) THPOH- $\text{NH}_3$ .

A number of views have been advanced to interpret the mechanism of oxidation by  $\text{NO}_2$ . Nitrogen dioxide is a specific reagent which oxidizes the primary hydroxyl groups at C-6 to acid groups. The degree of oxidation of the cellulose is determined by the duration of the oxidation, its temperature, and the amount of  $\text{NO}_2$ . Parkinson<sup>30</sup> studied the oxidation of cellulose by nitrogen dioxide in carbon tetrachloride and showed that the reaction preferentially takes place in the accessible (amorphous) regions. Kenyon and co-workers<sup>31</sup> proposed the formation of  $\text{HNO}_3$  from  $\text{NO}_2$  in the presence of moisture and subsequent nitration and oxidation of the C-6 hydroxyl group. Combination of  $\text{NO}_2$  with free water forms nitrous acid in situ on the fabric. The presence of acids would suggest that a direct attack of the glycosidic linkages could occur. This method of decomposition would be predominant in the case of exposure in the absence of light. In the presence of light, there would be the possibility of accelerated damage. Such damage is evident from the plots of breaking strength change (Fig. 2) where it is shown that light-off conditions produce less strength loss than light-on conditions for the same length of exposure.

The exposure of untreated cotton to  $\text{NO}_2$  in the presence of light caused minor changes in energy to rupture and D.P. (Table IV) after 50 hr. After 150 hr severe degradation of the fabric occurred with a 54% decrease in the energy to rupture. This change in rate of degradation suggests two things: (1) an initial buildup of reactive species must take place, and (2) the portion of the cellulose polymeric structure attacked initially is in readily accessible noncrystalline regions. The attack on the less accessible crystalline structures would proceed more slowly



TABLE IV  
Physical Properties of Fabrics Exposed to NO<sub>2</sub> in a Weather-Ometer

Hours	Light off				Light on			
	Breaking strength, kg	Elongation, mm	Energy to rupture, kg-cm	D.P.	Breaking strength, kg	Elongation, mm	Energy to Rupture, kg-cm	D.P.
0	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	3600	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	3600
50	—	—	—	—	19.9 ± 0.6	9.8 ± 0.4	13.4 ± 0.8	3219
100	17.6 ± 0.4	7.7 ± 0.2	8.5 ± 0.3	1960	16.4 ± 0.5	9.1 ± 0.3	11.3 ± 0.4	2161
150	15.7 ± 1.7	7.4 ± 0.4	7.5 ± 1.0	1640	13.5 ± 0.6	6.7 ± 0.4	6.3 ± 0.5	1348
0	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	3300	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	3300
20	—	—	—	—	18.3 ± 0.9	7.5 ± 0.3	8.1 ± 0.3	—
50	18.6 ± 0.5	8.1 ± 0.4	8.6 ± 0.4	—	18.4 ± 0.6	8.1 ± 0.5	8.7 ± 0.5	—
100	18.7 ± 0.4	7.1 ± 0.2	8.5 ± 0.3	3463	18.7 ± 0.2	8.9 ± 0.2	9.8 ± 0.2	2960
150	20.0 ± 0.4	7.1 ± 0.2	9.1 ± 0.4	2600	19.3 ± 0.3	7.3 ± 0.2	8.8 ± 0.3	2633
0	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	3100	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	3100
50	—	—	—	—	25.5 ± 0.5	7.7 ± 0.3	11.6 ± 0.9	—
100	26.0 ± 0.5	6.5 ± 0.2	12.3 ± 0.4	3120	24.0 ± 0.6	7.5 ± 0.1	12.9 ± 1.2	2077
150	25.0 ± 1.1	7.0 ± 0.1	10.8 ± 0.6	3120	21.7 ± 0.4	7.0 ± 0.2	9.6 ± 1.0	1755

as evidenced by the slower rate of degradation after 100 hr of exposure. The same glycosidic bonds in the cellulose chain are broken by two methods. First, with light there is photo-oxidation of carbon atoms carrying hydroxyl groups weakening the glycosidic linkages sufficiently so that photolytic cleavage can occur. Secondly, in the presence of water the nitrogen dioxide can form acid which in turn cleaves the original or weakened glycosidic bonds.

#### *Degradation by Sulfur Dioxide*

The degradation of cotton cellulose by  $\text{SO}_2$  results from the acid hydrolysis of glycosidic bonds. The  $\text{SO}_2$  in the presence of free water forms sulfurous acid as follows:



This acid acts to hydrolyze the cellulose by the mechanism discussed for the case of nitrous acid. The reaction of  $\text{SO}_2$  with the fabric without light after 150 hr of exposure resulted in a 35% loss in breaking strength, a 47.8% loss in energy to rupture, and a drop in D.P. from 3600 to 1600 (Table V, Fig. 3). This degradation is due to acid hydrolysis. After exposure to  $\text{SO}_2$  with light for 165 hr, the degradation was more severe resulting in a 45.7% breaking strength loss, a 60% loss in energy to rupture, and a drop in D.P. to 1060. The greater degree of degradation is due to both photo-oxidation and to acid hydrolysis. Photo-oxidation can occur independently or in combination with the acid hydrolysis reaction to produce accelerated damage.

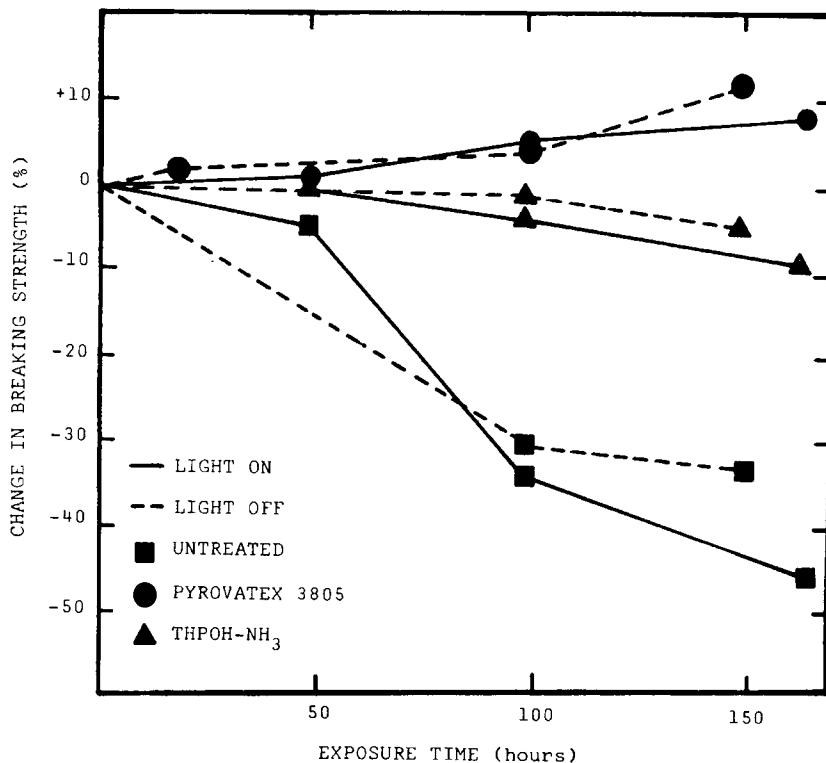


Fig. 3. Weather-Ometer exposure of fabrics to  $\text{SO}_2$  with and without xenon arc light: (■) untreated; (●) Pyrovatex 3805; (▲) THPOH-NH<sub>3</sub>.

TABLE V  
Physical Properties of Cotton Fabrics After Exposure to SO<sub>2</sub> in a Weather-Ometer

Hours	Light off			Light on			D.P.
	Breaking strength, kg	Elongation, mm	Energy to rupture, kg-cm	Breaking strength, kg	Elongation, mm	Energy to rupture, kg-cm	
0	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	3600
50	—	—	—	22.0 ± 0.6	7.2 ± 0.2	13.6 ± 0.8	—
100	16.2 ± 1.4	8.8 ± 0.8	8.0 ± 1.3	15.4 ± 0.8	7.6 ± 0.4	7.4 ± 0.6	1352
150	15.2 ± 1.5	8.3 ± 0.4	7.1 ± 1.1	—	—	—	—
165	—	—	—	12.7 ± 0.4	6.7 ± 0.3	5.4 ± 0.4	1060
0	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	3300
22	18.6 ± 0.8	7.5 ± 0.2	8.3 ± 0.6	—	—	—	—
50	—	—	—	18.4 ± 0.5	7.7 ± 0.3	8.2 ± 0.6	—
100	19.2 ± 0.8	6.5 ± 0.5	8.7 ± 0.4	19.4 ± 0.9	7.3 ± 0.2	8.8 ± 0.4	3290
150	20.4 ± 0.4	7.1 ± 0.3	9.8 ± 0.4	—	—	—	—
165	—	—	—	19.9 ± 0.9	7.3 ± 0.2	9.4 ± 0.3	3320
0	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	3100
50	—	—	—	26.2 ± 0.6	7.4 ± 0.8	13.0 ± 1.2	—
100	25.8 ± 1.1	6.7 ± 0.4	11.2 ± 0.8	25.0 ± 0.1	6.4 ± 0.4	11.0 ± 0.4	2464
150	24.9 ± 1.1	6.1 ± 0.2	10.0 ± 0.8	—	—	—	—
165	—	—	—	24.0 ± 0.7	7.0 ± 0.2	10.8 ± 0.3	2320

Untreated Cotton

3600

1620

1600

Pyrovatex 3805

3300

2874

2165

THPOH-NH<sub>3</sub>

3100

2735

2155

TABLE VI  
Physical Properties of Fabrics After Exposure to a Mixture of NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, and Xenon Arc  
Light in a Weather-Ometer

Hours	Breaking strength, kg	Elongation, mm	Energy to rupture, kg-cm	D.P.
Untreated Cotton				
0	23.4 ± 1.0	9.4 ± 0.3	13.6 ± 1.2	3600
100	13.2 ± 0.4	11.8 ± 0.3	7.0 ± 0.6	1574
150	10.7 ± 0.9	6.8 ± 0.5	4.2 ± 0.6	839
Pyrovatex 3805				
0	18.3 ± 0.6	7.4 ± 0.1	8.0 ± 0.6	3300
16	18.1 ± 0.6	7.1 ± 0.1	7.7 ± 0.2	—
48	18.4 ± 0.4	8.0 ± 0.1	8.0 ± 0.6	—
61	19.0 ± 0.7	8.1 ± 0.3	8.1 ± 0.3	—
100	19.3 ± 0.9	7.6 ± 0.2	9.5 ± 0.4	3130
150	20.4 ± 0.5	7.1 ± 0.1	9.1 ± 0.3	2153
THPOH-NH <sub>3</sub>				
0	26.2 ± 0.6	5.8 ± 0.5	11.0 ± 0.8	3100
100	23.9 ± 0.9	7.8 ± 0.3	11.2 ± 0.6	2311
150	20.7 ± 0.9	6.7 ± 0.2	8.9 ± 0.3	1523

#### *Degradation by Ozone*

Ozone acts primarily as an oxidant. Direct oxidation of cellulose by O<sub>3</sub> at low concentrations is not appreciable,<sup>12</sup> but under moist conditions degradation of the cellulose does occur. The rate of degradation was very slow and is negligible compared to other forms of weathering. These observations have been confirmed in this study. Exposure to O<sub>3</sub> for 100 hr in the presence of light produced only a moderate change in D.P. (3600 for untreated to 2679) which can be accounted for by the action of light only. In fact, O<sub>3</sub> appears to protect the cellulose from damage due to light. After 100 hr of exposure of the untreated cotton to light only, the D.P. was 1608 (Table III).

#### *Effects of Combination of Gases*

The combined action of NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub> with light produced major changes in the physical and chemical properties (Table VI and Fig. 4) of the untreated control. The D.P. of the cellulose was lowered from an initial value of 3600 to 839 after 150 hr, indicating substantial cleavage in the cellulose macromolecule. This degradation occurs by action of light and gases by the mechanisms previously described. After 100 hr of exposure to all three gases in the absence of light, the change in D.P. was greater than for the same duration of exposure to SO<sub>2</sub> (Table V) or NO<sub>2</sub> (Table IV) alone which is due to a higher concentration of acids. Action of the gases in the dark proceeds by acid hydrolysis.

#### **THPOH-NH<sub>3</sub>-Treated Fabric**

The effects of weathering on the physical and chemical properties of THPOH-NH<sub>3</sub>-treated fabric were significantly less than for the untreated fabric.

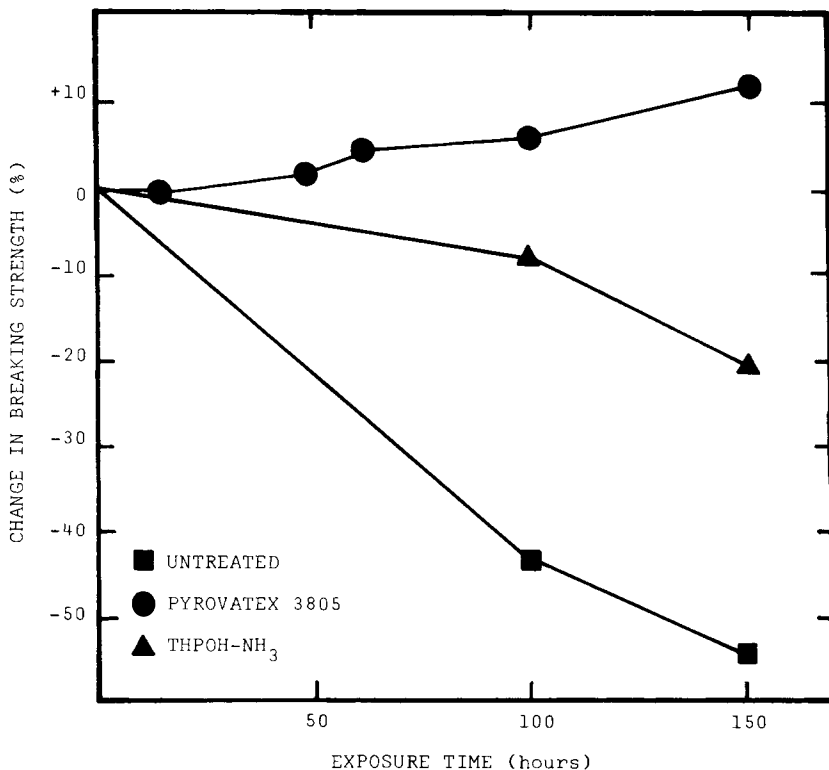


Fig. 4. Weather-Ometer exposure of fabrics to a mixture of  $\text{NO}_2$ ,  $\text{SO}_2$ , and  $\text{O}_3$  with xenon arc light: (■) untreated; (●) Pyrovatex 3805; (▲) THPOH-NH<sub>3</sub>.

#### *Effects of Weathering on Physical Properties*

The presence of the rather heavy coating of trifunctional polymer on the surface of the fiber as well as in the lumen has a rather important effect on the physical properties of the fiber. The initial finished fabric had a higher breaking strength than the untreated fabric (Table III). This increase in breaking strength may be viewed as the sum of the strength of the polymeric coating and the strength of the cellulose fiber.<sup>23,24</sup> The fabric samples coated with THPOH-NH<sub>3</sub> polymer exhibited an unusual breaking pattern. Most cotton raveled strip samples break at random places across the strip, with yarns breaking as much as 2 to 2.5 in. from each other in the linear direction. The THPOH-NH<sub>3</sub> fabrics broke almost straight across, with yarns breaking no more than 1/4 in. from the center of the break. This breaking pattern suggests that the fabric is somewhat inflexible. The inflexibility was also evident from the extension at break (Table III) which was reduced by at least 40%. Thus, the small increase in breaking strength and the large loss in extension at break resulted in a lowering of the total energy-to-rupture value to less than that for the untreated fabric. The presence of these two counterbalancing forces also caused a moderation in energy-to-rupture values obtained for the weathered samples (Tables IV, V and VI). As breaking strength was lost due to weathering, the stiffness of the fabric also decreased causing an increase in extension at break. Thus, large changes in energy to rupture were not observed.

Compared to the unexposed THPOH-NH<sub>3</sub>-treated fabric, a moderate decrease

in breaking strength of the THPOH-NH<sub>3</sub> fabric samples after 150 hr of exposure under conditions of all gases with light (Table VI, Fig. 4) and NO<sub>2</sub> with light (Table IV, Fig. 2) was observed—21% and 18%, respectively. The breaking strength losses under other exposure conditions were less than 9% (Tables III and V and Figs. 1 and 3). This suggests that the polymer coating provides some degree of protection of the cellulose from degradation by light and gases. This protection is less in the presence of all gases or NO<sub>2</sub>. When the treated fabric was exposed to NO<sub>2</sub> without light, chain cleavage did not occur because the D.P. of these samples was unchanged from that of the initial finished fabric (see Table IV). This indicates that the differences occurring in the two cases of moderate degradation must be from a coupled action of the light with the NO<sub>2</sub>. Postulated reactions of NO<sub>2</sub> with treated cellulose have been described previously.<sup>30,31</sup> Similar reactions are expected to occur in the treated fabrics with some alteration in the rate constants for these reactions.

The elemental analysis data (Table VII) for samples from these weathering tests reveal that 10% to 20% of the phosphorus and a corresponding quantity of nitrogen were lost. One might conclude that the loss of strength may be due solely or predominantly to the loss of polymeric material which was contributing to the breaking strength of the fabric. However, the viscosity data showed a marked drop in the D.P. of these samples. A 50% loss in D.P. for the case of all gases with light (Table VI) and a 43% loss for the case of NO<sub>2</sub> with light (Table IV) were observed. Surely, a loss in strength is possible with a 20% loss of finish; but considering the nature of the polymer, it is more likely that the polymeric material removed by weathering was from the scaly external layers shown in the SEM photomicrographs (Figs. 5 and 6). One would expect these external flakes to contribute little or nothing to the overall strength of the fabric. The more likely case is that strength loss is due to a decrease in D.P. of the cellulose fiber brought about by the same reaction described for the untreated fabric. The difference in degradation of the untreated and THPOH-NH<sub>3</sub>-treated fabric can be attributed to the shielding of light from the fabric as well as a decrease in free water on the fiber surfaces due to the hydrophobic nature of the polymeric finish.

The phosphorus-to-nitrogen atom ratios for this finish for most exposure conditions were approximately 0.95 (Table VII). These ratios approach the theoretical value of 1.0 for infinite polymer which reduces the availability of acid for cleavage of the cellulose linkages, but this reaction is probable and should occur to some degree. The viscosity data indicate there is a modest reduction in D.P. after exposure to SO<sub>2</sub> with or without light (Table V). Obviously, there is sufficient penetration to cause some acid cleavage of the cellulose but not enough cleavage to observe by strength measurements. There are no significant differences in the physical and chemical properties of the THPOH-NH<sub>3</sub>-treated fabric after exposure to SO<sub>2</sub> with or without light (Table V, Fig. 3).

#### *Flammability Properties*

Elemental analysis data (Table VII) indicate a loss of some finish for the THPOH-NH<sub>3</sub>-finished fabric after 150 hr of exposure to light with and without gases present, but little or no finish was lost in the absence of light. The oxygen index (O.I.) data (Table VII) indicated a change in O.I. from 28.5 to 27.5 for most exposures. Thus, the minor loss in finish had little effect on the flammability

TABLE VII  
Elemental Analysis and Oxygen Index for THPOH-NH<sub>3</sub>-Treated Fabric After Exposure in a Weather-Ometer

Gas	Hours	Light off				Light on			
		%P	%N	P/N <sup>a</sup>	O.I. <sup>b</sup>	%P	%N	P/N <sup>a</sup>	O.I. <sup>b</sup>
None	0	5.1	2.4	0.96	28.5	5.1	2.4	0.96	28.5
	100	—	—	—	—	4.8	2.0	1.09	27.5
	150	—	—	—	—	4.2	2.0	0.95	27.5
NO <sub>2</sub>	100	5.0	2.3	0.98	28.0	4.0	1.9	0.95	27.5
	150	4.9	2.1	1.05	27.0	4.0	1.9	0.95	27.0
SO <sub>2</sub>	50	—	—	—	—	5.0	2.3	1.00	28.5
	100	5.1	2.4	0.96	28.0	4.9	2.1	1.05	28.0
	150	5.1	2.4	0.96	27.0	4.6	2.1	0.99	27.5
SO <sub>2</sub> , NO <sub>2</sub> , O <sub>3</sub>	100	5.1	2.3	1.00	27.5	4.9	2.3	0.96	27.5
	150	—	—	—	—	4.2	2.0	0.95	27.5

<sup>a</sup> Atom ratio.

<sup>b</sup> Oxygen index.

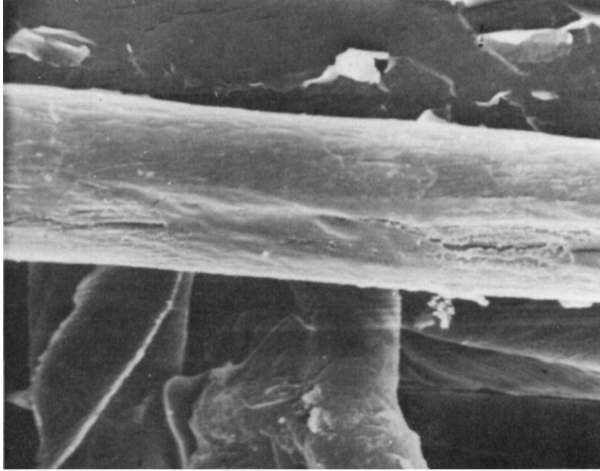


Fig. 5. Scanning electron photomicrograph of THPOH-NH<sub>3</sub>-treated cotton (2300 $\times$ ).

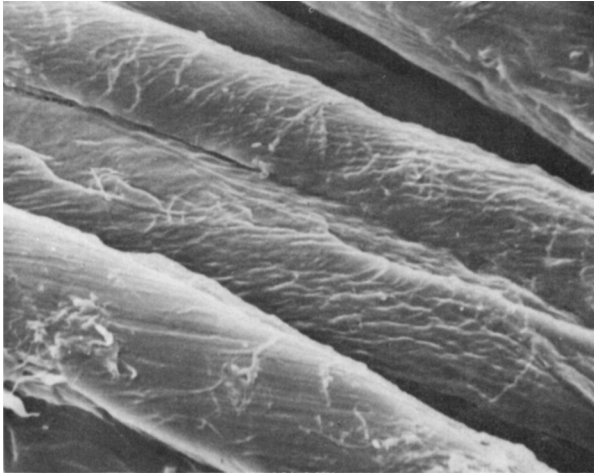


Fig. 6. Scanning electron photomicrograph of THPOH-NH<sub>3</sub>-treated cotton exposed to NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub> with xenon arc light for 150 hr and washed (2400 $\times$ ).

properties of the THPOH-NH<sub>3</sub>-finished fabrics. It is believed that the stability of this finish is due to the oxidation of the THPOH-NH<sub>3</sub> polymer during the initial finishing procedure since Mazzeno and co-workers<sup>32</sup> have previously shown that the unoxidized THPOH-NH<sub>3</sub> finish was susceptible to degradation by weathering.

### **Pyrovatex 3805-Treated Fabric**

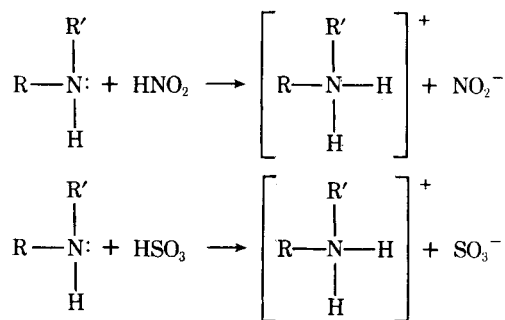
Weathering of the Pyrovatex 3805-treated fabric resulted in loss of flame retardant followed by an increase in the flammability of the treated fabric. The physical properties of the fabric were not appreciably affected. The changes in the physical properties will be discussed first.



*Effects of Weathering on Physical Properties*

All of the weathering exposures produced similar changes in breaking strength and energy-to-rupture values (Tables III–VI). These changes were reflected in recovery of strength lost as a result of finishing. Such changes can be correlated with loss of finish, i.e., the loss of some of the restraining crosslinks imposed by the melamine portion of the finish. The fact that the melamine finish is the major contributor to the initial reduction in strength properties after finishing can be seen from the results of tests performed with Aerotex 23 Special resin without the Pyrovatex 3805. A summary of these data is presented in Table VIII. There is a large loss in breaking strength of the treated fabric (23.4 to 14.6 kg), in extension to break (10 to 4.7 mm), and accordingly a loss in energy to rupture of more than 50%. The magnitude of these changes is related to the quantity of melamine polymerized on the fabric and to the degree of functionality of this reagent. After exposure to SO<sub>2</sub> and light for 100 and 150 hr, some of the above loss in physical properties was recovered. This supports the contention that the melamine affected the original loss in strength of the Pyrovatex 3805-finished fabric and that breaking of the crosslinks results in a recovery of strength. Note from the elemental analysis data in Table IX that the loss of melamine finish based on the nitrogen content was not at the same rate as the recovery in strength (Table V).

The Pyrovatex 3805-treated fabric not only recovered breaking strength but appeared to exhibit resistance to degradation of the cellulose fiber under the exposures tested. The D.P. data (Tables IV–VI) showed very minor reductions in the molecular weight of the cellulose itself. It is proposed that this resistance to cleavage of the glycosidic bond is due to the melamine portion of the finish which neutralizes the acid formed from the gases and H<sub>2</sub>O and prevents or reduces acid hydrolysis:



This proposition is supported by the data obtained with the Aerotex 23 Special resin-finished fabric. These data (Table VIII) show that after 150 hr of exposure to SO<sub>2</sub> and light, the D.P. of the cellulose was 3476, only slightly less than that for the original untreated fabric. This indicates that little or no acid hydrolysis of the cellulose occurred.

Exposure of the Pyrovatex 3805-treated fabric to light for 150 hr produced little change in D.P. (Table III); and when this fabric was exposed to all gases with light, a decrease in D.P. did not occur until after 100 hr of exposure (Table VI). There is no indication, therefore, of a significant photochemical effect on the action of the melamine as an inhibitor to acid cleavage of the cellulose. The losses in D.P. after 100 hr of exposure may be related to the loss of the finish.

TABLE VIII  
 Exposure of Aerotex 23 Special-Treated Fabric to Xenon Arc Light and SO<sub>2</sub> in a Weather-Ometer

Hours	B.S., <sup>a</sup> kg	B.S. gain, %	Elong., mm	Elong. gain, %	E.T.R., <sup>b</sup> kg-cm	E.T.R. gain, %	%N	D.S.	$\eta$	MW $\times 10^{-5}$	D.P.
0	14.6	0	4.7	0	6.0	0	1.51	—	—	—	—
100	16.4	12.3	5.5	17.0	7.6	26.8	1.43	—	—	—	—
150	16.7	14.4	5.6	19.2	8.4	40.0	1.32	2.91	25.2	10.18	3476

<sup>a</sup> Breaking strength.

<sup>b</sup> Energy to rupture.

TABLE IX  
Elemental Analysis and Oxygen Index Data for Pyrovatex 3805-Treated Fabric After Exposure in a Weather-Ometer

Gas	Hours	Light off				Light on			
		%P	%N	P/N <sup>a</sup>	O.I. <sup>b</sup>	%P	%N	P/N <sup>a</sup>	O.I. <sup>b</sup>
None	0	2.0	1.7	0.53	27.5	2.0	1.7	0.53	27.5
	150	—	—	—	—	1.5	1.1	0.61	23.5
NO <sub>2</sub>	50	2.0	1.4	0.66	26.5	1.9	1.7	0.51	27.5
	100	1.5	1.3	0.52	25.0	1.5	1.1	0.62	24.5
	150	1.2	1.2	0.45	25.0	1.5	1.1	0.62	25.0
SO <sub>2</sub>	50	1.9	1.4	0.62	27.5	1.8	1.6	0.51	27.0
	100	1.1	1.1	0.45	24.5	1.3	1.3	0.45	26.0
	150	1.1	1.0	0.50	24.5	—	—	—	—
	165	—	—	—	—	1.5	1.1	0.62	25.0
SO <sub>2</sub> , NO <sub>2</sub> , O <sub>3</sub>	16	—	—	—	—	2.0	1.7	0.53	27.5
	48	—	—	—	—	2.0	1.7	0.53	27.5
	61	—	—	—	—	1.7	1.4	0.55	27.5
	100	—	—	—	—	0.8	1.0	0.54	23.5
	150	—	—	—	—	0.8	1.0	0.36	22.5

<sup>a</sup> Atom ratio.

<sup>b</sup> Oxygen index.

Scanning electron micrographs (Fig. 7) of the weathered fibers showed a major change in the fiber surfaces after 150 hr of exposure to all gases with light. The outer layer of cellulose was removed, revealing the inner fiber structure, and deposits on the surface were observed. These deposits are probably crosslinked cellulose remaining after removal of the outer surface of the fiber. Removal of this outer surface would be consistent with the large loss of finish and retention of high D.P. values. The surface layer of cellulose was probably removed when unprotected cellulose linkages were attacked which caused the splitting off of large layers of fiber surface. This action would not appreciably affect the D.P. values since viscosity-average molecular weight determinations measure only that which is left behind and not solubilized, either in the washing procedure or in the preparation of the cellulose nitrate derivatives.

#### *Flammability Properties*

The weathering of the Pyrovatex 3805-treated fabric resulted in a loss in finish, as evidenced by the elemental analysis data in Table IX, thus causing a reduction in the oxygen index values for the fabric. The oxygen index values for the Pyrovatex 3805-treated fabric were equal to or less than 25 after exposure for 150 hr under all conditions. One may therefore conclude that this finish would not withstand the weathering action of line drying and would probably fail the vertical flammability test (FF-3-71) after less than 30 line dryings.

#### SUMMARY

The data from this study indicate that severe degradation of the untreated fabric occurred under all weathering conditions. The individual gases caused significant damage to the fabric in the absence of light, but the degradation of the fabric was most severe with combined exposure to light and gas(es).

The degradation of the cellulose occurred by more than one process or mechanism. Under conditions of light, the degrading processes are chiefly photo-oxidative. With the combined exposure to gases and light, the photo-

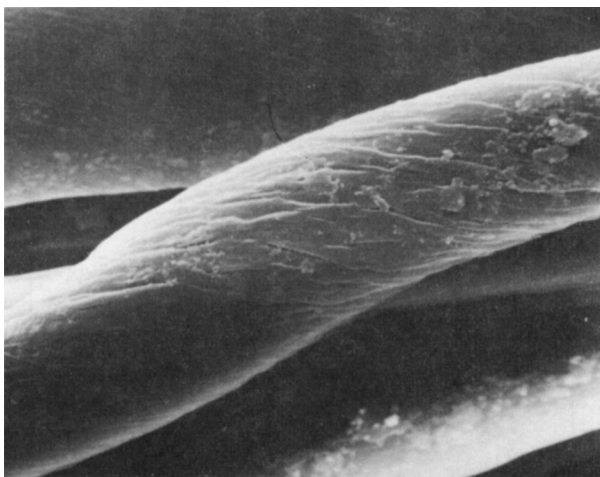


Fig. 7. Scanning electron photomicrography of Pyrovatex-treated cotton exposed to  $\text{NO}_2$ ,  $\text{SO}_2$ , and  $\text{O}_3$  with xenon arc light for 150 hr and washed (2350 $\times$ ).

oxidation occurs along with cleavage of the cellulose chains by acid hydrolysis. Exposure to the combined or individual gases resulted in degradation mainly by acid-catalyzed hydrolysis of the glycosidic linkages. The presence of the flame retardant finishes reduced the degradation of the fabric by the weathering exposures. The THPOH-NH<sub>3</sub> finish acted primarily as a shield with some possible interactions occurring to neutralize the acids formed by the combination of the NO<sub>2</sub> and SO<sub>2</sub> with water vapor. The Pyrovatex 3805 finish, which included Aerotex 23 resin, acted to prevent degradation of the cellulose polymer as evidenced by the D.P. data showing little change with weathering.

The flammability properties of the THPOH-NH<sub>3</sub>-treated fabric remained virtually unchanged after all the weathering exposures. The Pyrovatex 3805-treated fabric suffered significant loss of finish as shown by the loss of phosphorus and nitrogen. This loss of finish resulted in a lowering of the O.I. values for the fabric; and after 150 hr of exposure to any of the tested conditions, the O.I. was 25 or less.

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