

# The Effects of Weathering and Atmospheric Pollutants on Cotton Fabric and Cotton Fabric Treated with Selected Flame Retardants. II. Spectroscopic Studies\*

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## Synopsis

Spectroscopic studies of weathered flame retardant cotton fabrics were conducted. The weathering conditions included combined and independent exposure to xenon arc light and low concentrations of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> gases. Multiple internal reflectance infrared analysis of weathered Pyrovatex 3805-treated fabric showed that the finish removed after 150 hr of weathering exposure had the same structure as the original finish. Interferometer spectra of Pyrovatex 3805 and THPOH-NH<sub>3</sub> finishes on the fabric indicated no significant changes in the structure for both finishes after exposure to the various weathering conditions.

## INTRODUCTION

In a previous paper<sup>1</sup> data were presented showing the effects of xenon arc radiation and selected gases (SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>) on the physical properties of cotton fabric and cotton fabric treated with Pyrovatex 3805 and THPOH-NH<sub>3</sub> finishes, respectively. Although elemental analysis data indicated the relative concentrations of the finish components on the fabric, these data gave no information of the effect of the weathering exposures on the finishes. It is therefore of interest to present data relative to the nature of the fabric finishes after weathering. Unique spectroscopic techniques were used and will be discussed.

Fourier transform spectroscopy (FTS) or interferometric spectroscopy is a new application of the Michelson interferometer, circa 1890. The first two interferometers used for mid infrared FTS were both designed for astronomy. The first was developed by Connes<sup>2</sup> for extremely high-resolution measurements of weak sources and was overdesigned for normal chemical spectroscopy. The second, developed by Mertz,<sup>3</sup> has a much simpler design than Conne's interferometer. Its most important feature is its high scan speed. The theory of this and other rapid-scanning interferometers has been described in several articles.<sup>4-6</sup> The interferometer developed by Mertz yielded spectra of low resolution and did not meet with the general acceptance of the chemical community. Major modifications of rapid scan interferometers have been accomplished making it possible to obtain spectrum of high resolution (0.5 cm<sup>-1</sup>) at a scan speed of 10

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sec and of low resolution ( $8 \text{ cm}^{-1}$ ) at scan rates up to 100 scans/sec. Low<sup>6</sup> presented a very concise description of the interferogram obtained:

Such an interferogram does not at all resemble a spectrum. It is, in fact, not a spectrum, but the Fourier Transform of a spectrum, and as such, carries the desired intensity-frequency information within it. In principle, all the spectral information may be extracted by performing the appropriate inverse Fourier transformation. In practice, reducing an interferogram has not been easily accomplished until recently. The computations involved in data reduction are so complex, lengthy, and tedious that manual computation is out of the question. This difficulty, as well as the absence of suitable analog conversion devices, was one of the factors which kept Fourier Transform spectroscopy in obscurity. However, digital computer techniques and analog analysis are now readily available.

The interferogram can be recorded on magnetic tape, punched cards, paper tape, or directly in the core memory of a suitable computer. The Fourier Transform is then performed by digital means. This has the advantage that a number of corrections can be made, spectra can be ratioed, and so on. Fast computer programs are available for these computations, and the result is a normal spectrum.

## EXPERIMENTAL

Two flame retardant finishes, Pyrovatex 3805, which is an experimental form of Pyrovatex CP (N-methylol dimethyl phosphonopropionamide) developed by Ciba-Geigy, and THPOH, tetrakis(hydroxymethyl)phosphonium hydroxide, cured with  $\text{NH}_3$ , were applied to scoured, bleached, mercerized  $80 \times 80$  cotton print cloth. The Pyrovatex 3805 was applied in combination with Aerotex 23 Special resin (polymethylolmelamine). Finish application and fabric properties were described previously.<sup>1</sup>

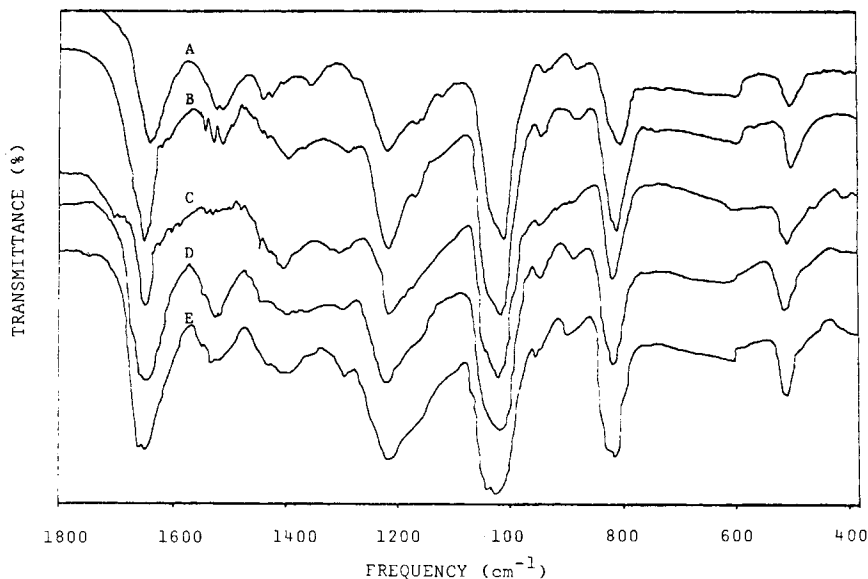


Fig. 1. Multiple internal reflectance infrared spectra of a thin film of finish extracted from Pyrovatex 3805-treated fabric: A, unweathered; B, 150 hr exposure to  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_3$ , and xenon arc light, unwashed; C, 150 hr, xenon arc light, unwashed; D, 150 hr,  $\text{NO}_2$ , xenon arc light, unwashed; E, 165 hr  $\text{SO}_2$ , xenon arc light, unwashed.

### Weathering

An Atlas xenon arc Weather-Ometer with capabilities for the controlled addition of ppm concentrations of  $\text{SO}_2$ ,  $\text{NO}_2$ , and  $\text{O}_3$  gases was used for the weathering exposure experiments. Samples of the fabrics before and after finishing were exposed to the gases singly and in combination, with or without xenon light, at  $35^\circ\text{C}$  and 90% relative humidity. These weathering experiments were described previously.<sup>1</sup>

### Washing

Samples of the weathered fabrics were washed once using AATCC Test Method 124-1973.<sup>7</sup>

### Synthesis of THPOH-NH<sub>3</sub>

A dilute aqueous solution of commercial-grade tetrakis (hydroxymethyl) phosphonium chloride supplied by Hooker Chemical Company was neutralized to pH 7 with dilute sodium hydroxide. Concentrated ammonium hydroxide was added to the solution slowly until a cloudiness occurred. The solution was stirred at room temperature for 4 hr. The white precipitate was removed by suction using a fritted glass filter. The reaction product was dried in a vacuum desiccator overnight. The final product was a white amorphous powder. A portion of the THPOH-NH<sub>3</sub> polymer was oxidized by dilute hydrogen peroxide in a water slurry for 1 hr. The product was recovered and dried in the usual manner.

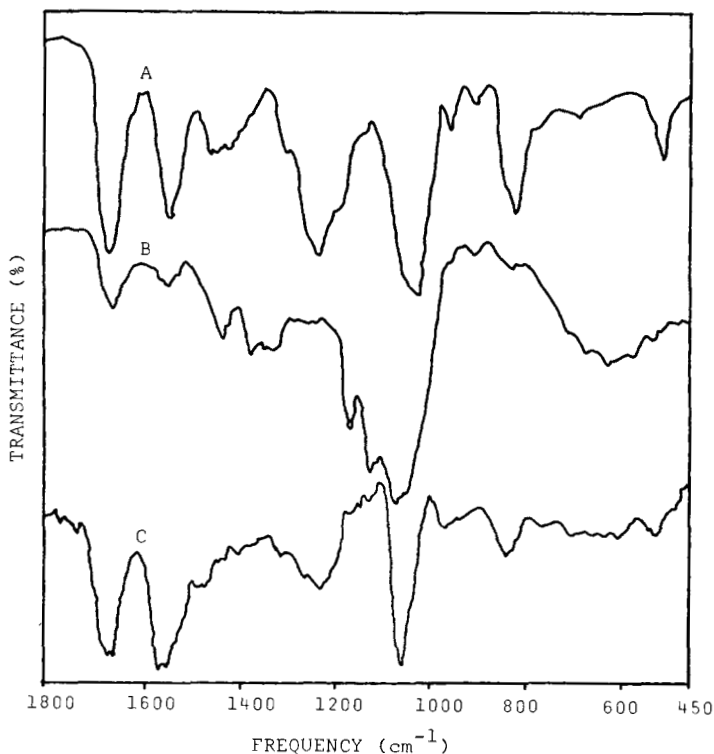


Fig. 2. Interferometer spectra: A, Pyrovatex 3805 thin film on KBr; B, Pyrovatex 3805-treated cotton; C, Pyrovatex 3805-treated cotton ratioed against the spectra of untreated cotton.

### Multiple Internal Reflectance Spectroscopy

Spectroscopic analysis of the flame retardants and flame retardant finishes used in this study was accomplished by two techniques. The first technique, infrared multiple internal reflection (MIR) spectroscopy, has recently been described in the literature.<sup>8</sup> Analysis of fabric finishes by MIR was accomplished by a combined solvent extraction-MIR technique because the concentration of finish on the surface of the fabric was too small for direct MIR analysis. Small strips of finished fabric were placed on the face of a KRS-5 crystal and wetted with 1-2 ml of methanol. The methanol was allowed to soak through the fabric onto the crystal face for approximately 30 sec. The fabric was then removed, and the solvent was allowed to evaporate, leaving a thin film of the extracted finish. The spectrum of the film was recorded using a Wilks Scientific Corporation dual-beam MIR apparatus and a Perkin-Elmer Model 457 infrared spectrophotometer.

### Fourier Transform Spectroscopy

The second spectroscopic technique used employed a FTS-14 Digilab interferometer equipped with a Digilab computer. All spectra obtained using this equipment was by direct transmission. The infrared spectrum of the liquid finishing reagents was obtained using a thin film on a salt plate. Spectra of fabric finishes were more difficult to obtain and required a special diamond cell sample preparation technique developed by Brasch<sup>9</sup> for obtaining transmission spectra of cotton fabrics on the FTS-14 interferometer. A single yarn was removed from the fabric sample, and the individual fibers were spread and separated. This

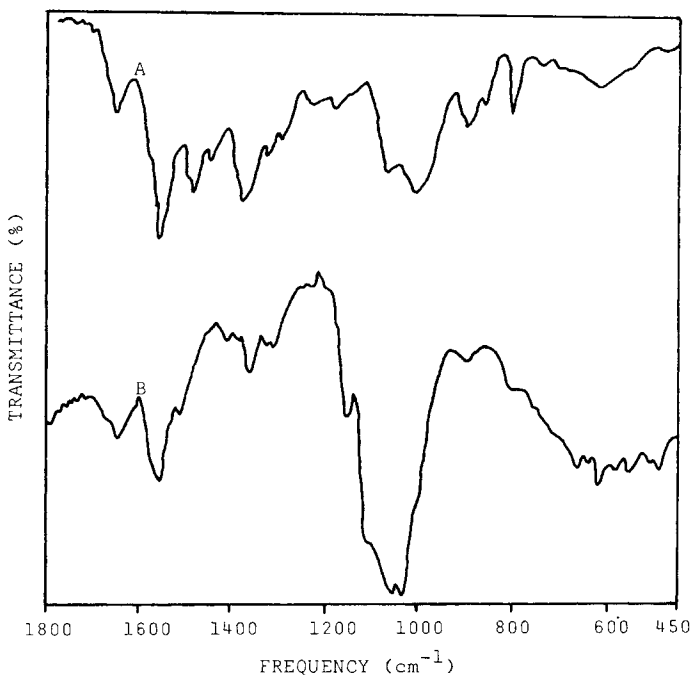


Fig. 3. Interferometer spectra: A, Aerotex 23 Special, thin film on KBr; B, Aerotex 23 Special-treated cotton fabric ratioed against untreated fabric.

thin layer of fibers was placed in a diamond pressure cell (2 mm × 2 mm) and repeatedly flattened between the diamond faces. The distribution of the fibers was observed by a light microscope with the light passing through the cell. When the fibers were uniformly distributed and a minimum of void space was evident, a final pressure of approximately 75,000 psi was applied and maintained. The transmission interferogram of the fiber sample was then taken using the FTS-14 spectrometer. The sample was scanned 200–400 times at a scan speed of 3 sec. The resultant interferogram was placed in memory storage on a magnetic disc. The spectra of the untreated cotton fabric, treated fabric, and treated fabric that had been weathered were taken and stored as described. To obtain the equivalent of infrared spectra, the Digilab computer performed a Fourier transform of the interferogram. The data were obtained in usual form by a computer plot on an XY recorder. The advantage of this technique is that by selecting an untreated cotton reference sample of proper thickness, the computer can subtract the reference spectrum from the spectrum of the finished cotton sample, the resultant spectrum being that of the finish on the fabric. Thus, one may look at the absorbance of the finish in the region where cellulose normally blanks out any other absorbance and make an evaluation of the effect of weathering on the flame retardant finish in situ.

Spectra of the solid THPOH-NH<sub>3</sub> polymer and the THPOH-NH<sub>3</sub> polymer oxidized with peroxide were also obtained using the diamond cell.

## DISCUSSION OF RESULTS

Weathered samples of the treated fabrics were examined before and after washing. The unwashed samples retained all of the finish present in the samples before weathering while the fabrics that were washed after weathering lost finish.<sup>1</sup>

### Multiple Internal Reflectance Infrared Analysis

In order to determine the nature of the degraded finish, these unwashed samples were solvent extracted by the procedure previously described. Multiple internal reflectance infrared analysis was performed on the thin films acquired by extraction. The spectra indicated that no finish was lost from the weathered THPOH-NH<sub>3</sub>-treated fabric before or after washing.

In the case of the weathered Pyrovatex 3805-treated fabric, the washing procedure removed all easily extractible material. Only with the weathered unwashed and unweathered Pyrovatex 3805-treated fabric was suitable material extractible for analysis. A comparison of the material extracted from the unweathered Pyrovatex 3805-finished fabric and that from the weathered fabric can be made from the spectra in Figure 1. These spectra indicate that the material extracted is the same in all cases. The material has the spectral characteristics of the Pyrovatex 3805 reagent used in the initial finishing procedure. This implies that the finish is being removed intact with no apparent structural change.

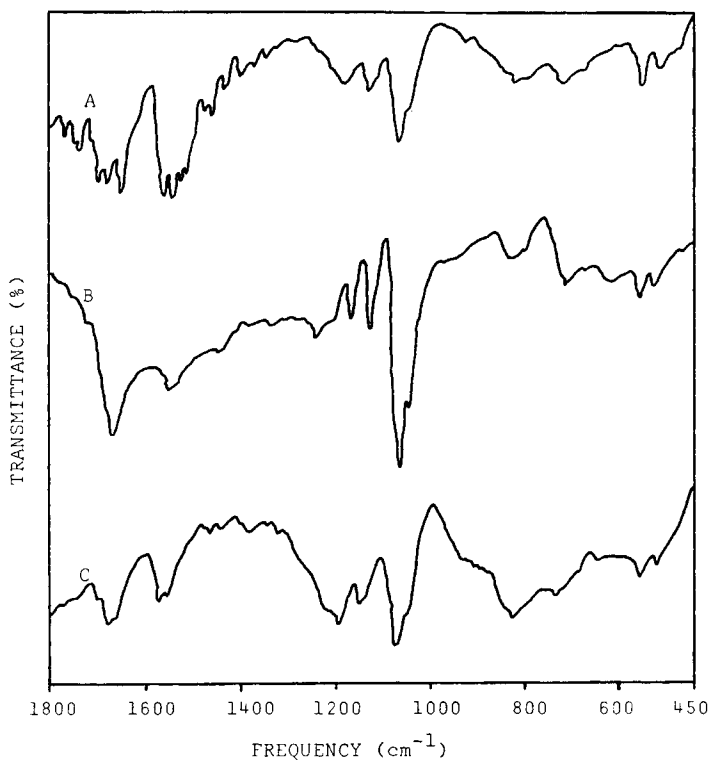
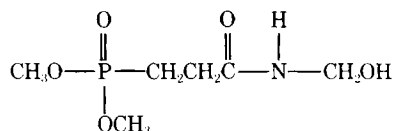


Fig. 4. Interferometer spectra of Pyrovatex 3805 finish on cotton fabric after Weather-Ometer exposure to  $\text{NO}_2$ ,  $\text{SO}_2$ , and  $\text{O}_3$ : A, 150 hr of exposure to xenon arc light, washed after exposure; B, same as A, unwashed; C, 100 hr of exposure without light, washed.

### Fourier Transform Spectroscopy

To ascertain the nature of the finish left behind after weathering and washing, it was necessary to employ a more sophisticated technique. A technique was developed whereby direct transmission spectra could be obtained from the cellulose fabric samples. The spectra were recorded using a Digilab FTS-14 interferometer using the technique previously described. Spectra of untreated and treated cellulose samples were compared employing computer techniques. The results of these comparisons were plotted in the form of conventional infrared spectra. By this technique the infrared spectra of the finish, in situ on the fabric, were obtained without the presence of an interfering cellulose spectrum. Figure 2 gives the spectra of the Pyrovatex 3805 reagent, the Pyrovatex 3805-finished cotton cellulose, and the Pyrovatex 3805 finish on the cellulose with the spectra of the cellulose removed. These spectra indicate that no major modification of the Pyrovatex 3805 compound occurred in the finishing process. Thus, what we see in the interferogram of the finish is the infrared spectrum of N-methyloldimethylphosphonopropionamide:



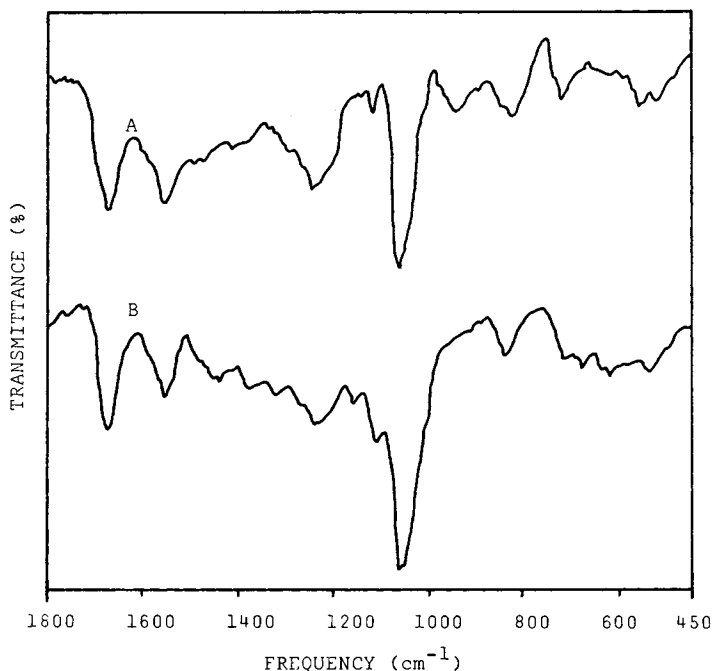


Fig. 5. Interferometer spectra of Pyrovatex 3805 finish on cotton fabric after 150 hr of Weather-Ometer exposure to  $\text{NO}_2$ : A, xenon arc light, washed; B, no light, washed.

By the use of this technique one should be capable of discerning any changes in the Pyrovatex 3805 structure if any changes were brought about by the conditions of weathering.

The other component of the Pyrovatex 3805 finish, Aerotex 23 Special, had an interferometer spectrum as shown in Figure 3. The spectrum of the Aerotex 23 Special finish after curing onto cotton fabric is also presented. It should be noted that these spectra cannot be compared directly in terms of the total intensity of the entire spectrum. These spectra were obtained by repetitive scanning and spectral ratioing, and for the final presentation, the resultant spectra were scale expanded using factors relative to the strongest peak in the spectra. Thus, the peak intensities from two different spectra cannot be directly compared. Comparisons that are valid are between some group frequency intensities with a single spectrum, frequencies of absorption bands, and changes in peak shape.

The spectrum of the Pyrovatex 3805 reagent (Fig. 2) shows major absorption bands at  $1660\text{--}1680\text{ cm}^{-1}$  (amide carbonyl),  $1550\text{ cm}^{-1}$  (amide hydrogen),  $1250\text{ cm}^{-1}$  (phosphonate group frequency), and  $1050\text{ cm}^{-1}$  (P—O—C group frequencies). From Figure 2, comparison of the Pyrovatex 3805 spectrum (A) with the combined Pyrovatex 3805–cellulose spectra (B) indicates that the major spectral interference of cellulose occurs between  $1000$  and  $1100\text{ cm}^{-1}$ . This is the region for C—O—C group frequencies and overlaps with the P—O—C group frequency absorption of the Pyrovatex 3805 and also the C—O—C group frequency of the polymerized Pyrovatex 3805–Aerotex 23 special finish. Extensive experimentation with the ratio technique for subtracting the cellulose spectrum from the combined cellulose–finish spectrum has established that the absorption bands for contributions from the finish in the region of  $1000\text{--}1100\text{ cm}^{-1}$  can be



Fig. 6. Interferometer spectra of Pyrovatex finish on cotton fabric after Weather-Ometer exposure to  $\text{SO}_2$ : A, 165 hr, xenon arc light, washed; B, 150 hr, no light, washed.

separated from those of the cellulose. It has been established that the absorption curve C (Fig. 2) represents the absorption curve for the Pyrovatex 3805 finish only and that the position and general shape of the absorption bands at 1050 and 1250  $\text{cm}^{-1}$  are real and significant.

Figure 4 presents the interferometer spectra of Pyrovatex 3805-finished fabric after weathering under the following conditions: spectrum A, 150 hr of exposure to all gases with light after washing; spectrum B, same as spectrum A but prior to washing; spectrum C, 100 hr of exposure to all gases with light after washing. These spectra indicate the presence of the amide group frequencies at 1665  $\text{cm}^{-1}$  in the same general position and with the same shape as was observed prior to weathering. There appears to be a change in the position and shape of the absorption band previously noted at 1250  $\text{cm}^{-1}$  for the unweathered sample. This shift of the 1270  $\text{cm}^{-1}$  absorption band to lower wavenumbers is evident in spectra A and C of Figure 4. These spectra represent conditions of all gases but differ in that the sample in spectrum A was weathered with light and without light. A slight shift in the 1050  $\text{cm}^{-1}$  absorption band also occurs, this shift being to higher wavenumbers. Spectrum C, weathered but unwashed under the same conditions as for the sample in spectrum A, shows a separation of the absorptions at 1050  $\text{cm}^{-1}$  and a broader band at 1250  $\text{cm}^{-1}$ . With the knowledge that the finish removed by washing is essentially the finish unchanged by weathering, one might suggest that spectrum B is the superposition of loosened but



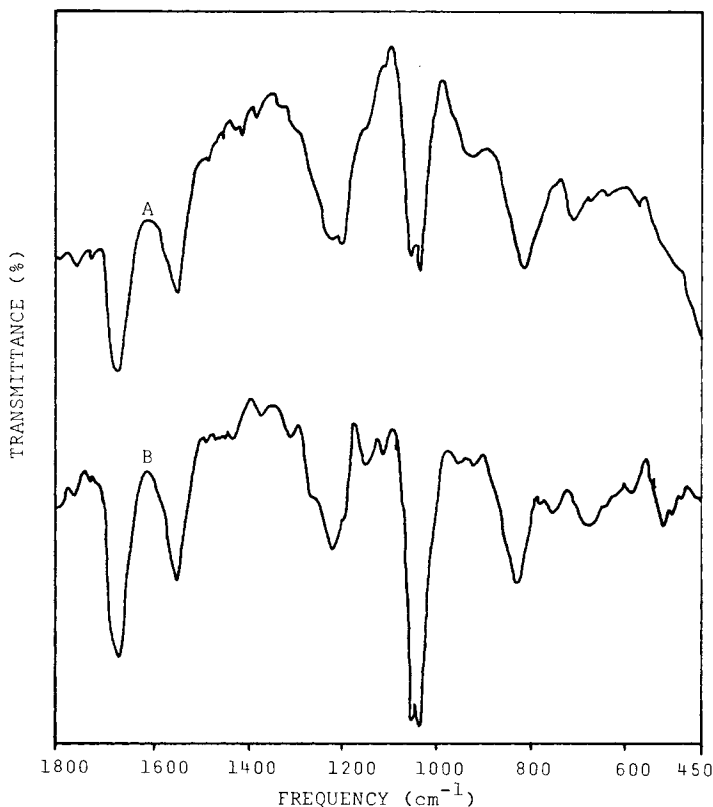


Fig. 7. Interferometer spectra of Pyrovatex 3805 finish on cotton fabric after Weather-Ometer exposure: A, 100 hr, O<sub>3</sub>, xenon arc light, washed; B, 150 hr, xenon arc light, washed.

structurally unchanged finish; however, the finish remaining after washing (A) may be slightly modified in structure.

The spectra of samples weathered in the presence of NO<sub>2</sub> with and without light are presented in Figure 5. There was no discernible change in these spectra relative to the unweathered sample.

The spectra for weathering in the presence of SO<sub>2</sub> with and without light are shown in Figure 6. Again, there were no observable shifts in the group frequency absorptions. It should be noted that the apparent change in the ratio of absorption at 1250 and 1050 cm<sup>-1</sup> is not real. This change is caused by an overcompensation for the cellulose absorption near 1050 cm<sup>-1</sup> reducing the 1050 cm<sup>-1</sup> absorption of the finish relative to the rest of the finish absorption. After scale expansion, this reduction becomes magnified.

The spectra of samples weathered in the presence of ozone with light and samples weathered using no added gases with only light present are shown in Figure 7. These spectra showed no changes in finish absorption from that of the unweathered sample. They give a very clear presentation of the Pyrovatex 3805 finish absorption as compared to samples from other weathering tests. This is probably due to the intensity of recorded spectra before scale expansion. The unexpanded spectra showed qualitative changes in absorption intensities corresponding to the amount of finish present. As noted from the previously in-

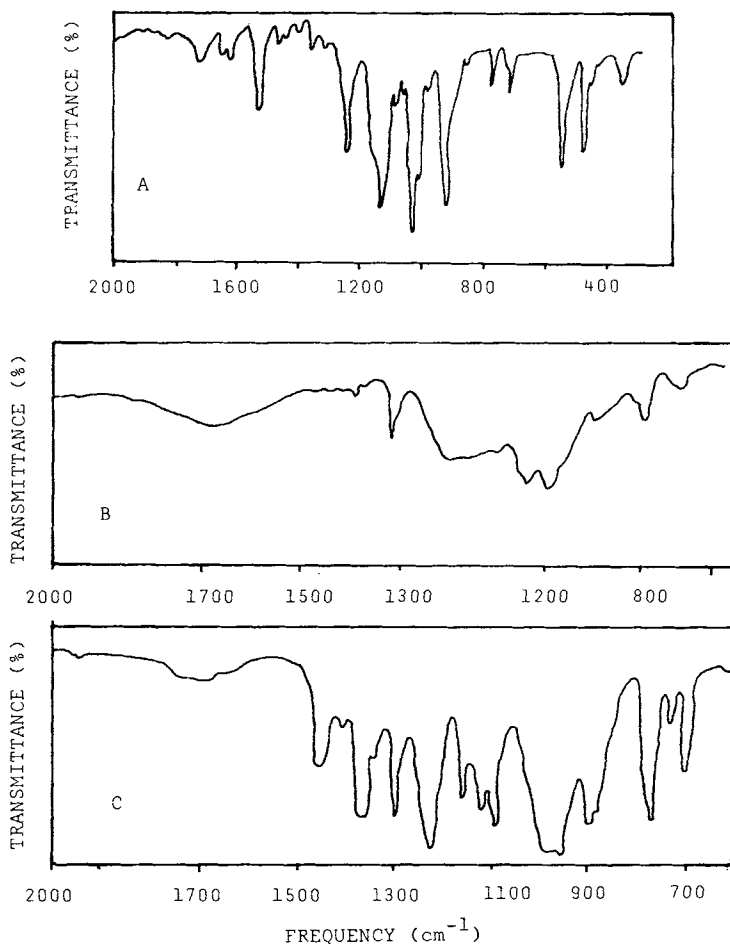


Fig. 8. Infrared spectra of phosphonic acid derivatives: A, (3-aminopropyl)phosphonic acid; B, methylphosphonic acid O-ethyl ester; C, phosphonic acid methyl-O-O-bis(isopropyl) ester.<sup>11</sup>

produced elemental analysis data, the loss of finish was quite significant in several of the weathering tests.

The interferometer spectra of the Pyrovatex 3805 finish after exposure to the various weathering conditions (see Figs. 4-7) appeared unchanged from that of the unweathered finish, with two exceptions. The exceptions were after the weathering exposures under conditions of all gases ( $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_3$ ) in the presence of xenon arc light and these gases without light. After exposure under these conditions, the absorption bands occurring at  $1250\text{ cm}^{-1}$  (phosphono group frequency) and  $1050\text{ cm}^{-1}$  (P—O—C and C—O—C group frequencies) appeared to shift toward each other (see Fig. 5). The obvious interpretation of this shift is that a change occurred in the structure of the phosphonate portion of the Pyrovatex 3805 compound. There is no indication of any change in absorption bands for the amide carbonyl and amide hydrogen; thus, no significant hydrolysis of the amide linkage is believed to have occurred. Another possible change which could occur under these conditions would be acid hydrolysis of the phosphonate

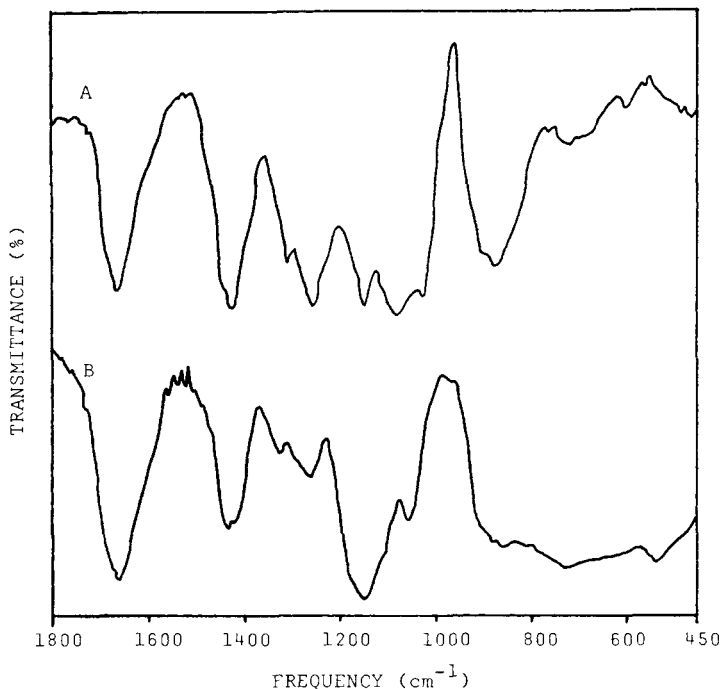
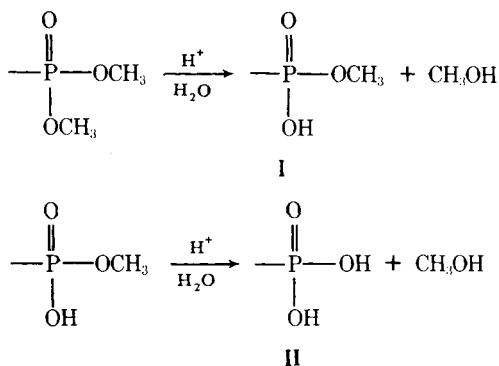


Fig. 9. Interferometer spectra of THPOH-NH<sub>3</sub> polymer: A, unoxidized; B, after oxidation with H<sub>2</sub>O<sub>2</sub>.

methyl esters changing the ester groups to acid groups as shown below:



The hydrolysis of the Pyrovatex methyl esters had been a problem in the commercial use of this finish.<sup>10</sup> Infrared spectra of the hydrolysis products (I, II) of the Pyrovatex molecule are not available. Spectra of compounds of related structure are shown in Figure 8. These spectra are of a free phosphonic acid (A), a monoester derivative (B), and a diester derivative (C). Examination of these spectra indicates that no comparison can be made from spectra of compounds of similar structure if more than one part of the molecule is different. To define the actual change which occurred after weathering of the Pyrovatex 3805 finish under conditions of all gases, one would have to compare the spectra of the original finish with that of the monoester and free acid forms of the compound. These spectra would have to be of the Pyrovatex derivatives finished on cotton

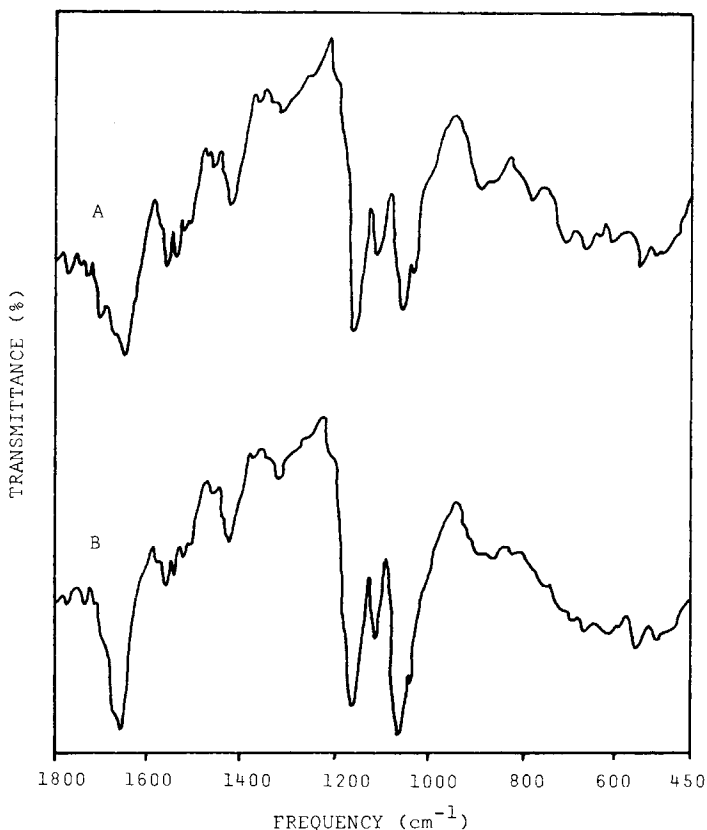


Fig. 10. Interferometer spectra of THPOH-NH<sub>3</sub> finish on cotton fabric: A, unweathered; B, After 150 hr of exposure to NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, and xenon arc light, washed.

fabric to prove that hydrolysis of the Pyrovatex 3805 finish occurred during weathering.

The THPOH-NH<sub>3</sub> finish was polymerized directly onto the cellulose fabric and oxidized in situ. To obtain the spectrum of the polymer, it was necessary to synthesize the polymer and to oxidize it. The interferometer spectra of the THPOH-NH<sub>3</sub> polymer before and after oxidation are presented in Figure 9. These spectra indicate a shift in absorption band frequencies and intensities of those bands relative to the phosphorus bonding. The shifts are a result of the conversion of the phosphine to the phosphine oxide changing the valence of phosphorus from +3 to +5.

The spectrum of the unweathered THPOH-NH<sub>3</sub> finish in situ on the fabric (cellulose absorption subtracted) and the corresponding spectrum of this finish after 150 hr of exposure to all gases with light are shown in Figure 10. The spectra of the finish after exposure to light in the presence of NO<sub>2</sub>, SO<sub>2</sub>, and all gases (sample unwashed) are presented in Figure 11, spectra A, B, and C, respectively. A spectral comparison of the weathered finish with the unweathered finish under the conditions stated showed no changes in absorption, therefore no changes in structure. The slight differences in spectrum B of Figure 11, exposure to SO<sub>2</sub> for 165 hr and washed, are probably due to a slight overcompensation for the cellulose spectra.

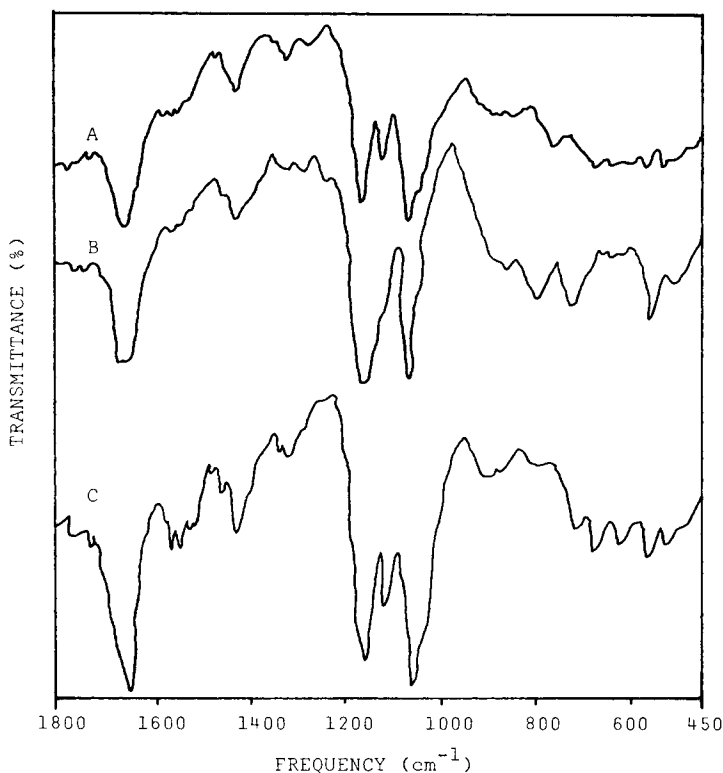


Fig. 11. Interferometer spectra of THPOH-NH<sub>3</sub> finish on cotton fabric after xenon arc light exposure in a Weather-Ometer: A, 150 hr NO<sub>2</sub>, washed; B, 165 hr SO<sub>2</sub>, washed; C, 150 hr NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, unwashed.

### SUMMARY

Two spectroscopic techniques were used to evaluate the nature of flame retardant finishes on cotton fabric before and after weathering exposure. Solvent extraction of the finishes followed by infrared analysis using an internal reflectance procedure revealed that the finishes removed from the fabric by the solvent were identical spectroscopically to the original finishes. The second spectroscopic technique—Fourier transform spectroscopy—provided a new and unique method of observing finishes on fabrics. By this technique it was possible to look at the finishes in situ on the fabric. The resulting FTS-infrared spectra indicated that, with but two exceptions, the weathering of the fabric and finishes with various combinations of xenon arc light and added pollution gases (NO<sub>2</sub>, SO<sub>2</sub>, and O<sub>3</sub>) caused no significant change in the structure of the flame retardant finishes. Previous work<sup>1</sup> had shown that in particular the Pyrovatex 3805 finish was removed from the fabric after long periods of weathering, but this weathering did not in general change the structural characteristics of the finish on the fabrics or the structure of the extractable finish. The FTS-IR spectra of Pyrovatex 3805 exposed to the combined weathering of SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> with xenon arc light indicated a possible change in the phosphono structure of the finish. However, the interpretation of this shift cannot be made with any confidence without a direct comparison with the spectra of model compounds depicting the proposed structural changes.

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