Electron Spectroscopy for Chemical Analyses (ESCA)— A Tool for Studying Treated Textiles

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Synopsis

Electron spectroscopy for chemical analysis (ESCA) has been successfully used to determine the location of flame-retardant polymers or reagents and crosslinking and oil/water-repellent reagents in relation to fiber surfaces of chemically modified cotton fabrics and cotton/polyester blends. Changes in intensity of characteristic ESCA element signals were followed as the particle size of the treated fabric varied. Dimethyloldihydroxyethyleneurea (DMDHEU) and the flame-retardant polymer formed from tetrakis(hydroxymethyl)phosphonium chloride (Thpc) and urea penetrate and are homogeneously deposited throughout cotton fabrics. The oil/water-repellent finish, FC-218, and the flame retardants from the THPOH/NH_3 reaction and tris(dibromopropyl) phosphate are deposited on the surfaces of both cotton and polyester fibers.

INTRODUCTION

Electron spectroscopy for chemical analyses (ESCA) introduced by K Siegbahn[1] is an important analytical tool for studying surfaces of solids. This technique yields information on the chemical composition (elemental analysis), the chemical state (bonding and oxidation), and the location of atom types within the sample.

In brief, monochromatic x-rays impinge upon a sample, interact with atoms of all elements contained in the bulk sample, and eject core level electrons from these atoms. Only electrons originating from atoms lying within 50 Å of the surface have a high probability of escaping from the sample with a measurable kinetic energy (E_{KE}). From E_{KE} and the energy value of the incident x-radiation ($E_{x\text{-ray}}$), binding energy (E_{BE}) of the electron can be calculated. This E_{BE} represents the energy of attraction originally experienced by the electron in the unperturbed atom of the sample. To a first approximation, E_{BE} is related to E_{KE} and $E_{x\text{-ray}}$ by the following equation:

$$E_{BE} = E_{x\text{-ray}} - E_{KE} + \text{constant} \qquad (1)$$

The E_{BE} is influenced by the nuclear charge, oxidation state, or formal charge of the atom from which it is ejected as well as bonding of that atom to electron-rich or electron-deficient atoms. The number of electrons with a specific E_{KE} is directly proportional to the concentration of a particular atom within about 50 Å of the sample surface.

ESCA showed that free amine and amine hydrosalts were present in diethylaminoethyl (DEAE) cottons.[2] The degree of conversion of tertiary

amine groups to quaternary ammonium groups by subsequent treatment of DEAE cotton with a number of alkyl halides was also determined by this technique.[3]

ESCA was also used to investigate cottons that were made flame retardant by treatment with various nitrogen-containing compounds, in conjunction with methylolated phosphorus compounds.[4]　Durability of such flame retardants depends on the oxidation state of phosphorus in the final polymer.[5] ESCA clearly showed that in some flame retardants, phosphorus was oxidized to its highest state during the treatment, whereas in others, total oxidation of phosphorus required post-H_2O_2 treatment.　In addition, we used ESCA to monitor air oxidation of a flame-retardant finish that was not given a post-H_2O_2 treatment, but simply exposed to the atmosphere for a period of weeks.[4]

In previous studies, the use of ESCA to detect changes in valence state of a particular element was emphasized.　For example, relative amounts of tertiary and quaternary nitrogen in DEAE cottons, or selective amounts of phosphine and phosphine oxide in selected flame-retardant cottons that had been subjected to chemical changes, were followed successfully via ESCA.

This report, which is concerned with the sensitivity of ESCA for studying chemical treatments of textiles, highlights precautions that must be taken in interpretation of spectra for quantitative analyses.　Specific examples are given on its use for determining distribution of reagents in cottons and in blends of 50/50 cotton/polyester that were chemically modified to yield flame-retardant, wrinkle-resistant, and soil-resistant fabrics.

EXPERIMENTAL

Reagents

Chemicals from the indicated commercial sources were used without further purification:　tetrakis(hydroxymethyl)phosphonium chloride (Thpc), Hooker Chemical Corporation; Fixapret CP, Badische Aniline-Soda Fabrick AG; Permafresh 183, Sun Chemical Corporation; urea, Baker Chemical Company; tris(2,3-dibromopropyl) phosphate (TDBPP), Michigan Chemical Corporation; Tween-20 and 61, ICI America Incorporated; FC-218, 3M Corporation.

Fabrics and Treatment

Fabrics were 80 × 80 cotton or 50/50 cotton–polyester printcloth, approximately 3.2 oz/yd², that had been desized, scoured, and bleached with peroxide.

A variety of methods were employed to impart flame, wrinkle, and/or soiling resistance to fabric; most were adaptations of previously published methods.

Flame Resistance

THPOH/NH₃.　Fabric was padded with a 35% aqueous solution of THPOH, dried, and cured 10 min in an ammonia chamber.[6]

THPOH/Amide. Fabric was padded with solution containing 26% Thpc, 7% urea, 5% trimethylolmelamine, 4% NaOH, and 48% H_2O, dried at 80°C for 2 min, and cured at 160°C for 3 min.[7]

Thpc/Urea/Na$_2$HPO$_4$. Fabric was padded with a solution of 27% Thpc, 8% urea, 3% Na_2HPO_4, 4% NaOH, and 58% H_2O, dried at 80°C for 2 min, and cured at 160°C for 2 min.[8]

Thpc/Urea/Na$_2$HPO$_4$/TDBPP. Fabric was padded with an emulsion prepared by mixing an aqueous and a perchloroethylene solution. The aqueous portion was 53% of the total weight and contained 47% Thpc, 15% urea, 32% H_2O, 4% Na_2HPO_4, and 2% Tween 20. The perchloroethylene portion contained 25% tris(2,3-dibromopropyl) phosphate (TDBPP), 31% perchloroethylene, 2% Tween 61, and 42% H_2O. Fabric was dried at 80°C for 2 min and cured at 160°C for 2 min.

TDBPP. An emulsion was prepared by mixing an aqueous portion (53%) containing 2% Tween 20 and 98% H_2O with a perchloroethylene portion containing the same chemicals as in part D. The fabric was dried and cured as in part D.

Wrinkle Resistance

An aqueous solution containing 10% by weight of a technically pure dimethyloldihydroxyethyleneurea (DMDHEU) obtained by diluting Fixapert CP-40 was made $0.03M$ with respect to $Zn(NO_3)_2$ and used to pad fabrics, which were dried at 60°C for 7 min and cured at 160°C for 3 min.[9]

Soil Resistance

FC-218/PR-183. Permafresh-183 and $0.03M$ $MgCl_2$ catalyst were added to a commercial aqueous emulsion of a fluorocarbon polymer, FC-218. The fabrics were padded with the emulsion, dried at 60°C for 7 min, then cured at 160°C for 3 min.

Analyses

Conventional Wet Analyses. Nitrogen was determined by the Kjeldahl method with an accuracy of ±0.2% at a concentration level of 1–2%. Phosphorus was determined gravimetrically as ammonium phosphomolybdate, following H_2SO_4/HNO_3 digestion of the fabric, with an accuracy of ±0.05% at a concentration level of 0.1–1.0%. Fluorine and bromine were determined after the sample was burned in an oxygen flask; "AMADAC-F" reagent was used for the fluorine and sodium hypochlorite for the bromine determinations.

Electron Emission (ESCA). ESCA examinations were made of fabric, fabrics ground to pass a 20-mesh screen, and of ball-milled samples. Double-back adhesive tape was used to mount samples on the probe. Samples were analyzed on a Varian IEE 15 spectrometer equipped with a magnesium anode. Spectra were recorded with a filament current of 120 mA and x-ray voltage of 9 kV in a vacuum of 1×10^{-6} torr.
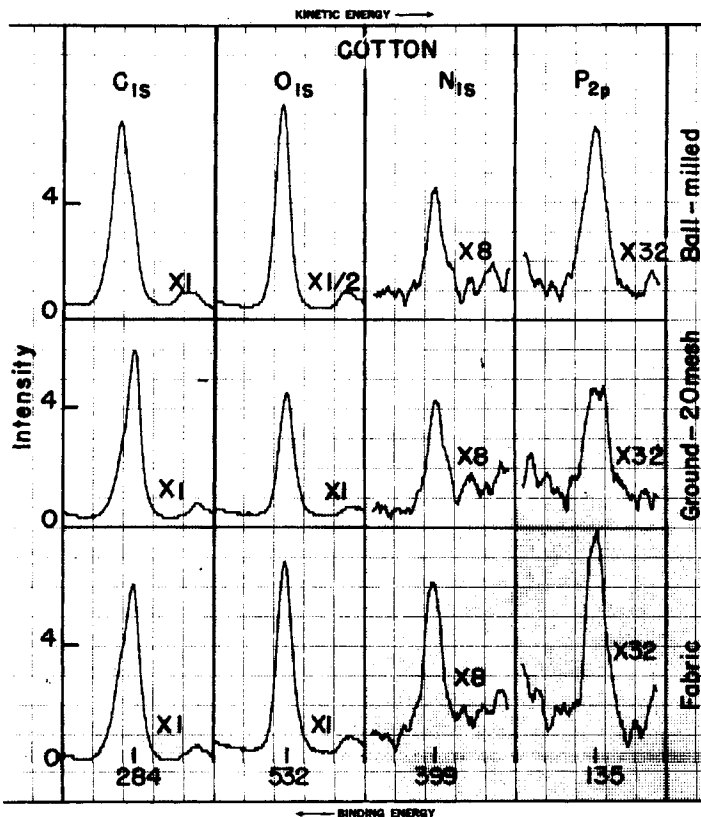
Fig. 1. ESCA spectra of untreated cotton. Spectra recorded with scan width 20 eV, scan time 20 sec; 10 scans each recorded for C_{1s} and O_{1s} regions, and 50 scans each for N_{1s} and P_{2p} regions.

RESULTS AND DISCUSSION

Combined properties of resilience and flame resistance, or of resilience and oil repellency, can be produced by either treating fabric with a solution or emulsion of the crosslinking and flame-retardant reagents, or by applying a crosslinking reagent and then the reagent that coats the surface. Because reagents penetrate fibers differently, their location in the final product might be altered by the method used to apply them. Since ESCA is a useful tool for examining only the outer layers or surfaces of fibers, it is ideally suited to study effects of various fabric treatments.

Differing amounts of fiber surfaces can be exposed to the x-rays if the treated fabrics are ground to several particle sizes. The strength of the ESCA signal (determined by either height or area) of an element that is dispersed uniformly throughout the fiber is insensitive to particle size; that of an element deposited only on the surface decreases as the particle size of the ground fabric decreases. Conversely, the signal strength arising from an element deposited only beneath the surface increases as the particle size decreases.

Sensitivity of ESCA to surface concentration as opposed to bulk concentration can be seen from differences in spectra obtained with fabric before and
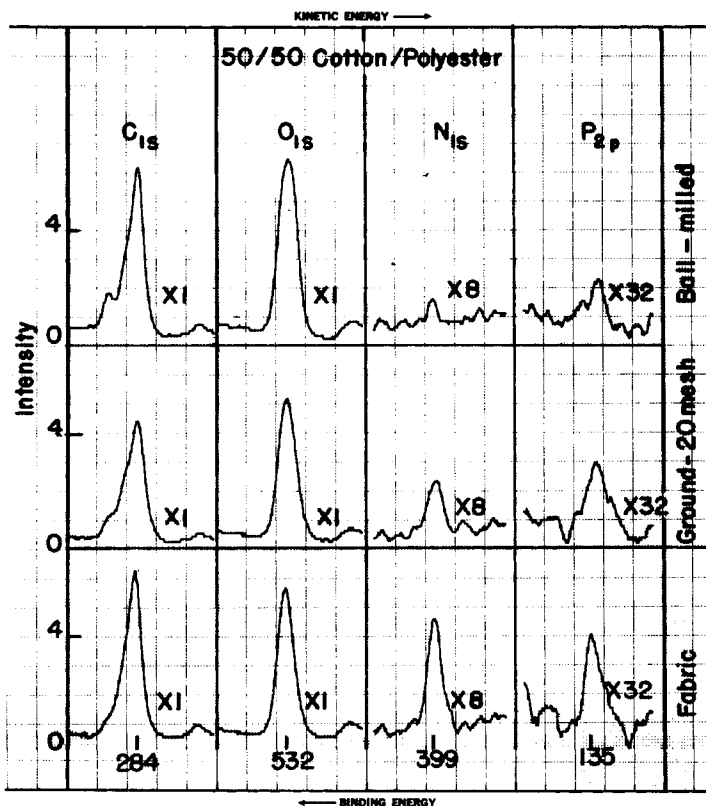
Fig. 2. ESCA spectra of untreated 50/50 cotton/polyester blend. Spectra recorded with scan width 20 eV, scan time 20 sec; 10 scans recorded for C_{1s} and O_{1s} regions, 50 scans each for N_{1s} and P_{2p} regions.

after ball milling or grinding to pass a 20-mesh screen. The C_{1s}, O_{1s}, N_{1s}, and P_{2p} spectra of untreated cotton (Fig. 1) and untreated 50/50 cotton/poly-ester blend (Fig. 2) are typical. Because of low concentration of nitrogen and phosphorus (0.2%) in each sample, the N_{1s} and P_{2p} signals were recorded after 50 scans, while the C_{1s} and O_{1s} were recorded after only 10 scans. Sample particle size affected spectra of the 50/50 blend more than that of cotton. The N_{1s}, C_{1s}, O_{1s}, and P_{2p} signals heights were relatively constant when the cotton was fabric, ground to 20-mesh, or ball milled. The N_{1s} and P_{2p} signals were greatly reduced when the 50/50 blend fabric was ball milled, but only slightly reduced when the fabric was ground. Data in Figures 1 and 2 suggest that nitrogen and phosphorus were evenly distributed throughout the all-cotton fabric, but were on or near the surface of the 50/50 cotton/polyester blend.

ESCA can distinguish like elements of different chemical environments if the difference in E_{BE} is 0.5 eV or more. Specifically, fluorocarbons, carbonyl carbons, and saturated hydrocarbons can be distinguished by their C_{1s} spectra. Carbon has the highest binding energy when attached to fluorine, next, when attached to a carbonyl oxygen, and lowest, when attached to other carbons and hydrogens in a chain. Since polyester contains carboxyl groups, the C_{1s} signal for those carbon atoms should be detectable at 288.4 eV. The C_{1s}

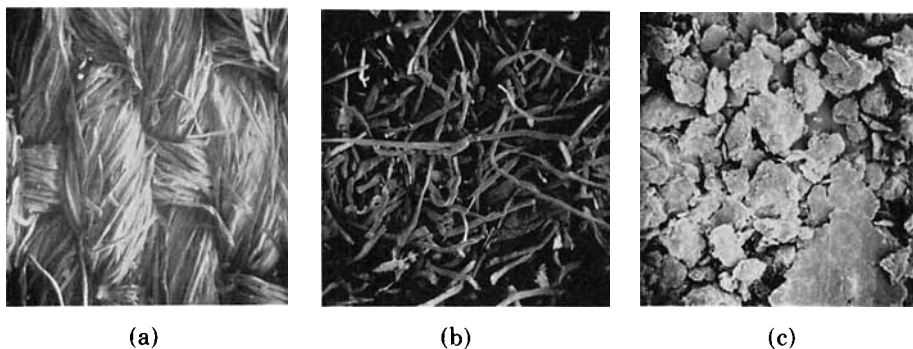(a)   (b)   (c)

Fig. 3. Scanning electron micrographs of 50/50 cotton/polyester fabric (a), 20-mesh ground (b), and ball milled (c) mounted on adhesive tape backing. (a) and (b) magnified 100×; (c) 500×.
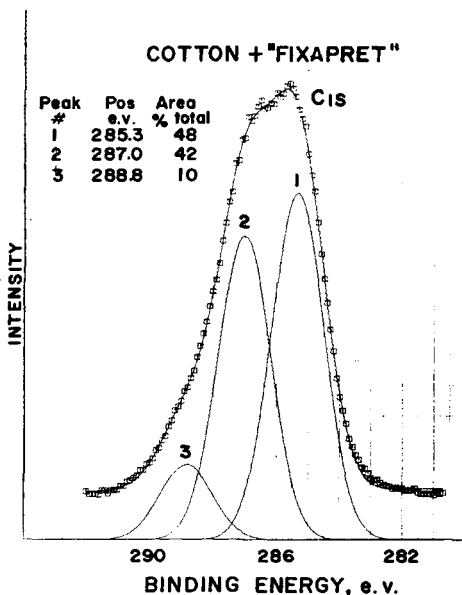

Fig. 4. Computer resolution of C_{1s} ESCA spectral data obtained from ball-milled samples of cotton fabric treated with Fixapret CP-40.

spectra in Figure 2 show emergence of a peak at 288.4 eV for the ground sample, and an increase in intensity of the signal for the ball-milled sample. Signal increases as particle sizes decrease can be attributed either to cotton fibers overlapping polyester fibers on surfaces or to the coating of all fibers with some of the products of chemical treatment. In either case, electrons ejected from the polyester are insulated from the detector because they are deenergized by interacting with the surface material. The signal is intensified because additional surfaces, normally below the fabric surface, are exposed when particle size of the ground fabric diminishes.

We eliminated the possibility that the higher E_{BE} of a C_{1s} observed on decrease in particle size of the blend may have been caused by Scotch "magic
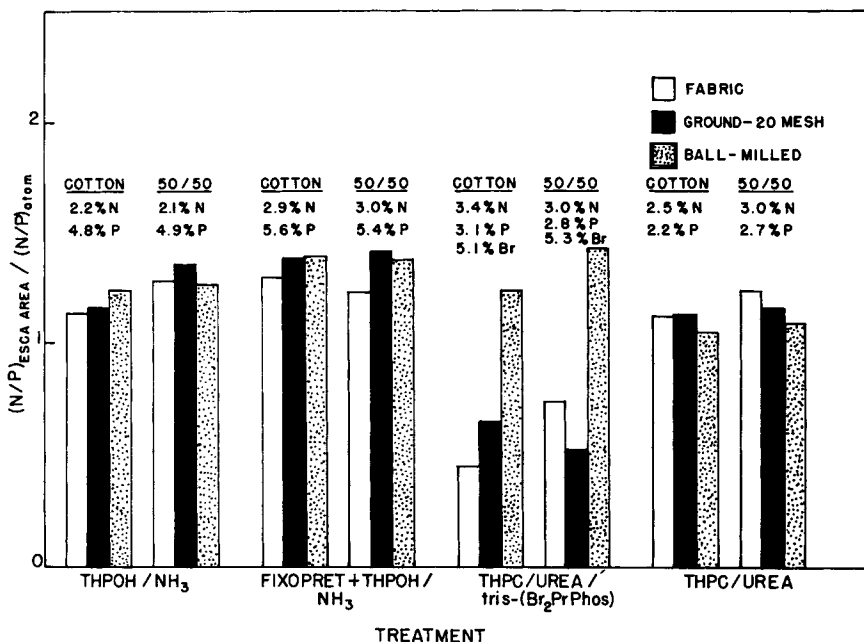
Fig. 5. Comparison of ESCA N_{1s} and P_{2p} areas and analytical nitrogen and phosphorus contents of treated cotton and 50/50 cotton/polyester.

tape" used to bind particles to the sample holder. Only ESCA spectra of the magic tape and the blended fabric, ground or ball milled, show peaks at 288.4 eV. All cotton samples completely covered the tape since the 288.4 eV C_{1s} peak was absent. Use of another kind of tape having a C_{1s} peak at 284.2 eV to bind samples of the blended fabrics resulted in a C_{1s} spectrum identical to that obtained with the magic tape binder. The peak at 288.4 eV appeared in the spectra of the small particle-size blend mounted on the tape which had no C_{1s} signal at 288.4 eV. Very little tape is visible between the fibers or particles of the blended fabric or ground fabric as observed in the scanning electron micrographs of the tape-mounted samples (Fig. 3). Similar micrographs were observed for the tape-mounted cotton samples.

Fixapret CP-40 (DMDHEU), used to impart wrinkle resistance to cotton and cotton/polyester blends, reacts with available cellulose hydroxyls to incorporate methylolated urea groups in the product. The cotton contained 0.9% and the blend contained 1.1% nitrogen after reaction with DMDHEU. Very little carbonyl carbons in relation to the carbons of the substrate (cotton and polyester) was present, so the carbonyl carbon signal from the added urea was not clearly discernible via ESCA spectra. Its presence, however, can be detected qualitatively by comparing ratios of the heights of the signal at 288.4 eV to the peak maximum for the samples before and after treatment. With each fabric, this ratio for the treated samples was higher than for the control. A computer analysis of the data for the C_{1s} spectra of the ball-milled cotton treated with DMDHEU gave the three components shown in Figure 4. The peak associated with the carbonyl carbons is located at 288.8 eV and represents 10% of the total carbon signal. If this resin is distributed
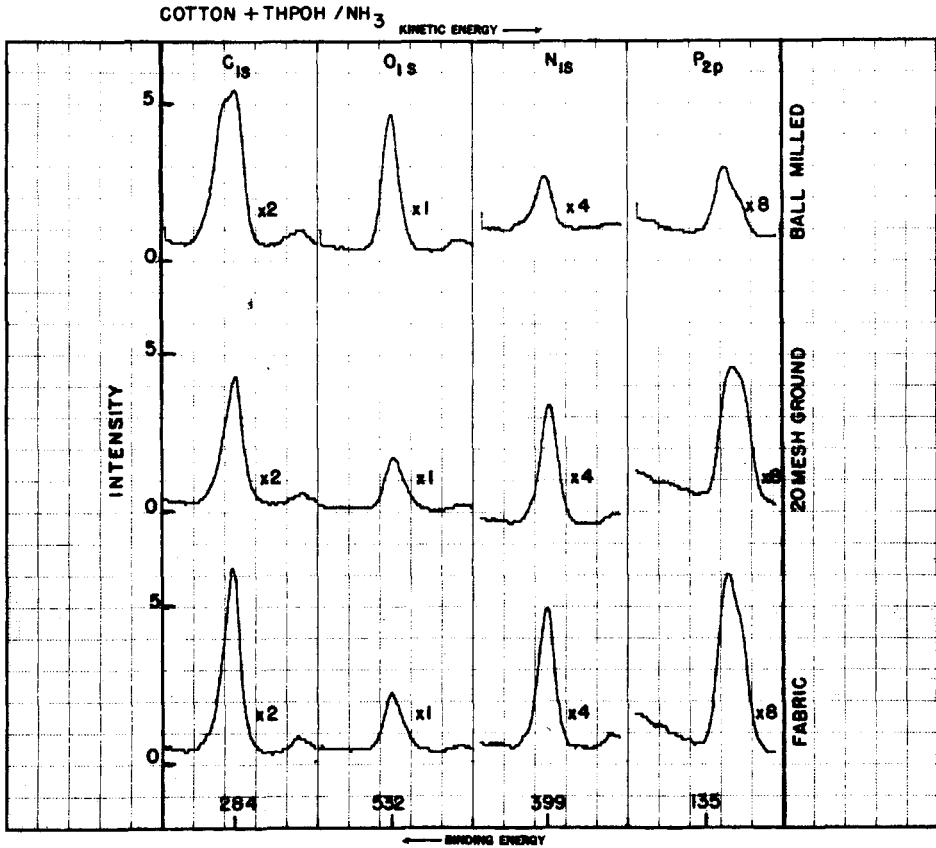
Fig. 6. C_{1s}, O_{1s}, N_{1s}, and P_{2p} ESCA spectra of cotton treated with THPOH/NH₃. C_{1s} and O_{1s}, 10 scans each; N_{1s} and P_{2p}, 50 scans each; 2.2% N and 4.8% P in fabric.

evenly throughout cotton fibers, there should be little difference between the peak ratio of the C_{1s} and N_{1s} signals as particle size changes. The peaks were recorded under identical scan conditions, except for the number of scans required to produce the peak. The C_{1s}-to-N_{1s} peak area ratios were 9.3, 11.7, and 12.7 for the DMDHEU-treated cottons analyzed as fabric, 20-mesh ground, and ball milled, respectively. Although particle sizes of ground and ball-milled samples differ greatly, the C-to-N area ratios are equal within experimental error, indicating a uniform distribution of nitrogen throughout the cotton. In contrast, the C-to-N peak area ratio of the ESCA spectra of the finished blend fabric differed from the ratios obtained on ground and ball-milled treated blends. These ratios were 7.0, 6.4, and 15.2, respectively. The C/N ratio increase for the ball-milled blend indicates that the reagent does not penetrate the polyester.

All-cotton and 50/50 polyester blend fabrics, after treatment with several flame-retardant finishes, were examined in all three forms by ESCA. The C_{1s} and O_{1s} spectra were recorded after 10 scans, the Br_{3d} spectrum after 20 scans, and the N_{1s} and P_{2p} spectra after 50 scans. Peak areas were measured by weighing cutouts of the Xeroxed spectra. Comparison of peak areas of different elements is equivalent to comparison of the concentrations of the
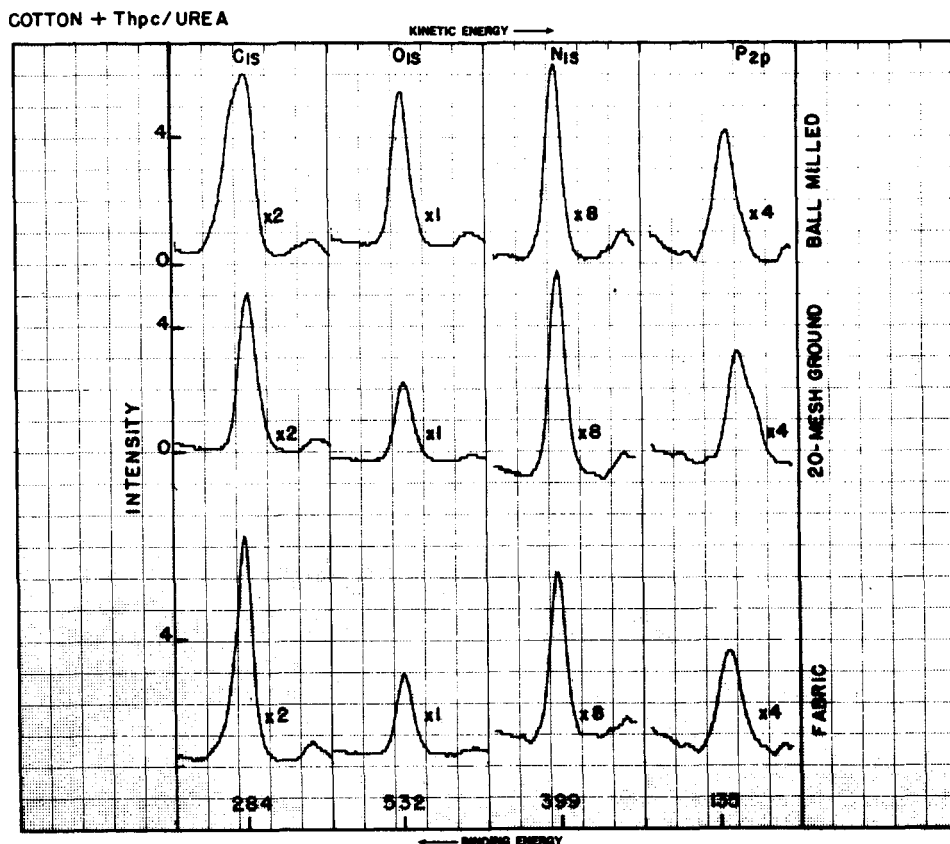
Fig. 7. C_{1s}, N_{1s}, O_{1s}, and P_{2p} ESCA spectra of cotton treated with Thpc/urea. C_{1s} and O_{1s}, 10 scans each; N_{1s} and P_{2p}, 50 scans each; 2.5% N and 2.2% P in fabric.

particular atoms present on the sample surface. Wagner[11] stated that the N_{1s} ESCA peak area was 1.05 times more sensitive than the P_{2p} peak area. We were interested in the peak area ratio in the ESCA of our flame-retardant fabrics to determine if nitrogen and phosphorus were uniformly distributed. The N/P ESCA peak areas in Figure 5 compare each treated fabric before and after grinding or ball milling to the N/P atom ratio, determined by wet chemical analyses. With the exception of the fabric treated with Thpc/urea/ TDBPP, the ratio is not affected by change in particle size of the sample.

With THPOH–NH$_3$ or Thpc–urea flame-retardant finishes, all of the phosphorus in the finished fabric is incorporated into a polymer which also contains all of the nitrogen present. Whether the polymer is on the surface or uniformly distributed, the $(N/P)_{ESCA}/(N/P)$ atom ratio is independent of particle size resulting from grinding or ball milling. With the addition of a phosphate, as in the Thpc/urea/TDBPP treatment, the phosphate phosphorus of the TDBPP does not become part of the P–N polymer and is probably located on the surface of the Thpc–urea polymer. Increase of the ratio with ball milling probably results from an increase in relative amounts of N on surfaces of particles exposed to ESCA.

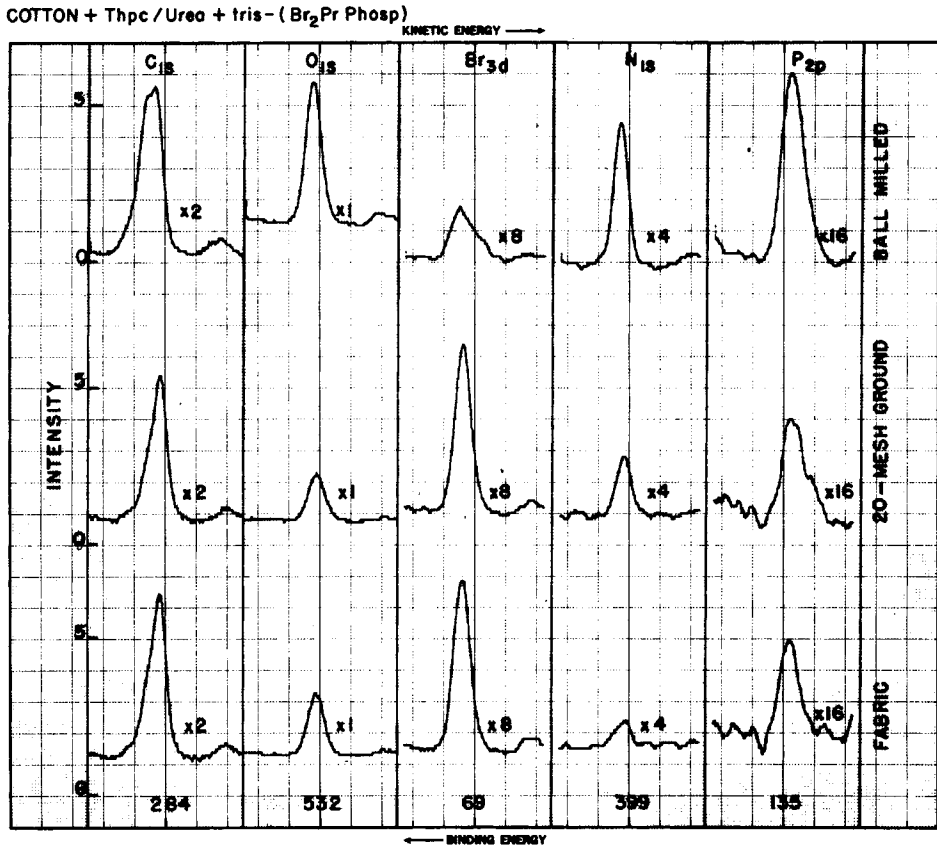Location of resins in relation to the surface of treated fabrics is helpful in

COTTON + Thpc / Urea + tris-(Br$_2$Pr Phosp)

Fig. 8. C$_{1s}$, O$_{1s}$, Br$_{3d}$, N$_{1s}$, and P$_{2p}$ ESCA spectra of cotton treated with Thpc/urea/trisdibro-mopropyl phosphate. C$_{1s}$ and O$_{1s}$, 10 scans each; Br$_{3d}$, 20 scans; N$_{1s}$ and P$_{2p}$, 50 scans each; 3.4% N, 3.1% P, and 5.1% Br in fabric.

understanding the role of polymers and compounds in the flame-retardant processes. ESCA spectra of cotton treated with THPOH/NH$_3$ (Fig. 6) show decreases in N$_{1s}$ and P$_{2p}$ signals only after ball milling of the fabric, indicating that the flame-retardant polymer coats the fiber surface and does not penetrate it. The constancy of N$_{1s}$ and P$_{2p}$ signals for fabric and ground samples of cotton treated with Thpc/urea (Fig. 7) indicates that this flame-retardant polymer is distributed uniformly throughout the fiber system.

Conventional water-soluble reagents that produce flame retardance in all-cotton fabrics are not effective for cotton–polyester blends because the reagents are not distributed uniformly in the polyester. However, reagents that coat fiber surfaces are effective for coating both cotton and polyester fibers. Halogenated phosphates as flame retardants for polyesters are as effective as Thpc/urea for cotton. A water–perchloroethylene emulsion of Thpc/urea and TDBPP was applied to a cotton and to a 50/50 cotton/polyester fabric. It is assumed that the phosphate coats the surfaces and that the Thpc/urea penetrates the cotton. However, it has been difficult to confirm this hypothesis by conventional means.

The C$_{1s}$, O$_{1s}$, N$_{1s}$, P$_{2p}$, and Br$_{3d}$ signal strengths of ESCA spectra of the
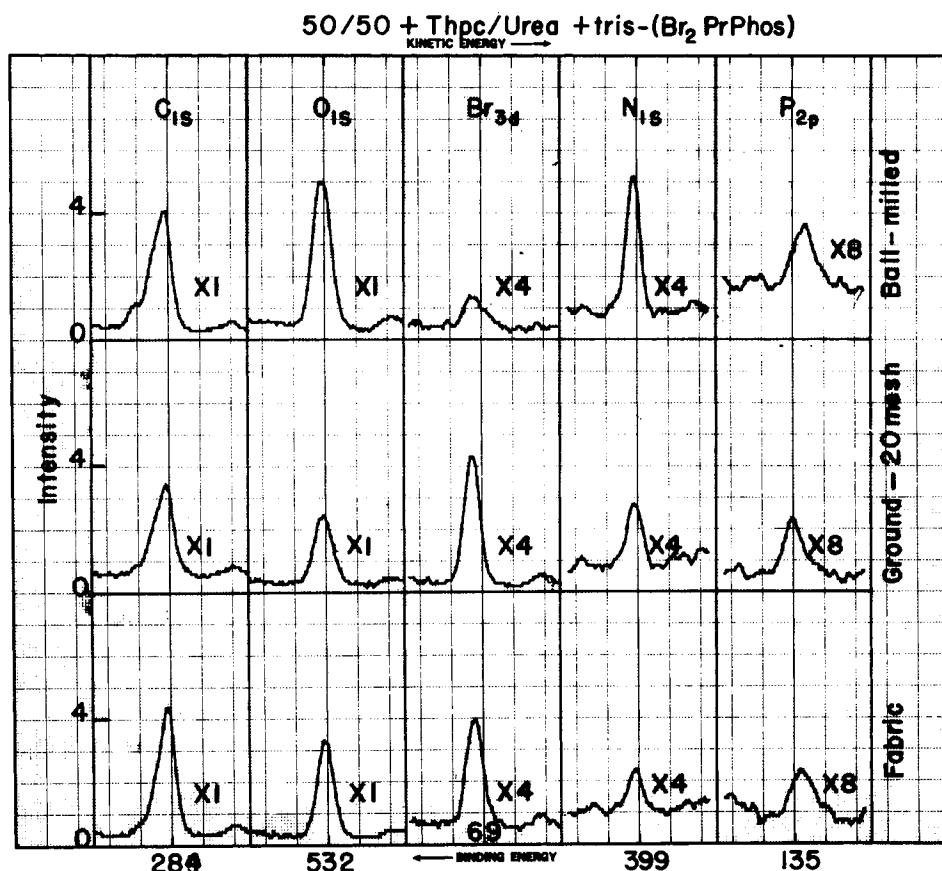
50/50 + Thpc/Urea + tris-(Br₂ PrPhos)

Fig. 9. C_{1s}, O_{1s}, Br_{3d}, N_{1s}, and P_{2p} ESCA spectra of 50/50 cotton/polyester blend treated with Thpc/urea/trisdibromopropyl phosphate. C_{1s} and O_{1s}, 10 scans each; Br_{3d}, 20 scans; N_{1s} and P_{2p}, 50 scans each; 3.0% N, 2.8% P, and 5.3% Br in fabric.

three samples of cotton (Fig. 8) and of cotton/polyester blend (Fig. 9) after treatment with the emulsion of Thpc/urea and TDBPP were compared to determine distribution of the reagents in the two substrates. Like the spectra of cotton treated with emulsion, those of the blend fabric exhibit an increase in N_{1s} and a decrease in Br_{3d} signals when particle size of the sample is reduced. The decrease of the Br_{3d} signal indicates that the TDBPP is on, not beneath, the surface. The increase in N_{1s} is a sign that the compound containing nitrogen is beneath the surface of the fiber. However, since this N_{1s} signal from the blend did not increase when particle size decreased to the same extent as that from the all-cotton sample, the nitrogen compound must have penetrated only the cotton surface. The constancy of the P_{2p} signal of the blend samples and its increase in all-cotton samples as particle size was reduced indicate that the phosphorus of the phosphate (TDBPP) coats both cotton and polyester surfaces, whereas the phosphorus of the Thpc penetrates cotton fiber only.

Oil repellency, together with wrinkle resistance, can be imparted to cotton by treatment with an emulsion containing a fluorocarbon polymer and a crosslinking reagent, such as the combination of FC-218 and PR-183.[10] The
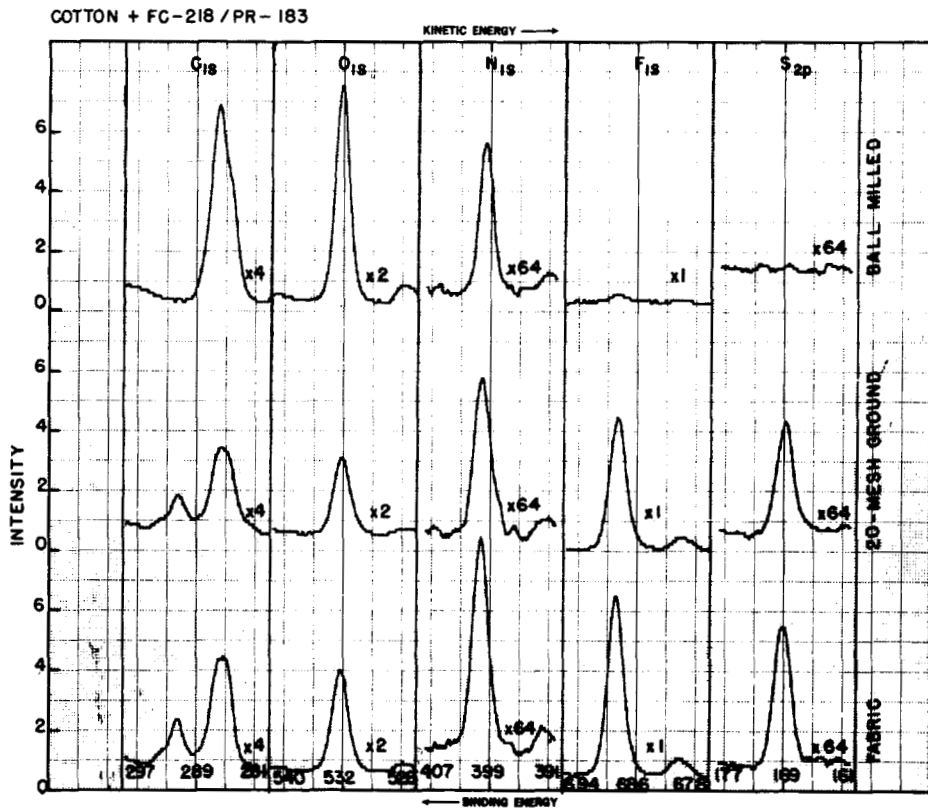
Fig. 10. C_{1s}, O_{1s}, N_{1s}, F_{1s}, and S_{2p} ESCA spectra of cotton treated with an emulsion of FC-218 and PR-183. Each signal recorded after 10 scans.

FC-218 polymer contains C, N, O, F, and S, whereas the PR-183 polymer contains only C, N, and O. Figure 10 is an illustration of these ESCA data. The F_{1s}, S_{2p}, and fluorine-containing C_{1s} signals are only slightly detectable in the ball-milled sample, whereas the N_{1s} signal is relatively constant in all samples, indicating that the FC-218 is on the surface only but that the PR-183 is distributed throughout the sample.

SUMMARY

If treated fabrics are analyzed by ESCA to determine location of polymers or reagents used to impart flame retardancy, wrinkle resistance, or oil/water repellency, the samples must be examined both in fabric form and as a ball-milled powder. From changes in signal intensities as particle sizes change, it can be determined whether a reagent penetrates uniformly throughout the fiber or whether it is deposited only on or beneath the surface. For example, the crosslinking reagent DMDHEU is distributed uniformly throughout a treated cotton fabric, whereas the oil-repellent finish FC-218 is deposited on the fiber surface only.

References

1. K. Siegbahn, C. Nordling, A. Faklman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S-E Karlson, I. Lindgren, and B. Lindberg, *ESCA Atomic, Molecular and Solid State Structures Studied by Means of Electron Spectroscopy*, Almquist and Wiksells AB, Stockholm, 1967.

2. D. M. Soignet, R. J. Berni, and R. R. Benerito, *Anal. Chem.*, **46,** 941 (1974).

3. D. M. Perrier and R. R. Benerito, *J. Appl. Polym. Sci.*, **19,** 3211 (1975).

4. D. M. Soignet, R. J. Berni, and R. R. Benerito, *Text. Res. J.*, **45**(1), 28 (1974).

5. D. J. Daigle, W. A. Reeves, and J. V. Beninate, *J. Fire Flammability*, **1,** 178 (1970).

6. J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Amer. Dyest. Rep.,* **57**(25), 74 (1968).

7. J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Text. Res. J.*, **38,** 267 (1968).

8. D. J. Donaldson, F. L. Normand, G. L. Drake, Jr., and W. A. Reeves, *J. Coated Fabr.,* **3,** 250 (1974).

9. E. J. Gonzales, R. R. Benerito, R. J. Berni, and H. M. Zacharis, *Text. Tes. J.,* **36**(6), 571 (1966).

10. W. J. Connick and S. E. Ellzey, *Amer. Dyest. Rep.*, **61**(11), 55 (1972).

11. C. D. Wagner, *Anal. Chem.*, **44**(6), 1050 (1972).