

3—**Surface Characterization of Textiles Using SEM**

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I—**Introduction**

In modern materials science, structural characterization is basic to a thorough understanding of the nature of a material. The microscope has played an important part in formulating structural concepts in polymeric materials. The light microscope (LM) provided information on the external structure of bulk and fibrillar polymers, and the transmission electron microscope (TEM) permitted ultrastructural information to be obtained. However, natural concepts of external and internal surface structures were difficult to envision due to the low resolution and depth of focus in the LM, and due to the necessity of dealing with microareas of the sample at high magnifications in the TEM. The scanning electron microscope (SEM) produces surface images that are realistic, three-dimensional reproductions of the sample, and its depth of focus and range of magnifications fill the gap between the LM and the TEM. It has thus opened a whole new field in fiber structure studies.

Fiber scientists have relied heavily on the microscope for gaining information on their product for many years. In 1836 a microscopical study of shape, diameter, maturity, and variability of properties of the cotton fiber was given at the Privy Council of King William IV in a report on the status of the textile industry of Great Britain [1]. Application of electron microscopy to a study of cotton fiber structure was made in the early 1940s by Ruska and Kretschmer [2], by Eisenhut and Kuhn [3], and by Barnes and Burton [4], and this instrument has continued to be used in the study of the fine structure of fibers and changes in structure due to chemical modifications. This "new" microscope was also used for characterization of synthetic fibers as they were developed and came into commercial production [5]. Because of the limited ability of the TEM to provide gross information

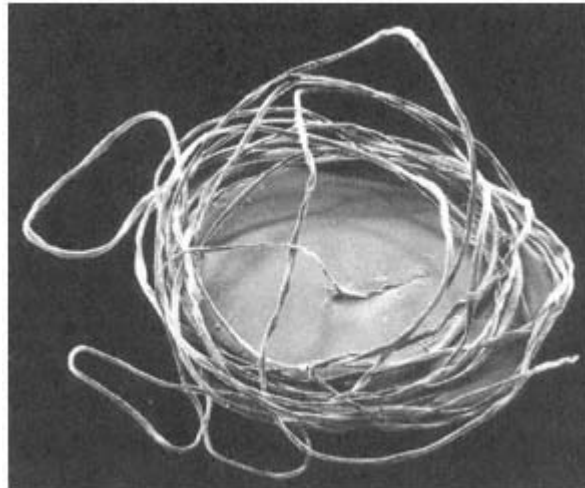


Figure 1
Single coiled cotton fiber showing the extreme
length—diameter dimensions.

on fiber structure, fiber scientists were quick to realize the potential for application of the newly developed SEM in this field. Though the instrument did not become commercially available until 1965, it was used to study fibers as early as the mid 1950s. At the conference on Electron Microscopy of Fibers at the University of Leeds in January 1956, Wells described the examination of fibers in the SEM [6]. During developmental work on the SEM at Cambridge University, Smith and Attack of the Pulp and Paper Institute of Canada showed the potential of this instrument in pulp and paper research [7]. When this instrument was commercialized, two of the first three produced were used in textile fiber laboratories. The SEM not only is used in structural studies and basic and developmental research, but also has found great application in industrial troubleshooting and for dramatic illustration.

Most textile fibers, both natural and synthetic, are organic polymers that manifest some characteristic morphological structure with easily discernable features. In natural fibers such as cotton and wool, this structure is genetically determined and may be influenced by variety or growing conditions. Synthetic fibers or filaments are designed and engineered to a predetermined structure. These special structural features may be used for fiber identification, for prediction of fiber characteristics, or for determination of changes that have occurred in the fiber due to chemical reaction and finishing, or to damage by insects, fungus, heat, wear, or chemical attack. Study of deformations or of rupture due to deformation can provide useful information on internal morphology as well as on reaction deformation.

II— Sample Preparation

Preparation of fiber samples for SEM is relatively simple, especially as compared to TEM preparation, but it should be carried out with care since even simple preparative techniques, if poorly done, result in poor micrographs or erroneous interpretations. Because of the poor conductivity of most polymers, a layer of conducting material must be applied to their surfaces before SEM examination. Echlin and Hyde [8] list five parameters to be considered in choosing a coating material:

1. Conductivity
2. Mechanical stability
3. Secondary electron emission
4. Backscattered primaries
5. Beam penetration

Poor sample conductivity causes buildup of surface electrons, producing variations in surface potential, or "charging." Charging manifests itself as various image distortions and excessively bright overglow, which prevents true image production. Poor conductivity also reduces thermal dissipation, which may lead to

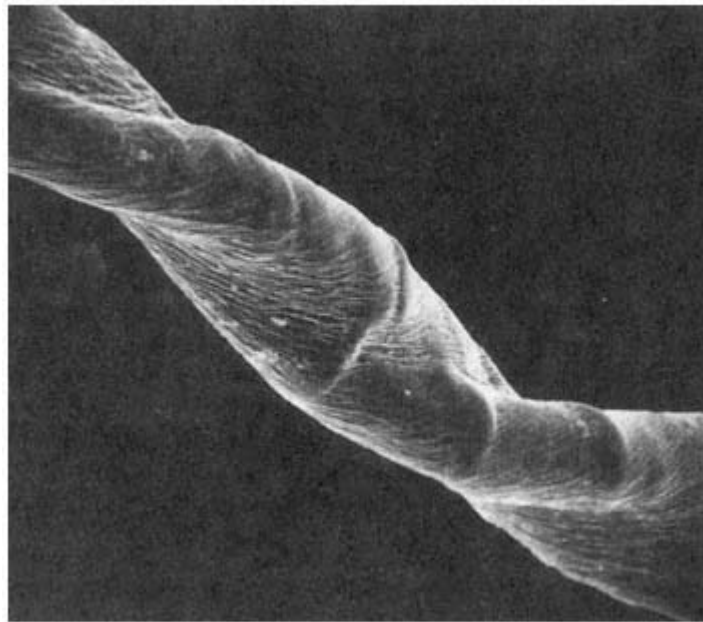


Figure 2
Enlarged fiber segment showing the wrinkled primary wall surface.

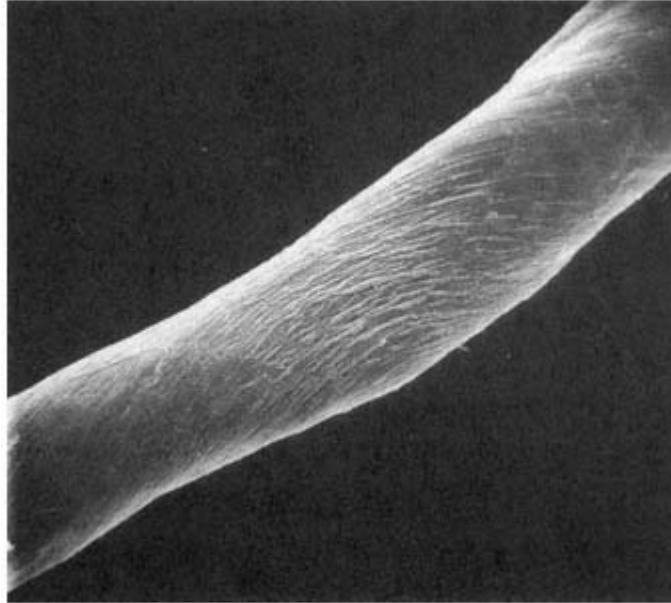


Figure 3
Enlarged fiber segment in which the surface wrinkles indicate a change in the direction of the underlying fibrillar spiral (a reversal).

local sample movement or even heat damage. In addition, polymers, which are usually materials of low atomic density, are readily penetrated by a high-keV (electron voltage) electron beam, causing loss of surface detail. Coating with a microlayer of metal is the most widely used method to suppress charging and decrease beam penetration. Low beam penetration is especially important in polymers since secondary electron emission (those electrons emitted by the sample due to bombardment of the electron beam) is their primary mode of image generation, and deep penetration reduces the number of surface secondaries produced. The amount of metal to be applied depends on the sample and the magnification or resolution to be achieved. Most literature sources specify a 200–300 Å metal layer, which, to be effective in eliminating charging, must be continuous. Continuity may be easily achieved with fibers or even yarns, but the geometry of fabrics presents a problem for obtaining continuous films. However, since most yarn and fabric samples are studied at low magnifications, thicker coatings (500–600 Å) may be applied without obscuring any information available at these magnifications. Such coatings are likely to be continuous over the sample surface as well as from sample to stub. Specimen-to-stub conductivity can be improved by use of conductive tape or paint. Caution should be used in applying conductive paint since it can wick into fibrous samples. As the need for use of higher magnifica-

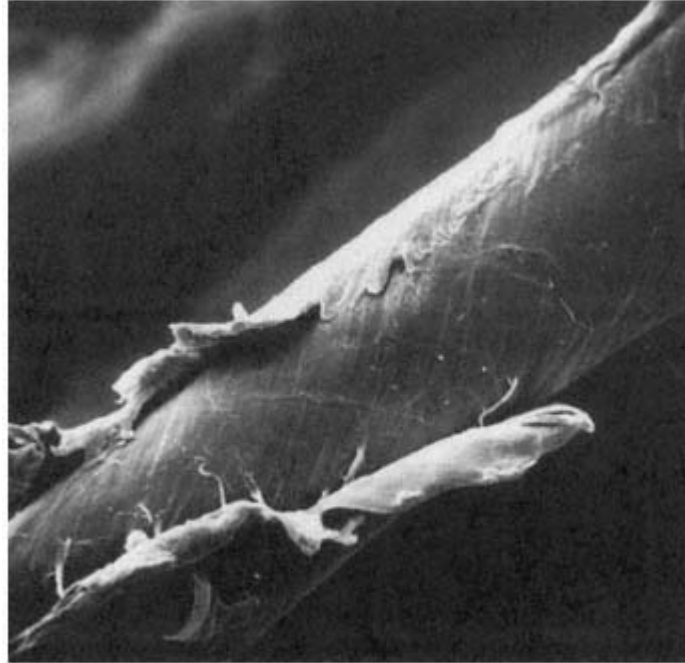


Figure 4
Enlarged fiber segment showing a peeled primary wall,
and the underlying fibrillar spiral.

tions arises, sample coating thicknesses should be reduced to improve resolution of sample features.

A— ***Metal Coating***

Of the several methods that have been used to suppress charging; currently the most satisfactory method is metal coating by sputtering. The other method for metal coating that is used in some laboratories is vacuum evaporation, because this equipment is often already available for TEM preparation methods. Procedures other than metal coating have been used but with less success. Pfefferkorn et al. [9] discussed use of metal foil screening, gas discharge etching, and use of "wet" samples. Lane described the use of a humidity chamber to control charging. This method has been incorporated into the design of a scanning electron microscope with a controlled humidity chamber in which no sample coating is used. This instrument is called an environmental electron microscope and is discussed in Section V. Sikorski et al. [10], who was one of the first to use the SEM in fiber science, advocated the use of antistatic agents (usually solutions of organic liquids) rather

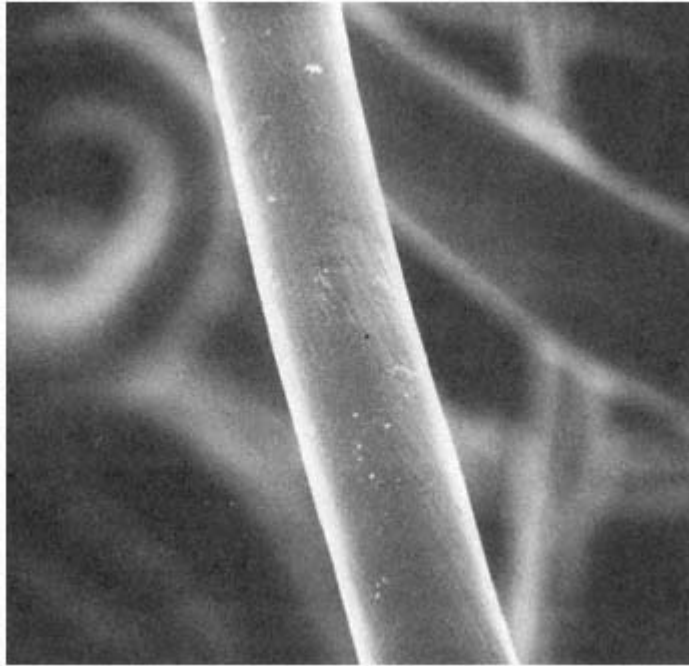


Figure 5
Tubular mercerized cotton fiber, showing a smoother surface.

than metal coating. This method has not achieved very great acceptance as a means of charge suppression.

The widely used sputtering method is achieved by bombarding a conductive metal with

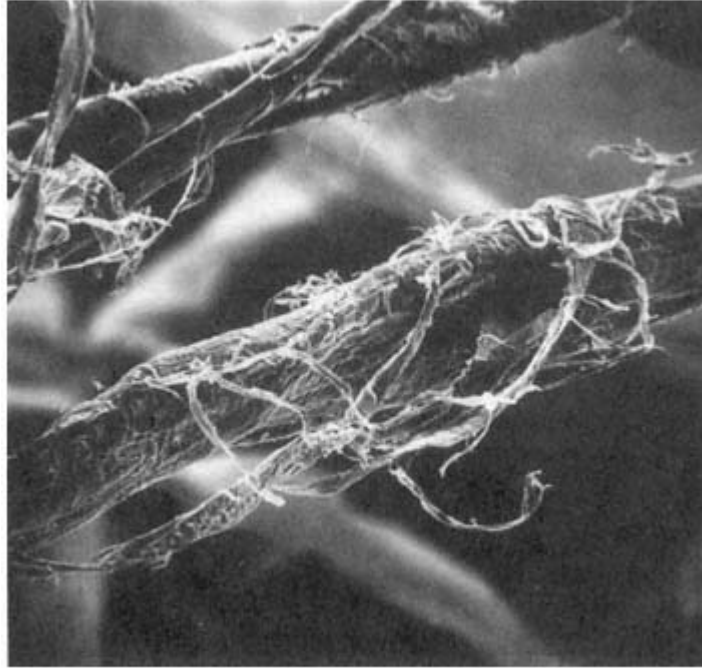


Figure 6
Wet-abraded fiber showing stringy fibrillation.

vide a very satisfactory means of sample coating. Depending on the heat lability of the polymer, care must be taken to protect it from the radiant heat of the filament. The specimen should be placed as far as possible from the source, and if necessary a shuttered aperture may be placed between the source and the specimen.

B—

Coating Materials and Thickness

Choice of coating materials is of prime consideration. Even though it is a relatively poor electrical and thermal conductor, carbon has been used rather extensively as an evaporant [11]. Actually, carbon is best used as an undercoat in conjunction with heavy metal coating, since carbon on vaporizing is reflected inside the vacuum chamber and approaches the sample in directions not possible with metal atoms, thus providing a more uniform film. A metal film can then be overlaid onto the carbon to provide better conductance (unless x-ray analyses are to be done). Although silver and aluminum are the cheapest and easiest metals for coatings, they can be used only when the specimen is to be examined immediately upon coating, since these films deteriorate rapidly on storage. This is of particular concern in preparing fabrics, since fabric construction tends to encourage slight move-

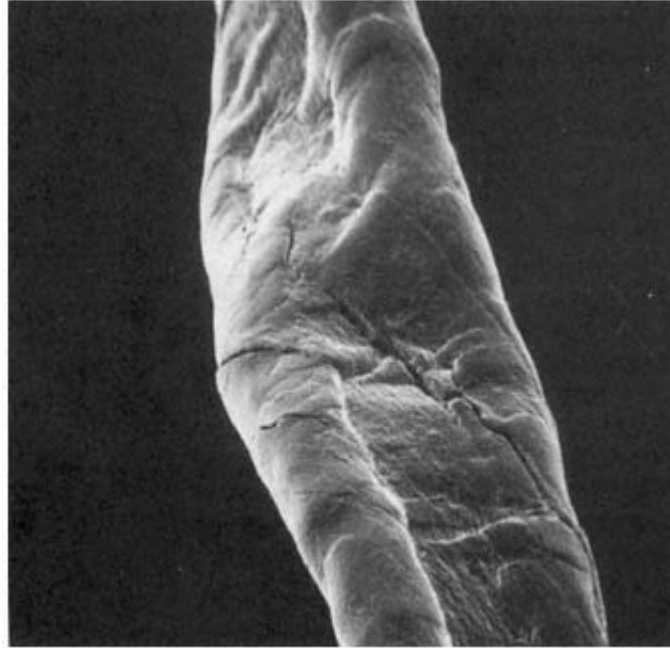


Figure 7
Dry-abraded fiber showing cracks in the surface.

ment ever after the sample is mounted and coated. Movement can cause the film to crack, making it useless as a conductor. Gold and gold—palladium (60–40%, w/w) are probably the best choices as coating materials, since they form relatively stable films, and their higher atomic densities produce greater quantities of secondary electrons with thin coating.

Coating thickness may be measured in several ways [8], none of which probably gives an accurate determination for specimens with very irregular surfaces. For this reason it is difficult to propose that a yarn or fabric surface should have a uniform coating of any particular thickness. While coating thickness may be more critical for samples at high magnifications where maximum resolution is needed, the prime goal for samples photographed at low magnifications is to rid the sample of charging, and with irregular fabrics, thicker coatings than those normally recommended may be necessary. If it is certain that the sample surface is grounded to the stub, and charging occurs after a normal coating procedure, the specimen should be recoated. Such heavy coatings may render the sample useless for studying detailed structures at high magnifications, but do permit examination at the low magnifications of interest.



Figure 8
Blunt end of a broken, dry-abraded fiber.

Coating also affects the type of information obtained from the sample. If analyses other than secondary electron collection are to be made on a sample, this should be taken into account during sample preparation, since elemental analyses require coating with a material such as carbon that does not normally produce extraneous, unrelated sample information. Although carbon alone is not considered a good textile coating material for charge suppression, it can be used when elemental analyses are to be made.

C—

Sample-Holder Attachment

In preparation, the samples to be examined are simply cut to a size consistent with the mounting stub and attached to the stub with some type of adhesive. For fabric samples, double-coated adhesive tape is very convenient. This tape is applied to the stub, trimmed so that it does not quite meet the edge, and the fabric is firmly pressed into it. Tape tends to craze in the vacuum and does not provide an esthetic background for fibers, yarns, or particulate polymers at low magnification. A smoother background is usually obtained by the use of a liquid glue. The choice

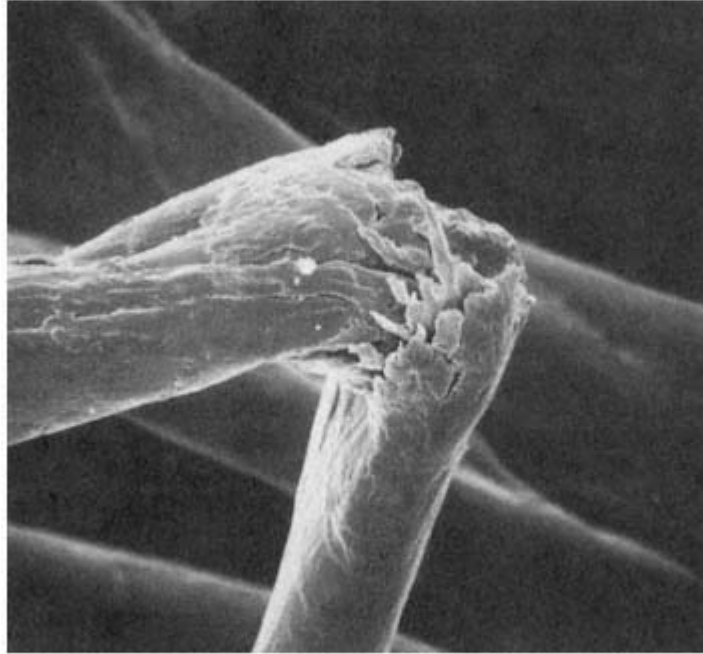


Figure 9
Snapped, dry-abraded fiber.

of glue is not critical, but it should be one that does not seriously outgas in the vacuum, or whose solvent does not affect the sample to be examined. One problem in using glue is that if the sample is applied while the glue is still liquid, it tends to infiltrate the sample and presents an interpretation problem. Once most glues have solidified to the point at which they do not infiltrate, they are usually not tacky enough to securely hold the specimen to the stub. A glue that remains tacky on drying may be obtained by dissolving the adhesive from cellophane adhesive tape in an appropriate solvent. A semiliquid coating of this adhesive is placed on the specimen stub and allowed to dry to tackiness. The specimen may then be pressed onto the stub without infiltration. The liquidity of the adhesive may be adjusted to choice by use of various amounts of solvent.

Fibrous samples may also be mounted by using adhesive on only the ends of the fibers. However, this type of mounting does not restrict specimen motion, which can cause cracking of the conductive film, or specimen drift during examination. Mounting stubs have been devised for examination of fibers under special conditions.



Figure 10
Fungus-damaged fiber after sodium hydroxide swelling.

Special sample preparation aids, such as carbon and metallic tapes, that make sample preparation easier are available from specialty microscopy supply houses. Transfer glues are available in sizes that cover SEM specimen stubs. These tacky glues are attached to a waxy paper and can be transferred to the stub by pressing the sticky surface to the stub and removing the paper. This product provides a tacky, strongly adhesive surface that does not wick into the sample. Silver paints and pastes are also available, but these should be used with caution to prevent infiltration into the sample or interference with elemental analyses.

III— Microscope Operating Conditions

Optimum operating conditions of the SEM for examination of fibers may be somewhat different than for other materials. Parameters that provide good results for samples of high atomic number will not likely provide the same success with most fibers. For that reason it is necessary for the fiber microscopist to have at least a

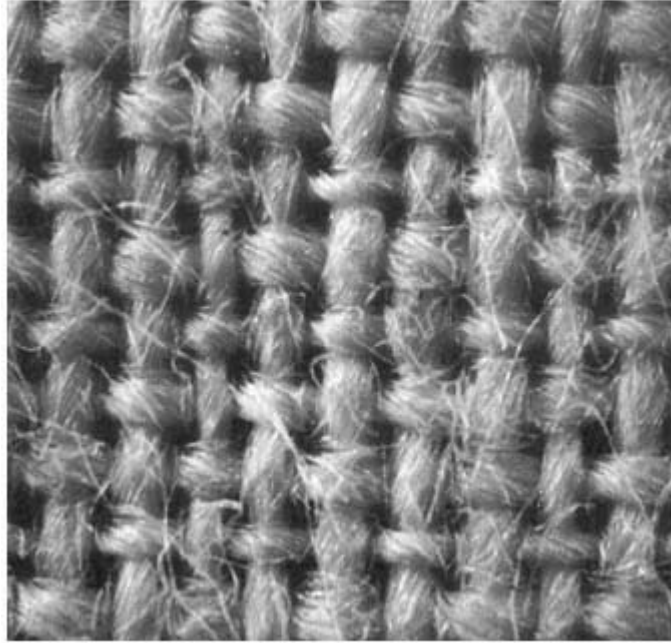


Figure 11
Cotton fabric surface (LM).

basic understanding of the theory of operation of the SEM in order to set operating conditions that will provide the best results with textile samples.

A—
Beam Voltage

Polymers, generally materials of low density, allow greater penetration of the electron beam than do samples of higher atomic number. If a high-keV beam is used, this penetration produces signal from areas of the specimen below the surface and results in images of lower contrast and a loss of detail. Reduction of the beam voltage to 5 keV gives an image of considerably more detail but reduces the resolving capability of the SEM. However, the increased detail brought about by reducing the beam penetration overbalances this loss in resolution, especially at low magnifications. Use of low voltage is especially important when very thin specimens such as fibrillated or sectioned fibers are studied. Even with most coated specimens, low voltages are recommended as an additional means of reducing charging in fibers. Since resolution is lost by the use of low voltage, care must be taken in SEM operation to set other parameters to give the greatest possible resolution. If chosen operating parameters produce an image with a high signal-to-noise ratio

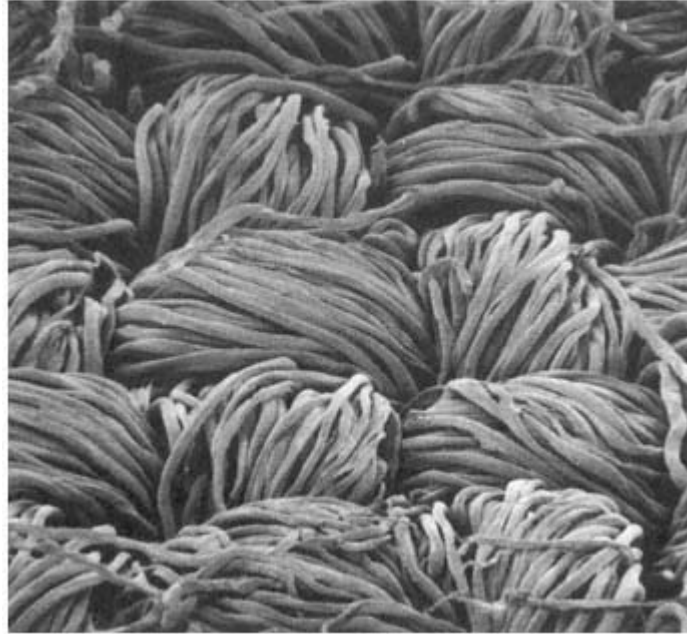


Figure 12
Cotton fabric surface (SEM).

(a great amount of background noise as compared to the signal generated by the sample), this increased noise may be overcome by using longer exposure times. Exposures of 100 sec are commonly used. Use of a shorter working distance is another means of increasing resolution. With careful operation, acceptable resolutions can be achieved even at very low voltages.

B—
Sample Signals

Micrographs usually associated with the SEM are produced by collecting secondary electrons, those emitted by the sample due to bombardment of the electron beam and whose energy is less than 50 eV. They produce the spatially pleasing micrographs that provide surface structural information. Particularly in polymers with low atomic numbers, metallic coatings can control the depth of penetration of the beam and prevent excitation of electrons deep within the sample. They can also help prevent "edge effects," seen as bright areas, on samples that are thinner on the edge than in the center.

Information not available from secondary electrons can also be obtained by collection of other signals emitted from the sample. Backscattered electrons are

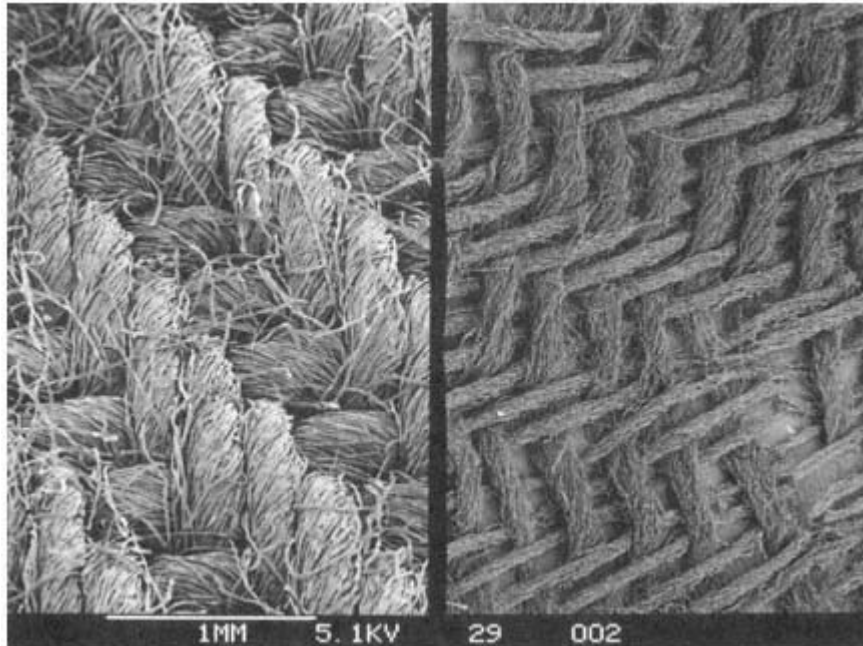


Figure 13
Unburned (left) and charred (right) cotton twill fabric, showing shrinkage that occurs during burning.

those electrons from the primary beam that penetrate the sample and are returned through the penetrated surface. Their energy is close to the incident beam energy. These electrons, having energy higher than that of secondary electrons, are less readily affected by charging forces. Therefore, use of the backscattered mode is one way to photograph samples that continue to charge even after coating. However, backscattered electrons contain different information than do secondary electrons, and the micrograph attained will not have the exact same surface image as those attained with secondary electrons alone. Backscattered electrons do contain Z (atomic number) information, and areas of changes in elemental composition may be noted by changes in contrast in the sample image.

A more definitive method for gaining elemental information from the sample is to collect x-rays that are produced in the sample due to rearrangements of the electrons in the atomic structure after emission of secondary electrons. These x-rays are characteristic of the element from which they are emitted, and can be identified by measuring their energies (energy-dispersive analysis) or their wavelengths (Wavelength analysis). Spectral analysis of energy-dispersive x-rays (EDS) has been a useful tool in textile finishing studies. This method not only can be used for quantitative and qualitative analyses of the sample, but is spatially

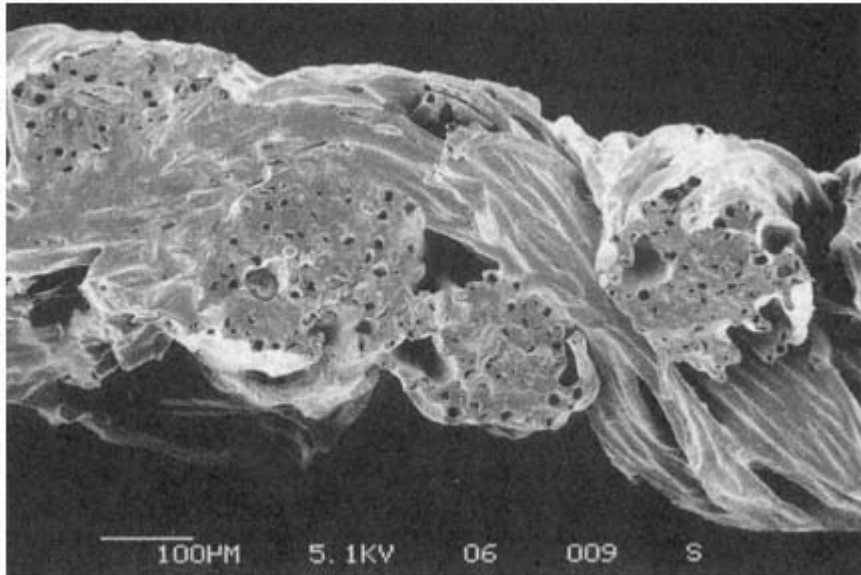


Figure 14
Fabric cross section of a cotton-polyester char.

consistent with secondary images, allowing locations of various elements in the sample to be shown. Qualitative energy-dispersive analysis of textile products is relatively simple, while quantitative analyses are more difficult.

IV— Applications of Sem to Textiles

Natural fibers may be either of plant or animal origin. Cotton and wood fibers are the two plant fibers of greatest commercial importance. Others include flax, ramie, jute, and sisal. The natural animal fibers are wool, other animal hair, and silk. Until the production of synthetic fibers, cotton, flax (linen), wool, and silk were the principal textile fibers. A survey of textile literature shows that the SEM has been used to characterize many different textile fibers. Jute was studied by A. K. Mukhopadhyay et al. [12, 13] and P. K. Ray et al. [14]. Mukherjee and Satyanarayana studied the structure and properties of vegetable fibers such as sisal [15]. Cheek and Roussel compared mercerization of ramie, flax, and cotton [16], and Cheek and Struszczyk showed effects of liquid ammonia and sodium hydroxide on viscose [17]. Structure and properties of coir fibers (coconut palm) were investigated by Satyanarayana et al. [18]. SEM of wool fibers has been carried out by Brady et al. [19], Hafey and Watt [20], and Ito et al. [21]. One of the first commercial SEMs was used by Billica to study synthetic fibers. A report on techniques and general applications of SEM for synthetic fibers was published by Billica and

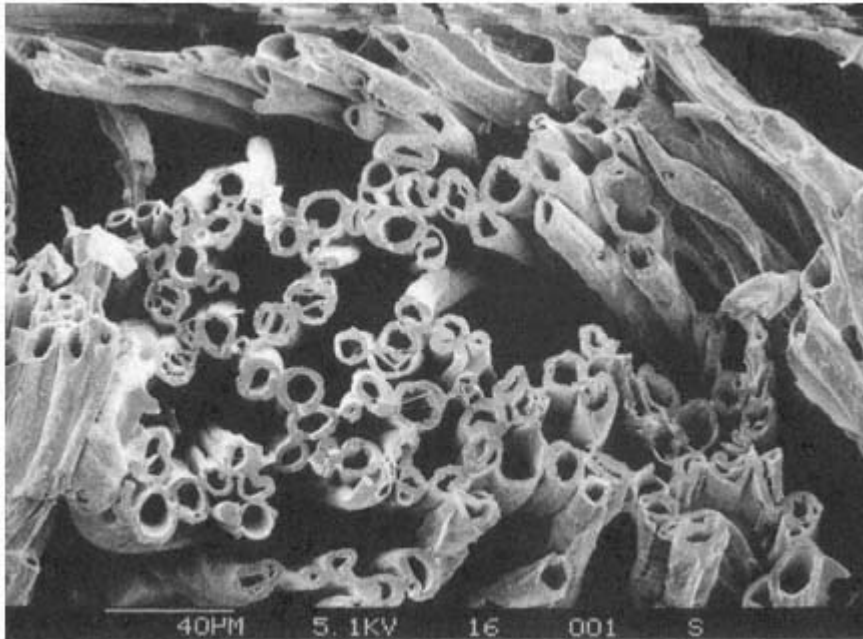


Figure 15

Char of a cotton yarn from a flame-retardant-finished fabric, showing fibers with compressed walls and enlarged lumens.

Van Veld [22]. More recent examples of synthetic fiber work can be found in publications by Stowell and Card [23] and Subramanian et al. [24] (nylon), Ansell [25] (polyester), Kulshreshtha et al. [26] (acrylic), and Schwartz et al. [27] (polyethylene). Structural characteristics can often be used for fiber identification. Saw-bridge and Ford have shown longitudinal and cross-sectional views of many natural and manmade fibers [28]. Sich [29] compared SEM and light microscopy for identifying animal fibers. Problems of abrasion and pilling were studied by Pack [30], and damage to a wide range of fibers was reported by Zeronian et al. [31]. Cotton fibers and fabrics have been studied extensively using the SEM. General methods for microscopy of cellulosic textiles have been reviewed by Rollins et al. [32]. One of the earliest applications of SEM to the cotton fiber was the various studies of fiber fracture by Hearle and Lomas [33]. SEM has been used often to examine cotton fabric abrasion. An example of this is shown in the work of Dweltz et al. [34]. Raheel and co-workers have published a series of papers on modifying wear life of cotton fabrics [35]. Obendorf et al. have extensively studied fabric soiling [36]. The effect of chemical modification on cotton was shown by Ghosh and Dalai [37]. References are made in this chapter to SEM applications for many types of fibers, but the major emphasis is on the cotton fiber because that is the area that the author has most extensively studied.

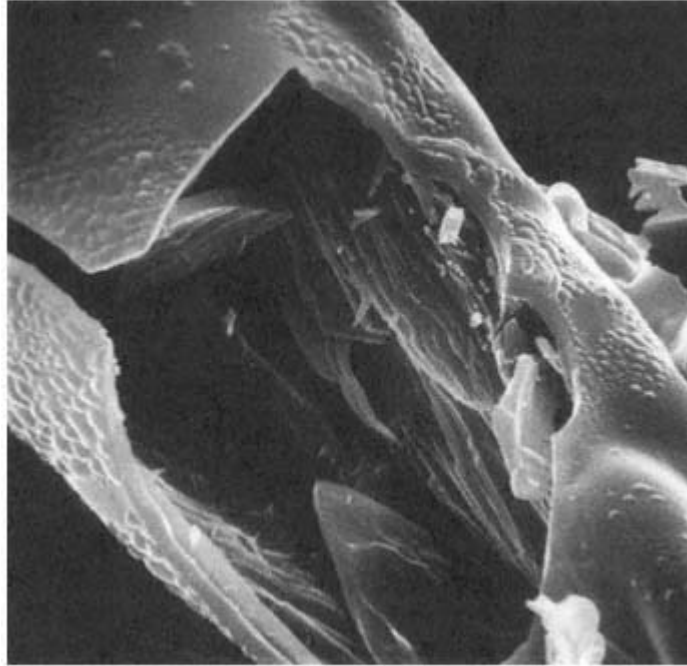


Figure 16
Charred fiber from a flame-retardant-finished fabric. The break in the wall shows the collapsed internal structure.

A—

Cotton Fiber Morphology

Cotton is a seed hair that grows in tubular form, developing thickness by depositing layers of cellulose fibrils inside the cell wall (primary wall) and enclosing the central canal, or lumen. These fibrillar layers spiral around the axis of the fiber at an angle of approximately 45 degrees. Periodically the direction of this angle reverses. This point is called a reversal, and the change in spiral angle affects fiber strength at that position. When the boll opens, the fibers dry out and collapse, shrinking and forming twists or convolutions. The spacing of the convolutions is not constant, and their direction may alternate from clockwise to counterclockwise. The size of the fiber is dependent on genetic variety, growth conditions, and degree of maturity, but the average length of spinnable cottons is from 0.5 to 1.5 in. The diameter of the fibers varies from 12 to 22 μm . As a textile fiber, cotton is a "dead" biological substance; thus fixation and other preservation procedures are not necessary for microscopy unless the undried, "living" fiber is to be studied. The general morphological structure of the cotton fiber has been determined by LM, and detailed surface features have been studied by replication procedures in the TEM. However, SEM provides a more natural view of fiber gross struc-

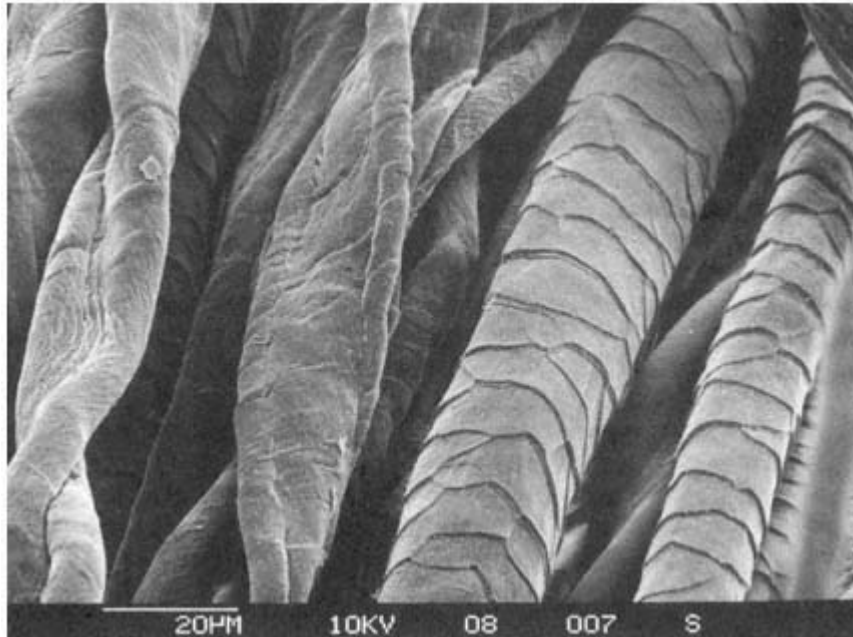


Figure 17
Surface of a blended cotton—wool fabric.

tures. The extreme of the length—diameter dimensions of the cotton fiber may be seen by viewing the fiber in coiled form (Fig. 1). The coiled fiber was prepared by rolling a single fiber around a needle, setting the point of the needle down on the tacky sample stub, and pushing the fiber down the needle to the stub. The shrunken, twisted morphology of the fiber is evident at this magnification. Higher magnifications of portions of the fiber show the wrinkled surface of the coated primary wail (Fig. 2) and a reversal, made evident by a change in the direction of the wrinkles (Fig. 3). In many areas of the fiber, ridges or compression marks are evident on the fiber surface. If the r primary wail is broken, the main body of the fiber is exposed, showing the spiral of the fibrils around the fiber axis (Fig. 4).

B— *Nature of Changes in Fibers*

Changes in characteristic structural features are often evident in the SEM. When chemical finishing causes visual changes in fibers or fabrics, it is possible to use SEM to determine whether a specific finish has been given, as well as to see the extent that the finish has changed the nature of the sample.

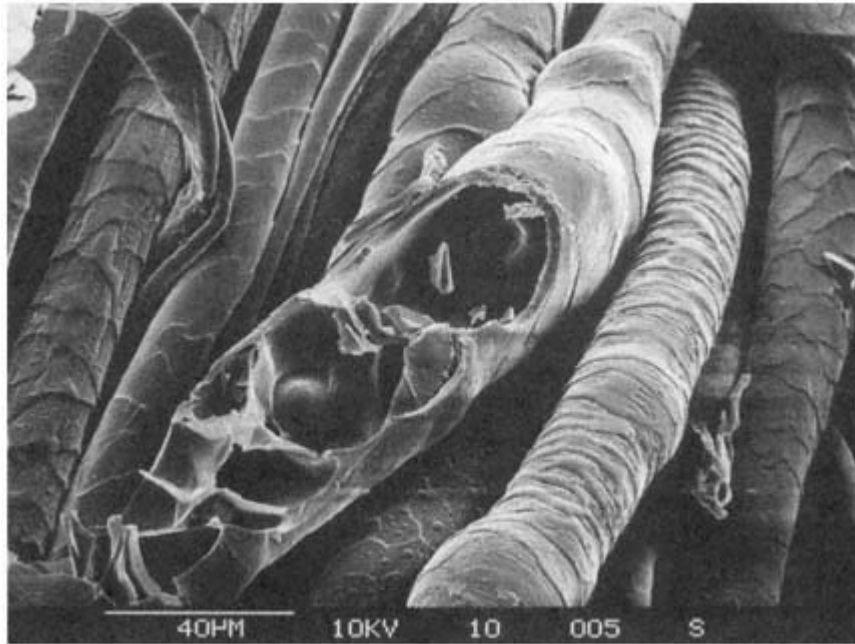


Figure 18
Swelled and ruptured wool fiber caused by heat.

1— Mercerization

Mercerization, a process of swelling the fiber in a caustic solution (usually NaOH), causes the wrinkled surface to become more smooth (Fig. 5) and the fiber to become more cylindrical. This treatment changes the crystalline structure of the cellulose, and improves textile properties of the fiber. Mercerization under laboratory conditions brings about more thorough conversion of the fiber cellulose, and thus of the fiber appearance, than do commercial processes. In many commercial mercerizations not all of the fibers in a yarn are swelled to the rounded structure seen in Fig. 5. Processes are usually developed that produce the desired increase in absorption, dyeability, hand or sheen. These do not always require full mercerization.

2— Fiber Damage

The study of damaged cotton fibers in the SEM not only helps in understanding the nature and causes of the damage, but also indicates the nature of the inner structure of the fiber. Fibers damaged by washing and drying processes were shown by Goynes et al. [38]. When cotton fibers are abraded wet in repetitive rubbing ac-

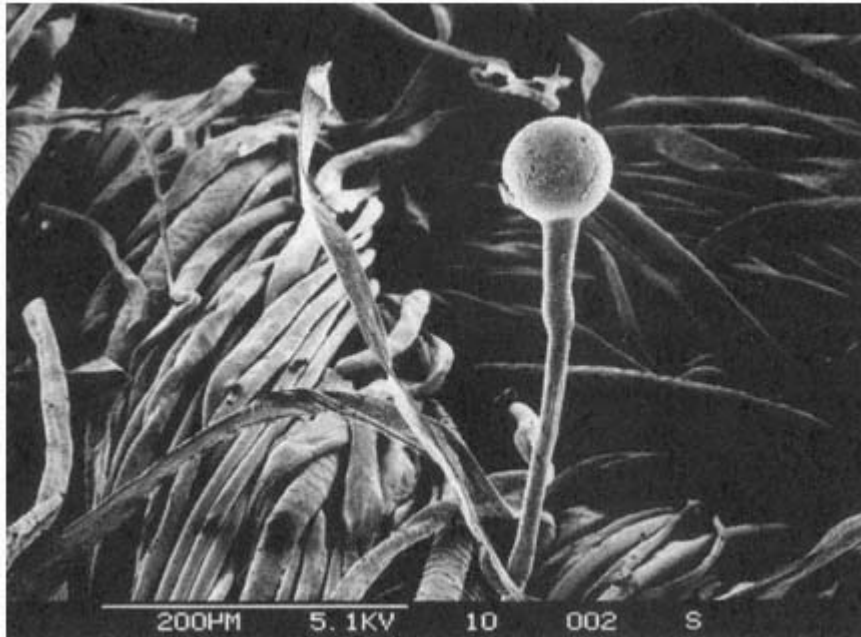


Figure 19
Melted globular tip on polyester fiber on the surface of a blended
cotton—wool—polyester fabric that had been heated.

tions, such as can happen in a washing machine, the fibers separate into small, stringy bundles of fibrils (Fig. 6). When dry abrasion damage occurs, such as that from machine drying, instead of fibrillating, the fibers become brittle and usually crack in the direction of the spiral of the secondary layers around the fiber axis (Fig. 7). Cracks may also occur at fiat fiber edges. Fiber breaks caused by dry abrasion leave blunt ends with little fibrillation (Fig. 8.). These types of damage illustrate the effect of moisture on the fibrillate structure of the fiber. Wet fibers swell, separating the fibrils and allowing them to be separated by frictional forces. As fibers are dried, the fibrils are drawn closer together, and hydrogen-bonding forces prevent fibrillation. Overdrying causes the fibers to become very brittle, and in some instances they have the appearance of being snapped by abrasion (Fig. 9). Fiber damage from other causes such as fungus and heat can also be identified using the SEM. Figure 10 illustrates damage to the cotton fiber due to fungal attack. The damage has been made more evident by swelling the damaged fiber in NaOH.

C—

Fabric Structure

The SEM is a particularly valuable tool for studying textile fabrics because it is difficult to completely examine the surface of a fabric in the light microscope due

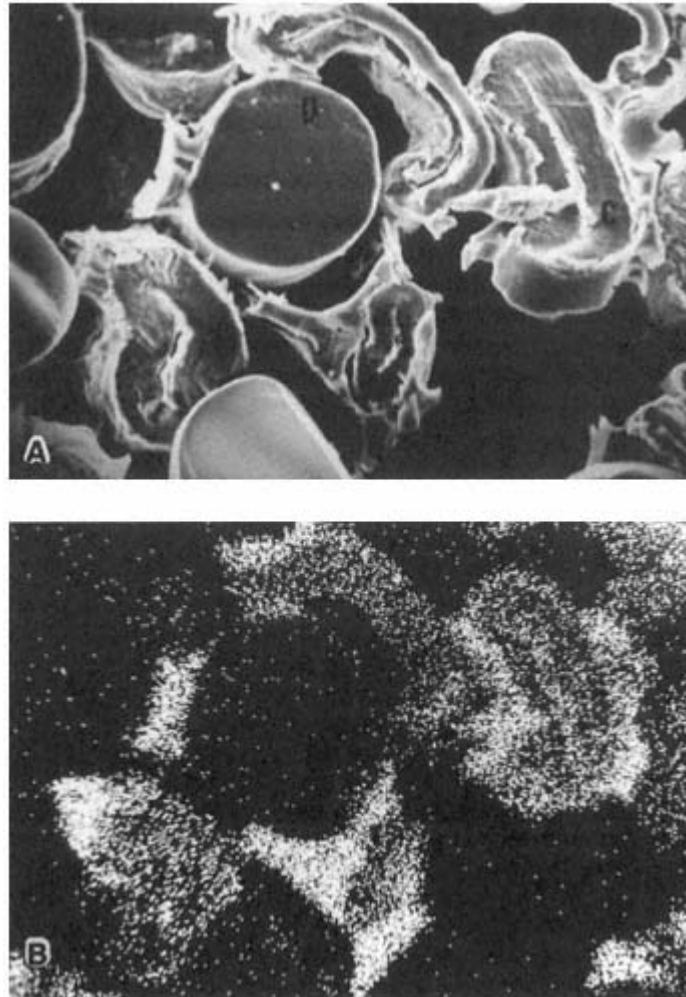


Figure 20

Cross sections from a flame-retardant—finished cotton—polyester fabric (top) showing finishing chemical between fiber sections, and a corresponding energy-dispersive x-ray map (bottom) showing location of phosphorus in the deposited chemical and the cotton fibers but not in the polyester fibers.

to its low depth of focus. The depth of focus in the SEM is great enough to study such parameters as fabric construction, damage, or surface deposition of chemical finishing agents. A comparison of LM and SEM fabric surfaces is illustrated in Figs. 11 (LM) and 12 (SEM), which show the increased information available from the SEM. Although light microscopy has provided important information in

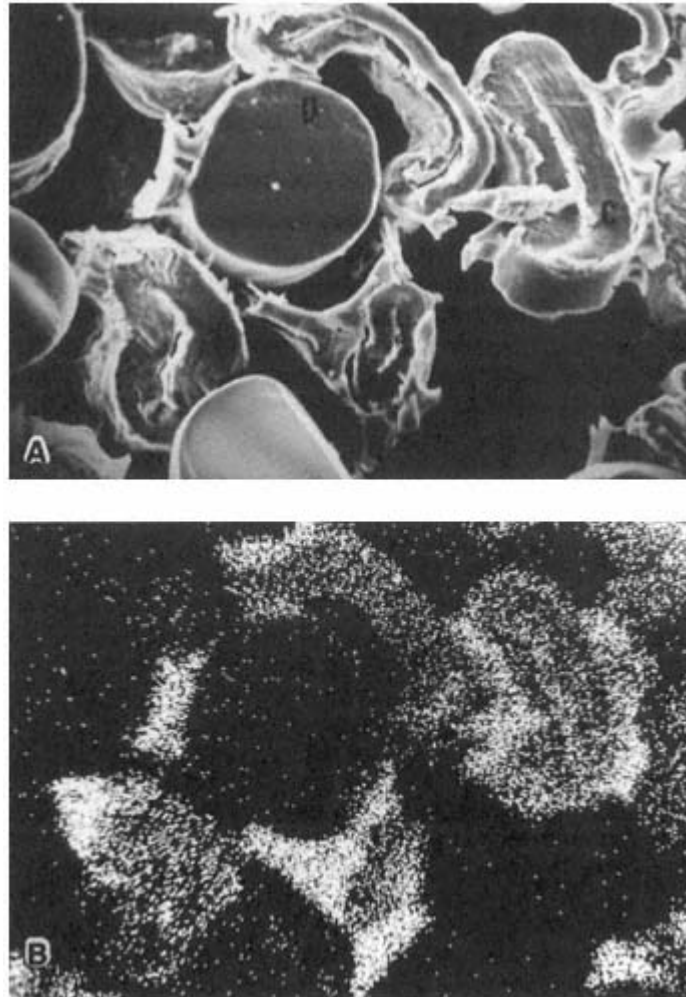


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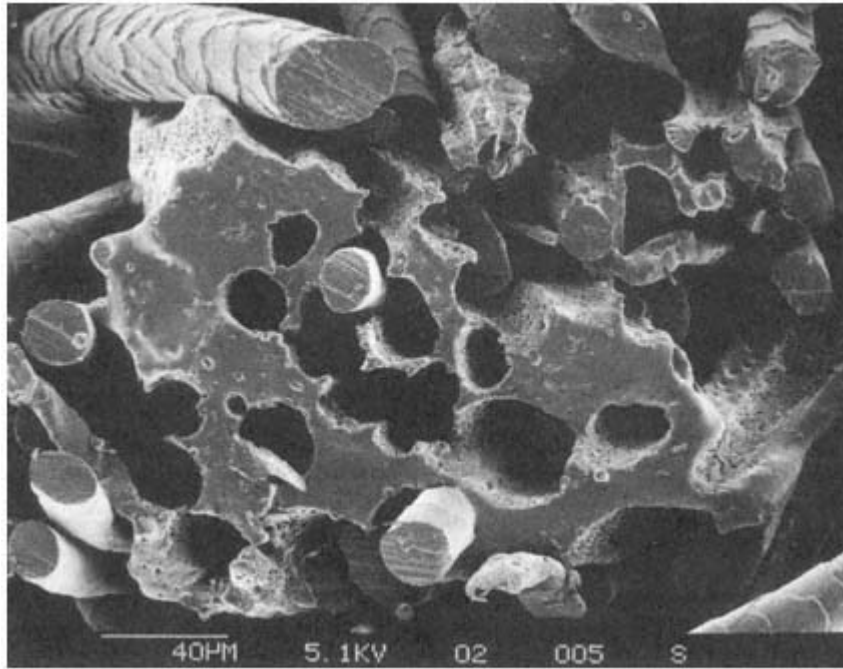


Figure 22

Yarn cross section from a wool fabric treated for thermal adaptability, showing poor adhesion of the fibers to the treatment polymer.

phology due to chemicals deposited on fiber surfaces can be seen by use of secondary electron microscopy. However, chemicals that penetrate the fiber surface are difficult to see by use of the secondary image even when internal surfaces of the fiber are studied. These internally deposited or reacted chemicals are more easily studied by use of one of the elemental analysis procedures (EDS, for example).

Treating cotton textiles with phosphorus-containing flame-retardant (FR) finishes reduces fabric flammability. When an untreated cotton fabric is burned under atmospheric conditions, it produces a wispy, fragile char. Figure 13 compares an unburned and burned cotton twill and illustrates the shrinkage that occurs on burning. Because of the melting and flow character of polyester fibers, fabrics blended of cotton and polyester form a more solid char, as shown in the fabric cross section in Fig. 14. Proper finishing with a flame-retardant agent may not produce noticeable differences in the appearance of the fabric surface but does change the nature of the char greatly. Figure 15 is a cross section of an FR-treated yarn char, showing the enlarged lumen area of the fibers that occurs when the wall of the fiber compresses. In Fig. 16, detailed structure of the internal charred, finished cotton

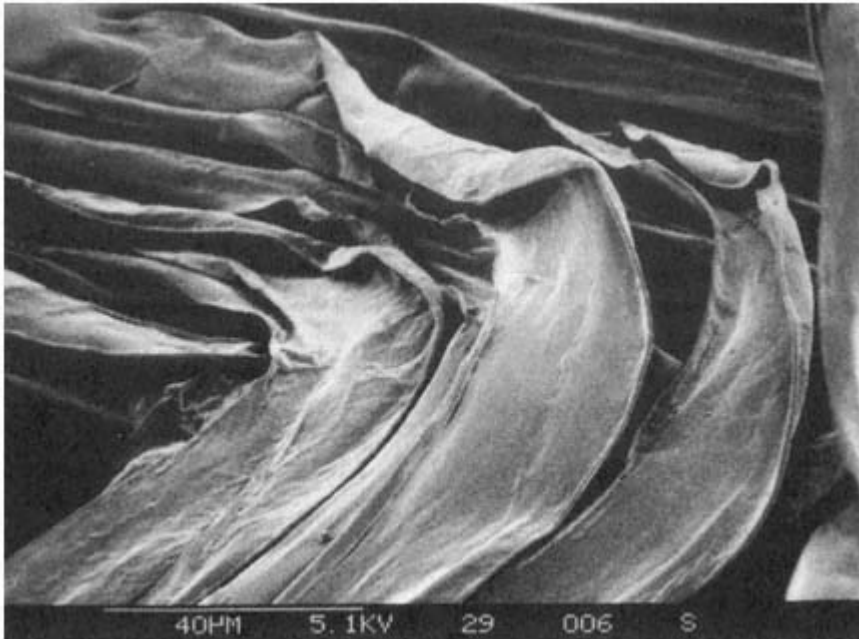


Figure 23

Undeveloped, ribbon-like cotton fibers from an undeveloped seed (mote).

fiber can be seen. The resultant char is stronger than that of an untreated fabric. The presence of fibers other than cotton in blended fabrics changes the burning rates and the resultant char length of these fabrics, as well as the structure of the resultant chars. A blended cotton/wool fabric surface is shown in Fig. 17. When this fabric was burned, the approaching heat edge first visually affected the wool fibers. Swelling and rupture of wool fibers is shown in Fig. 18. When polyester fibers are also included in the blend, those fiber ends that are raised above the fabric surface show the first reaction to heat by melting and forming globules. These melted fiber ends are illustrated in Fig. 19. The effect of heat on cotton polyester and wool fibers has been shown by Goynes et al. [39, 40].

Chemicals within the fiber cannot be detected by surface SEM. Energydispersive x-ray microanalysis provides a means of determining locations of specific elements within the fiber, and can show selective interactions with different fibers in blended fabrics. For this procedure, yams from treated fabrics were embedded in a polymerizable liquid, and the hardened block was sectioned with a microtome [32]. Sections were collected on a carbon disk and the embedment polymer was removed using a solvent. The disk was then attached to a sample stub and prepared for examination by coating with carbon. A secondary electron image

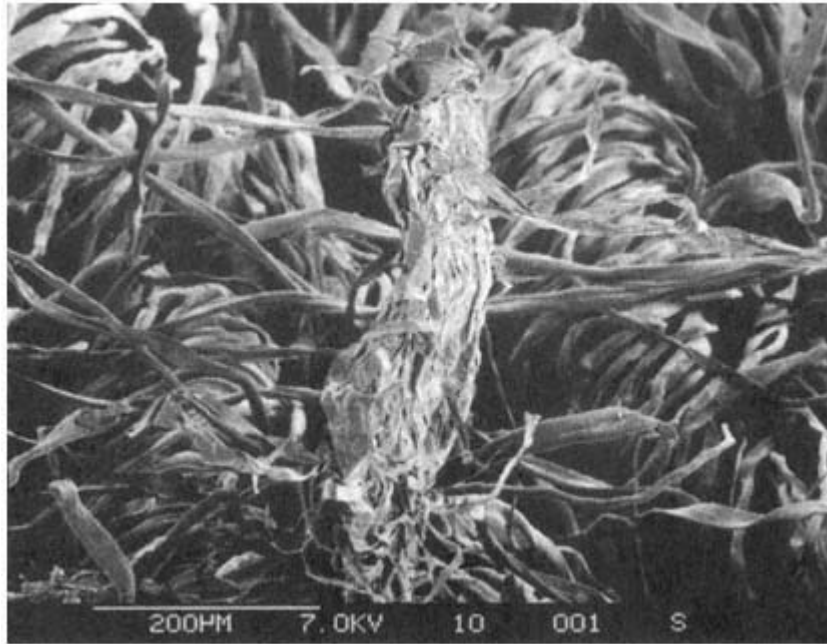


Figure 24
"White speck" defect on the surface of a dyed cotton fabric.

was generated and recorded (Fig. 20a), and then an elemental spectra was generated by EDS analysis. Peaks were identified, the element of interest (phosphorus) was selected, and an elemental map corresponding to the secondary image was recorded (Fig. 20b). Comparison of the two images shows that the phosphorus flame-retardant chemical is deposited heavily on fiber surfaces and in spaces between the fibers, and that it is also within cotton fibers but not within polyester sections. Such analyses provide valuable information in formulating more efficient finishes [41].

b—
Thermal Adaptability

Another type of textile finish in which the SEM has provided useful information is the production of thermally adaptable fabrics by use of polyethylene glycol solutions [42]. These fabrics were designed to increase wearer comfort by liberating heat, thus providing a warming effect, when they are cooled, and by absorbing heat, producing a cooling effect, when they are heated. Figure 21, a yam cross section from a treated cotton fabric, shows that the treating polymer had filled the spaces between the fibers. This fiber/polymer binding produces a yam that is essentially a low-temperature composite structure, a polymer matrix of embedded fibers. This type of bonding was found to be necessary to a good finish. All fibers did not bind well in the formulation used, as

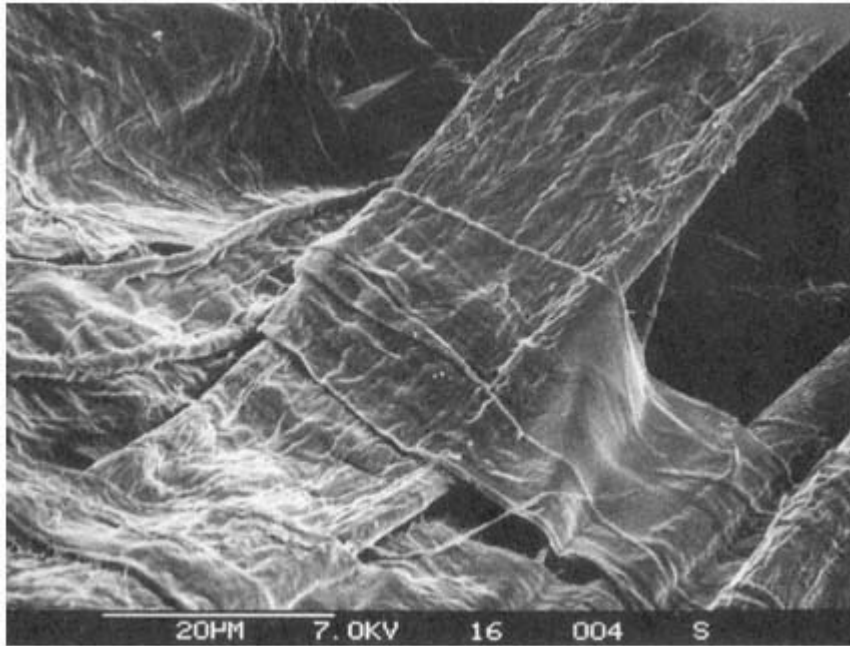


Figure 25
Enlarged area of "white speck" defect, showing that it is made-up of flat, undeveloped fibers.

is shown by the treated wool yam section shown in Fig. 22. To achieve a well-bonded fiber matrix, it was necessary to use a finishing procedure specifically designed for wool fibers.

2—

Fabric Defects

The SEM is also valuable in textile problem solving in areas other than finishing. Imperfections on fabric surfaces can produce fabrics that are not acceptable for marketing. In dark-dyed fabrics imperfections can be seen as small specks of undyed materials that appear white on the dark surface. An SEM study of such "white specks" showed them to be clumps of undeveloped, flat, ribbon-like fibers. These undeveloped fibers are produced by undeveloped seed (motes). Their growth was interrupted before the internal layers of cellulose fibrils were deposited. Thus they became tubes that flattened into ribbons on drying. These fibers, which show up as white specks, do not contain enough cellulose to dye in the process used for cotton fabrics. Figure 23 shows a bundle of such flat fibers from a mote. Knots of these compressed fibers can be carried through textile processing and entangled into fibers on the fabric surface. An example of such a de-

fect on a fabric surface is shown in Fig. 24. Higher magnification of the defect more clearly shows the extremely thin fiber walls that form them (Fig. 25). Judicious use of SEM operation parameters was required to obtain this image of a very thin fiber overlying another fiber. A keV level high enough to resolve the details of the structure was necessary, but a keV level whose energy penetrated the thin fiber without generating secondary electrons would not have defined the fiber.

V—

New Instrumental Techniques

The SEM is a relatively new tool for studying textiles. Many of the techniques developed for application of this microscience were intended to be used with nonbiological materials that have higher atomic numbers than do most textile materials. Because of the great variance in properties between biological and nonbiological materials, these techniques have had to be adapted for use with textiles. Even with these limitations, a casual literature survey indicates that SEM has provided a valuable means of developing textile information that was otherwise unavailable. Instrumental developments continue. One of the greatest obstacles to use of the SEM with biological materials is the necessity for the sample to be in the high-vacuum, low-moisture microscope chamber for examination. These conditions are not ideal for textile study. To overcome these disadvantages, a microscope that operates at a lower chamber pressure, and in which moisture can be increased, is currently on the market. It is called an environmental scanning electron microscope (ESEM) because conditions in the microscope chamber are more closely related to normal environmental conditions than are those commonly used in the SEM [43]. While the theory of operation of this microscope is promising, in actual practice it does not provide optimal operating conditions for textiles. Because of the moisture in the chamber, samples need not be coated before examination. However, coated fibers provide a better image than do uncoated due to reduction of beam penetration; ESEM fiber images often have bright edges with poor contrast, and do not relate well to images obtained from the SEM. Care also has to be taken that surfaces do not have water condensed on them, or details of the fiber surface can be obscured. The microscope does, however, offer the possibility of performing dynamic experiments within the chamber, such as stretching and breaking fibers, and observing effects of wetting and drying on the sample. Tao and Collier have shown results of some textile applications of the ESEM [44].

VI—

Future Outlook

The many interactions that occur between the primary electron beam and the atoms in the sample provide a great avenue for further development of SEM applications to textiles. Cathodoluminescence, production of visible light by interaction with the electron beam, has already found some limited application. Tech-

niques such as Auger analysis and electron energy loss analysis (EELS) will eventually be available for textile applications as progress is made in methodology. Energy-dispersive analyses using conventional detector windows are limited to elements of atomic number sodium or above. Windowless detectors are now available for detection of light-element electrons. Even these, however, are not easily applied to textile materials, since many textiles are composed of carbon, hydrogen, and oxygen. Detection of light elements in such a matrix has not yet been highly successful. Progress in detector improvement and in the limits of both qualitative and quantitative elemental detectability is being made by instrument manufacturers. This offers the possibility of better EDS analyses in the future. New methods for electron beam generation, such as field emission, are now available. The field emission gun greatly increases resolution in the microscope and provides more detailed views of surfaces, especially at low keV.

VII—

Summary

SEM and related techniques have provided a means of better visual understanding of textile fibers and fabrics and has improved concepts of the role of unit interactions in fibrous matrices. The methods are valuable in both basic research and in process evaluation. Limitations are present in microscope capabilities, such as resolution, and in sample preparation. As improvements are made in these areas more information on textile structures will be available. Opportunities for gaining even greater understanding of fiber and fabric structures will continue to develop as innovations in associated microscopical technology become commercially available and are adapted to use with special materials such as textiles.

Acknowledgment

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4—**Investigation of Textiles by Analytical Pyrolysis**

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I—**Introduction**

There are numerous methods that are used to investigate and identify polymers, fibers, and the textiles they make up. These include reaction to burning, solubility, optical and electron microscopy, infrared spectrophotometry, and thermal analysis. Each of these methods gives information that is valuable in identification of the fiber and any modifications to the fiber that may have been done. The application of analytical pyrolysis is another method that can provide a powerful approach to polymer, fiber and textile investigations.

Two generally agreed on definitions in the field of pyrolysis techniques are [1]:

Pyrolysis: a chemical degradation reaction that is induced by thermal energy alone.

Analytical pyrolysis: the characterization of a material or a chemical process by the instrumental analysis of its pyrolysate.

Pyrolysis is the chemical process where heat energy breaks down large molecules into smaller fragment molecules. It is done by the direct application of high temperature energy to the substrates. The molecular bonds in the large molecules are broken by thermolysis, and characteristic smaller molecules are created. The terms thermolysis and thermal reaction are often used in place of pyrolysis [2]. Examples of pyrolysis to produce information about the nature of organic materials include the production of isoprene from natural rubber, the destructive distillation of wood to yield methanol, and the range of chemicals derived from coal tar, produced by the pyrolysis of coal. It is important to understand that reactions caused

by heating with the involvement of catalysts, or the simultaneous or subsequent reaction with ambient oxygen, do not constitute pyrolysis.

The types of reactions that are a part of pyrolysis are dissociation into free radicals, elimination of small molecules, and carbon—carbon fission. Because of the size of the polymer molecules, you may have random scission at many points along the polymer backbone, or scission of the side groups in either a random or systematic fashion. There may also be reversion of the polymer back to monomer, dimer, or other oligomers. Given the large sizes of many of the molecules that are part of the substances examined, it is not surprising that pyrolysis gives rise to complex mixtures of products resulting from the many possible reactions. When pyrolysis is coupled with separation of the volatile fragments by gas chromatography (PY-GC), one has a simple analytical method that can be applied to all manner of substances and materials to gain information regarding their nature and identity. The result of such an analysis is referred to as a pyrogram. An example for cotton is given in Fig. 1. The addition of mass spectrometry to identify the individual fragments (Py-GC-MS) gives one a very powerful tool that can be applied to a wide range of chemical problems. One very significant advantage to this method is that only a few milligrams of the specimen are necessary to give clear identification.

Analytical pyrolysis is particularly suited to analysis of polymers, whether they are natural proteins or polysaccharides, or manufactured plastics, adhesives, paints, or fibers. The literature on analytical pyrolysis is voluminous and covers a

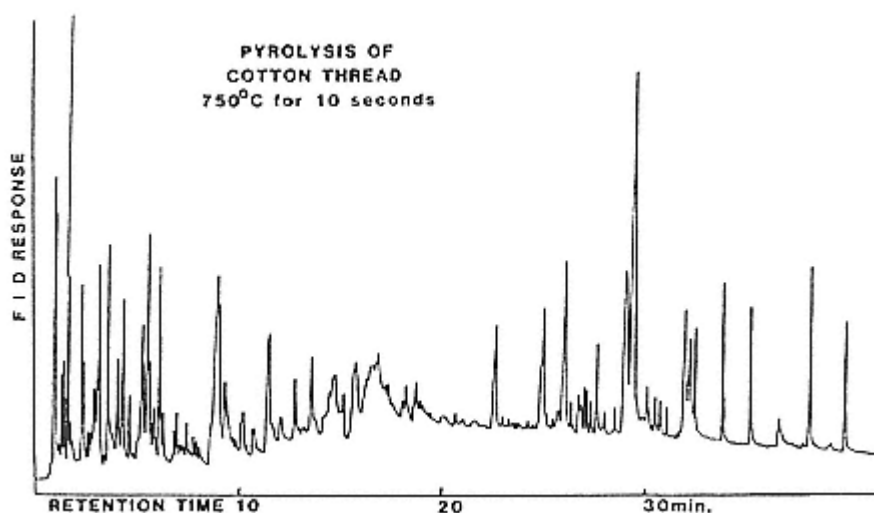


Figure 1
Pyrogram of cotton fiber, 750°C
(From Ref. 41.)

broad range of areas, including biomass conversion [3], plant cell walls [4], microorganisms [5,6], wood lignin [7], characterization of suspended matter in sea water [8], smoke aerosols [9,10], food sciences [11], tobacco smoke [12], coffee flavors [13], and forensics. In the following sections, the method of analytical pyrolysis and its use are described, and applications to polymers, fibers, finishes, and dyes are surveyed.

II—

Instrumentation and Analysis

Analytical pyrolysis is normally done by using a pulse of heat to quickly heat the sample and break it down into the individual components. The sample size is usually 10 to 100 μ . Pyrolyses can be run at heating rates ranging from 0.01°C per second to 20,000°C per second. Very slow rates result in pyrograms that resemble those produced by pulse pyrolyses at lower end-point temperatures. Lower rates may permit one to see more of the primary pyrolysis products, which may be formed at lower temperatures and then removed before secondary reactions occur [14]. The process of pyrolysis can be linked to gas chromatography (GC), mass spectrometry (MS) or Fourier-transform infrared spectroscopy (FTIR), either individually (PY-GC, PY-MS, PY-FTIR) or in combination (PY-GC-MS). Each of these has particular advantages. Certainly, PY-GC is the most widely used and the most widely reported in the literature. Pyrolysis is dynamic, with a flow of carrier gas sweeping volatile products away from the pyrolysis zone to the gas chromatograph, mass spectrometer, or the FTIR.

A—

Pyrolyzers

The instruments employed for the pyrolysis step are usually either resistance-heated filaments, inductively heated filaments or wires, microfurnaces, or radiative laser heating. Most of these pyrolyzers are small units that can be inserted into a gas chromatograph or mass spectrometry port, or linked with an interface. While each type of pyrolyzer has certain advantages and disadvantages, the most widely used type is the resistance-heated filament or coil.

1—

Resistance Heating

In the resistance-heated pyrolyzer the sample is placed on platinum filament or inside a platinum coil that is part of the pyrolysis probe. The temperature rise time (TRT) is dependent on the probe type. For the instrument cited most often in the literature [15] a temperature of 600°C can be reached in 8 msec with the ribbon filament; or 600 msec for the coil with a quartz tube included within the coil. The temperatures reached can be varied from ambient to 1400°C. With models now available, the temperatures are exact, and are reproducible. The quartz tube is used to help hold certain kinds of samples in place and to minimize possible catalytic effects from the platinum.

The resistance-heated pyrolyzer has the general advantages of a fast temperature rise time, a good temperature range, and the ability to program the heating in a flexible way. It has the additional advantage of being widely used with numerous publications citing applications. Disadvantages include the possibility of catalytic effects (although few problems with this are cited in the literature), and the fact that the temperature actually experienced by the sample may be difficult to determine exactly.

2—

Inductive Heating

The inductively heated filament pyrolyzers are usually referred to as the Curiepoint method. This refers to the property of ferromagnetic metals or alloys (Fe, Ni, Co) whereby when subjected to radiofrequency radiation they heat up rapidly by the absorption of the energy. At their "Curie point," which is specific for each material, the energy absorption ceases and the material stabilizes at the characteristic temperature. The temperature—time characteristics of the filament are determined by the ferromagnetic properties of the sample holder, its dimensions, and the power of the radiofrequency field applied to it [16]. The end-point temperature occurs at the temperature where the wire loses its ferromagnetic properties. This temperature is very reproducible and is determined by the composition of the ferromagnetic material chosen. The temperature can be varied between 160 and 1040°C [17]. The heating rates are normally in the range of 1000–10,000°C per second.

The primary advantage of this type of pyrolysis is the ability to have exact control of the temperature because of the Curie-point principle [18]. A number of wires are available with Curie points between 300 and 981 °C. The temperature rise time (TRT) is dependent on the composition and geometry of the wire and power of the oscillator.

3—

Microfurnaces

This type of instrument can have several designs. One incorporates a very small quartz tube maintained in a furnace assembly at the pyrolysis temperature by a thermocouple feedback controller [19]. The pyrolysis is isothermal, and liquid or solid samples can be injected directly into the furnace. Short lengths of sample are injected directly into the quartz furnace with a "solids injecting syringe." Another design, available in Japan, utilizes a small sample holder made of platinum, which is then dropped into the reactor zone [20]. The key to getting a fast TRT is to eliminate dead space in the furnace. Oguri [17] modified the maintenance oven so that the heated area of the transfer needle was increased to improve the analysis of the high-molecular-weight pyrolysates. Improved programs resulted, particularly for high-molecular-weight products. A heated aluminum block prevented the condensation of the pyrolysates in the sample and transfer tubes.

In both designs the advantages seem to be the control of the fragmentation temperature and sure reproducibility of that temperature, thus improving the replication of the programs. A disadvantage would be less flexibility in programming the thermal conditions.

4—

Radiative Heating

This is usually done with a carbon dioxide laser source. The advantage for this method is that the sample can be heated in remote locations or on any material. The disadvantages are the lack of reasonably priced instruments and the difficulty of controlling accurately both the TRT and the final temperature. A new instrument has recently been described that utilizes an Nd—Cr—GGG laser [21].

B—

Techniques for Characterization

1—

Pyrolysis—Gas Chromatography

Pyrolysis—gas chromatography is a relatively simple and inexpensive experimental technique. A pyrolysis unit is linked directly or by an interface to the gas chromatograph. The pyrolysis products are formed and then moved away by carrier gas

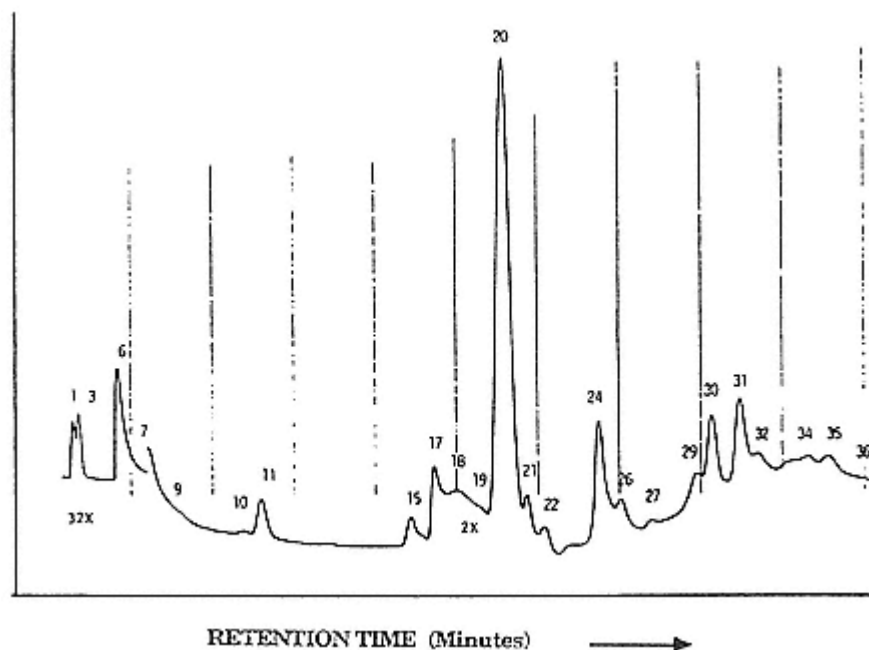


Figure 2
Pyrogram of cotton fiber, 805°C.
(From Ref. 32.)

to the gas chromatograph. The result is a pyrogram, as shown in Fig. 2. This method uses very small samples, is very sensitive, and the chromatograms obtained are much less complicated than the mass spectra in PY-MS. In addition, the power of the method can be increased by using mass spectrometry. The mass spectrometry can be combined with PY-GC by a suitable interface so that each of the GC peaks can be mass analyzed. Table 1 presents the results of the analysis of the Fig. 2 pyrogram. This method can be most useful for initial investigations of a product so that PY-GC can be used on the material with much smaller sample sizes [22]. The drawbacks include the need to take particular care in reproducing all conditions, the very large amount of data that a program gives, and the length of time involved (30 min to 1 hr) in running one sample.

Table 1 Identification of Volatile Pyrolysis Products for Cotton Fabrics

GC peak	Compounds identified	Molecular weight	Identification by GC/MS ^a
1	Carbon monoxide	28	P
3	Carbon dioxide	44	P
6	Water	18	P
7	Propene	46	HP
11	Oxirane	44	HP
12	Butene	56	HP
15	Furan	68	HP
16	Dimethyl ether	46	HP
17	Acetone	58	HP
20	Glycolaldehyde	60	HP
21	Acetic acid	60	HP
23	2,3-Butanedione	86	HP
24	1-Hydroxy-2-propanone	74	HP
26	3-Methyl-3-butene-2-one	84	LP
27	2,5-Dimethylfuran	96	HP
28	3-Hydroxy-2-butanone	88	HP
30	Acetic anhydride	102	HP
31	Fufural	96	HP
32	2-Furan methanol	98	LP
35	1-(2-Furanyl)ethanone	110	LP
36	5-Methyl-2-Furaldehyde	110	HP
38	2-Hydroxy-2-cyclopentene-1-one	112	HP

^aP = positively identified by the mass spectrum and retention time on GC, HP = high-purity fit with the standard spectrum in the MS library (800–850), LP = relatively low-purity fit with the standard spectrum of the MS library (800–850).

Source: Ref. 32.

The conditions used for gas chromatography can have an important effect on the pyrogram obtained. Certain GC instruments may require a different interface between the pyrolyzer and the GC. One can use either packed or capillary columns. Capillary columns of chemically inert fused silica have high numbers of theoretical plates and can give better resolution, and therefore more details in the pyrogram, than packed columns [23]. See, for comparison, Fig. 1—capillary column versus Fig. 2—packed column for the same material. The smaller peak width means a lower detection limit of an individual component is possible [24]. On the other hand, capillary columns generally take a longer time to produce a pyrogram and usually require smaller samples and splitting of the carrier gas stream. The use of a cryogenic focusing step can allow very small samples, splitless injection, and prevention of the loss of low-molecular-weight compound resolution [25]. The smaller sample size can present some problems in handling and can raise questions regarding the representative nature of the microgram sample used. A packed column will allow larger samples to be used, but resolution is lost and thermal gradients within the sample are likely.

If properly controlled pyrolysis is coupled with gas chromatographic separation, one can obtain pyrograms that are repeatable. The pyrograms of cotton in Figs. 1 and 2 are each replicable, even though they are significantly different in detail. These pyrograms both were of cotton, but done with different gas chromatographic columns and conditions. When the same instrument and conditions are used, and care is taken with the condition of the pyrolyzer and sample preparation, then the pyrograms obtained on successive specimens of the same sample will be virtually identical. Both of the pyrograms in Figs. 1 and 2 will be useful for many purposes. The extra detail in Fig. 1 will aid in mechanistic studies and will be very useful in detecting small differences in the materials. Figure 2 is probably just as useful as Fig. 1 for fingerprint identification purposes.

2—

Pyrolysis—Mass Spectrometry

When mass spectrometry is used directly in conjunction with pyrolysis the sample is introduced directly into the ion source and the mass spectrometer itself provides the pyrolytic system. The mass spectral profiles produced by pyrolysis—mass spectrometry (PY-MS) are highly characteristic and reproducible and can be used as fingerprints [26]. The data produced are automatically available to the computer for storage and manipulation. The runs can be conducted in a few minutes, and analysis time is short. The drawbacks are that PY-MS is less sensitive than PY-GC and the results can be complicated with the MS cracking patterns superimposed. The equipment is more expensive than that for PY-GC, although the relatively low-cost GC-MS units now on the market may well change this in the future.

Two important considerations for both of the methods presented are that high temperature rise time (TRT) and small sample size are critical to obtain repro-

ducible results. If these are achieved, reproducibility will be good. If TRT is slower and sample size larger, then much more attention to the actual heating program will be required to obtain useable results. In large samples there may be diffusion control of volatile product evolution, which will restrict the rate of escape of the pyrolysis products. Increased residence time may lead to increased probability of forming secondary products, thus obscuring the true pyrolysis profile and leading to false conclusions [22].

3—

Pyrolysis—Infrared Spectroscopy

Pyrolysis can be combined with infrared spectroscopy to aid in the identification of polymers and fibers. The first applications of this method used a pyrolysis chamber where the resulting vapors were trapped and the infrared spectrum of the resulting mixture was taken. A typical study was that done on a variety of flameretardant—treated fabrics where the fabrics were pyrolyzed at intervals of 200°C from 200 to 1200°C [27].

Pyrolysis—Fourier transform infrared spectroscopy (PY-FTIR) of polymers provides a reproducible pyrogram that is used as a fingerprint for polymer identification [28] or for polymer quality control [29]. This technique can be useful in quick determinations of polymer identify. Pyrolysis of the sample directly into the infrared beam using a unique interface enables spectra to be obtained before side reactions and condensation occur. For example, the direct PY-FTIR of polystyrene gave a spectrum almost identical to the styrene monomer. The nylons were easily distinguished through the relative strength of the C-H stretching bands near 3000 cm⁻¹ compared to the amide stretching band at 1650 cm⁻¹. The analysis can be done in a fraction of the 20–60 min that a typical pyrolysis—gas chromatography run requires. In addition, PY-FTIR lends itself directly to studies of evolved gas during thermal treatment and processes.

C—

Analysis of Results

1—

Fingerprints

The product of pyrolysis—gas chromatography is a pyrogram. These plots of compounds in the pyrolyzate by retention time are truly "fingerprints." To be useful, the experimenter must pay attention to details such as sample size, preparation, and the long-term reproducibility of the GC column performance. Fingerprints can be used to identify a polymer or a fiber and to detect small changes made in a given material. The use of fingerprints does not require knowledge of the composition of the pyrolysis products, nor how they relate to the original molecular structure. It should be understood that when using fingerprints that interlaboratory reproducibility is difficult, since instruments and techniques will inevitably vary. Certainly, a key to the success of fingerprints is their use in conjunction with a site-established library of pyrograms. On the other hand, fingerprints cannot be

used to identify polymers in commercial mixtures, or with complicated compositions in the presence of other polymers where the individual constituent programs are superimposed [30]. The absence of compositional information prevents identifying polymers that are similar in nature, with slight differences in macromolecular structure, but having different properties.

2—

Classification System

Another example of an identification approach is that used by Milina et al. [31] to quickly identify low-molecular-weight substances from their pyrograms. There are some similarities to the empirical approach used by Hardin and Wang [32] and it may be worthwhile in application to fibers. The system does not incorporate data from the entire pyrogram but only uses three characteristics to ensure a unique recognition of a pyrogram. Pyrograms are presented to the computer by giving relative retention times and areas of individual peaks. Calculations were done by using a maximum of 10 peaks, with the requirement that any peak used was larger than one percent of the total area subtended by the pyrogram. The characteristic values used were:

1. $PI = \sum A_i T_i$, pyrolysis index, where A is the area and T is the relative retention time of the individual peaks
2. $C = A_i T_i$, the ratio of two adjacent peaks
3. T_{max} , the relative retention time of the most intense peak

No one of the three characteristics permitted the complete recognition of the pyrograms, but the simultaneous use of all three resulted in 100% recognition of all compounds.

3—

Compositional Analysis

Comparisons between pyrograms that are similar and complex can pose seemingly intractable analysis problems. Fifty or more individual components in a pyrogram are not unusual, and small changes can be difficult to differentiate. Compositional analysis relies on the identification of individual pyrolysis products. This method uses preliminary chromatographic investigation of the polymers to establish a relationship between pyrolysis products and the polymer composition [30]. Once the presence of repeating units, cyclic oligomers, mass markers, fragments, and series is correlated to known polymer structures, then unknown samples can be run and their patterns can be used to establish molecular structure. For those samples clearly different, there are no problems. For those close in structure, one must pay close attention to pyrogram quality. There may be differences in quantitative distribution rather than each possessing unique fragments. Composition analysis of copolymers or polymer blends (or copolymer fibers or fiber blends) can be done by pyrolyzing pure components to establish the chromatographic peaks characteristic of each component. The composition of

true copolymers and blends is then established by calibration charts created from the pure components [33].

4—

Computational Techniques

In order to deal with the complexity of many pyrograms and to use pyrograms to detect small changes in the polymers or fibers, it is necessary to use methods that try to rationalize data and make them amenable to statistical analysis. Truly complex pyrograms can have up to 200 components. Only more complex methods of pattern recognition techniques can give the differentiation needed.

The general term applied to this approach is chemometrics. This approach has been greatly enhanced by the spectacular rise of the capabilities of small computers. One definition of chemometrics is "the application of numerical techniques to the identification of, or discrimination between, chemical substances" [34]. This is a particularly important approach for analytical pyrolysis in trying to use the method to give the maximum amount of information to detect small changes in materials as a result of treatments.

One approach was applied to untreated cotton and cotton treated with inorganic salts. Small changes in the pyrograms were evident but a systematic analysis was needed. The analysis involved classifications of the volatiles into groups, with partial correlation coefficients for each volatile. Sign matrix analysis was used to group the compounds to determine the mechanisms of the reactions involved [35]. A number of other studies can be looked at for more sophisticated examples. These include the work by Jones [16], where statistical procedures were coupled with discriminate analysis, the probability method developed by Ryabikova et al. [36], and the compositional analysis of carbon fiber composites by Bradna and Zima [37]. There are applications of chemometrics to pyrolysis mass spectrometry of rubber triblends by Lattimer et al. [38], and to polyesters and polyethers by Georgakopoulos [39]. Chapters on chemometrics and their application to pyrolysis can be found in Irwin's book on analytical pyrolysis [40] and Maddock and Ottley's Chapter 3 in Wampler's handbook [41].

D—

Reproducibility

The question of reproducibility with analytical pyrolysis methods was reviewed by Wampler and Levy [42]. Sample size and geometry both affect the transfer of heat. The smaller the sample size, the less the thermal gradient will be and the more likely it is that pyrolysis will be uniform. Generally, a sample size in the low micrograms range will produce better and more reproducible results than larger samples. The best geometry for the sample is a thin film, preferably melted onto the filament. When melting is not possible the reproducibility of the sample shape becomes crucial. Homogeneity should be sought by grinding, powdering, and mixing of the sample when possible.

Contamination from several sources has to be acknowledged as possible and avoided. Successive pyrograms of the same substance that show erratic behavior may simply be the result of introducing finger oil to certain samples. In addition, the pyrolyzer itself could be a source of reproducibility problems. Quartz linings to minifurnaces, or quartz tubes for resistance heated pyrolyzers, can obviate problems if metal catalysis is suspected. Sample transfer as a source of erratic results will depend on the tightness of connections and the maintenance of an evenly heated transfer system.

If sampling and handling techniques are carded out with proper attention, then reproducibility can be quite good. The instruments currently available, when used properly, are capable of giving replications with relative standard deviations of less than 3%, and sometimes much better than this [42].

III— Polymers

Analytical pyrolysis is particularly well suited to characterize polymers and fibers and to detect small changes in the chemical composition of these materials. It is a rapid and very sensitive method that can provide structural information for polymers and fibers. Pyrolysis does not depend on polymers or fibers being solvent soluble, and can readily handle cross-linked polymers with three-dimensional networks. It works by thermal nonoxidative breakdown of the long polymer chains into a series of structure-specific smaller volatile compounds. Three kinds of reactions may result from the applications of high heat to polymers:

1. Crosslinking within the polymer
2. Chain scission leading to a decrease in the molecular weight
3. Large yields of small molecules, including monomeric and oligomeric moieties

The latter effect is typically seen if heat is applied quickly and a high temperature is reached in a very short time. Various quantitative studies have shown that pyrolysis processes in polymers give little or no evidence for recombination reactions that create new or different molecules [43]. Therefore, if pyrolysis conditions are kept constant, the sample should always degrade into the same constituent molecules. When the degradation products are swept into a chromatograph under particular given conditions, the resulting chromatogram will always be the same and a fingerprint is obtained.

The limitations of pyrolysis—gas chromatography in its early days included difficulty in getting sufficient separation of degradation products and problems with identification of the individual products. The first reference to the use of pyrolysis in examining polymeric products was that by Davison et al. in 1954 [44], when they suggested pyrolyzing the samples and then separately separating the products by gas chromatography. They gave the results for eight polymers. Later,

other workers [45,46] combined the pyrolysis apparatus with the gas chromatograph and showed that it could be a general tool for the identification of polymers and quantification of groups within the polymers. There were also studies that applied the beginning method to groups of polymers such as the acrylics and the polyurethanes [47–51].

Nelson et al. [52] examined a large group of plastics and showed that the method could be extended to various classes of polymers and that milligrams and submilligram quantities could be used. They concluded that reproducibility was adequate for identification purposes and that the method could have general application. Since the early 1960s, when this work was done, the method of analytical pyrolysis has become a widely used method for polymers, and hundreds of papers have been published. The bibliography by Wampler [41] contains 140 references on synthetic polymers for the years 1980–1989 alone.

IV— Fibers

The amount of information about polymers and analytical pyrolysis is voluminous. The articles and book chapters that deal specifically with fibers are much less so, though certainly significant. In general, information is contained in articles concerned with forensic investigations or aimed towards a textile audience. Early studies on fibers included those by Haase and Rau [53], Janiak and Damerau [54] and Gunther et al. [55], where natural and synthetic fibers were pyrolyzed to produce fingerprint programs. In other early work [56], blends of fibers were also included. Forensic applications involving fibers are discussed by Wheals and Noble [57], Saferstein and Manura [58], Hughes et al. [59], Wheals [60,61], and Challinor [62]. There are several references that are concerned with the application of analytical pyrolysis to fibers in general. These include the early work by Janiak [63], the publication on identification of textile materials by the Textile Institute [64], and articles by Chrighton [65] and Focher et al. [66].

Hardin and Wang [32] examined a wide range of examples of textile applications and created pyrograms for cotton and treated cottons, nylon, acetate, acrylic, polyester, and aramid. See Figs. 3–7 for examples of polypropylene, acrylic, Nomex aramid, acetate, and polyester fibers. Perlstein, in a comprehensive study [67], examined the pyrograms from polyester, nylon 66, aramids, acrylic, polypropylene, cellulose, and protein fibers. Blends of polyester and wool, polyester and cotton, polyester and polypropylene, and others were also examined. The pyrograms were interpreted with the aid of diagnostic peaks for degradation products, rather than by the pattern recognition method. Diagnostic peaks proved especially useful in identification of fiber blends. Wright et al. [68] used a furnacetype pyrolyzer to examine PY-GC profiles of nylon 6, polypropylene, polyethylene, and polyester fibers. They noted that these pyrograms are typically very complex and used heart-cutting, cold-trapping, and back-flushing techniques to

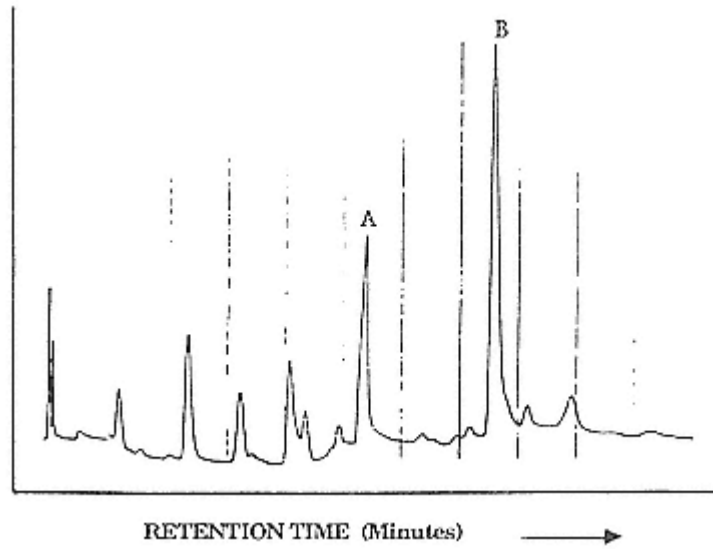


Figure 3
Pyrogram of acetate fiber.
(From Ref. 32.)

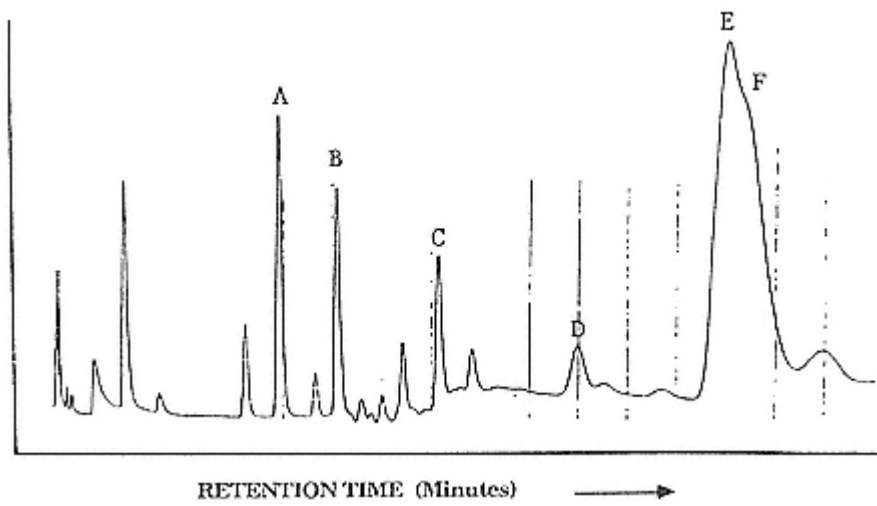


Figure 4
Pyrogram of acrylic fiber.
(From Ref. 32.)

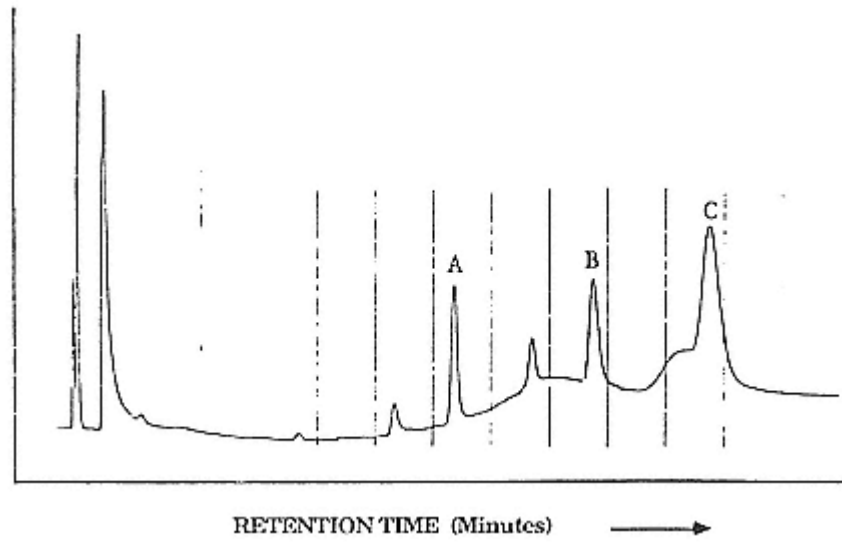


Figure 5
Pyrogram of Nomex aramid fiber.
(From Ref. 32.)

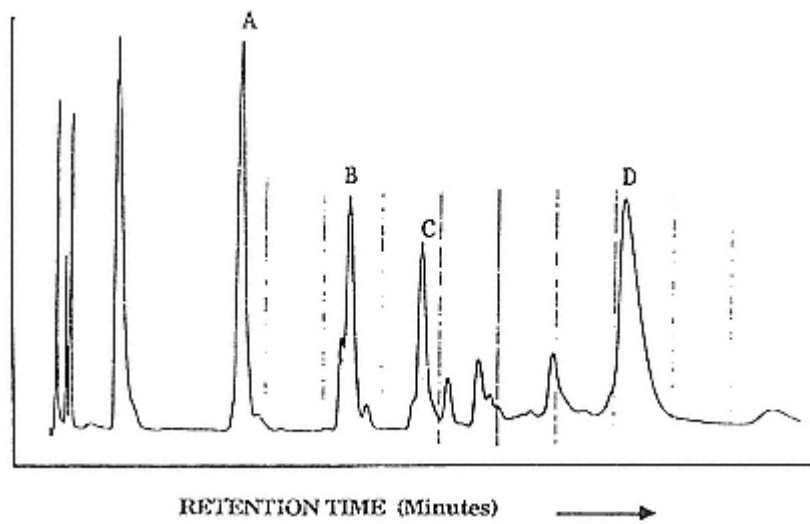


Figure 6
Pyrogram of polypropylene fiber.
(From Ref. 32.)

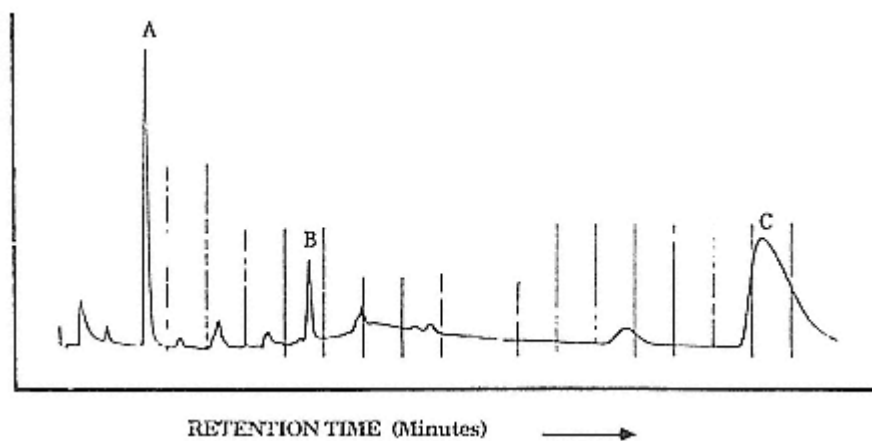


Figure 7
Pyrogram of polyester fiber.
(From Ref. 32.)

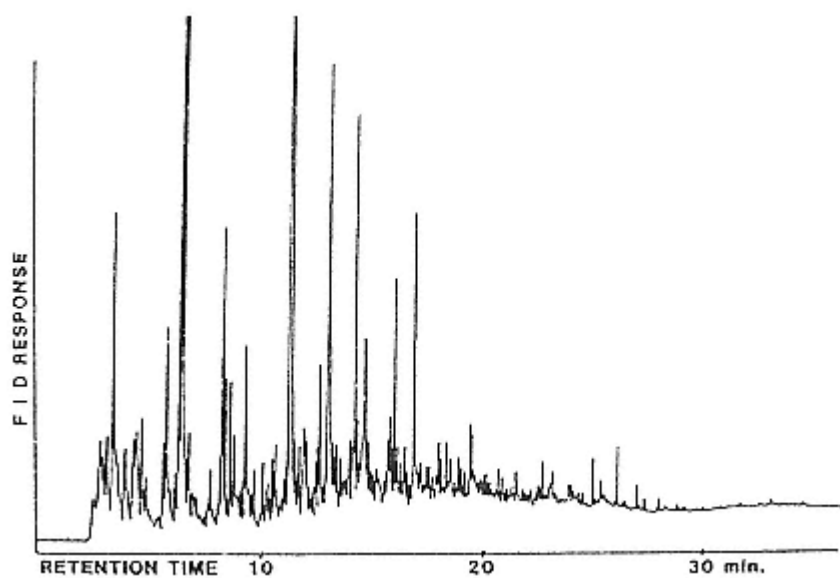


Figure 8
Pyrogram of raw wool.
(From Ref. 41.)

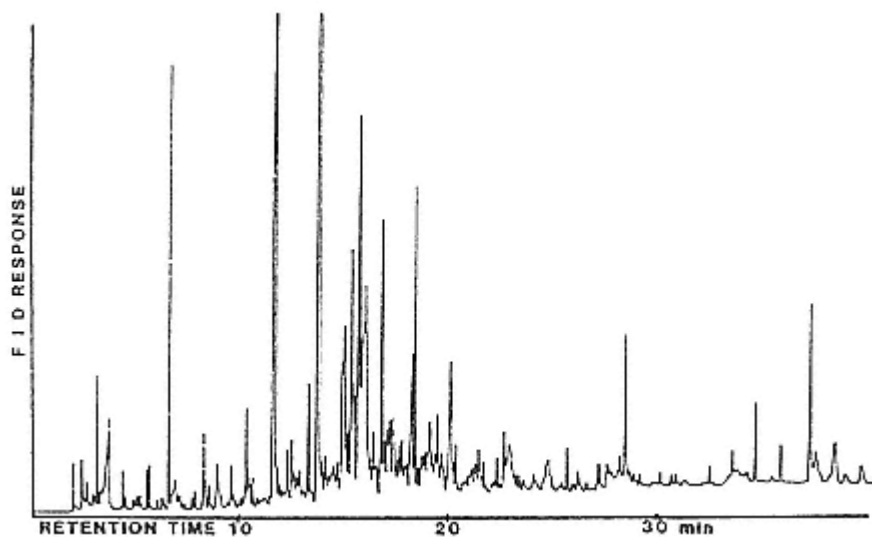


Figure 9
Pyrogram of silk fiber.
(From Ref. 41.)

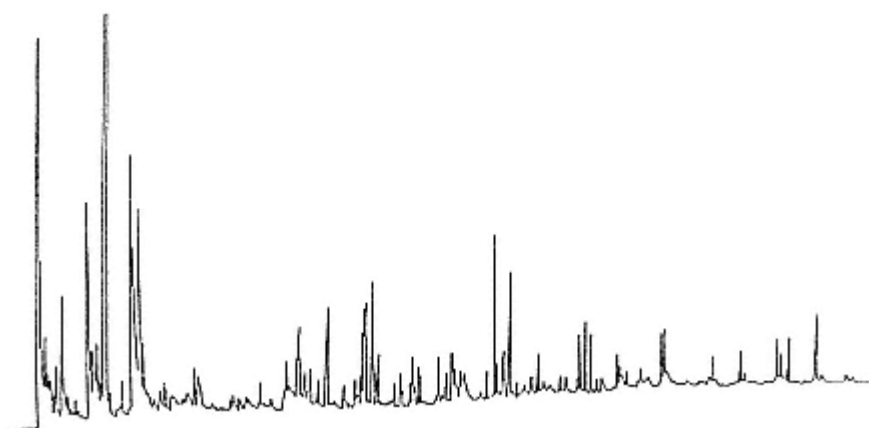


Figure 10
Pyrogram of nylon 6/6.
(From Ref. 41.)

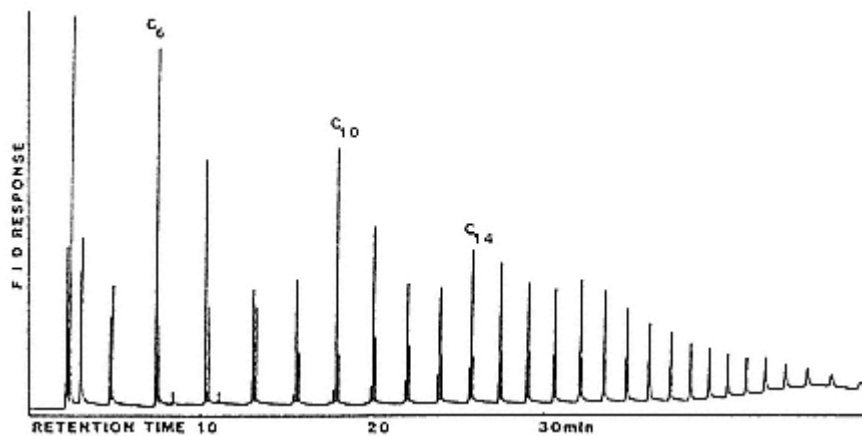


Figure 11
Pyrogram of polyethylene.
(From Ref. 41.)

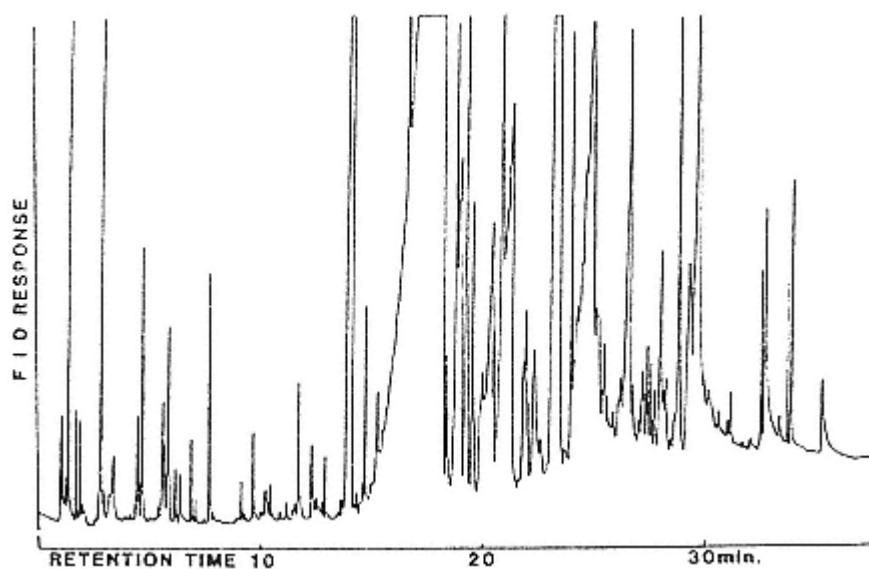


Figure 12
Pyrogram of polyester fiber.
(From Ref. 41.)

eliminate less valuable information from the programs and shorten the scan time. In his handbook on pyrolysis [41], Wampler includes an index of sample pyrograms, including several fibers. Figures 8–12 are from that source.

A—

Polyesters

Polyethylene terephthalate (PET) is by far the most common polymer used for polyester fiber. When pyrolyzed, it typically yields compounds such as benzene, benzoic acid, biphenyl, and vinyl terephthalate [69]. Hardin and Wang [32], Peristein [67], and Wright et al. [68] all show pyrograms of polyester, each characteristic of the particular conditions and setup. Day and Wiles [70] examined PET untreated and treated with TRIS, the now-banned flame retardant. Ordeyaar and Rowan [71] studied the interaction of polyester and cotton blends during pyrolysis. Yang and Hardin used a different approach to gain quantitative determinations of cotton and polyester in blends of unknown composition [72]. Instead of separating the individual compounds after pyrolysis, the pyrolyzates were moved quickly through the column and the total area of the reaction products peaks was measured. By using calibration charts created by known blend composition samples, the blend ratios in unknowns could be determined accurately and quickly.

B—

Nylons

Several studies have dealt with specifically with nylons. In early work Krull examined stabilized nylon 6 [73]. A detailed study of nylons was done by Ohtani et al. [74]. They examined 12 different nylons (5 aminocarboxylic and 7 dicarboxylic types). These were pyrolyzed in a microfurnace with peaks separated by glass capillary GC and then identification of the peaks by mass spectrometry. Characteristic degradation products were identified and general mechanisms of degradation formulated. Challinor [62] showed how nonpolar capillary columns can be used to clearly differentiate nylon 6 and nylon 66 (Fig. 13).

C—

Acrylics

Differentiation between microgram quantities of acrylic and modacrylic fibers was demonstrated by Bortnish et al. [75]. Further studies of polyacrylonitrile were done by Ferguaoor and Mahapotra [76]. Urbas and Kullik [77] analyzed the production of toxic compounds from nitrogen-containing fibers like the acrylics. The copolymer constituents of acrylic fibers were qualitatively and quantitatively determined by Saglam [78]. Methyl acrylate and methyl methacrylate were determined by dissolving the fibers in dimethyl formamide, depositing the solution on a platinum spiral, pyrolyzing, and then separating the products by gas chromatography. The compositions arrived at agreed with other methods.

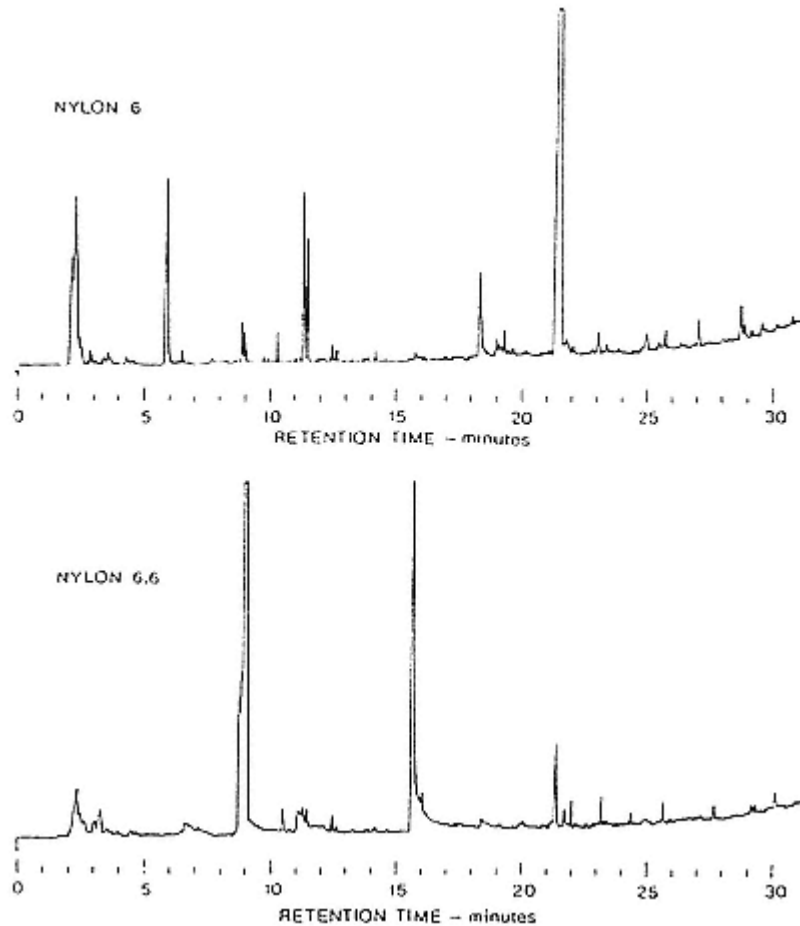


Figure 13
Comparison of pyrograms for two nylon fibers.
(From Ref. 62.)

D— Proteins

Analytical pyrolysis work on protein fibers has interesting links with animal and human hair and other proteins. Some of the earliest studies in PY-GC of wool dealt with analysis of volatile gases, particularly those that might be toxic. Kerrit and Kullik [79] looked at the evolution of some toxic gases (CO_2 , CH_4 , H_2S , and CS_2) from amino acids and at differences between wools from various sources and silk. Urbas and Kullik took the work further into other nitrogen-containing fibers such polyacrylic and polyamide fibers [80].

Several studies relate directly to wool. Danielson and Rogers examined tryptophan in proteins by PY-GC [81]. This done by on pyrolysis followed by GC separation of skatole, a unique pyrolysis product of tryptophan. Urbas and Kullik [82] analyzed untreated and flame-proofed wools. A series of detailed papers on wool from Marmer, Magidman and colleagues dealt with detection and characterization of commercially applied chemical agents, tryptophan and tyrosine in wool [83–85]. Characteristic peaks from benzoylated wool, from wool treated with the insect resistant agent Mitin FF, and from wool treated with Lisoamin yellow 26 were examined, all of which gave characteristic GC peaks. The latter two studies examined compositional changes induced by various kinds of chemical treatment normally done in textile processing. Py-GC was used to quantitate tryptophan in wool using product ratios (indole to *para*-cresol + phenol) and by detecting tyrosyl residues caused by chemical processing of wool.

Perlstein also examined wool and silk for diagnostic peaks in their pyrograms [67]. Although both are proteins, the difference in their mix of amino acids allows easy identification. Specific studies concerning human hair that linked PY-GC to MS were those by Munson and Vick [86] and Ishizawa and Misawa [87].

E—

Cellulosics

There is a voluminous literature dealing with the pyrolysis of cellulose and its relationship to such interests as biomass conversion, flame retardancy, and flammability in general. Analytical pyrolyses of cellulosic fibers are exemplified by the PY-GC work on rayon fibers by Heinsoo et al. [88], Perlstein's comprehensive fiber identification paper [67], the series of papers by Hardin and co-workers [32,72,89–92], the examination of microcrystalline cellulose by Pouwels et al. [93], the PY-MS work on polysaccharides by Lomax et al. [94], and the review paper on the application of PY-GC to the paper and textile industries by Ferrari [95]. An ancillary study was the thermal characterization of milkweed fibers by Gu et al. [96]; which included differential thermal analysis (DTA), FTIR, and pyrolysis. The data were compared with those from cellulose, hemicellulose, and lignin.

V—

Finishes and Dyes

There is a limited amount of literature dealing with the application of analytical pyrolysis to finishes and dyes. Cope [97] used a small furnace at 400°C to pyrolyze two commercial fire resistant finishes, tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH) and N-methylol dimethylphosphonium propionamide (Pyrovatex CP), and cotton fabrics after they had been treated with these agents. The THPOH was also applied to a 80/20 cotton/Nomex blend fabric. The now-banned flame retardant TRIS—tris(2,3-dibromopropyl) phosphate—was pyrolyzed alone

and after being applied to a polyester (PET) fabric. Day and Wiles [70] also examined this flame retardant on polyester. Another study by Thoma and Hutzinger examined a series of brominated flame retardants by PY-GC-MS [98].

The THPOH and Pyrovatex CP finishes both react with fibers. The pyrograms of the neat finish and the pyrograms of the finished fabric showed little similarity. The TRIS, on the other hand, did not react with the PET but was absorbed physically within the fiber structure. The principal peaks of TRIS pyrolyzed alone were present when the treated fabric was pyrolyzed, although the latter pyrogram was much less complex.

Hardin and Wang [32] compared the pyrograms from unfinished cotton and THPOH-NH₃ and Pyrovatex CP—treated cotton (Figs. 14–16). The pyrograms for all three contained the same compound peaks, although the relative amounts of the lower molecular weight compounds and the intense peak for glycolaldehyde were distinctive. With both finishes the amount of glycolaldehyde was greatly suppressed. In other studies by Hardin and colleagues analytical pyrolysis was used to investigate the effect of organophosphorus flame retardants on the flammability of cotton cellulose [91,92] and the effect of deposited salts on the pyrolysis of untreated cotton cellulose [89,90].

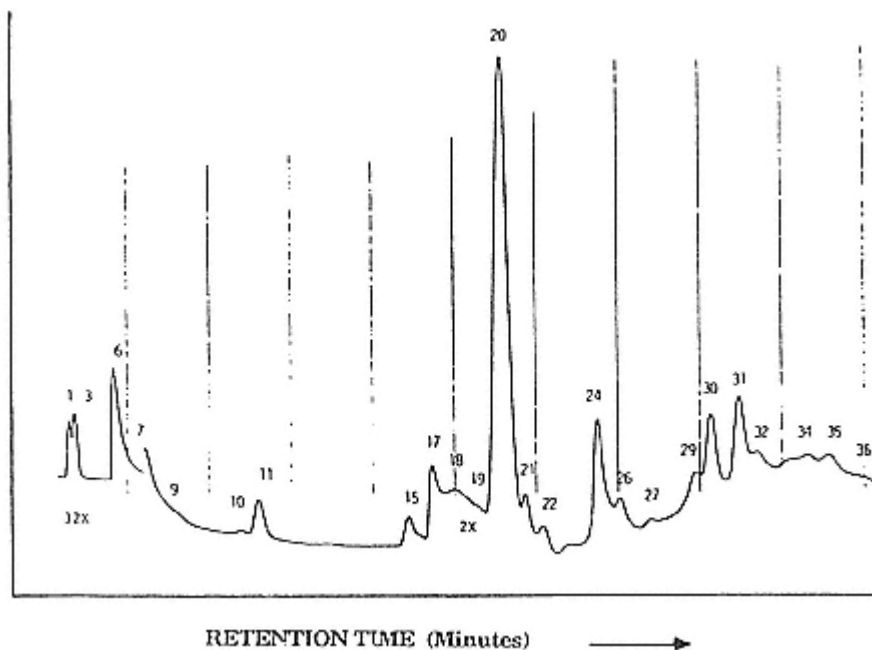


Figure 14
Pyrogram of unfinished cotton.
(From Ref. 32.)

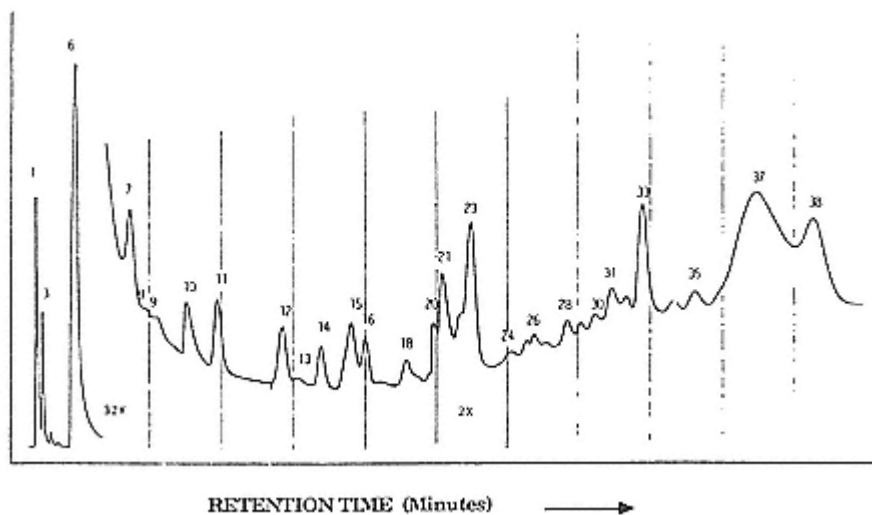


Figure 15
Pyrogram of THPOH-NH3 finished cotton.
(From Ref. 32.)

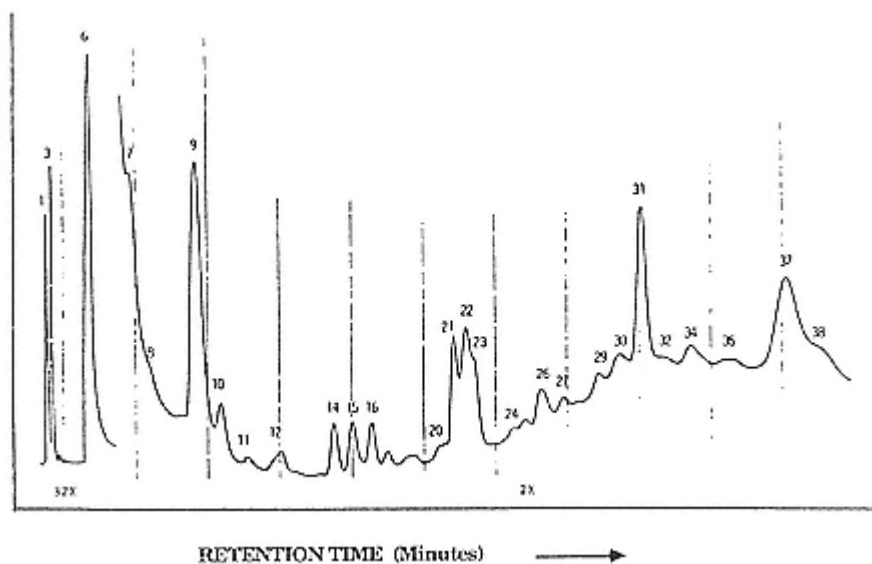


Figure 16
Pyrogram of Pyrovatex CP finished cotton.
(From Ref. 32.)

Hercosett cationic resin is a diethyltriamine condensed with adipic acid and crosslinked with epichlorohydrin. It is the most widely used finish for shrinkproofing wool. Cutler et al. developed a sensitive and accurate method for measuring the level of the agent on fabrics using PY-GC [99]. The method is based on pyrolysis—gas chromatography. A small sample was pyrolyzed at 764°C and conveyed to a capillary column for the detection of cyclopentanone, the primary pyrolyzate of adipic acid. A linear correlation was shown to exist between the Hercosett content of wool and the ratio of the cyclopentanone peak to a nearby reference peak arising from wool protein. The method, which takes about 2 hr, is faster and more accurate than other methods that might be used, and can give the amount of Hercosett by setting up a standard curve.

In other work on textile finishes the emphasis was on using analytical pyrolysis to identify finish materials. Casanovas and Rovira [100] used PY-GC to identify acrylic copolymers and their mixtures with formaldehyde and melamine resins used in textiles. The pyrolysis products formed could be used to identify the copolymers and the mixtures. Hardin and Wang [32] presented pyrograms for sizing materials such as corn starches, modified potato starches, hydroxypropyl methylcellulose, and two different polyvinyl alcohols (Figs. 17–22).

The identification of aniline dyes by PY-GC-MS was demonstrated by Abbey et al. [101]. Four dyes were obtained from commercial sources and five others were synthesized. The samples used were about 2 µg pellets. The pyrolysis products were identified using computer database searches. The products obtained were complete subunits of the original dyes, making it easy to get information about the original structure. It was also possible to quantify the amount of dye

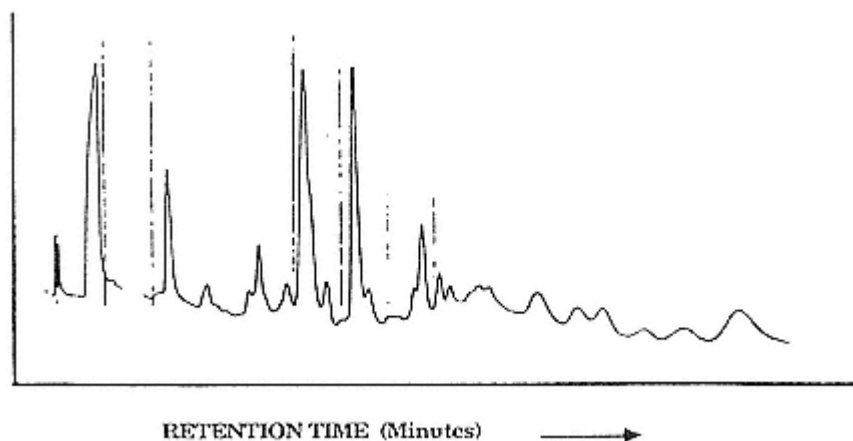


Figure 17
Pyrogram of potato starch.
(From Ref. 32.)

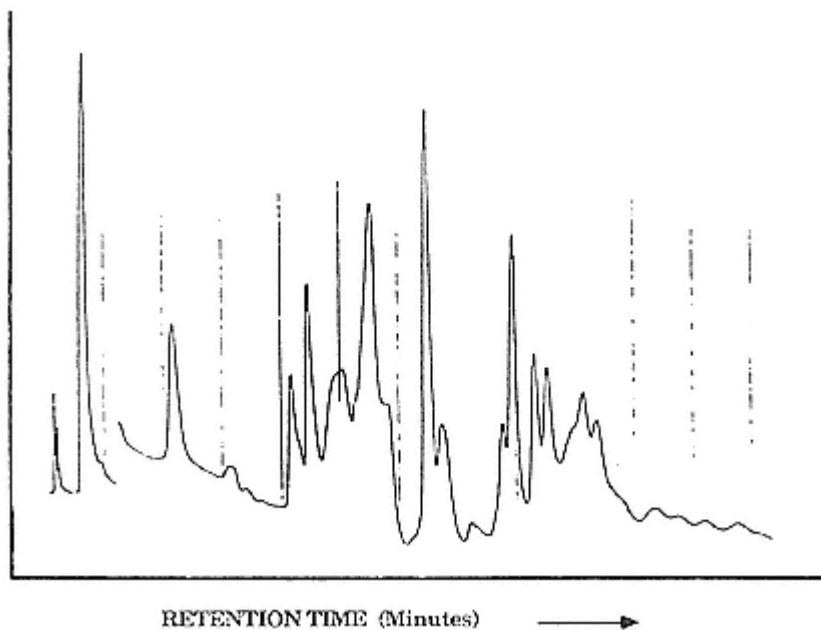


Figure 18
Pyrogram of corn starch.
(From Ref. 32.)

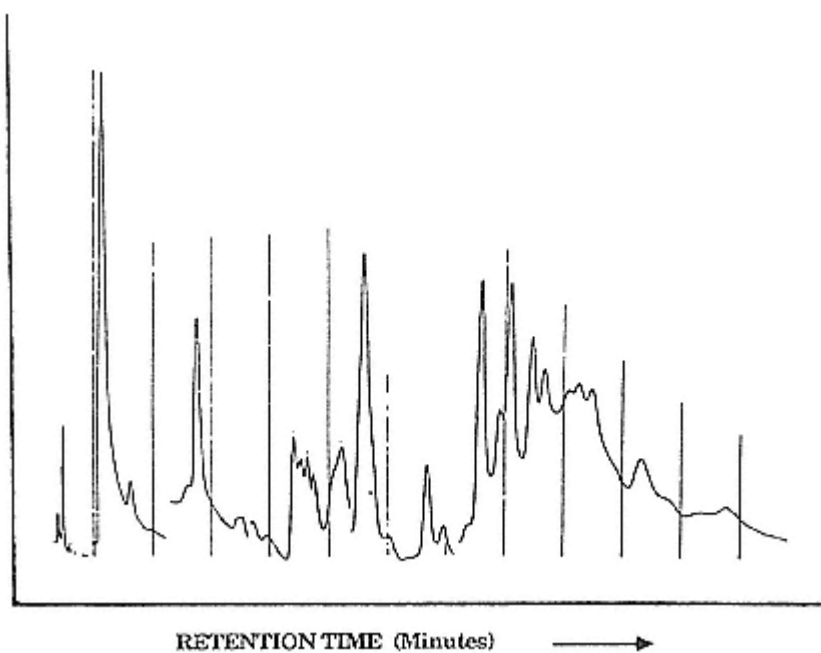


Figure 19
Pyrogram of hydroxypropyl potato starch.
(From Ref. 32.)

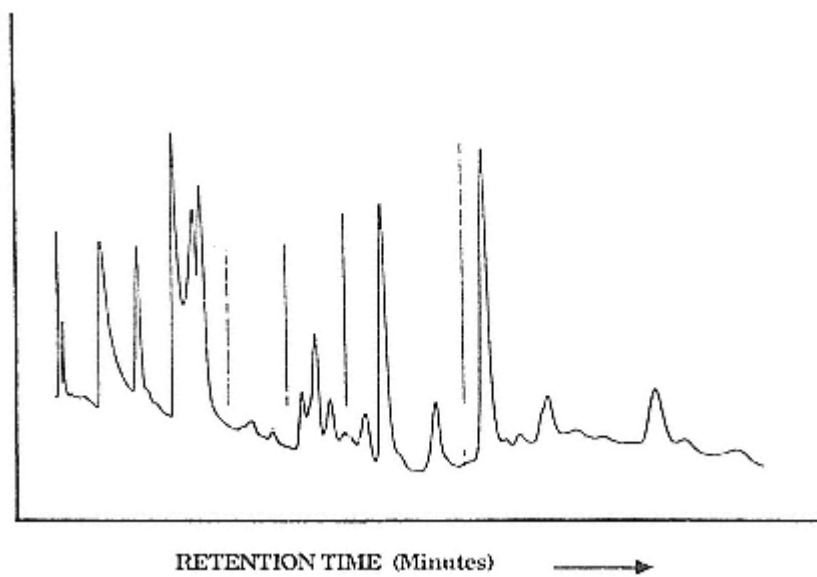


Figure 20
Pyrogram of hydroxypropyl methyl cellulose.
(From Ref. 32.)

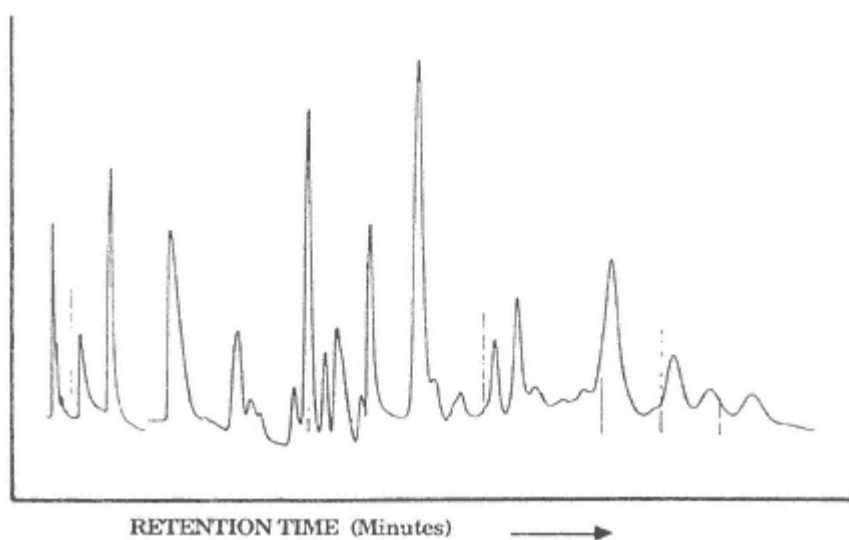


Figure 21
Pyrogram of polyvinyl alcohol, 88% hydrolyzed.
(From Ref. 32.)

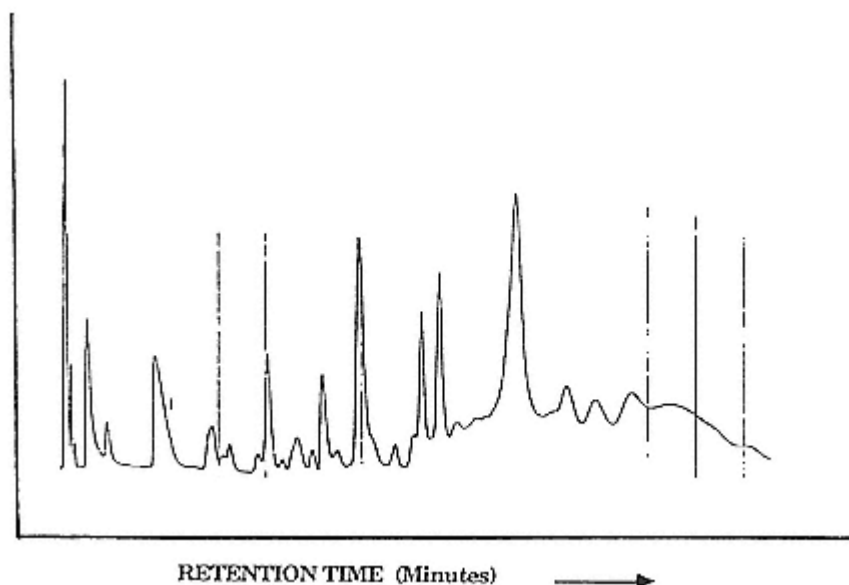


Figure 22
Pyrogram of polyvinyl alcohol copolymer.
(From Ref. 32.)

pyrolyzed. The method was applied to several environmental waste samples and was shown to be useful in the rapid identification of aniline-based dyes in the environment.

VI— Reviews on Analytical Pyrolysis

There are a number of good sources of information available on analytical pyrolysis. These contain much information on polymers and some specific information on the application of the method to fibers. Journal articles include reviews by Wolf et al. [102], Irwin [103], Liebman and Levy [104], Jones [16], and Shedrinsky et al. [105]. There is also an extensive bibliography by Wampler that covers analytical pyrolysis applications from 1980 to 1989 [106]. The section on instrumentation in the bibliography contains 34 references, that on biopolymers has 34 references, and there are more than 140 references on synthetic polymers. Articles focused on PY-MS include Haverkamp and Kistemaker [107], Gale et al. [108], Pausch et al. [109], Israel et al. [110], and Garozzo and Montaudo [26].

Books on analytical pyrolysis include the monograph on pyrolysis—gas chromatography by May et al. [111], the compendium and atlas by Meuzelaar et al. [112], comprehensive reviews by Irwin [40] and Voorhees [113], and the book de-

voted to analytical pyrolysis and polymers by Liebman and Levy [114]. In addition, there is a recently published analytical pyrolysis handbook edited by Wampler that contains chapters giving an overview of the method, instrumentation and analysis, and various sections on polymers and fibers [41]. Other sources include the chapter on polymer identification using PY-GC by Brown [115] and the section on pyrolysis techniques in Crompton [14].

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