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# SCANNING ELECTRON MICROSCOPE EXAMINATION OF COTTON LINTERS AND WOOD PULP FIBERS BEFORE AND AFTER NITRATION AND GUN PROPELLANT MANUFACTURE

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The prime ingredient in all operational military gun propellants is nitrocellulose (NC). The properties of the NC are a function of the source of the cellulose, any processes used to prepare the cellulose for nitration, and the nitration process. The purpose of this paper is to analyze the morphology of several standard types of cellulose feedstocks from a variety of biological sources and preparative processes. The feedstocks examined were cotton linters, and sulfite or sulfate treated softwood and hardwood

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pulp fibers. Prior to nitration the cotton linters are well formed and intact with smooth surfaces. The wood pulp fibers are broken and crushed from the mechanical pulping processes with the surfaces of the fibers erroded and porous due to the purifying sulfate or sulfite processes. After nitration the surfaces of the linters and pulp fibers show increased porosity and degradation of the mechanical structure of the fibers with the cotton linters showing less damage than the pulp fibers. The increased porosity of the wood pulp fibers indicate why these fibers, after nitration, are generally more soluble than nitrated linters. In both types of cellulose, the cell walls are still intact with the microfibrils showing little damage. The cellulose microfibrils consist of long chains of the polymer, beta, (1-4) D-glucose grouped together to form bundles from .008 to .03 micrometer wide. These microfibrils are held together by hydrogen bonds and appear as striations on the surface of the fibers. The bundles of microfibrils are held together through covalent linkages by a variety of bonding materials, including lignin in wood pulp, and form the main structural element in the cell wall. Several extruded single and double base propellants were examined. The manufacturing process appears to destroy the mechanical structure of the cell wall while leaving most of the microfibrils intact and lying in long strands parallel to the direction of extrusion. In the double base ball propellant WC 870 and the triple base M30A1 samples analyzed, the microfibrils have been completely solvated with no fibrous structure remaining. From these observations it is proposed that the total solvation of the microfibrils results in the formation of a brittle, crystalline NC matrix. This correlates well with the known mechanical properties of fully solvated NC propellants such as M30 and advanced nitramine propellants using NC as the binder. This suggests improved mechanical properties can be obtained by retaining some of the microfibrils and/or using plasticizers to prevent the formation of the brittle NC matrix.

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# I. INTRODUCTION

The prime ingredient in almost all military gun propellants is nitrocellulose (NC). This material is used as either the major ingredient, as in single base propellants which contain approximately 98 percent NC by weight, or as an energetic polymeric binder as in triple base and composite propellants which usually contain between 15 percent and 50 percent NC by weight. The NC is formed by reacting cellulose with a mixture of nitric and sulfuric acids. The cellulose used is obtained from either cotton (fibers) or wood pulp fibers. This cellulose is a biological material, and its properties as nitrocellulose will be a function of its biological source, preparation processes, and nitration processes. The purpose of this paper is to analyze the morphology of several standard types of cellulose feed stocks from a variety of biological sources and preparative processes. These celluloses were then compared with a variety of nitrocelluloses made from similar cellulose feedstocks at the Radford Army Ammunition Plant, Radford, Virginia. The morphological effects of the resulting nitrocellulose on processing into finished gun propellants was then examined. Since nitrocellulose is obtained from biological cellulose feedstocks, the biological sources and growth processes must be examined before we can describe and understand the morphology of cellulose prior to and after it is nitrated. The two prime cellulose feedstocks are wood pulp fibers and cotton linters.

## A. Cellulose Fibers

Wood pulp fibers are the fibrous residue remaining after the mechanical chipping of pulp wood followed by disintegration of the wood chips with a hot solution of either calcium bisulfite (sulphite pulp) or sodium hydroxide (sulfate pulp).[1,2] These chemical processes are designed to remove the lignin and other impurities from the cellulose fibers. The sulphite process generally yields the purer cellulose fibers. High quality nitrocellulose should have no impurities remaining after nitration.

The two main classes of trees yielding cellulose fibers are softwood or coniferous trees and hardwood or deciduous trees. The cellular structure of both types of trees is a highly complex subject, but some general features are common to both types and will prove useful to examine.

The bulk of wood pulp cellulose comes from the xylem. The xylem is that part of a tree which has ceased to grow and provides mechanical

[1] *F. Keith Hall, "Wood Pulp," Scientific American, pp. 52-62, April 1974.*

[2] *R. Norris Shreve and Joseph A. Brink, Jr., Chemical Process Industries, 4th Edition, McGraw-Hill Book Co., New York, 1977, pp. 545-565.*

strength and conveys sap to the growing portions of the tree.[3,4] The xylem provides the main bulk of tree trunks and larger branches. The structure consists of elongated parallel cells with cell walls that have been thickened by the deposition of layers of cellulose and strengthened by lignin. Each wood cell is bound to the adjacent cells by an intercellular material whose composition is species dependent. In the cellulose extraction of wood, which consists of chemical action with mechanical agitation, most of the lignin and other impurities are dissolved, and the fiber structure is disintegrated longitudinally. The result is a fibrous material in the form of flat ribbons, usually with flattened internal canals. The structure of the cell wall is somewhat porous due to the strong chemical attack and the removal of lignin. Table 1 lists the typical impurities found in wood. The fibers of coniferous wood pulp are the remains of cellular elements known as tracheids which are elongated single cells. In hardwood pulp, the fibers consist primarily of the sap-carrying vessels which were formed by the fusion of rows of shorter cells.

Table 1. Wood Pulp Impurities

- Lignin (20-30%)
- Hemicelluloses (10-20%)
- Pentosans (10-15%)
- Waxes, Proteins, Fats (Trace)

Cotton fibers are the hairs or trichomes formed on the epidermis of the cotton seed.[3] These trichomes are extruded from the seed during the first stages of growth and are covered with part of the waxy cuticle of the seed.[4] The dried trichome is marked by very characteristic twists or convolutions that occur at irregular intervals along its length, producing a flat convoluted ribbon. The cuticle is extremely thin and is not found after the trichome has been nitrated. The structure of the cotton exterior cell wall consists of parallel bundles of spiral wrapped fibrils making an angle of about $30^{\circ}$ to the axis of the fiber. (See Figures 1(a) and 6(a).)

The cotton linters used for nitration are the short (0.05-0.5 cm) trichomes remaining on the seed after the longer (2-10 cm) fibers have been removed. These cotton linters consist of two basic types. The first is like the longer fibers with a fairly wide and flattened central lumen or canal and many convolutions. The second type consists of short, round fibers tapering to a point with thick cell walls and a narrow lumen. Both types of fibers are typically 10-25 μm wide. Acceptable nitration quality

[3] *Frank D. Miles, Cellulose Nitrate, Interscience Publishers Inc., New York, 1955.*

[4] *Myron C. Ledbetter, and Keith R. Porter, Introduction to the Fine Structure of Plant Cells, Springer-Verlag, New York, Heidelberg, Berlin, pp.37-99, 1970.*

fibers of both wood pulp and cotton cellulose consist of the remains of one or more cell walls containing at least 95 percent cellulose.

B. The Physical Structure of Cellulose

Cellulose is a rigid, linear, crystalline polymeric material consisting of beta, (1-4)-linked D-glucosepyranose molecules. (See Figure 1.) The average chain length is determined by the structural purpose of the cellulose in the plant cell wall and the species of the plant. Cell wall cellulose consists of highly crystalline and regular regions of pure cellulose interspaced with small regions of irregular or amorphous cellulose. These amorphous regions usually contain small amounts of impurities. Present theory describes the beta-linked glucose chains in the crystalline regions as forming flat ribbons with the glucose rings of each chain lying in the same plane while the hydroxyl groups on the glucose molecules protrude above and below the plane of the cellulose ribbon.[5,6] (See Figures 2 and 3.) Bundles of these cellulose ribbons are called microfibrils. The microfibrils vary in width from 0.008 to 0.03 μm and are approximately half as thick as they are wide.[3,6] The microfibril bundles are held together by hydrogen bonds formed between the protruding hydroxyl groups of the flat glucose molecule. (See Figure 2.) The hydrogen bonding in these microfibrils is very strong with the microfibrils remaining intact except under severe processing conditions. Typical processing conditions include elevated temperatures, strong solvents, acids, and bases.

The main structural unit of cellulose in the plant wall consists of these cellulose microfibrils bonded together in a polymeric matrix much like filament-wound rocket motor casings where the filaments are bonded together by polymeric resins. The microfibrils are covalently bonded together by various polymeric sugars and proteins.[5] A model of this structure is seen in Figure 3. The covalent bonded microfibrils are often found grouped into fibrils. These cellulose fibrils are generally between 0.05-0.3 μm in diameter with an average diameter of approximately 0.15 μm and up to 20 cm or more in length. The presence of the fibrils and their length, and the exact composition and amount of the fibril bonding materials are determined primarily by plant species and function, with the microfibrils serving as the main building unit of the fibrils. These fibrils then form the various structured features found in the plant cell wall.

C. Cellulose and Plant Cell Growth

Plant cells grow by first forming a primary or outer cell wall after the nucleus has divided during cell division (mitosis).[4] This primary cell wall consists of layered cellulose fibrils. In cotton linters, this primary wall consists of dense spiral wrapped layers of cellulose fibrils. In wood cells, this primary cell wall is formed of matted fibrils resembling matted

[5] *Peter Albersheim, "The Walls of Growing Plant Cells," Scientific American, pp. 81-95, April 1974.*

[6] *R. Stuart Tipson, Editor, Advances in Carbohydrate Chemistry and Biochemistry, Academic Press, Vol. 26, pp.297-349. New York, 1971.*

felt. This primary cell wall is usually coated with an outer protective or bonding layer. In cotton fibers, this is a waxy cuticle to protect the exposed cell wall, as cotton fibers in the cotton ball consist of single chains of plant cells connected end-to-end. In wood pulp fibers, the individual rows of plant cells are coated by intercellular materials that connect adjoining cell walls together. Schematic drawings of typical cotton and wood cells are seen in Figure 4.

As the cell matures, a secondary cell wall ($S_1$) is formed right next to the interior of the primary cell wall. It is usually difficult to distinguish this initial secondary cell wall from the primary cell by optical means. The distinctive difference is that the $S_1$ cell wall is made of tightly wrapped layers of cellulose fibrils wound in a spiral pattern. Also, the $S_1$ cell wall is usually better defined and more dense than the primary cell wall. As the cell continues to mature, the middle layer of the secondary cell wall ($S_2$) is formed. This $S_2$ wall is generally not as dense as the primary and $S_1$ cell wall, but is much thicker and provides the main bulk of a plant cell wall. Cell wall growth is usually terminated by the construction of a final and more dense inner wall ($S_3$) that surrounds the protoplasm of the young plant cell. As a general rule, each secondary cell wall is formed of alternating angles of spiral wrapped cellulose fibrils. The angles of the spiral wrapping and the thickness of these layers are determined by the species, the maturity of the cell, and growth conditions.

As the plant matures to full size, the successive layers of fibrils in most cell walls are thought to slowly unwind and become more and more parallel.[5] In a mature cell wall, the alternating angles of the cellulose fibrils are still present to provide structural integrity. The strength of these multipurpose structures is readily seen in these wood pulp xylem cells as they support the entire weight of the tree while serving as transport vessels for the fluids found in the tree. While the basic cellulose structure is the same in most plants, each species has its own unique characteristics. Thus, cotton linters possess a highly defined, spiral-wrapped pattern of the fibrils while the fibrils in wood pulp fibers, which consists mainly of mature xylem cells, appear almost parallel. (See Figure 4.)

As the plant cell reaches its maximum length and maturity, two main processes occur. The first is the deposition of lignin. Lignin is a complex polymer of condensed, substituted phenols. It is water insoluable and highly resistant to chemical attack. Lignin is the major binder for the cellulose in the cell wall and provides the strength and rigidity of woody tissues. The amount of lignin deposited will control the flexibility of the cell wall. Other materials deposited during maturation involve hemicelluloses, pectin, and some proteins. This process occurs in both trees and in the woody portions of cotton plants. The cotton fibers contain little lignin and are thus very flexible. The final step in the process is drying up of the protoplasm of the cell and cessation of growth. The end result is a plant cell with a rigid cell wall composed of elongated cellulose fibrils surrounding a hollow center that is used to convey sap to

the growing regions of the plant. In wood pulp fiber, the dry weight of the fibers is 40-60 percent cellulose prior to processing while cotton linters contains 70-97 percent cellulose by dry weight.[3,7,8]

## II. METHODS AND MATERIALS

This investigation was performed by analyzing scanning electron microscope (SEM) microphotographs of various cellulose feedstock samples, celluloses nitrated at the Radford Army Ammunition Plant, and finished gun propellants. These samples included both cotton linters and wood pulp cellulose, nitrocelluloses made from cotton and wood pulp feedstocks, and finished gun propellants. The samples are described in Tables 2, 3, and 4.

Table 2. Radford Cellulose Feedstock Samples

| Type Cellulose | Source | Process | RAAP Lot No. |
|---|---|---|---|
| 1. Cotton Linter | Hercules Hopewell | --- | HPC-5756 |
| 2. Cotton Linter | Buckeye | --- | 5756 |
| 3. Wood Pulp | ITT Ravonier | Sulfite | 5749 |
| 4. Wood Pulp | ITT Ravonier | Sulfite | 5749 |
| 5. Hardwood (Dissolving Pulp) | International Paper Co. | --- | V-9063 |
| 6. Southern Pine | Buckeye | Pre-Hydrolyzed Sulfate (96% Alpha Cellulose) | --- |
| 7. Wood Pulp | Alaska Lumber & Paper Co. | Bleached Sulfite | --- |

*Note: Dashes indicate data not available.

The cellulose and nitrocellulose samples were provided by the Radford Army Ammunition Plant and picked from stock available at the time. The samples are of typical stocks on hand, and no effort was made to follow a given lot through nitration to the finished propellant. Thus, all the samples examined (cellulose, nitrocellulose and propellants) are related to each other only as being typical materials and products used in propellant manufacture.

[7] *Emil Ott, H. M. Spurlin, and M. W. Grafflin, Editors, Cellulose and Cellulose Derivatives, Vol. 5, Interscience Publishers Inc., New York, 1954.*

[8] *E. L. Akim, "Cellulose-Bellwether or Old Hat," Chem Tech, pp. 676-682, November 1978.*

Table 3. Radford Nitrocellulose Samples*

| | Sample | Type NC | Blend | % Nitrogen | | % $HNO_3$ | % $H_2SO_4$ | % $H_2O$ | Acid Boiling |
|---|---|---|---|---|---|---|---|---|---|
| 1 | A | BL-3 | C-1751 | 11.7 | Linter | 21.00 | 60.75 | 18.25 | 15 Hrs |
| 2 | B | BL-4 | C-40,001 | 12.2 | Linter | 20.00 | 62.60 | 17.40 | 15 Hrs |
| 3 | C | BL-1 | C-2600 | 13.4 | Linter | 24.50 | 65.50 | 10.00 | 40 Hrs |
| 4 | D | P-1 | CF-2008 | | Pulp | | | | |
| 5 | E | S-4 | A-4905 | 12.2 | Linter | 20.00 | 63.00 | 17.00 | 15 Hrs |
| 6 | F | BL-7 | C-70002 | 12.6 | Linter | 21.5 | 62.2 | 16.30 | 15 Hrs |
| 7 | G | P-7 | CF-2613 | | Pulp | 54.00 | 33.80 | 12.20 | 20 Hrs |
| 8 | H | C-10936y | 10,000y | Blend of P-1 & P-7 (Pulp) | | | | | |
| 9 | I | L-7 | CB-1049 | 12.6 | Sheeted Linter | 54.00 | 33.15 | 12.85 | 20 Hrs |
| 10 | J | BL-3 | C-80,003 | 11.7 | Linter | | | | |
| 11 | K | P-5 | CR-2393 | 12.0 | Pulp | 52.00 | 33.80 | 14.20 | 15 Hrs |
| 12 | L | S-5 | A-5710 | 12.0 | Linter | 20.00 | 62.20 | 17.30 | 15 Hrs |

*Note: 1. All material stabilized and then viscosity reduced by acid boiling followed by cutting through Jordon Beater. Material is then blended for propellant manufacture.

2. All materials were poached after cutting as follows: (Total boiling time during poaching equals 8 hrs. Material is then either used as is or blended for propellant manufacture.)

| | |
|---|---|
| 4 hr | soda ash boil |
| 2 hr | neutral boil |
| 1 hr | neutral boil |
| 1 hr | neutral boil |
| 8 hr | total boiling time |

Table 4. Finished Gun Propellant Morphological Samples

| Propellant | IMR 4350 | M10F | HC25B | M30A1A | WC870 |
|---|---|---|---|---|---|
| Type | Extruded Single Base | Extruded Single Base | Extruded Double Base | Extruded Triple Base | Ball Double Base |
| Ingredients (%) | | | | | |
| Nitrocellulose 13.15% N | 99.3 | 98.0 | 83.5 | | 84.8 |
| 13.1% N | | | | 28.0 | |
| 12.6% N | | | | | |
| Nitroglycerin | | | 9.0 | 19.0 | 10.0 |
| Nitroguanidine | | | | 50.0 | |
| Diphenylamine | 0.7 | 1.0 | 1.0 | | |
| Diphenyl Phthalate | | | 5.0 | | 5.2 |
| Ethyl Centralite | | | | 1.5 | |
| Graphite | | 0.1 | | | |
| Potassium Nitrate | | | 1.5 | | |
| Potassium Sulfate | | 0.9 | | 0.5 | |

The samples for SEM analysis were placed on collodial, graphite-coated, aluminum stubs and coated with 100 percent gold in an International Scientific Instrument PS-2 Sputter Coater. The linter and wood pulp fibers were placed directly onto the stubs at room temperature prior to gold coating. The liquid nitrogen fractured samples were prepared prior to stub mounting by soaking a small bundle of fibers in the liquid nitrogen. The frozen fibers were then immediately fractured with two pairs of forceps. The fractured fibers were then placed onto the aluminum stubs faceup.

The gun propellant samples were prepared by using a knife or razor blade to fracture the samples longitudinally (parallel to the direction of extrusion) and latitudinally ($90^{o}$ to the direction of extrusion) to provide an end-on view of the sample. These samples were then placed faceup onto a graphite coated stub. The graphite paint was used to hold the sample in place on the stub. The goal was to examine fractured surfaces rather than the cut surfaces of the propellant sample. The knife-cut regions tend to smear and appear smooth and featureless under the SEM.

All the samples were then examined in an International Scientific Instrument Super III-A Scanning Electron Microscope. To avoid burning the samples, a low acceleration voltage of 10 Kv was used along with minimum focus/examination times, particularly at magnification greater than 500X. The prime method used was to focus the image very quickly and study the resultant microphotographs (micrographs) rather than the direct image on the video screen.

For size determination, each micrograph contains some portion or all of a 55.5/μm sizing bar. The bar is made up of a 50/μm length, a 0.5 μm gap, and terminated with a 5/μm bar. Low magnifications will show the whole bar. High magnifications generally contain some of the end of the 50/μm bar, all of the 0.5/μm gap and some or all of the terminal 5/μm bar. Thus, a constant reference scale is available independent of the magnification. The micrographs also contain the approximate magnification of the original micrograph beneath the lower right corner and is not the actual magnification of the micrograph as printed in this report. These magnifications are included to simplify comparisons between the micrographs printed in this report.

Caution must be exercised in evaluating the SEM data as any single micrograph or even a large number of micrographs of a single sample area depicts only the object or region viewed and not necessarily the whole sample. To obtain a statistical sampling of even a small sample requires a very large number of micrographs. The field of microscopic gun propellant morphology is relatively new and, while the micrographs contain tremendous amounts of information, this information has yet to be correlated to processing changes and combustion characteristics. The goal of this study was to obtain a generalized view of the whole sample. The basic technique used was to first obtain a number of representative samples of a lot, then to prepare a small portion of each representative sample. Thus, a large lot of nitrocellulose was sampled in four or five places in the container; then each sample was broken into three portions. A small sample of each portion was then viewed under the SEM.

The sample in the SEM was first viewed at a low magnification to get a general view of the whole sample and to spot any regions that appear appreciably different. Each different area was noted for further examination. If no regions appeared significantly different, then three different regions on the sample were examined to obtain a good scan of the whole sample. The sample was viewed at higher magnifications, looking at areas of interest.

This technique was used on the first sample. The second and third samples of a given portion were similarily examined, not to map each sample, but to insure that a representative scan of the portion was being performed. Thus, if the second sample appeared similar to the first, only a very few micrographs were taken. Then, the third sample was examined to be sure it was also similar to the first and second samples. This technique does not provide micrographs of every possible structure in a given sample, but it does allow a generalized study of the whole sample with the minimum expenditure of time and expense. Thus, as one grows more familiar with a given sample type, fewer micrographs are required, and each micrograph is compared against the existing data base. The main goal of this technique is to obtain a generalized, pictorial record of the sample for comparative analysis.

This report includes micrographs typical of the samples examined rather than all the micrographs taken of each sample. The observations and interpretations presented are based on a large number of micrographs for each sample and sample type. Interpretation of the SEM micrographs should be considered as our best attempts at understanding the microscopic morphology of these materials. These interpretations are subject to future modifications as our understanding grows. Comments and/or suggestions on interpretating the results presented are welcomed by the authors.

## III. RESULTS AND DISCUSSION

Representative micrographs of the various samples examined are found in Figures 5 through 26. Each category of sample will be discussed as a group with specific micrographs being referenced when applicable.

### A. Cellulose Feed Stock Samples

1. Cotton Linter Celluloses. There were no major differences between the two cotton linter samples provided. (See Figures 5 through 9.) The linters were intact, showing little evidence of mechanical or chemical degradation. Chemical degradation is generally observed as partial or total solvation of the entire sample and/or various microstructures. Some fibers did show some surface tearing of the outer cellulose layers as seen in Figure 6(d). Both linter samples show the typical mix of flattened, convoluted ribbons and the round, tapered fibers seen in optical micrographs of cotton linters. The fiber surfaces appeared smooth and undamaged. The overall views of the samples showed few broken ends and/or short fragments.

The liquid nitrogen frozen linters, as seen in Figure 7, fractured with few cellulose strands, tufts and/or delaminations of the cell wall structure. This suggests that the fiber was relatively "crystalline" when fractured, resulting in a clean break. This also suggsts a relatively

uniform structure and purity of the cell wall. Some delamination or splintering of the fiber ends would be expected if the $S_2$ cell wall layers contained different mechanical structures and/or regions of differing chemical composition. This fracturing evidence alone is not conclusive of structural or chemical homogeneity.

2. Woodpulp Cellulose.

a. Softwood Pulp (Sulfate and Sulfite Processed). The softwood pulp fibers (Figures 8 through 12) show evidence of both mechanical and chemical damage. The overall views of all these samples show many broken ends and short fragments as compared to the long fibers found in the original trees. Most of the fibers exhibited hair-like structures on the surfaces, giving evidence of the tearing apart of the wood chips that occurs during processing. Figure 8(d) shows some of the chemical erosion that takes place during pulp processing. Here the chemical erosion appears as a partial solvation or "eating away" of regions of the cell wall with irregular surfaces and pits, but with generally smooth edges. The surfaces of the fibers appear roughened with many torn regions. Most of the fibers appear as flattened ribbons with the central lumen collapsed. The pits or pores typically seen in wood pulp cell walls can be seen in Figure 8(b) and 8(d). There is no readily apparent difference between the sulfate and sulfite processed pulps.

The liquid nitrogen fractured fibers did not appear to break as smoothly as the cotton linter fibers. (See Figures 9 and 12.) Figure 12 shows delamination of the secondary cell wall layer ($S_2$) with the central lumen readily visible. This suggests that either the fibers warmed up before they were fractured or that structural and/or chemical differences exist in these cell walls as compared to the other liquid nitrogen fractured samples.

b. Hardwood Pulp Fibers. The hardwood pulp fibers, seen in Figure 13, appear very similar to the softwood pulp fibers. The overall views of the sample show broken and torn fiber ends and numerous small, irregular fiber fragments. The main difference between the hardwood and softwood pulp fibers is that the hardwood fibers appear to show less mechanical damage to the fiber surfaces. Some of the hardwood fiber surfaces appear to be as smooth as those of the cotton linters.

In summary, it appears as a generalized observation that cotton linters are relatively undamaged while both kinds of wood pulp fibers show significant mechanical and chemical damage, with the hardwood fibers being less damaged than the softwood fibers.

B. Nitrocellulose Fibers

There appear to be no major differences between the cotton and wood pulp nitrocellulose linters. The cotton nitrocellulose fibers appear more mechanically intact than the wood pulp, but the difference is in degree rather than in kind.

1. Cotton Nitrocellulose. The cotton linter nitrocellulose samples (Figure 14 and 15) all appear very similar. The fibers show increased

mechanical damage compared to the cellulose linters. The nitrocellulose fibers show regions where the cell wall is split along the fibril structural pattern with the cellulose fibril bundles exposed. The surfaces show numerous smooth-edged pores that suggests partial solvation with subsequent rapid drying. Partial solvation of the cellulose occurs during nitration, especially by nitric acid, which is a strong solvent for cellulose.[3] Almost all nitration processes use one or more rapid drying steps.

The cracks in the cell walls expose the structure of the cellulose fibrils. One explanation for these cracks is that they are the result of the rapid drying of the solvent-swollen cellulose fibrils. This induces stress on the cell wall structure, and the cracks appear at weak points, cleavage planes, and at the end of fibril bundles. The fibrils preferentially separate parallel to the $30^{o}$ spiral twist of the fibrils seen in the cotton cellulose linter feedstock. This is seen in Figures 14(c) and 15(d). The depth of these separations generally appears to be on the order of 1 to 2 μm in most of the samples. This gives an indication of the depth of the outer layers ($S_1$) of the secondary cell wall. There was little evidence in all of the samples viewed of any cracks or fractures transverse to the fibril bundles. This suggests that the cotton linter fiber bundles are more or less continuous throughout the length of the cell wall and that the individual microfibrils are also very long relative to the length of the fiber.

2. Wood Pulp Nitrocellulose. All of the wood pulp nitrocellulose fibers appear very similar. These are seen in Figures 16 through 18. The fibers appear to show more mechanical damage than the feedstock, wood pulp cellulose fibers. The nitrocellulose fibers have many broken and torn ends and many short fragments. Many of these fibers appear to have been crushed or severely compressed. The fiber surfaces have numerous cracks and smooth-edged pores. These pores range from 0.05 to 0.3 μm in diameter, with an approximate average diameter of 0.1 μm.

The wood pulp nitrocellulose fiber surfaces look very similar to the cotton nitrocellulose fiber surfaces, especially at magnifications above 4000X. The main difference between the cotton and the wood nitrocellulose fiber surfaces is that the visible surface of the wood fibers appears to consist of the primary cell wall layer while the cotton fibers surfaces consist mainly of the outer ($S_1$) secondary cell wall layer.

The stress crackings visible on the wood nitrocellulose fiber surfaces as seen in Figures 14 through 16 appear to be less regular than those of cotton. The primary cell wall of wood is thicker than that of cotton, and is still intact in these nitrocellulose fibers. Some indication of the underlying secondary cell wall structure can be seen in Figures 17(c), (d), and (e) and in Figure 18(c). Figure 17(e) shows a region where the fibril bundles appear to have been separated into a network of microfibrils. This type of network and the overall surface cracks of the wood pulp fibers indicate that there are very few structural fracture planes in the fibril bundles and that the structure of the wood pulp primary wall is less ordered than that of the cotton fiber $S_1$ cell wall. This is consistent with the basic structure of plant cell walls previously discussed.

C. Gun Propellants

Figures 19 through 23 are of single base extruded gun propellants, IMR 4350 and M10. Figure 19 of IMR 4350 single base propellant is typical of how extruded single, double, and triple base propellants fractured longitudinally (parallel to the direction of extrusion) and latitudinally (perpendicular to the direction of extrusion). The smooth areas on the fractured surfaces are where the knife cut the propellant grain. It can be readily seen that the cut surfaces contain very little morphological information. These smooth regions are very similar to the kind of surfaces produced by microtoming propellant grains.

The extruded single, double, and triple base grains fractured like a large wood log. The grains fractured readily longitudinally. The lateral, end view fractures also split like a piece of wood with much splintering at the fractured surface. One would expect a nonfibrous material to fracture like a piece of ceramic rather than like a piece of wood. This behavior suggests that the extruded propellant grains are fibrous, that the fibers are oriented parallel to the direction of extrusion and that the fibers are relatively long in relation to their diameter. Figures 19 through 24, indeed, show the fibrous nature of the nitrocellulose in these typical single base propellants. The original grains were graphite glazed. The M10 propellant also contains graphite in the formulation. Similar single base formulations without graphite in the formulation appear translucent, with color ranging from light green to orange prior to graphite coating.

Figure 23 is of an M10 single base propellant grain frozen in liquid nitrogen and then fractured longitudinally. Figure 23(a) shows two cellulose fibers still intact. The remaining micrographs of this figure are higher magnification views of the lower fiber of Figure 23(a). Note the similarity of these micrographs, and, indeed, all of the higher magnification views of single and double base extruded propellants, and magnifications of the cotton and woodpulp nitrocellulose fibers. A general rule is that the higher the nitrogen content of nitrocellulose, the less soluble that nitrocellulose will be. A possible explanation for the observed morphology is that the basic structure appears to be a mat of shredded or unraveled fiber sheets of higher nitrogen content nitrocelluloses. These sheets appear to be delaminated or unwrapped sections of the secondary cell wall structure of the fiber. The two fibers seen in Figure 23(a) are partially delaminated.

The higher magnification micrographs of Figure 18 through 24 appear very similar to the high magnification views of the nitrocellulose fibers. These propellant micrographs show large numbers of smooth-edged pores of about 0.1 μm in diameter, and the laminar or sheet-like structure of the individual secondary cell wall layers of the nitrated cellulose fibrils is intact. The fibril strands average 0.05 μm in diameter. This is typical for all of these samples viewed. In general, the basic microfibril or fibrillar structure appears to be intact, with the mechanical mixing and solvent systems causing delamination and unwrapping of the primary and secondary cell wall structure. There also occurs some separation of the laminar fibrillar structure into small sheets or bundles of fibrils.

The HC25B extruded double base propellant seen in Figure 24 appears very similar to the extruded single base propellant micrographs. The major difference is that the fibrillar stucture is less distinct and the nitrocellulose appears to be more solvated. This could be due to the nitroglycerine plasticizer in the formulation. Plasticizers and solvents cause nitrocellulose fibrils to swell. This would make the fibrils less distinct. The nitrocellulose appears fibrous in nature and does not resemble gelatin, but rather a compressed mass of thin, fibrous flakes or sheets.

The M30A1 triple base propellant in Figure 25 appears markedly different from the single and double base extruded propellants. Figures 25(a) and (b) are longitudinal fractures at the outer edge of the grain. The graphite coating is readily visible at the top of these micrographs. Figures 25(c) and (d) are longitudinal fractured surfaces. The nitroguanidine crystals are oriented parallel to the direction of extrusion and appear roughly cylindrical in shape, with surfaces roughened with small bumps and/or pits. The crystals appear to be separated from each other by a thin layer of nonstructured binder. The nitrocellulose binder appears to be totally solvated, with all of the microfibrillar structure destroyed. Note that the NC used in this propellant contains only 12.6 percent nitrogen. In all of the triple base micrographs viewed, no evidence of the laminar sheets of secondary cell wall or even loose agglomerations of microfibrils has been seen. The original cell wall structure of the nitrocellulose fibers appears to be totally solvated during the mixing process due to the strong solvents and the high percentage of nitroglycerine to nitrocellulose (approximately 40:60) in standard triple base formulations. In the lateral fractures of Figures 25(c) and (d), the nitroguanidine crystals can be seen sticking out from the fracture surface. The holes are the pockets in the binder left by crystals that remained on the other half of the fractured pieces. Each crystal appears to be held in place by a featureless, gelatinous binder with little porosity.

While each nitroguanidine crystal in all the samples viewed appeared to be surrounded by the nitrocellulose binder system, not all the samples demonstrated the same amount of wetting by the binder. The micrographs presented in this report show the crystals to have an approximately 0.1 μm gap between the crystal surface and the binder over most of the crystal surface. Samples of a different M30 propellant showed no such gaps. A well-wetted surface with good adhesion between the binder and the crystal would show no difference between the binder and the crystal, making it very difficult to identify where the binder ends and the crystal surface begins. An SEM micrograph is a picture of the gold coating over the surface of the sample with the major differences seen being gaps (black areas) in the gold coating due to surface features. The responses of the different chemical species in a given sample to the electron beam is of secondary importance in this SEM effort.

The double base WC870 ball propellant seen in Figure 26 is made from a much different process than the extruded propellants previously discussed. This propellant is made by totally solvating the nitrocellulose in ethyl acetate. The micrographs show no fibrous structure in the propellant grains. The grains fractured very cleanly, with no splintering and relatively smooth fracture surfaces. Figure 26 shows only a porous

gelatinous type of material with no structure. The micrographs in this figure are all of the same grain. The overall view of the grain is in Figure 26(a). The coordinates on the side of this micrograph locate the other micrographs in this figure. Note how the porosity varies over different regions of the same grain.

## IV. CONCLUSIONS

The results of this study indicate that the SEM does not as yet provide enough useful information to quantitatively discriminate between the fine details of cellulose feedstocks and finished nitrocelluloses. The micrographs are useful in providing a qualitative assessment of the mechanical structure and quality of these fibers. This status is expected to change as our understanding of the SEM data increases. The SEM analysis of the finished gun propellants shows great promise as a useful production quality control tool. The micrographs readily provide information on thoroughness of mixing, solvation of ingredients, porosity (both at the macroscopic and microscopic levels), wetting and adhesion of binder to solid particulates, measurement of grain dimensions, adhesion of inhibitor coatings, and overall product mechanical integrity. While the above is only an initial list of potential useful SEM data, there is potential for even more useful data with an SEM coupled to an image analyzer where the micrographic data can be readily quantitized.

Prior to nitration, the cotton linters are well formed and intact with smooth surfaces. The wood pulp fibers are broken and crushed from the mechanical pulping processes, with the surfaces of the fibers eroded and porous due to the purifying sulfate or sulfite processes. After nitration, the surfaces of the linters and pulp fibers with the cotton linters show less damage than the pulp fibers. The increased porosity of the wood pulp fibers indicates why these fibers are generally more soluble than nitrate linters. In both types of cellulose, the cell walls are still intact, with the microfibrils showing little damage.

The cellulose microfibrils consist of long chains of the polymer (β, (1-4) D-glucose), grouped together to form microfibril bundles from 0.008 to 0.03 μm wide. These microfibrils are held together by hydrogen bonds and are very resistant to chemical attack. The nitrating conditions must be extreme to fully nitrate the cellulose; otherwise, only the surfaces on the microfibrils will be nitrated. The microfibrils appear as striations on the surfaces of the fibers. The bundles of microfibrils are held together through covalent linkages by a variety of bonding materials, including lignin in wood pulp. These bonding agents comprise the bulk of the cellulose impurities in all types of cellulose and are removed through the preparative processes and during nitration.

IMR and M10 single base and HC25B double base extruded gun propellants were analyzed. The manufacturing processes appear to have destroyed the mechanical structure of the cell walls, but most of the microfibrils are intact and are lying in long strands parallel to the direction of extrusion. In the double base WC870 ball propellant and the triple base M30A1 samples analyzed, the microfibrils have been broken up, with the internal morphology of the grains showing no fibrous nature. This destruction of the microfibrils is attributed to the strong solvents used in the manufacture of those propellants.

The relationship between morphology and mechanical properties appears to be strong. The single and double base extruded grains were more difficult to fracture in any direction compared to extruded triple base grains fractured in the same direction. In general, the single and double base grains were more resilient and less brittle than the triple base grains of M30 and M30A1. All grains fractured easier parallel to the direction of extrusion. The orientation of the fibrils in the single and double base grains and the nitroguanidine crystals in the triple base grains were parallel to the direction of extrusion in all samples.

The morphology of these extruded grains resembles composite structures, with the unsolvated fibrils and the nitroguanidine crystals acting as the filament filler and the solvated NC acting as the matrix binder. The wetting of the unsolvated NC fibrils by the solvated NC appears good, and as both the fibrils and the matrix are the same material, one would reasonably expect good bonding to take place. The surfaces of the unsolvated NC fibrils should be partially softened during the mixing cycle, thus providing a good surface for bonding by the solvated NC. This does not appear to be the case with the M30 triple base propellants.

The NC appeared to be totally solvated in the triple base grains, with no fibrous structure remaining in the NC. The overall strength of a grain will depend on the strength of the NC binder, the nitroguanidine crystals, and the adhesion between the binder and the crystal. The longitudinal fractures of the triple base grains show much of the surface of the crystals exposed. This suggests that the weak point in this system is the binder-crystal bond. The binder regions between and to the sides of the nitroguanidine crystals showed tufts and strands of binder when fractured at ambient temperature, with no evidence of tufts of binder adhering to the surface of the crystals. This suggests that the binder fractured around the crystals and that the fracture did not pass from the binder into the crystals as there was no evidence of any crystal fracturing in the longitudinal fracture surfaces.

One explanation is that, even in the case of good wetting, the binder does not adhere strongly to the crystals. When samples are fractured laterally, the stress is on the crystals and the fracture is more difficult. The nitroguanidine crystals appear to be somewhat flexible at room temperatures. This is evidenced by such fracture surfaces showing many bent crystals (figure not included). This flexibility would provide the grain with more resilience when stressed laterally. The poor adhesion interface between the NC binder and the crystals could also provide ready fracture planes in the longitudinal direction, thus explaining the ease with which these grains will fracture in the longitudinal direction, both at room temperature and when frozen by liquid nitrogen.

From the above, it is proposed that this breakdown of the microfibrils into cellulose macromolecules by solvation and mechanical action during processing results in the formation of a brittle crystalline NC matrix. This correlates well with the known mechanical properties of fully solvated NC propellants such as M30 and advanced nitramine propellants using NC as the matrix binder. This suggests improved mechanical properties of the binder can be obtained by retaining some of the microfibrils and/or using plasticizers or other polymers to prevent the formation of a brittle NC matrix.

## V. RECOMMENDATIONS

The data presented in this report suggest that much further morphological analysis is required of propellant ingredients, processing variables, and finished products coupled to the performance results of the finished formulations. The microporosity seen in the NC binders and the gaps around the triple-base nitroguanidine crystals suggest further studies on the effects of pore size and crystal wetting. Thus, it is recommended that basic research be performed to determine the initial pore diameters and the depths that various flames will enter as a function of pressure. The porosity also suggests studies on the mechanical and combustion properties of propellants as a function of pore size and binder-crystal adhesion over the range of temperatures and pressure rise gradients gun propellants experience in operational use.

The wealth of data presented in a single micrograph requires a large data base to successfully understand the information presented. It is recommended that workers in SEM analysis should first begin with the raw ingredients and follow each step of the process with SEM analysis to more fully understand the SEM data seen in the finished product. We will presently begin a study to follow a single lot of cellulose through each step of the nitration process, and finally through propellant manufacture. We hope to correlate these data with the changes in viscosity, polymer chain length, chemical composition, and ballistic performance in gun systems. The ultimate goal would be to perform this type of effort for each type of nitration process and each type of gun propellant, both those presently being produced and those under research and development.


## ACKNOWLEDGMENTS

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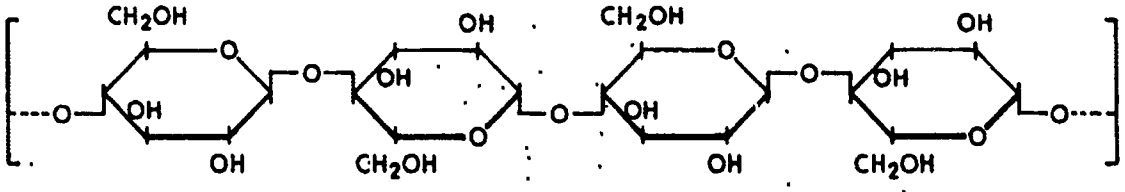



Figure 1. Cellulose [β(1,4) D-Glucosepyranose] Molecule

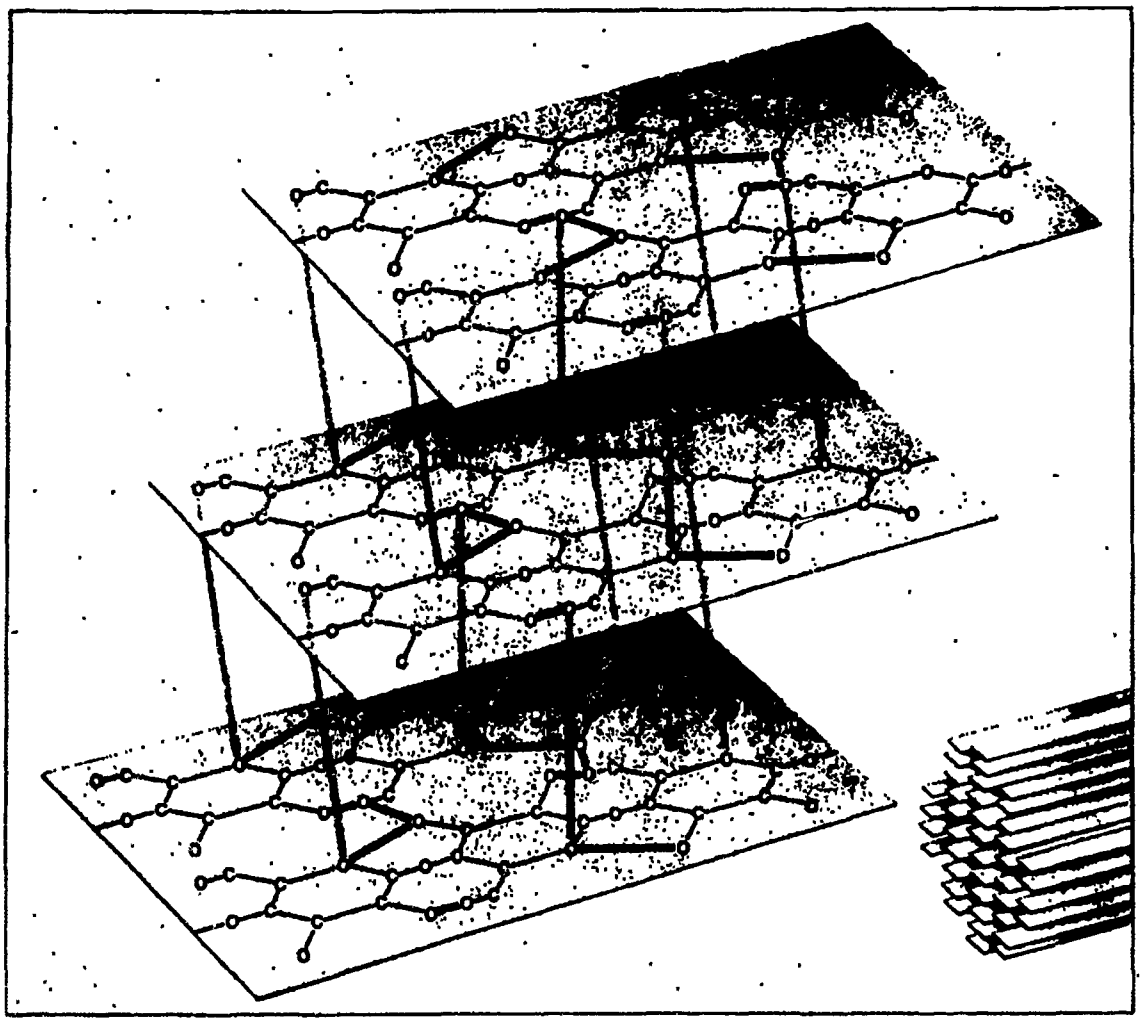


Figure 2. Model of Cellulose Microfibril (Reprinted from Scientific American Inc. by permission)

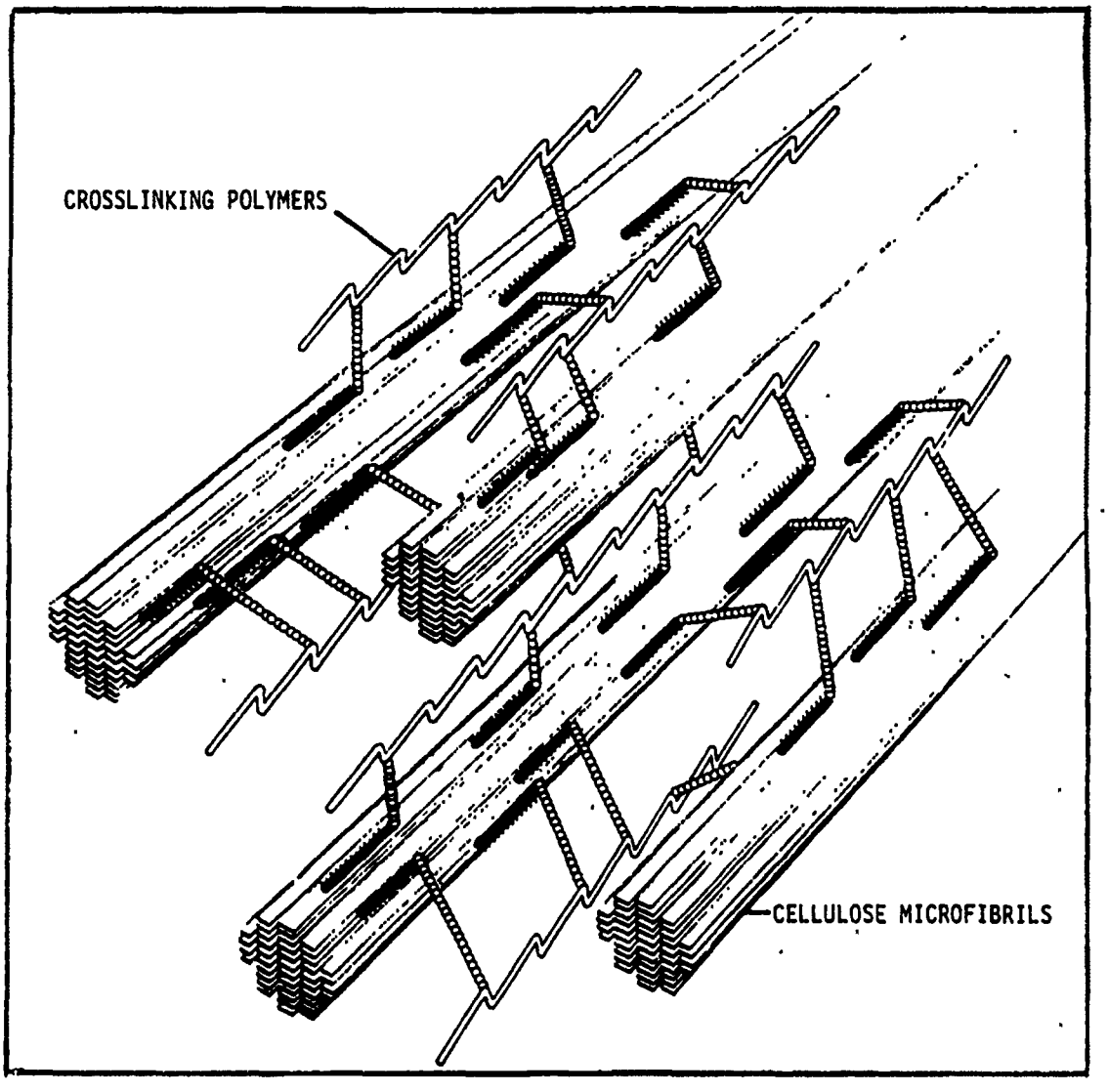



Figure 3. Model of Plant Cell Wall Bonding of Microfibril Bundles (Reprinted from Scientific American Inc. by permission)

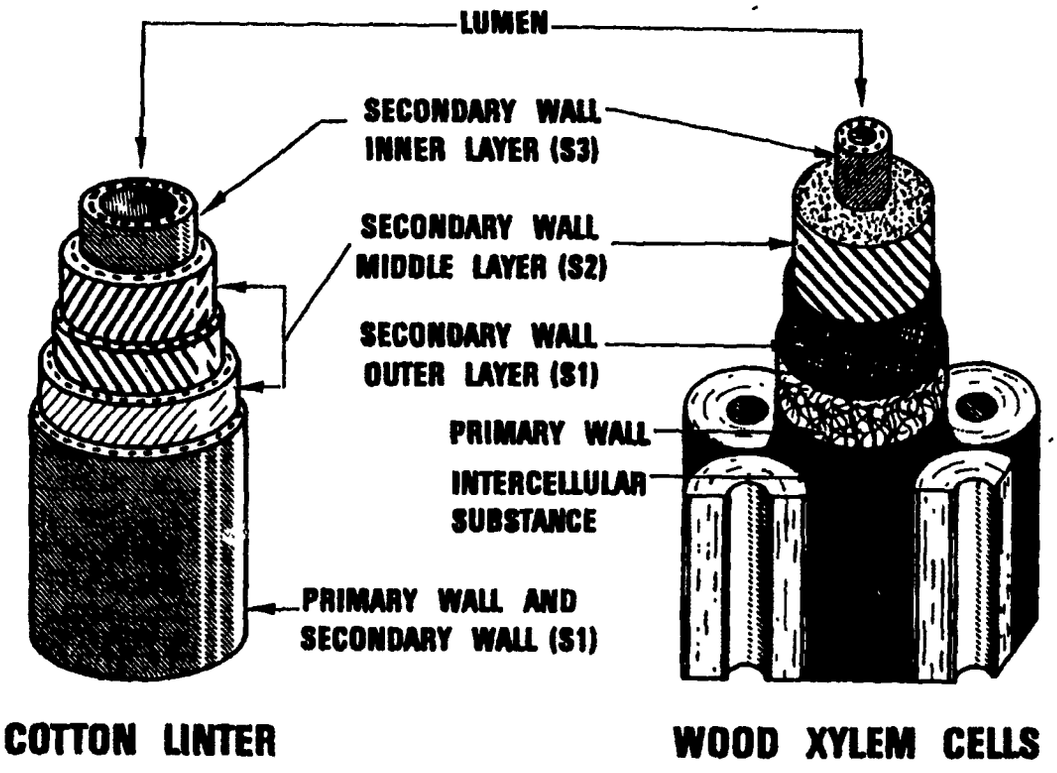
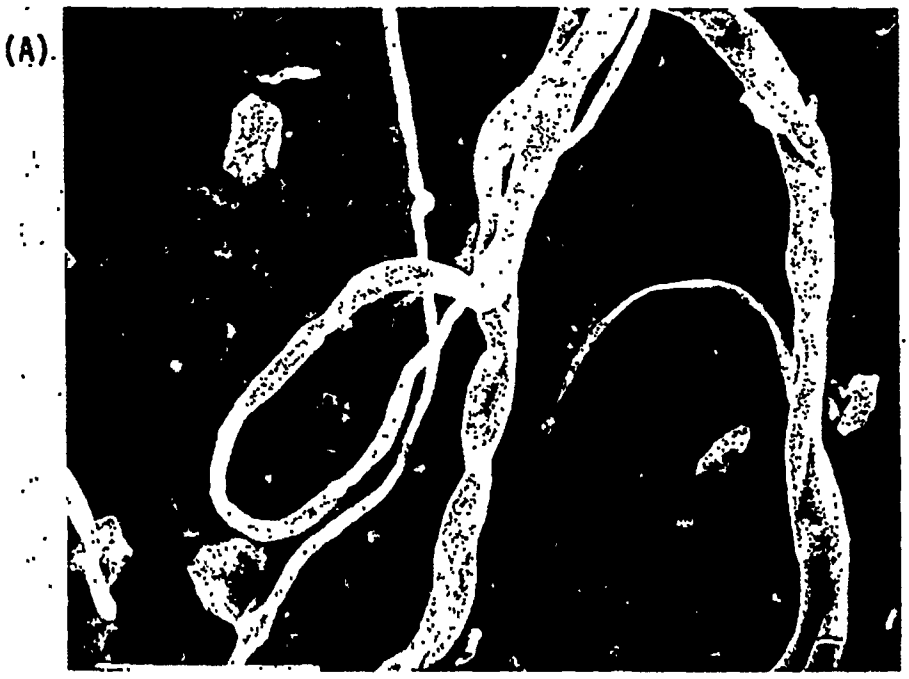



Figure 4. Model of Basic Cell Wall Structures of Cotton and Wood Cells Showing Laminar Structure of Cell Walls




375x


150-1500x

Figure 5. Buckeye Cotton Linter Cellulose Fibers

Comment: The surfaces of the linters are relatively smooth and intact. Micrographs A & B show both the collapsed, convoluted ribbons and the round linter fiber types. The magnifications listed on all the photomicrographs are from the original SEM micrographs. Due to changes of

(C)

2250x

(D)

7500x

Figure 5. (Cont'd)

Comment (Cont'd): image size during reproduction these values no longer give the actual magnification. These numbers are included for reference with all of the photomicrographs of this report. See description of micrograph white size bars on page 16.

(A)

375x

(B)

150-1500x

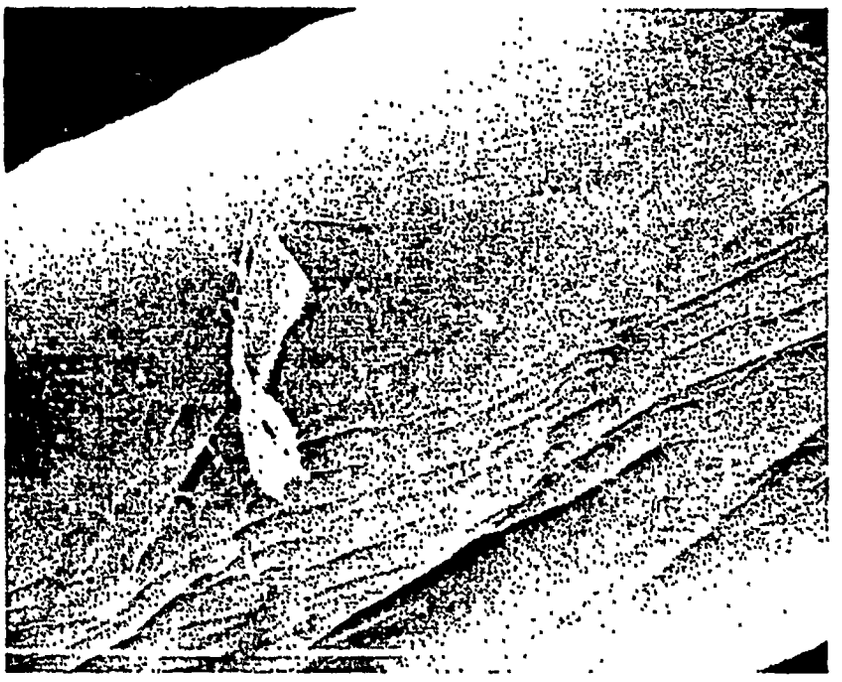
Figure 6. Hercules Hopewell Cotton Linter Cellulose Fibers

Comment: These linters show some mechanical damage. Micrograph C shows the typical cotton cellulose striations at 30° and the surface cracks at 60° to the fiber axis.

(C)

2250x

(D)



7500x

Figure 6. (Cont'd)

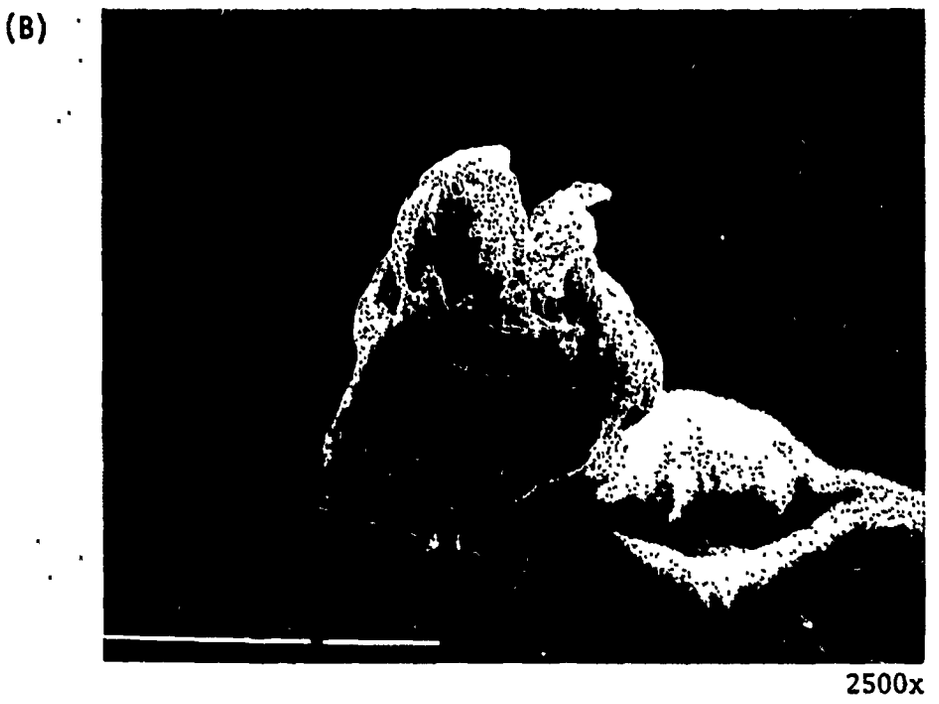
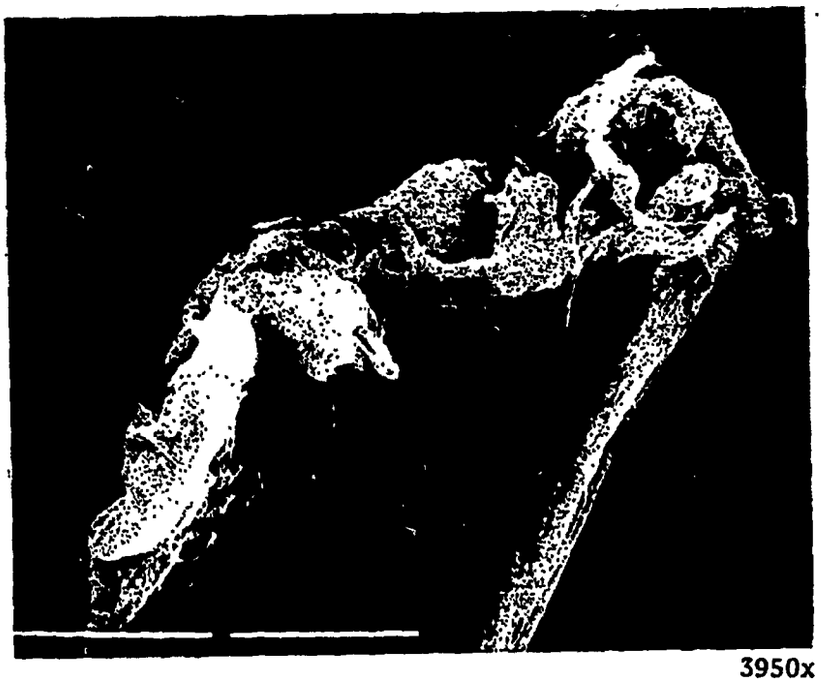




Figure 7. Fractured Buckeye Cotton Cellulose Fibers

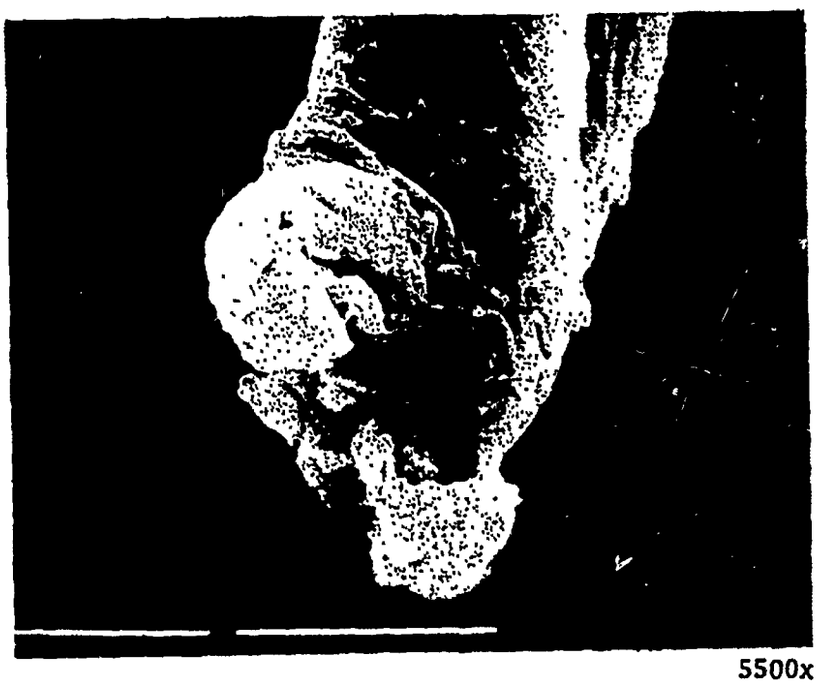
Comment: These fibers were frozen in liquid nitrogen and then fractured. Notice that there is little evidence of major delaminations of the cell wall layers at the fracture surfaces.

(C)



3950x

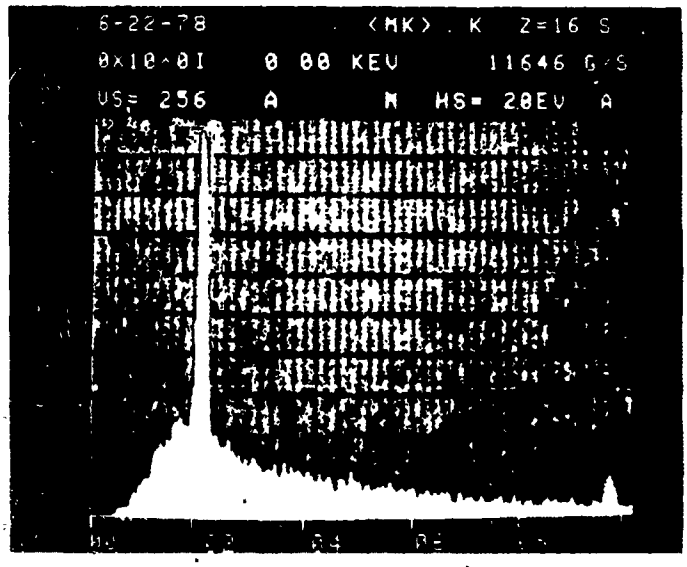
(D)



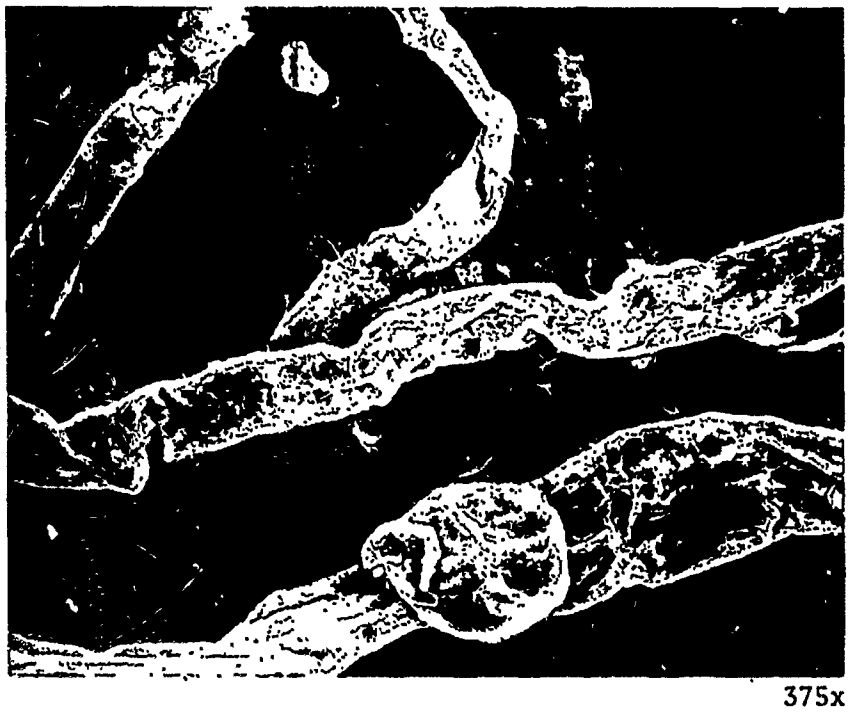
5500x

Figure 7. (Cont'd)

(A)




(B)

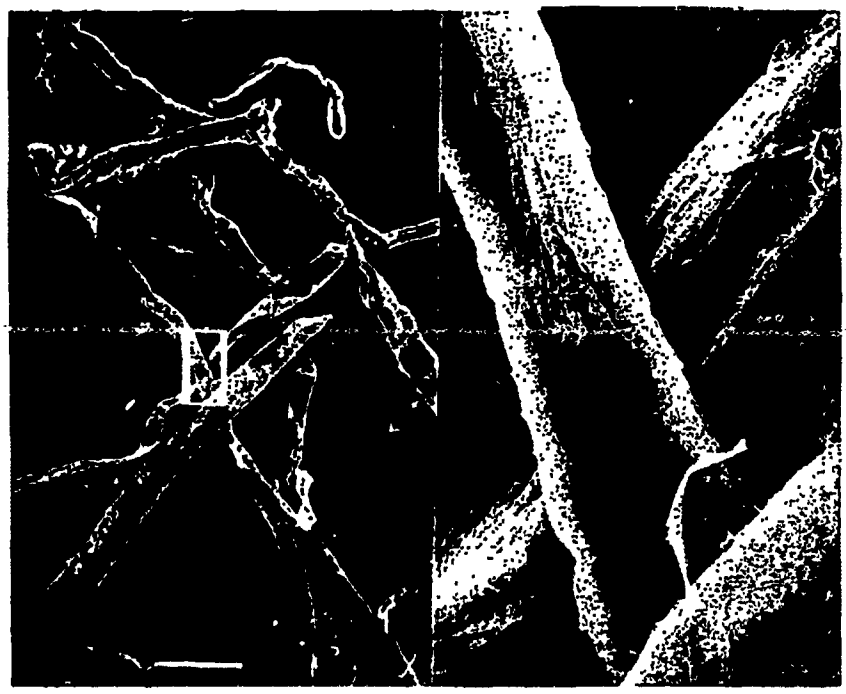


375x

Figure 8. ITT Rayonier Wood Pulp Cellulose Fibers

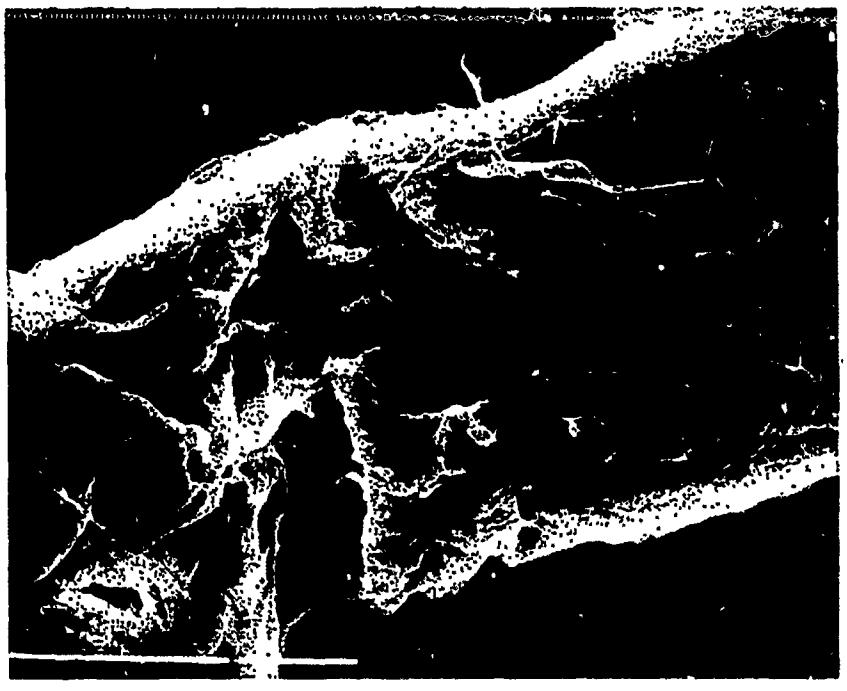
Comment: These fibers are from Lot No. 5478 and were sulfite processed. Picture A is of an x-ray scan of these fibers. The large peak shows the presence of sulfur in the fibers. Note the mechanical damage on the

(C)



150-1500x

(D)

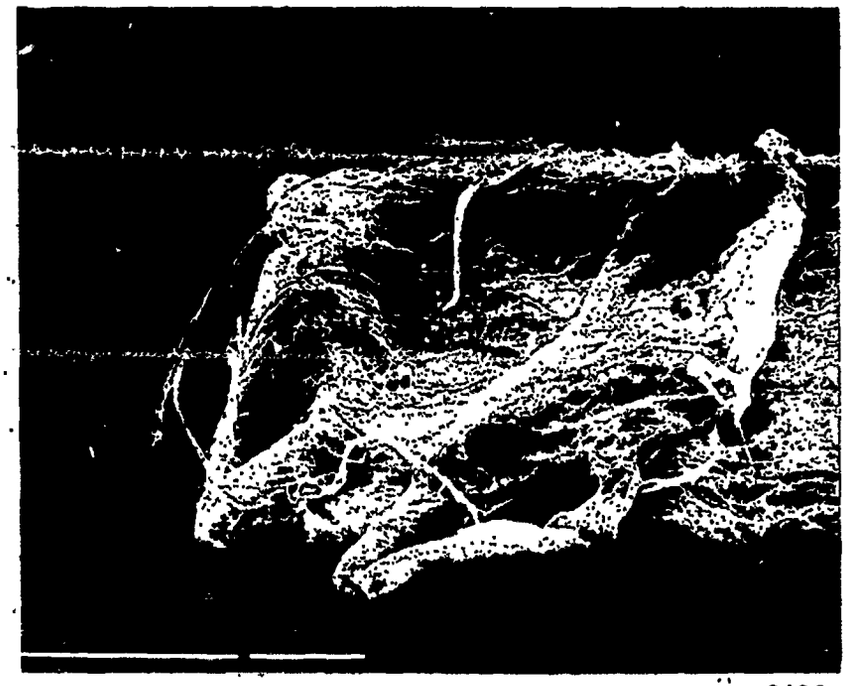


2500x

Figure 8. (Cont'd)

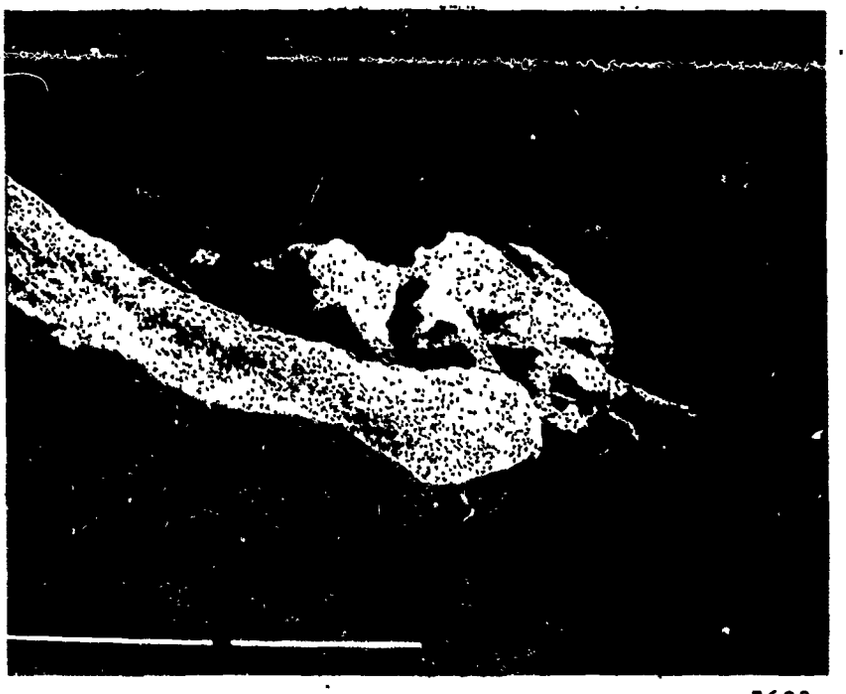
Comments (Cont'd): fibers as seen by the numerous hair-like projections (fibrils) on the fiber surfaces. Micrograph shows some possible chemical erosion of the fiber surface around the pits or holes in fiber cell walls.

(E)



2400x

(F)

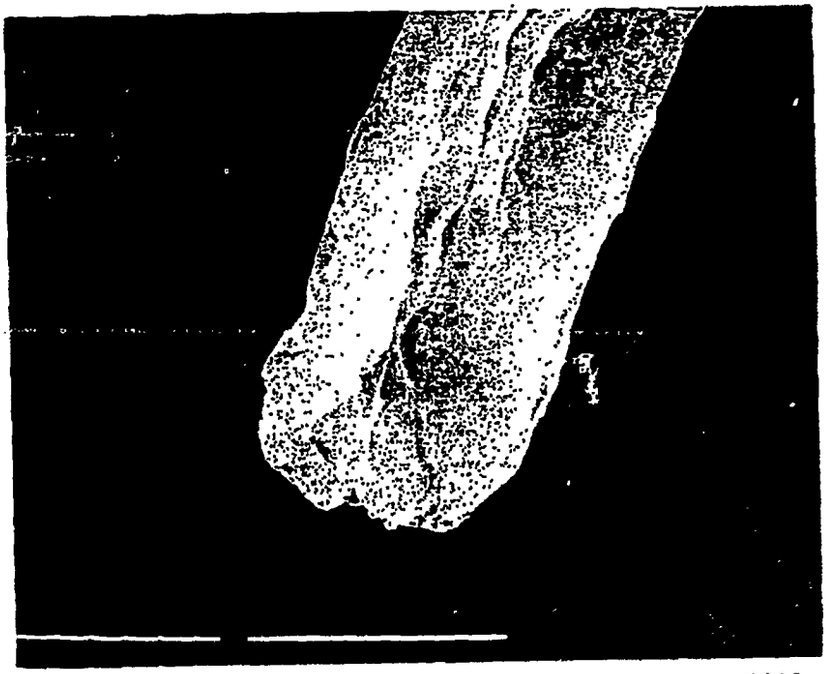


5600x

Figure 8. (Cont'd)

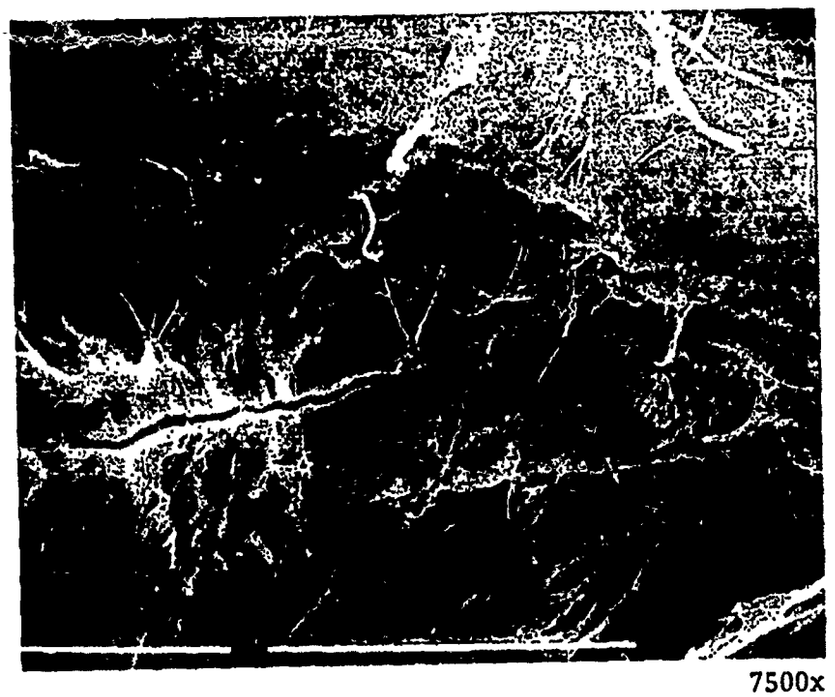
Comment (Cont'd): Micrograph E shows the outer cell wall layer delaminated and folded back along the fiber surface.

(G)



5600x

(H)



7500x

Figure 8. (Cont'd)

(A)

1200x

(B)

1600x

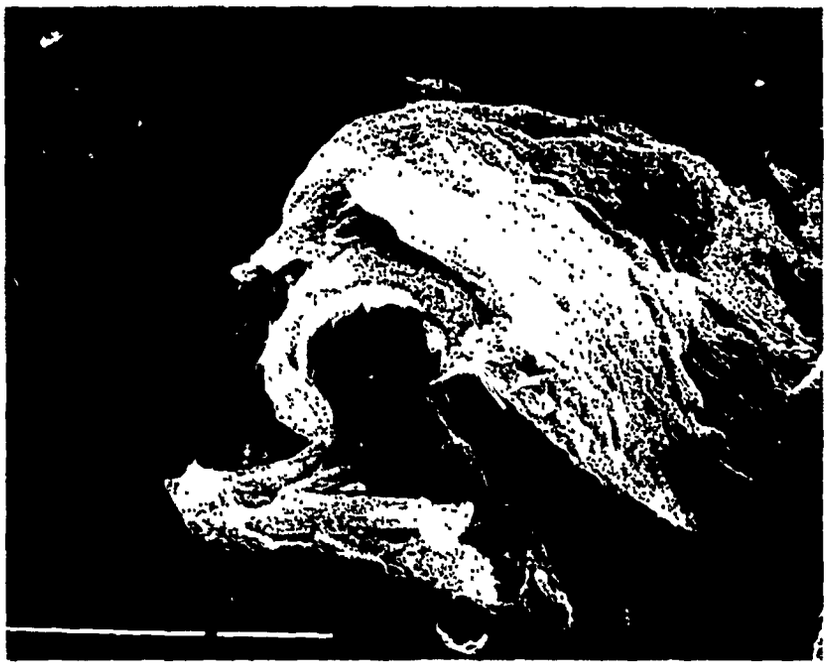
Figure 9. Fractured ITT Rayonier Wood Pulp Cellulose Fibers

Comment: These fibers are from Lot No. 5749 and were sulfite processed. These fibers were frozen in liquid nitrogen and then fractured. Note the delamination and splintering of the cell wall, indicating possible chemical and/or structural heterogeneity.

(C)

2400x

(D)



2400x

Figure 9. (Cont'd)

(E)

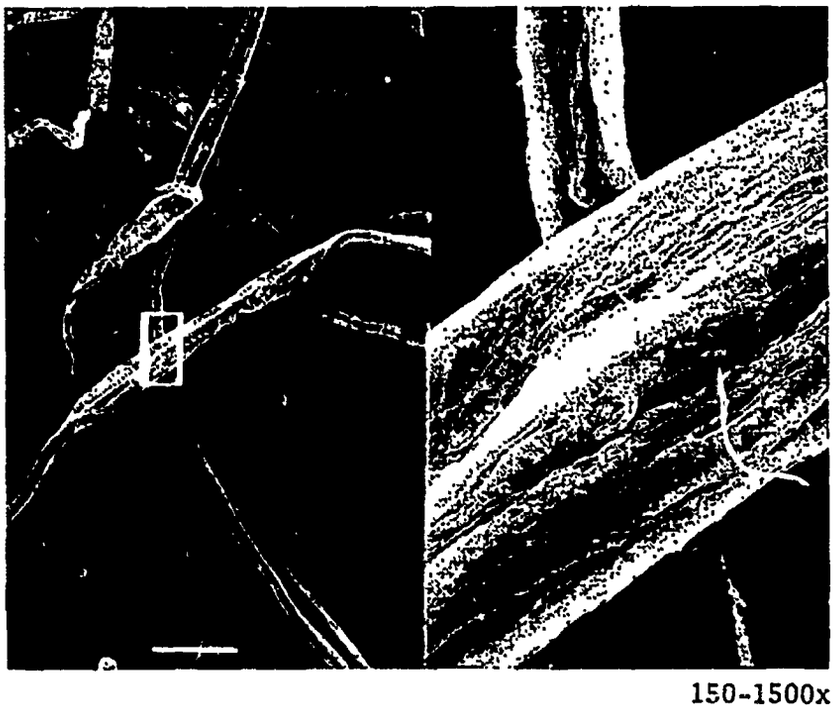
2400x

Figure 9. (Cont'd)

(A)

375x

(B)



150-1500x

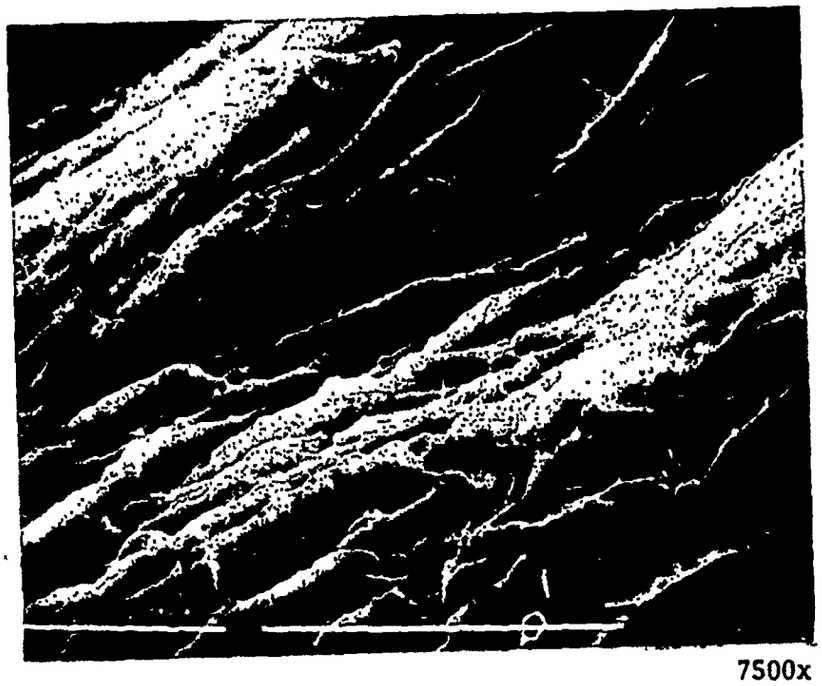
Figure 10. Buckeye Southern Pine Pulpwood Cellulose Fibers (Sulfate Processed)

Comment: This sample contains 96 percent alpha cellulose. Note the mechanical damage on the fiber surfaces.

(C)

2250x

(D)



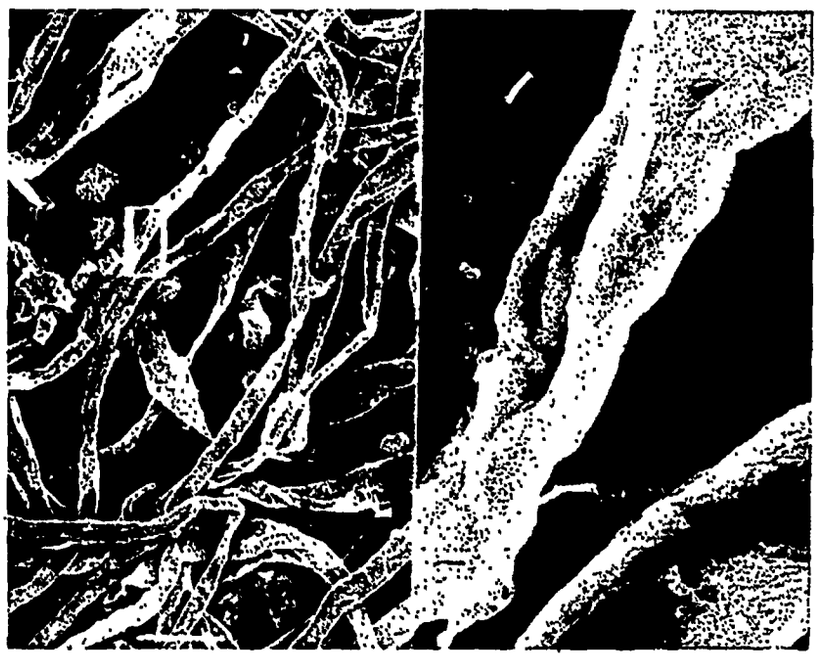
7500x

Figure 10. (Cont'd)

(A)

375x

(B)

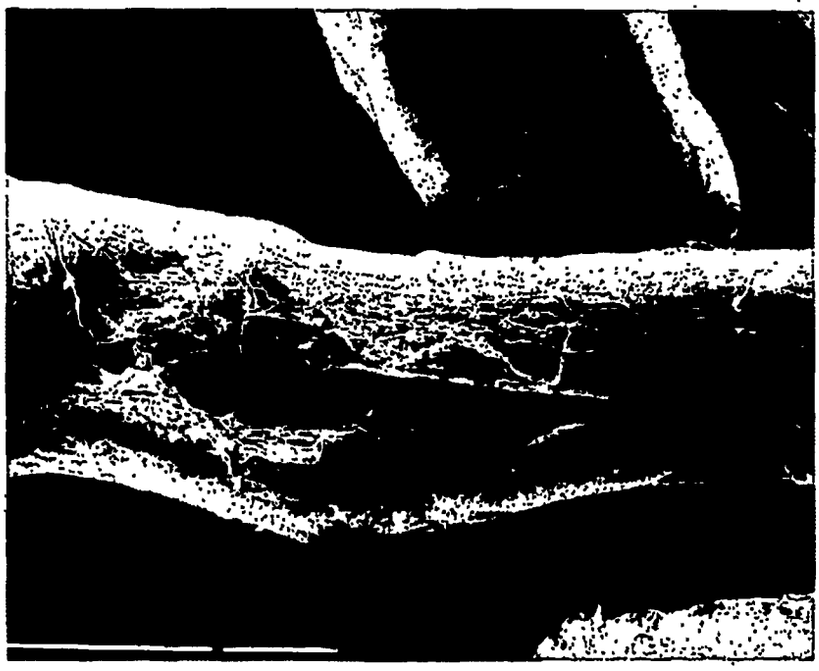


150-1500x

Figure 11. Alaska Lumber and Paper Company
Wood Pulp Cellulose Fibers

Comment: These fibers have been sulfate processed and bleached to increase the purity of the cellulose. Note the large number of fiber fragments in micrograph A.

(C)

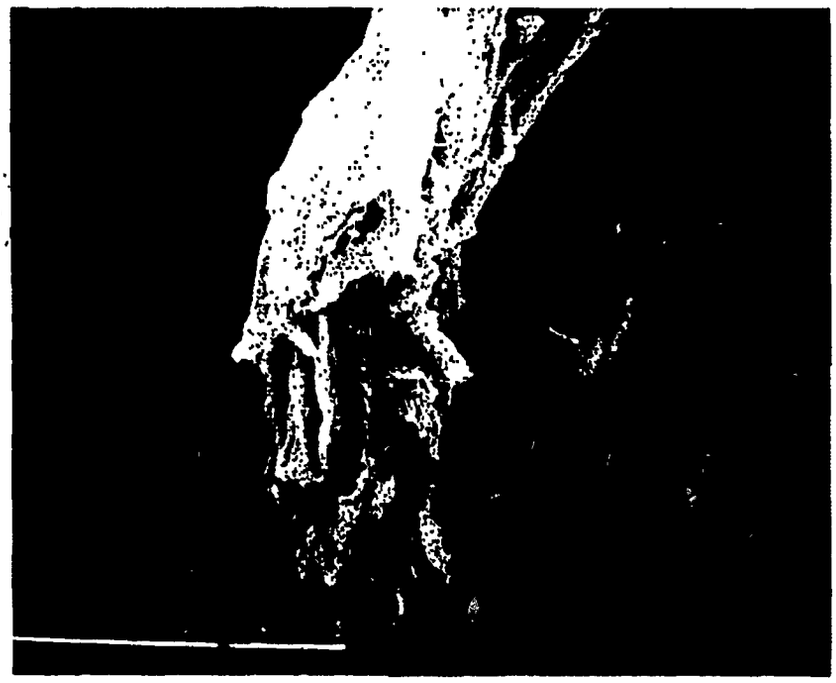


2250x

(D)

7500x

Figure 11. (Cont'd)



2400x

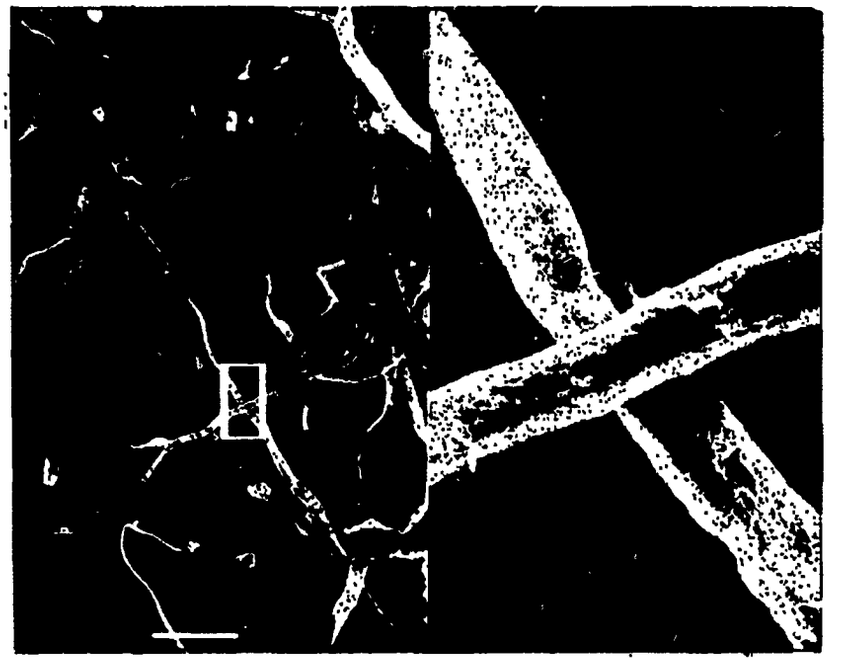
Figure 12. Fractured Wood Pulp Fibers

Comment: These sulfite processed fibers were frozen in liquid nitrogen and then fractured. Note the delamination of the secondary cell wall at the fracture surfaces.

(A)

375x

(B)

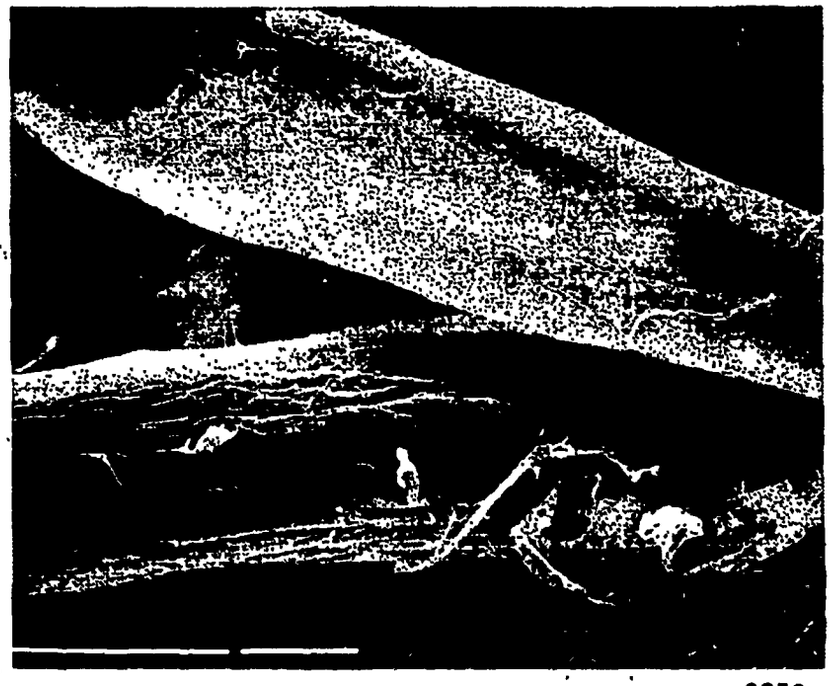


150-1500x

Figure 13. International Paper Company Hardwood Wood Pulp Cellulose Fibers

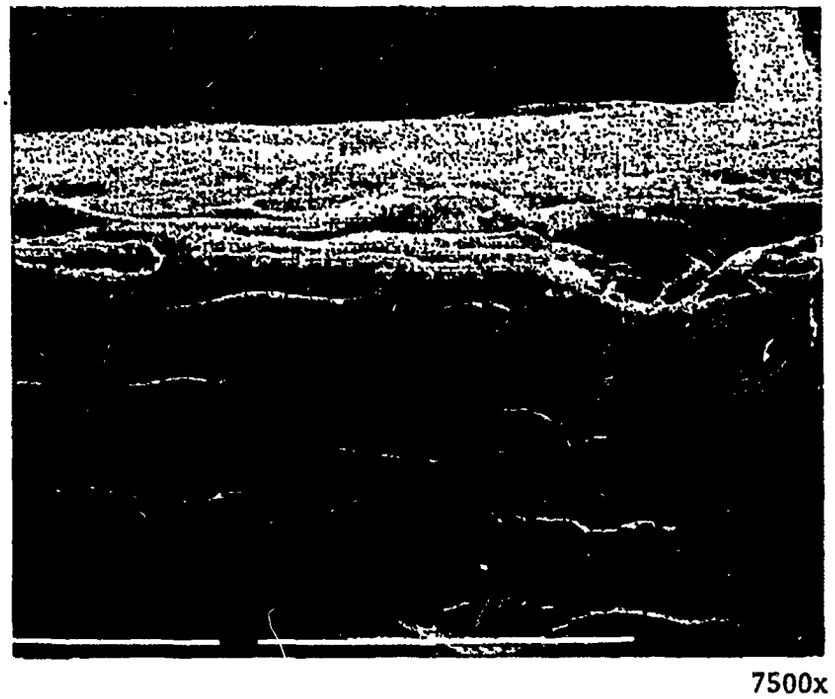
Comment: Most of these fibers appear as flattened ribbons with the central lumen collapsed. Note the evidence of structural damage to the fiber surfaces.

(C)



2250x

(D)



7500x

Figure 13. (Cont'd)

(A)

160x

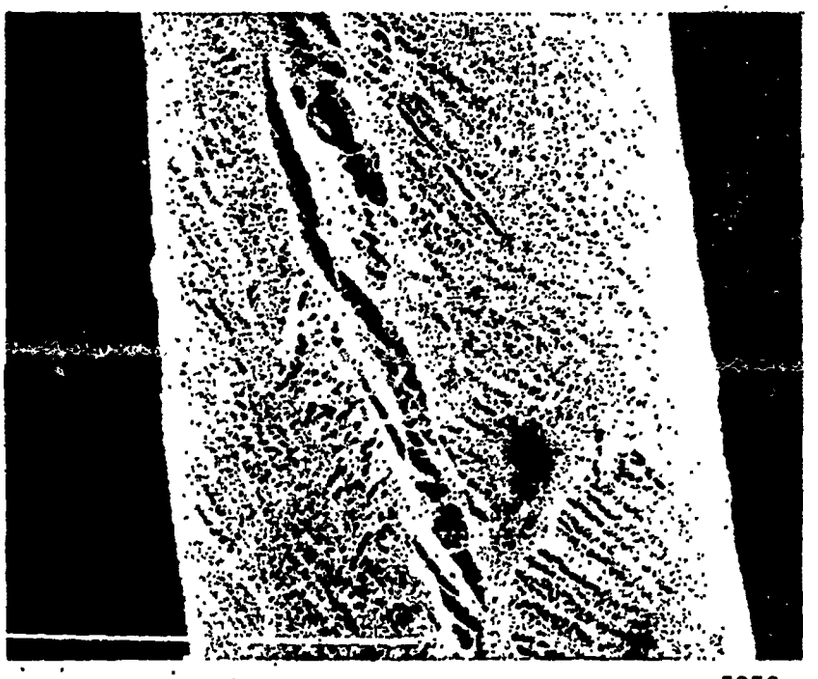
(B)

790x

Figure 14. Cotton Linter Nitrocellulose Fibers

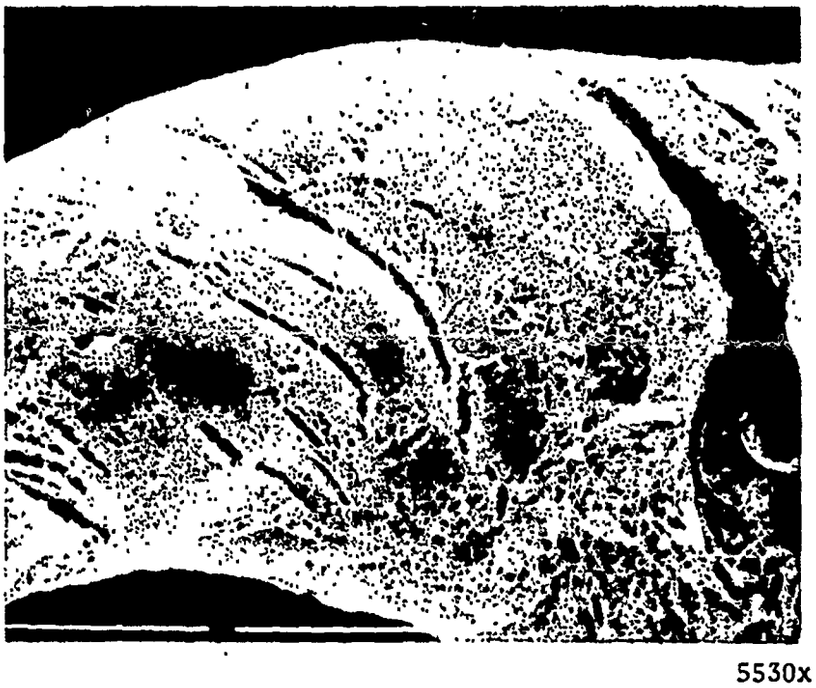
Comment: These fibers are from Lot BL-3. This sample contains 11.7 percent nitrogen. Note that the surfaces of the fibers are cracked and porous, with numerous, round, smooth-edged holes (approximately 0.1

(C)



3950x

(D)

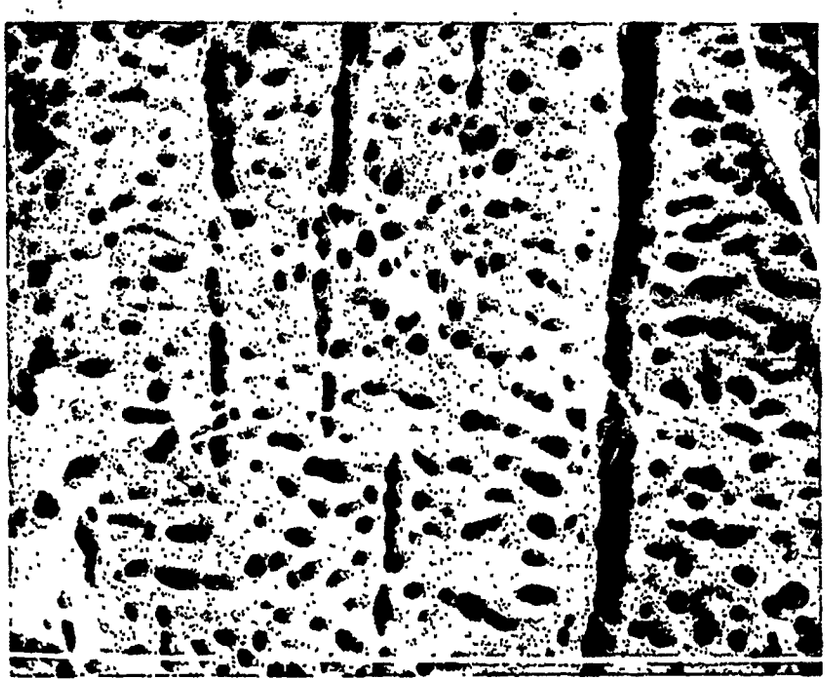


5530x

Figure 14. (Cont'd)

Comment (Cont'd): micron in diameter). The less dense secondary cell wall structure is visible beneath the cracks in the primary cell wall.

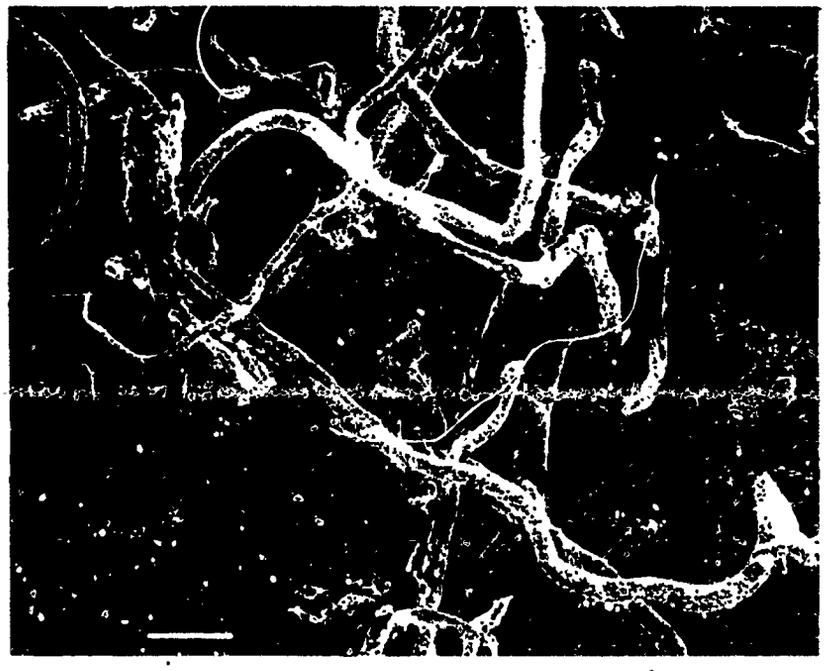
(E)



11850x

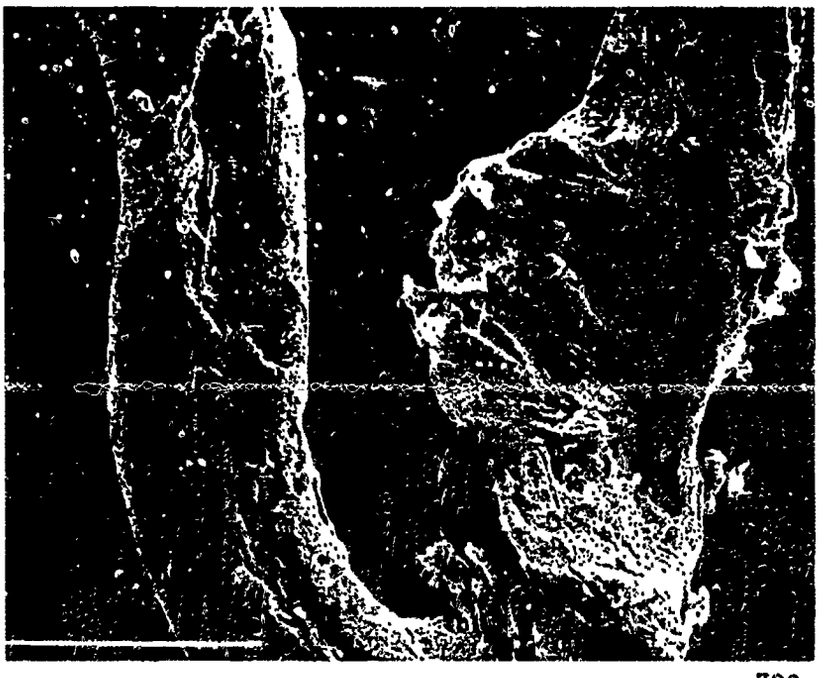
Figure 14.(Cont'd)

(A)



160x

(B)



790x

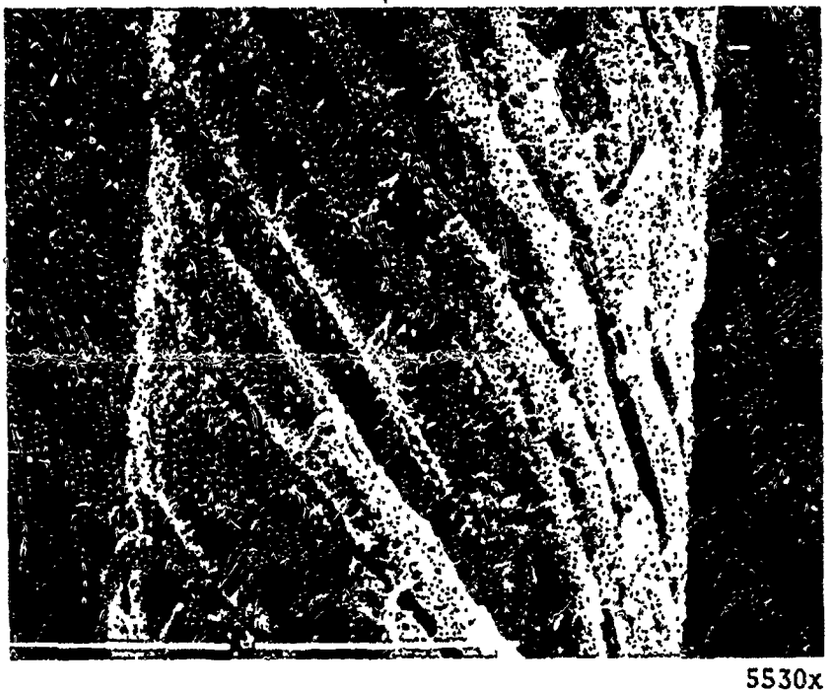
Figure 15. Cotton Linter Nitrocellulose Fibers

Comment: These fibers are from Lot No. BL-7. The fibers show extensive mechanical damage and a large number of small fiber fragments. (See micrograph A.) Micrograph D readily shows the 30° spiral-wrapped fibril bundles cracked and split apart.

(C)

3950x

(D)



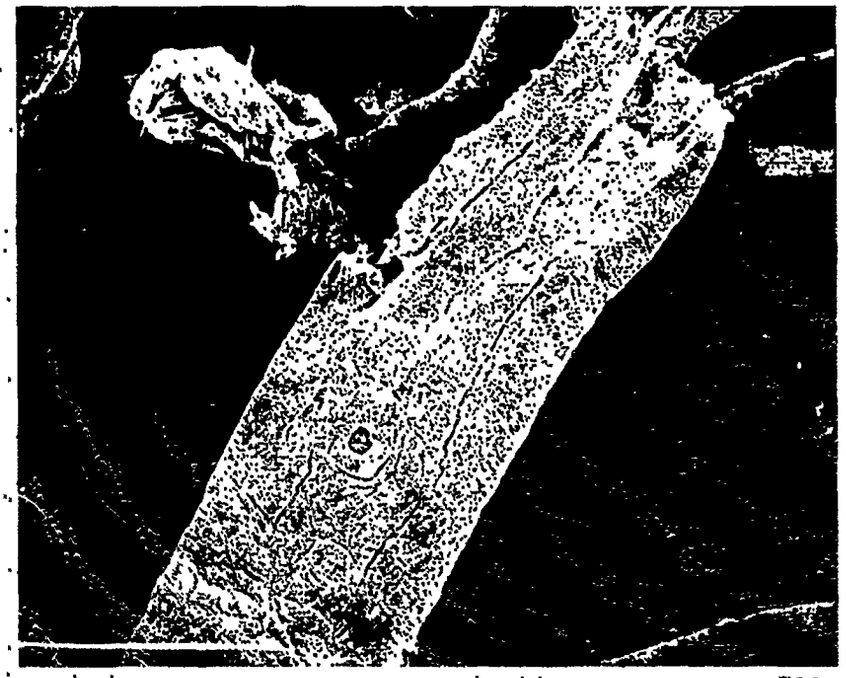
5530x

Figure 15. (Cont'd)

(A)

160x

(B)



790x

Figure 16. Southern Pine Nitrocellulose Fibers

Comment: These fibers are from Lot C-0936Y. The fibers show extensive mechanical damage with torn fiber ends and numerous small fragments. Note the bordered pits in micrographs C and D which are typical of

(C)

390-3900x

(D)

5530x

Figure 16. (Cont'd)

Comment (Cont'd): softwood fibers. The patterns of the cracks around the pits expose the structure of the fibrils around the pits.

(A)

160x

(B)

790x

Figure 17. Softwood Pulp Nitrocellulose Fibers

Comment: These fibers are a blend of Lots P-1 and P-7. The fibers display significant mechanical damage and crushing. Note the porosity of the fiber surfaces in micrographs C and E. Both micrographs show

(C)

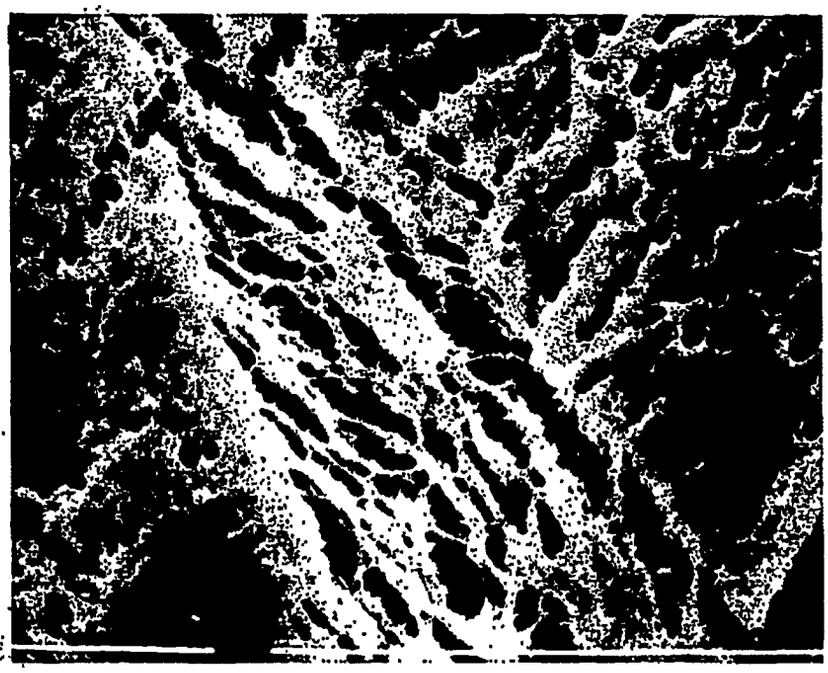
390-3900x

(D)

Figure 17. (Cont'd)

Comment (Cont'd): the round, smooth-edged pores along with a large number of cracks in the outer cell wall that expose the fibril structure in the inner cell wall layers.

(E)



11850x

Figure 17. (Cont'd)

(A)

160x

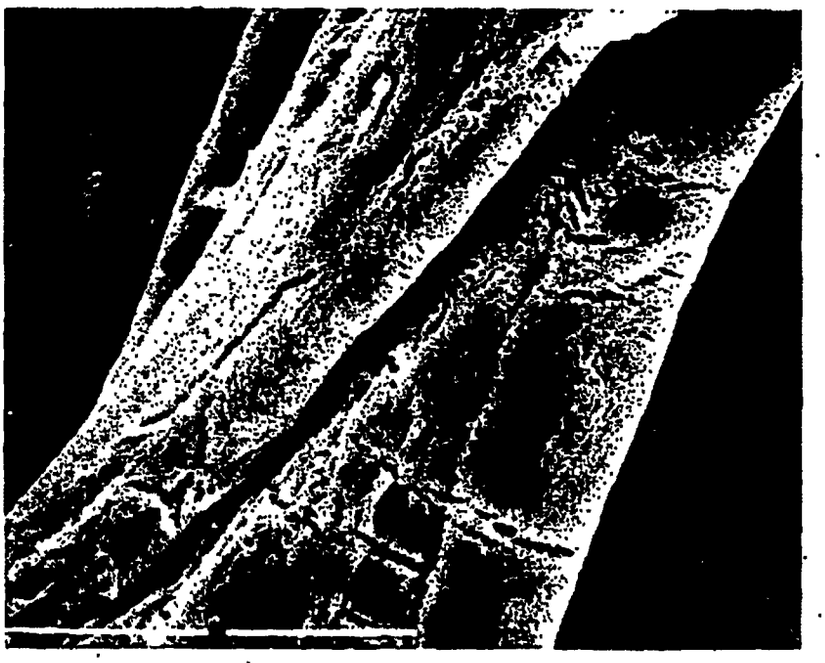
(B)

790x

Figure 18. Wood Pulp Nitrocellulose Fibers

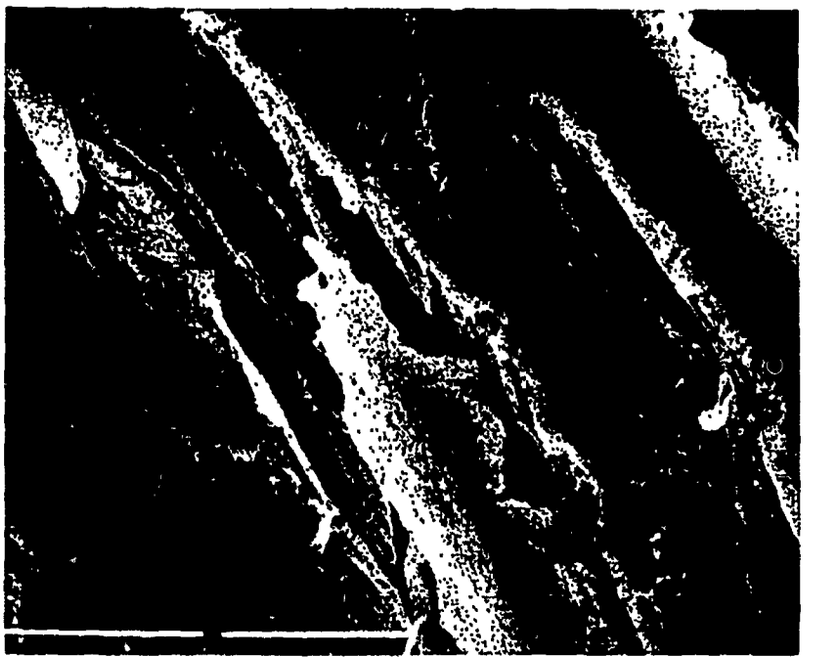
Comment: These fibers are from Lot P-1 and show mechanical damage with torn fiber ends, compressed fibers, and small fiber fragments.

(C)



3950x

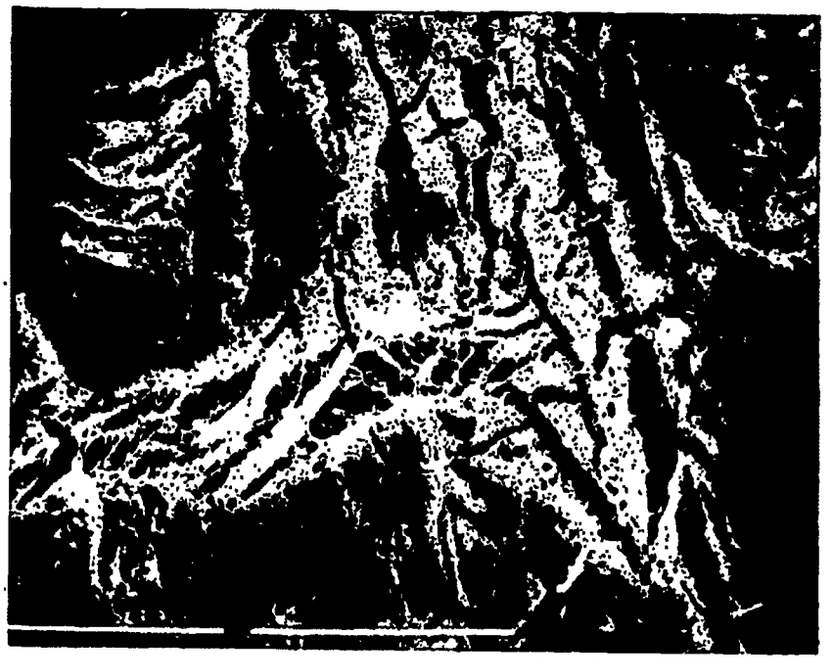
(D)



4000x

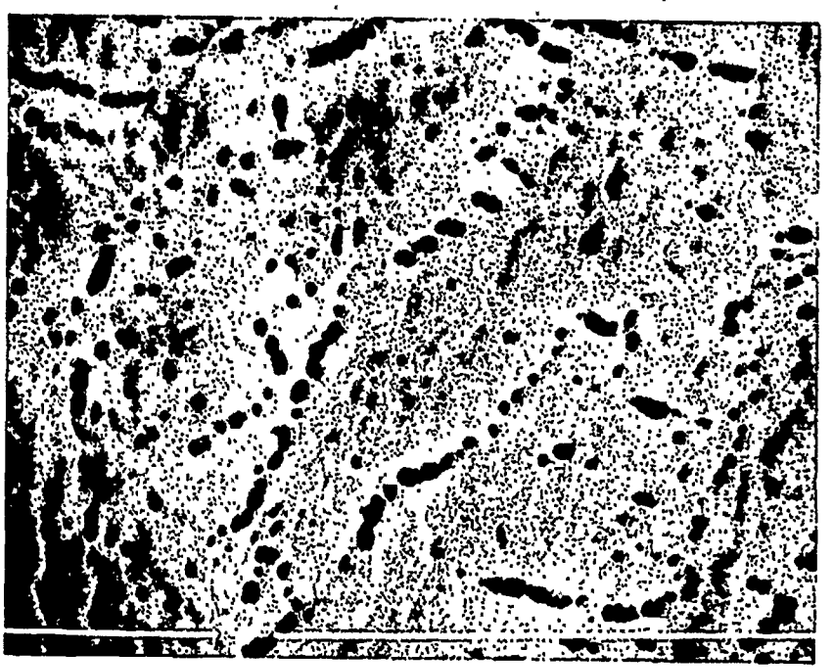
Figure 18. (Cont'd)

(E)



5530x

(F)



11850x

Figure 18. (Cont'd)

(A)

30X

Figure 19. IMR 4350 Single Base Extruded Propellant Grains

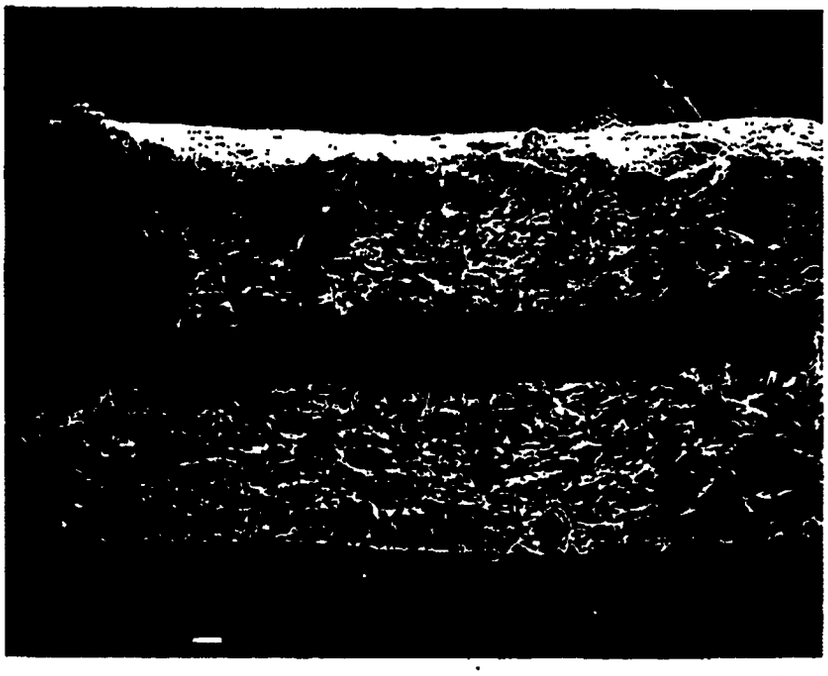
Comment: These grains were fractured at room temperature. Micrograph A. shows a grain fractured longitudinally or parallel to the direction of extrusion. The upper right corner of the left grain in this micrograph shows the region where the knife cut the grain during the fracture process. Micrograph B shows a grain fractured laterally or perpendicular to the direction of extrusion. Again, note the smooth region where the knife cut the grain.

(B)

50X

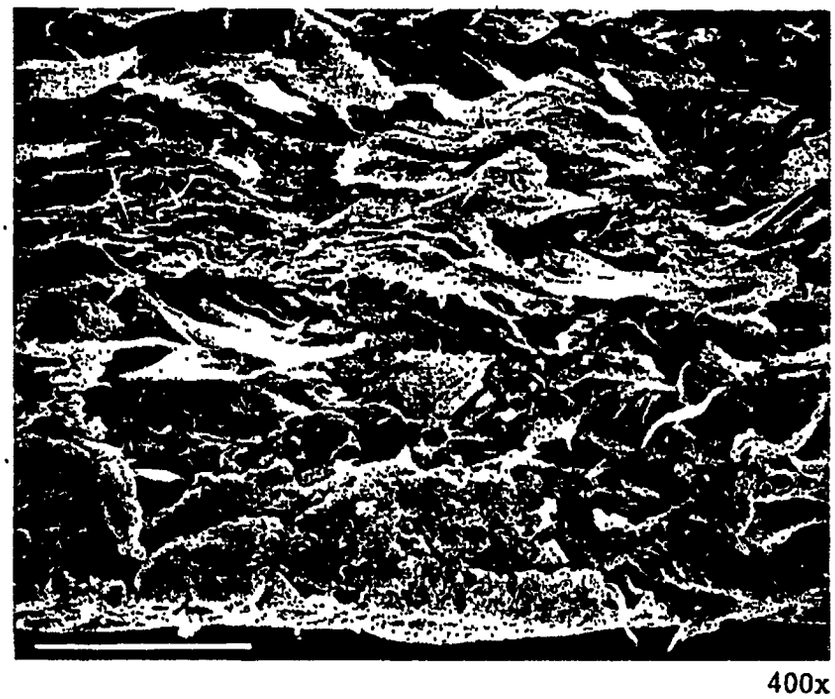
Figure 19. (Cont'd)

(A)



56x

(B)

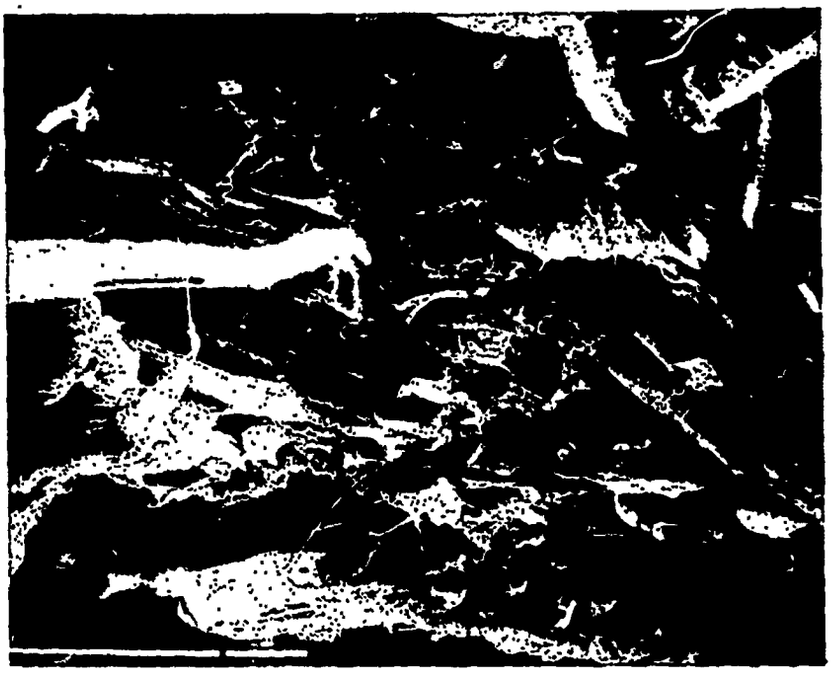


400x

Figure 20. IMR 4350 Single Base Grain Fractured Longitudinally

Comment: Micrograph D is a higher magnification view of the center region of micrograph C. Note that the fibers in the grain are orientated parallel to the direction of extrusion, and parallel to the perforation.

(C)



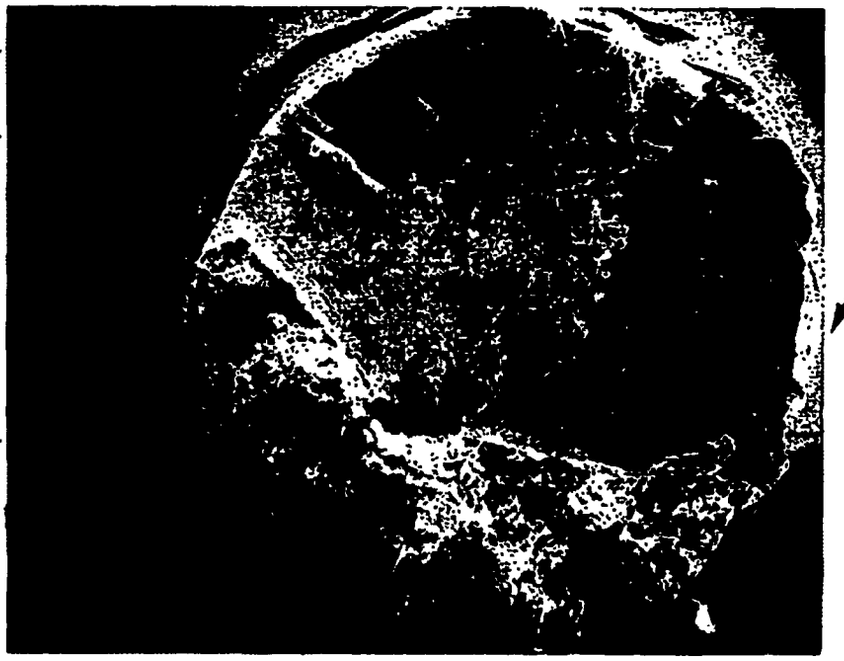
1600x

(D)

8000x

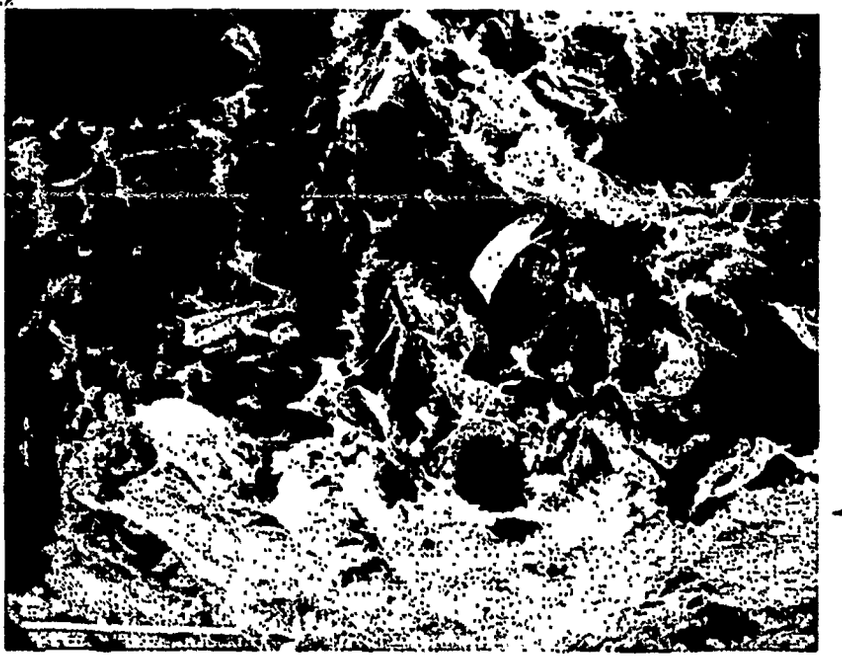
Figure 20. (Cont'd)

(A)



80x

(B)



400x

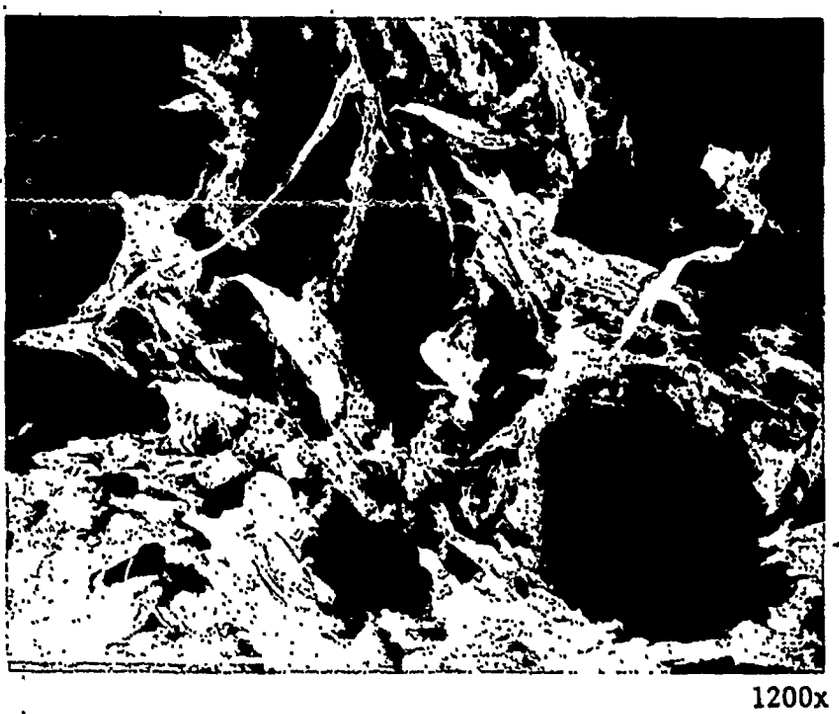
Figure 21. IMR 4350 Single Base Grain Fractured Laterally

Comment: This grain was fractured at room temperature. The arrows indicate the edge of outer grain surface which is graphite coated. Note the orientation of the fibers.

(C)

400x

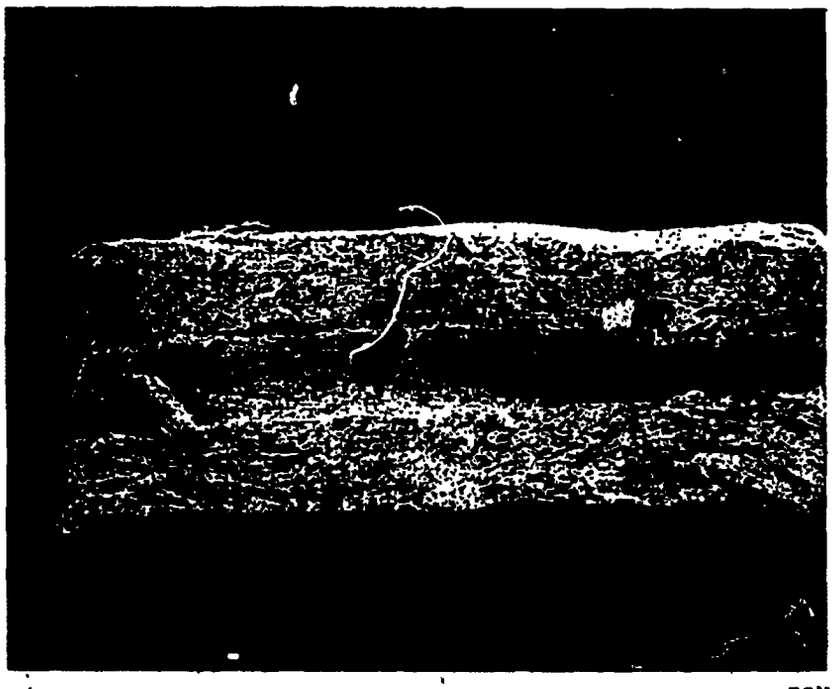
(D)



1200x

Figure 21. (Cont'd)

(A)



30X

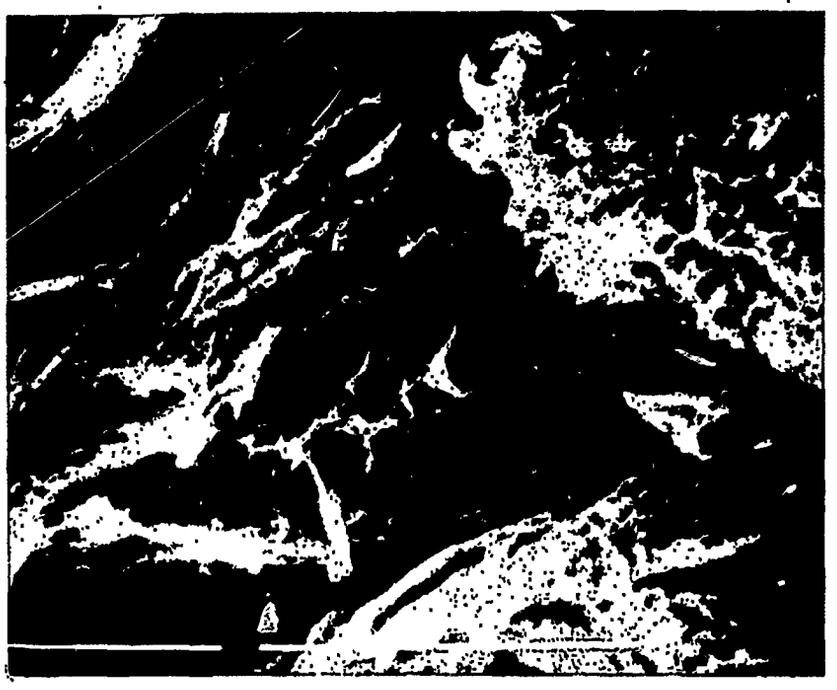
(B)

1600X

Figure 22. M10 Single Base Extruded Grain Fractured Longitudinally

Comment: This grain was fractured at room temperature. Note the similarity of the fibrous morphology with the IMR 4350 propellant.

(C)



8000x

Figure 22. (Cont'd)

(A)

800x

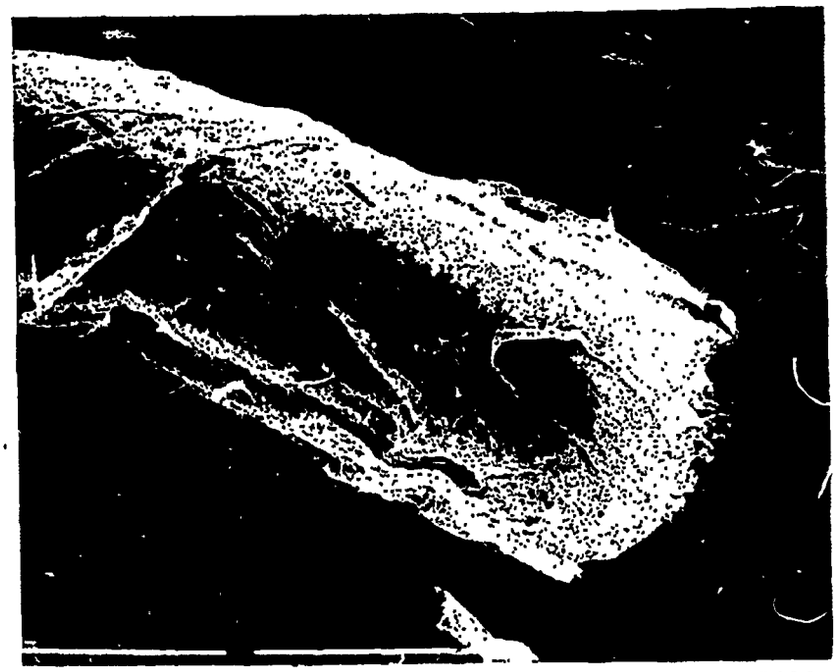
(B)

5600x

Figure 23. M10 Single Base Grain Fractured in Liquid Nitrogen

Comment: This grain was fractured longitudinally while being immersed in liquid nitrogen. Micrographs B, C, and D are higher magnification views of the intact fiber seen in the center region of micrograph A.

(C)



5600x

(D)

8000x

Figure 23. (Cont'd)

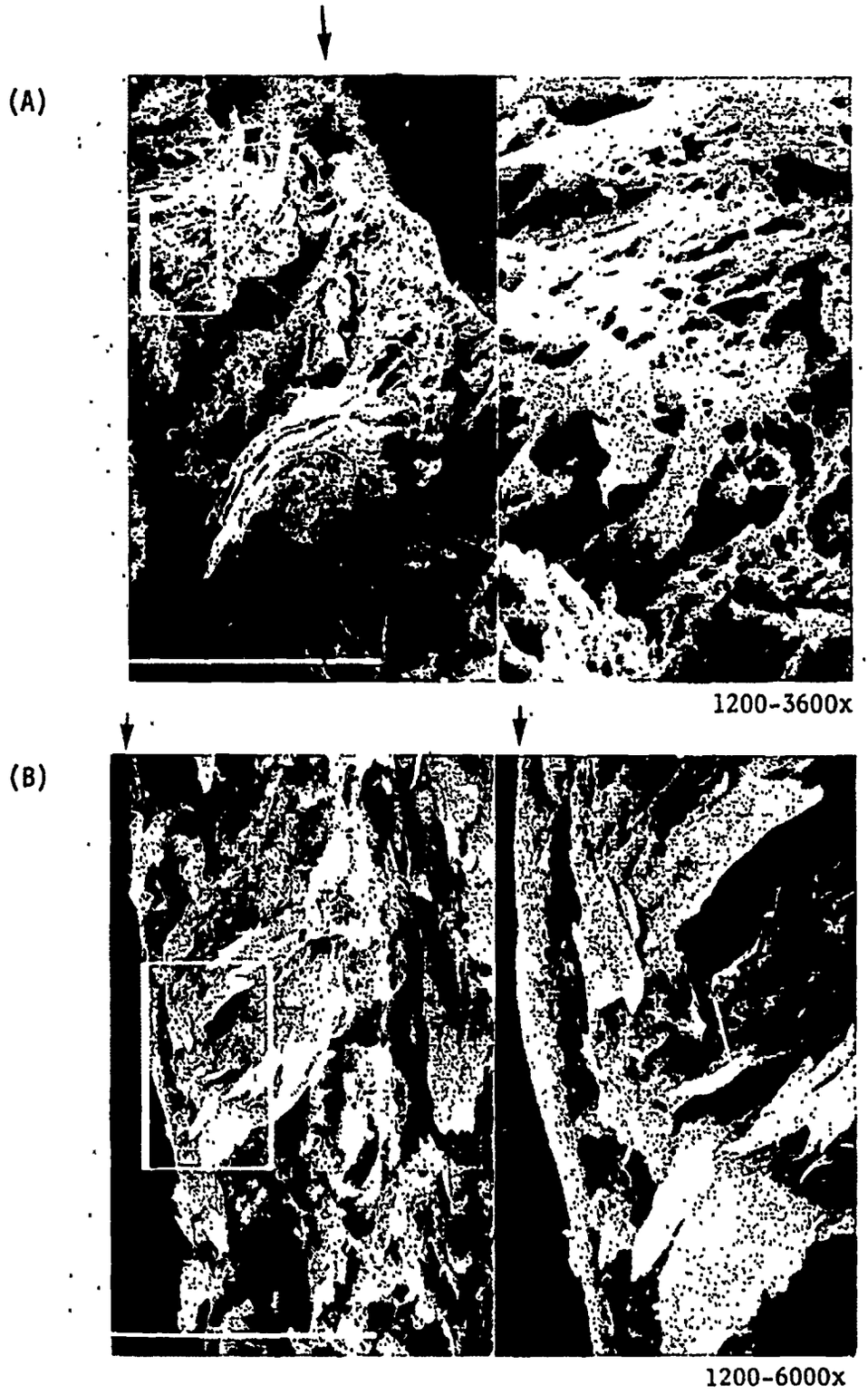



Figure 24. HC25B Extruded Double Base

Comment: These grains were fractured at room temperature. Micrograph A is a longitudinal fracture with the arrow indicating both the direction of extrusion and the outer grain surface. Micrograph B is a lateral fracture with the arrow indicating the edge of the perforation.

(A)

1200x

(B)

4000x

Figure 25. M30A1 Extruded Triple Base Propellant

Comment: These samples were fractured at room temperature. Micrographs A and B are of the same longitudinally fractured grain surface. The graphite coated exterior surface is visible at the top of each micrograph.

(C)

1200-6000x

(D)

2400x

Figure 25. (Cont'd)

Comment: The nitroguanidine needle-like crystals are parallel to the direction of extrusion which is indicated by the arrow. Micrographs C and D are of two different grains fractured laterally.

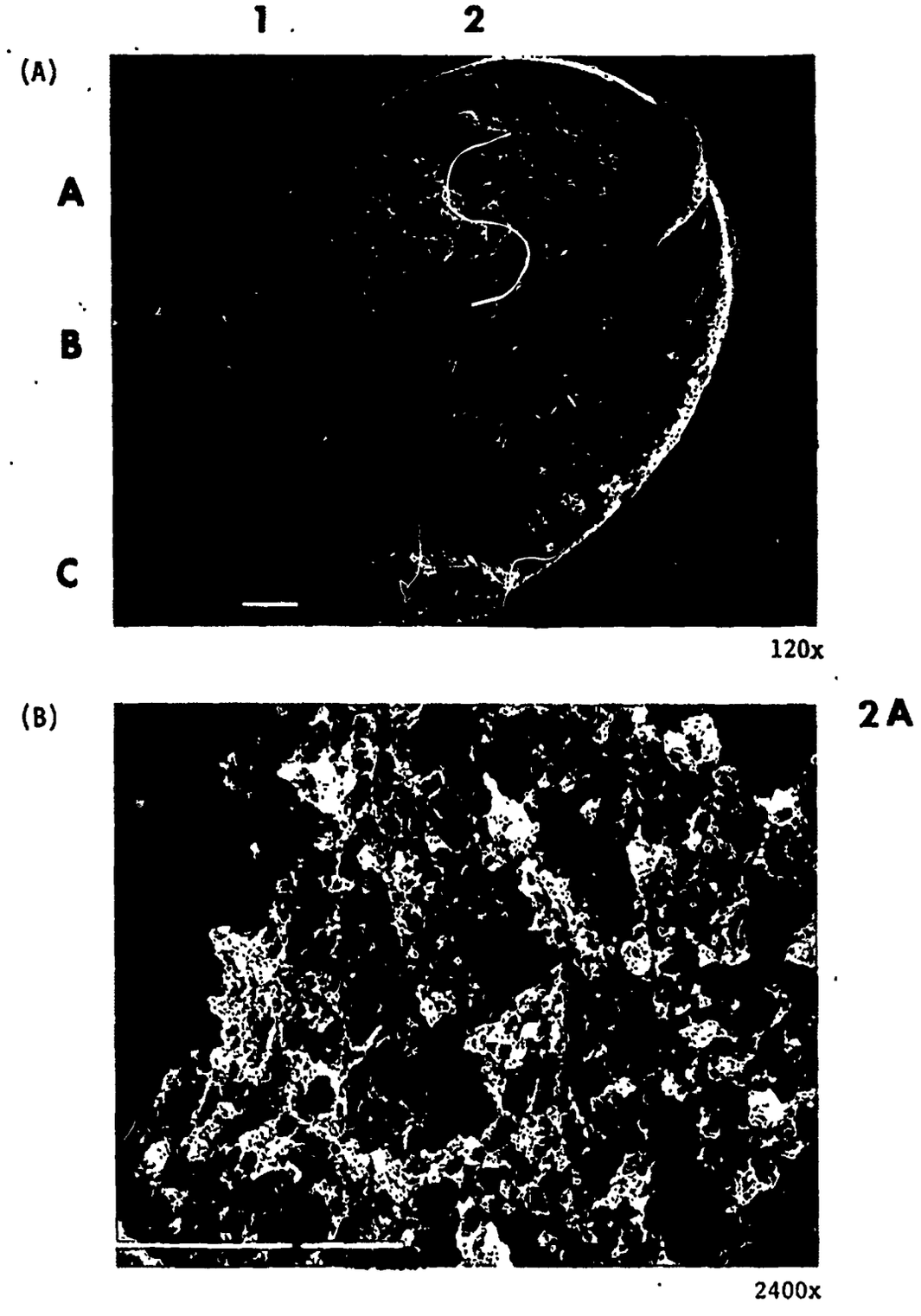
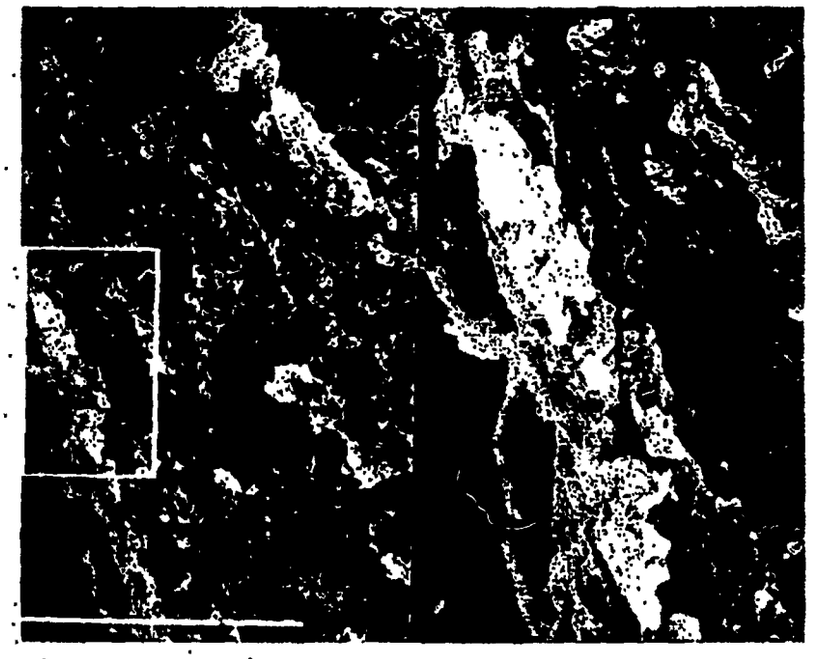



Figure 26. WC870 Double Base Ball Propellant Grain

Comment: All micrographs are of the same grain which was fractured at room temperature. The coordinates on the upper right corner of each micrograph reference the coordinates on micrograph A. Note the wide

(C)



1C

2400-7200X

(D)

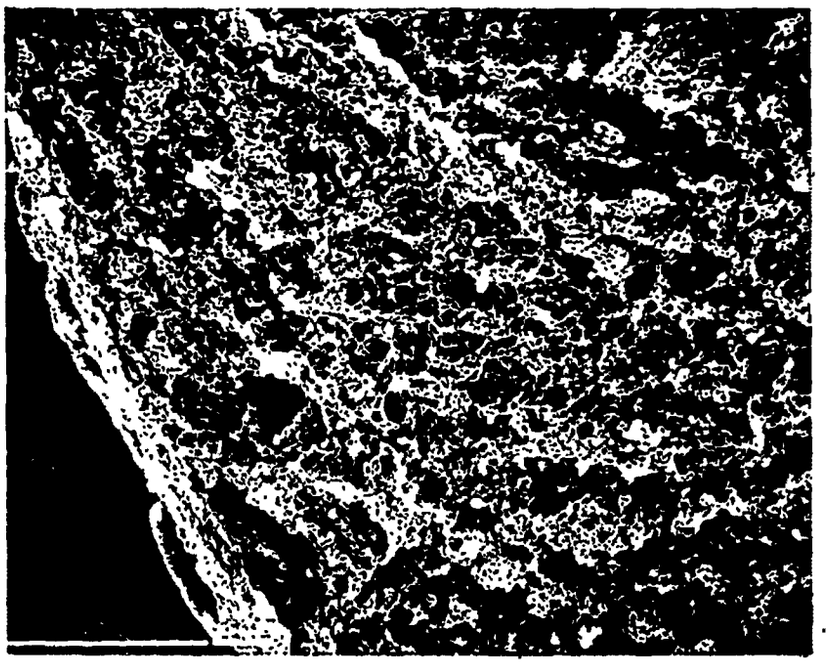
2C

2400-7200X

Figure 26. (Cont'd)

Comment (Cont'd): variety of morphologies present on this typical grain. Also note the lack of any fibrous structures in this propellant type.

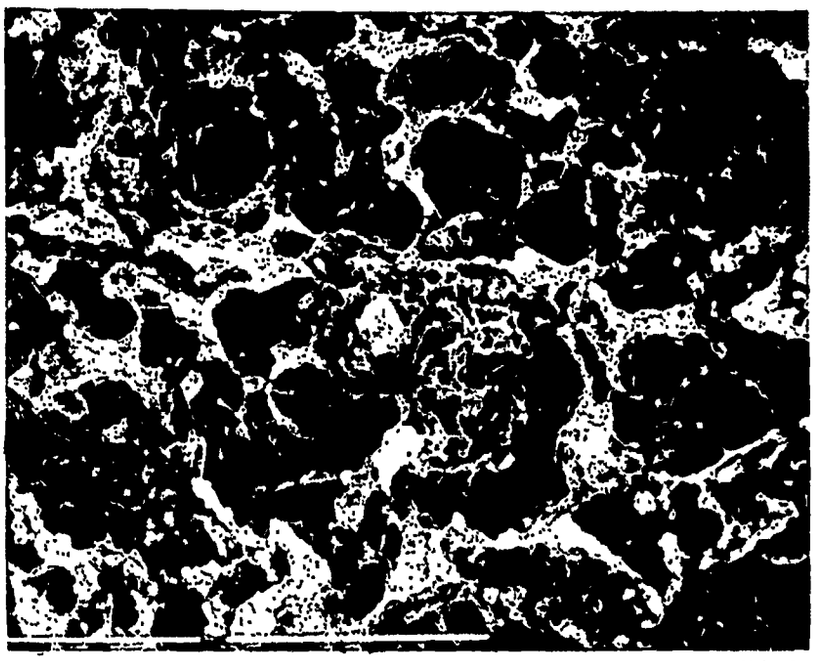
(E)



1B

1200x

(F)



1B

5600x

Figure 26. (Cont'd)

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