April 18, 1969

ASBESTOS REINFORCEMENTS AND FILLERS

Asbestos has been used by the plastics industry in large quantities since the development of phenol-formaldehyde resins in 1909. The longer grades have traditionally been used for reinforcement in the form of fibers, yarns or textiles and the shorter grades as fillers or extenders and, to some extent, for viscosity control. The utility of asbestos has been demonstrated in most types of resins and in myriad applications.

Asbestos, a comparative newcomer in industry, is one of the few important non-metallic minerals that the United States imports from foreign sources. Less than 10 per cent of our annual requirement is currently produced from domestic deposits while the remainder is imported largely from Canada. Since 1960, however, domestic production has been increasing rapidly with an estimated 1968 production valued at over 6 million dollars.

The name asbestos is a broad, commercial term that has been applied to a number of natural fibrous silicate minerals. They are all incombustible and can be separated by mechanical or chemical means into fibers of various lengths and thicknesses, but differ in chemical composition and other properties.

The low cost, exceptional mechanical properties, and resistance to heat of asbestos account for much of the growth of its use in plastic-asbestos products. It has recently been recognized that the asbestos unit fibril is a naturally occurring "whisker," i.e. an inorganic crystal grown under controlled pressures and temperature. Because of its

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high strength, stiffness, and aspect ratio, the asbestos fibril is an excellent whisker reinforcement. Maximum utilization of its desirable reinforcing characteristics requires a high degree of fibril liberation and the absence of extraneous gangue material.

Asbestos research is expanding the variety of products available with a strong trend to more highly refined fiber with higher standards of quality control. High performance, chemically modified asbestos products with altered surface properties are now in the market place. The industry is working to keep pace with the increasing sophistication of the plastics industry. Chemically "designed" asbestos products will be part of custom engineered plastic systems of the future.

THE ASBESTOS MINERALS

The six generally recognized varieties of asbestos include the fibrous form of serpentine, known as chrysotile, and five minerals of the amphibole group, anthophyllite, crocidolite, actinolite, tremolite, and amosite. Comparative properties of the asbestos minerals are shown in Table I.

Chrysotile

Chrysotile is the most plentiful and useful form of asbestos. Of the more than two billion pounds of asbestos used each year by the plastics industry, over 90 per cent is chrysotile. Its positive surface charge, softness and flexibility, and its low refractive index sets it apart from other asbestos. Chrysotile fiber diameters, less than 0.03 micron, are the smallest of any other commonly known fiber, as illustrated in Table II. It has exceptional mechanical strength, as

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shown in Table I. On these distinguishing characteristics most of the uses for chrysotile depend.

The crystal structure of chrysotile is similar to that of the kaolinite minerals consisting of alternate layers of tetrahedrally co-ordinated silica and octahedrally co-ordinated magnesiun hydroxide joined into a composite sheet. The outer surface of the chrysotile fibril, essentially magnesium hydroxide, is similar to the mineral brucite. Figure 1 is a representation of this structure showing the hydroxyl outer surface of the fibril. The magnesium hydroxide surface of chrysotile with its resultant cationic charge, determines its chemical affinity for many resin systems.

Because of a mismatch of the brucite and silica layers within the chrysotile structure, curved composite sheets are formed, resulting in closed cylinders of extreme length-to-diameter ratio (often as high as 1000:1). Evidence for the cylindrical structure of chrysotile has been obtained from X-ray and electron diffraction studies, and from electron micrographs. Recent high resolution electron microscopic studies in Japan have shown an average O.D. of the chrysotile fiber to be about 250 Å with an I.D. of about 140 Å. ~~Figure 2 is an electron micrograph showing the lattice image of sectioned chrysotile observed perpendicular to the fiber~~ axis. ~~The multi-spiral structure of the fiber and its hollow center~~ are ~~clearly visible~~.

Chrysotile occurs only in serpentinite rock bodies, most commonly as cross-fiber veins. These cross fibers, an electron micrograph of which is shown in Figure 3, vary in length up to two inches which are usually shortened during processing. In most mining operations

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with ore containing less than 15% asbestos, the fiber must be separated from its host rock by crushing and milling with subsequent grading. Chrysotile is graded by a Quebec standard according to fiber length, from the longest, Grade 3, to Grade 7 which is the shortest. The recent exploitation of short fiber chrysotile from a massive, matted, New Idria deposit in California, believed to be the largest in the Free World, is due to its unusual morphology, as shown in Figure 4. This deposit consists mainly of randomly oriented fibrils, most of which are in point contact with their neighbor, and fiber yields commonly exceed 50 per cent. Fiber purification is accomplished by conventional dry milling techniques as well as by newly developed hydraulic processes. Figures 5 and 6 show the fibril liberation possible through pneumatic and hydraulic processing, respectively. The high purity, colloidal fiber products, represented by Figure 6 resulting from hydraulic milling, are one example of the trend in the asbestos industry toward controlled, higher purity products.

Recently, commercial products based on chrysotile have been introduced which, by chemical modifications of the normal chrysotile fiber, have novel surface properties. These materials are used mainly for viscosity control in anti-sag and thixotropic applications.

The Amphiboles

Compared to chrysotile, the amphibole fibers are larger in cross section, harsh and hard. The amphibole asbestos minerals are anionic in surface charge and are more resistant to acids than chrysotile.

Anthophyllite fibers usually occur as fibrous masses containing randomly oriented cubic blocks of fiber up to 1 inch in length.

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They are generally used in insulating materials, as filtering media and as fillers in plastics, paints, and asbestos-cement products. Asbestos-reinforced polypropylene utilizes anthophyllite almost exclusively.

Crocidolite, or blue asbestos, is found principally in the Republic of South Africa. It is needle-like in structure and has exceptionally high mechanical strength. It is used in plastics where its pronounced color is not detrimental.

Tremolite and actinolite are very similar, except for the higher iron content of the latter. Both are in relatively short supply and are used mainly as filter media or fillers. Amosite is a yellowish-brown, long fiber which is harsh and brittle and is used mainly in thermal insulation.

THERMOPLASTICS

The largest single use for asbestos in thermoplastics is in vinyl-asbestos floor tile. It is also used in numerous sealants and mastics for the automotive and construction industries in compounds based on butyl rubber, vinyl plastisols, and asphalt. The volume of thermoplastic molding compounds, such as polypropylene, nylon, rigid PVC, and linear polyethylene, containing asbestos is steadily growing.

Short fiber chrysotile is incorporated into vinyl asbestos floor tile to improve heat resistance and dimensional stability.

Since 1965, the consumption of asbestos-reinforced polypropylene by the automotive industry has increased rapidly. This trend toward the use of short fiber products for reinforcement is dependent on the inherent strength and fibril geometry of asbestos. Table III shows the

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Increased stiffness, heat resistance and other properties of polypropylene containing 40% anthophyllite. Lowering the asbestos content to 20% is said to double or triple impact strength, improve stability and gloss while sacrificing only 25% in flexural modulus and 25°F in heat distortion temperature.

More recently, several manufacturers have introduced asbestos-reinforced nylon and polyolefin molding compounds. The mechanical and electrical properties of several nylon compounds containing 30% chrysotile are also shown in Table III. The performance of colloidal grades of chrysotile in this application is illustrative of the type of whisker reinforcement which occurs through optimum natural affinity of the fiber and the polymer matrix. High levels of reinforcement can be attained also in resins lacking this affinity by using high purity colloidal chrysotile and technology to improve fiber wetting and fiber dispersion. Recently disclosed "ceraplast" products, for example, exhibit threefold increases in tensile strength and modulus with 40 % asbestos in linear polyethylene. The fineness of chrysotile fibers permits dense structures with maximum resin fiber adhesion enhanced by the high surface area, ca. 60 $m^2/g.$, of the asbestos. An extension of this technology is reported to produce a number of products useful when transparency or translucency is desired in the composite. Transparent resins such as vinyls and ionomers can, in many cases, be reinforced with little loss in clarity since the diameter of colloidal asbestos is well under the wavelength of visible light. A photograph illustrating the clarity obtainable in a rigid PVC is shown in Figure 7. The reinforced material is reported to be improved in toughness and heat and fire resistance.

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The volume of short fiber chrysotile used in mastics, sealants, and adhesives of various types is increasing. From 5 to 60 per cent asbestos is used in adhesives to reduce crazing, shrinkage, and embrittlement. It also reduces cost, increases bulk, provides controlled penetration and resistance to heat in such adhesives as phenolics, urea, resorcinol, epoxy, nitrile, and reclaimed rubber, and silicates. In mastics and sealants, asbestos provides toughness, flow and penetration control, and reduced cost. The colloidal grades of chrysotile are reported to contribute additional performance and handling improvements to this type of product.

THERMOSETS

Asbestos filled or reinforced plastic products originated with phenolic molding compounds. However, these materials now include virtuall every type of thermosetting resin, including urea-formaldehyde, melamines, furanes, epoxies, polyesters, and silicones. Asbestos shorts and floats are used in molding compounds to produce desirable molding characteristics, good surface finish, and improved physical properties in the molded piece which may be employed as electrical insulation, heat insulation, or brake and clutch facings.

The amount of asbestos needed varies with the particular resin system and the fiber length and degree of openness of the asbestos. Each system has an optimum level for maximum mechanical strength. For example, in phenolics about 25% is typical for asbestos floats or as low as 5% colloidal chrysotile. This level may vary up to 60%, however, depending on the levels of chemical, thermal and impact resistance, and the electrical properties desired. Asbestos-filled phenolic and urea-formaldehyde resins are used in many electrical applications where heat resistance is also required. Asbestos-filled polyester and

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diallylphthalate compounds are also used in electrical applications. The asbestos-containing compounds offer the capability of molding with exceptional accuracy, ease of molding in metal inserts and the mass production of intricate shapes difficult to fabricate from other dielectric materials.

Polyester premixes, used to fabricate automotive parts, tractor and marine engine housings, and materials handling bins and containers, often employ short fiber chrysotile to provide flow control, improved surface appearances, reduced shrinkage, and low cost. The new low profile systems utilize asbestos for controlled shrinkage, improved mechanical strength, and heat resistance.

Phenolic-asbestos laminates used for rocket flame tubes are one example of the increased demand for asbestos-reinforced systems brought about by the requirements of the space age for heat, chemical, and shock resistance.

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TABLE I. COMPARATIVE PROPERTIES OF ASBESTOS MINERALS

Property	Chrysotile	Anthophyllite	Crocidolite	Actinolite	Tremolite	Amosite
Composition	$Mg_3Si_2O_5(OH)_4$	$Mg_7Si_8O_{22}(OH)_2$	$Na_2Fe_3Fe_2Si_8O_{22}(OH)_2$	$Ca_2Fe_5Si_8O_{22}(OH)_2$	$Mg_5Ca_2Si_8O_{22}(OH)_2$	$(Fe,Mg)_7Si_8O_{22}(OH)_2$
Crystal Habit	Fine, easily separable fibers	Prismatic crystals and fibers	Long brittle fibers	Prismatic crystals and fibers	Prismatic crystals and fibers	Prismatic crystals and fibers
Veining	Cross-, Slip-, & Massive-fiber	Slip- & Massive-fiber	Cross-fiber	Slip- & Massive-fiber	Slip- & Massive-fiber	Cross-fiber
Color	White, gray, green	Gray-white	Blue	Green	White, gray-white, green	Ash gray or brown
Luster	Silky	Vitreous to pearly	Silky to dull	Silky	Silky	Vitreous to pearly
Texture	Soft to harsh, also silky	Harsh	Soft to harsh	Harsh	Harsh	Harsh
Flexibility	Very good	Poor	Good	Poor	Poor	Good
Hardness	2.5-4	5.5-6	4	6	5.5	5.5-6
Fiber diameter, Å	~~180-200~~ 200-400	600-900	600-900	600-900	600-900	600-900
Tensile Strength, psi	~~281,000-436,000~~ 300,000-500,000	<4,000	400,000-600,000	<4,000	1,000-8,000	100,000-200,000
Modulus of Elasticity, psi	~~23.3~~ 23 x 10^6	-	~~27.1~~ 27 x 10^6	-	-	~~23.6~~ 24 x 10^6
Specific heat, Btu/lb,°F	0.266	0.210	0.201	0.217	0.212	0.193
Specific Gravity	2.4-2.6	2.8-3.1	3.2-3.3	3.0-3.2	2.9-3.2	3.1-3.3
Refractive Index (mean)	1.51-1.55	1.61	1.7	1.63	1.61	1.64
pH	9.5-10.3	9.4	9.1	9.5	9.5	9.1
Electric Charge in aqueous slurry	Positive	Negative	Negative	Negative	Negative	Negative
Resistance to Acids	Poor	Very good	Good	Fair	Good	Good

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TABLE III

PHYSICAL PROPERTIES OF ASBESTOS REINFORCED THERMOPLASTICS

	Polypropylene		Nylon (with 30% Asbestos)		
	Base Resin	40% Asbestos	Nylon 6	Nylon 6/10	Nylon 6
Tensile Strength, psi x 10^{-3}	5.0	4.8	20.0	14.0	20.0
Ultimate Elongation, %	200	5	-	-	-
Flexural Strength, psi x 10^{-3}	-	-	30.0	21.0	30.0
Flexural Modulus, psi x 10^{-6}	0.18	0.65	1.5	1.2	1.5
Izod Impact, ft.lb./in.					
Notched	0.4	0.5	0.9	0.8	0.8
Unnotched	-	-	13	14	12
Heat Deflection Temp., °F					
66 psi	230	290	-	-	-
264 psi	-	-	385	340	465
Deformation Under Load, 24 hr. @ 2000 psi, 122°F., %	3.5	1.6			
Specific Gravity	0.91	1.24			
Water Absorption, 24 hr., %	<0.01	0.02			
Coef. of Lin. Thermal Exp. 10^{-5} in./in./°F	3.8	2.1			
Mold Shrinkage, in./in.	0.015	0.01			
Dielectric Strength, S/T, VPM	650	450	450	450	450
Volume Resistivity, ohms/cm.	1.0×10^{17}	1.5×10^{15}	6.9×10^{11}	9.6×10^{12}	7.6×10
Arc Resistance, sec.	136	121	127	123	126
Dielectric Constant, @ 60 Hz	2.2	2.75	4.3	4.0	4.1
10^6 Hz	2.2	2.6	3.5	3.3	3.5
Dissipation Factor, @ 60 Hz	0.0002	0.007	0.053	0.031	0.03
10^6 Hz	0.0002	0.002	0.019	0.018	0.01

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FIG. I.

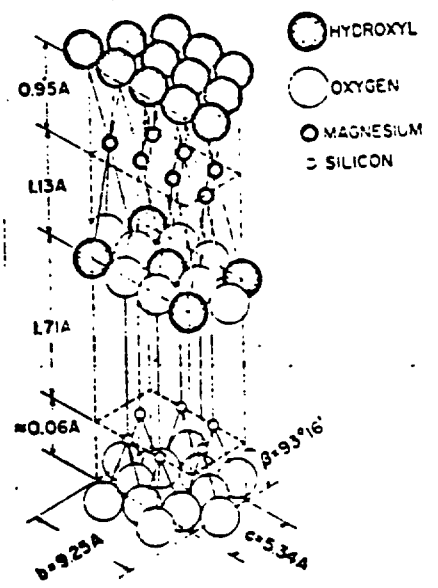


Fig. 1. Chrysotile structure (after Whittaker)

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FIG II

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ACTA CRYSTALLOGRAPHICA, VOL. 23, 1967—YADA
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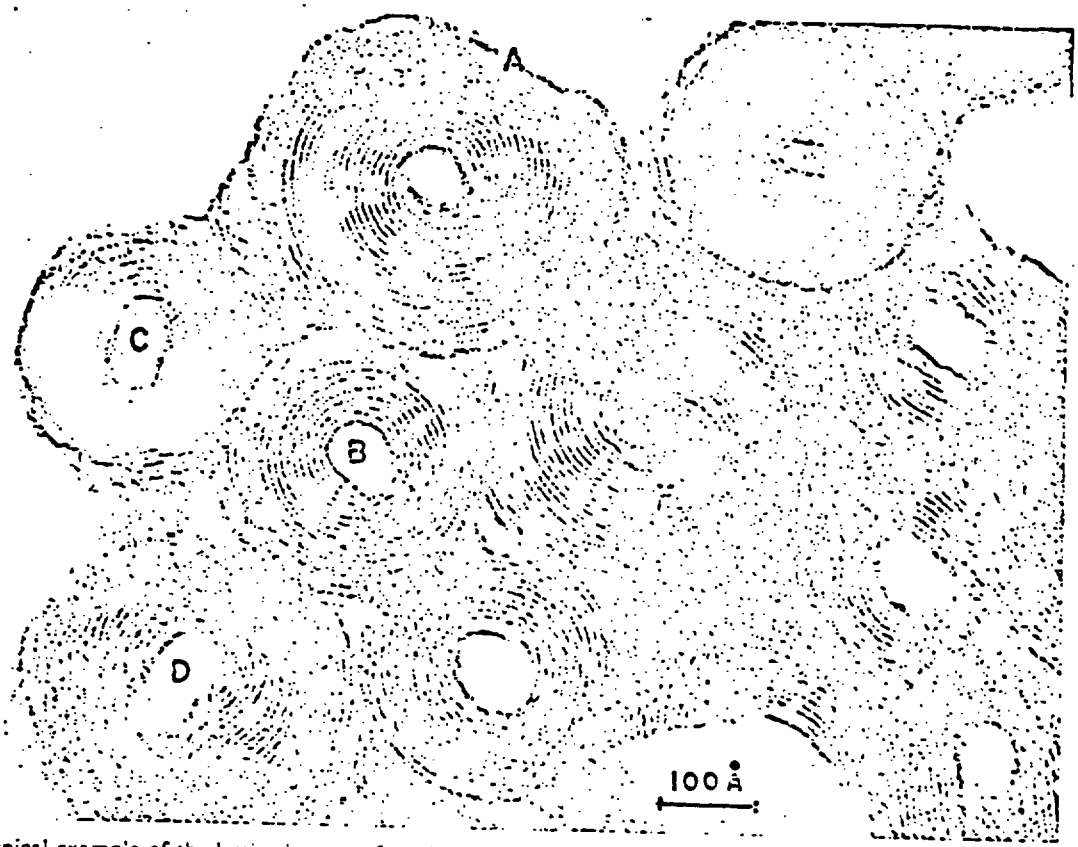


Fig. 7. A typical example of the lattice images of sectioned chrysotile observed from the direction parallel to the fiber axis.

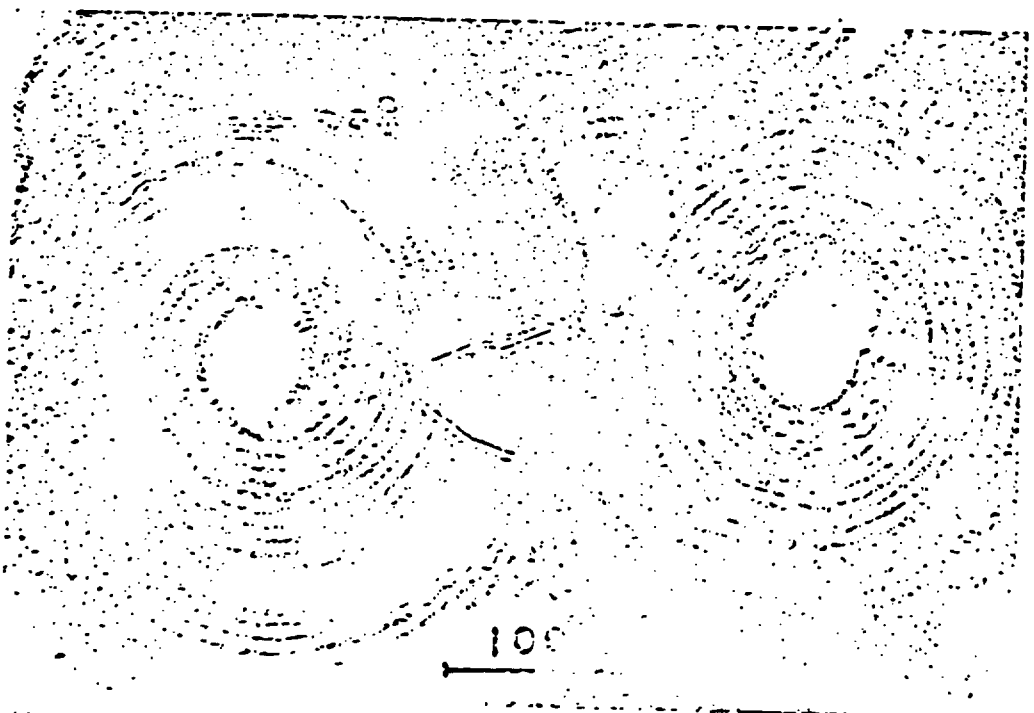
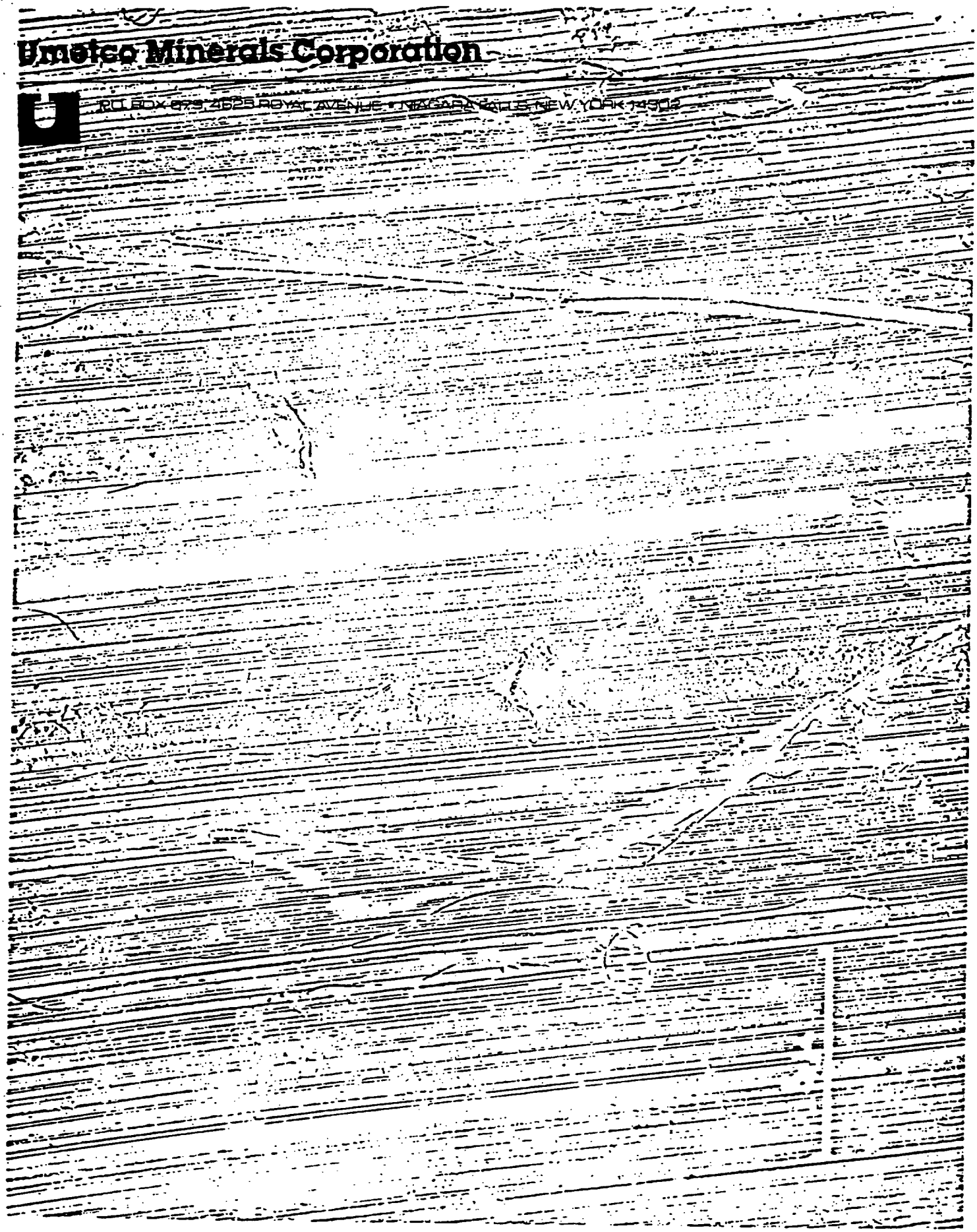


Fig. 8. Enlarged image of Fig. 7 (crystallites *A*, *B*) showing two kinds of fringe systems of the circumferential (001) and the radial (020) planes.

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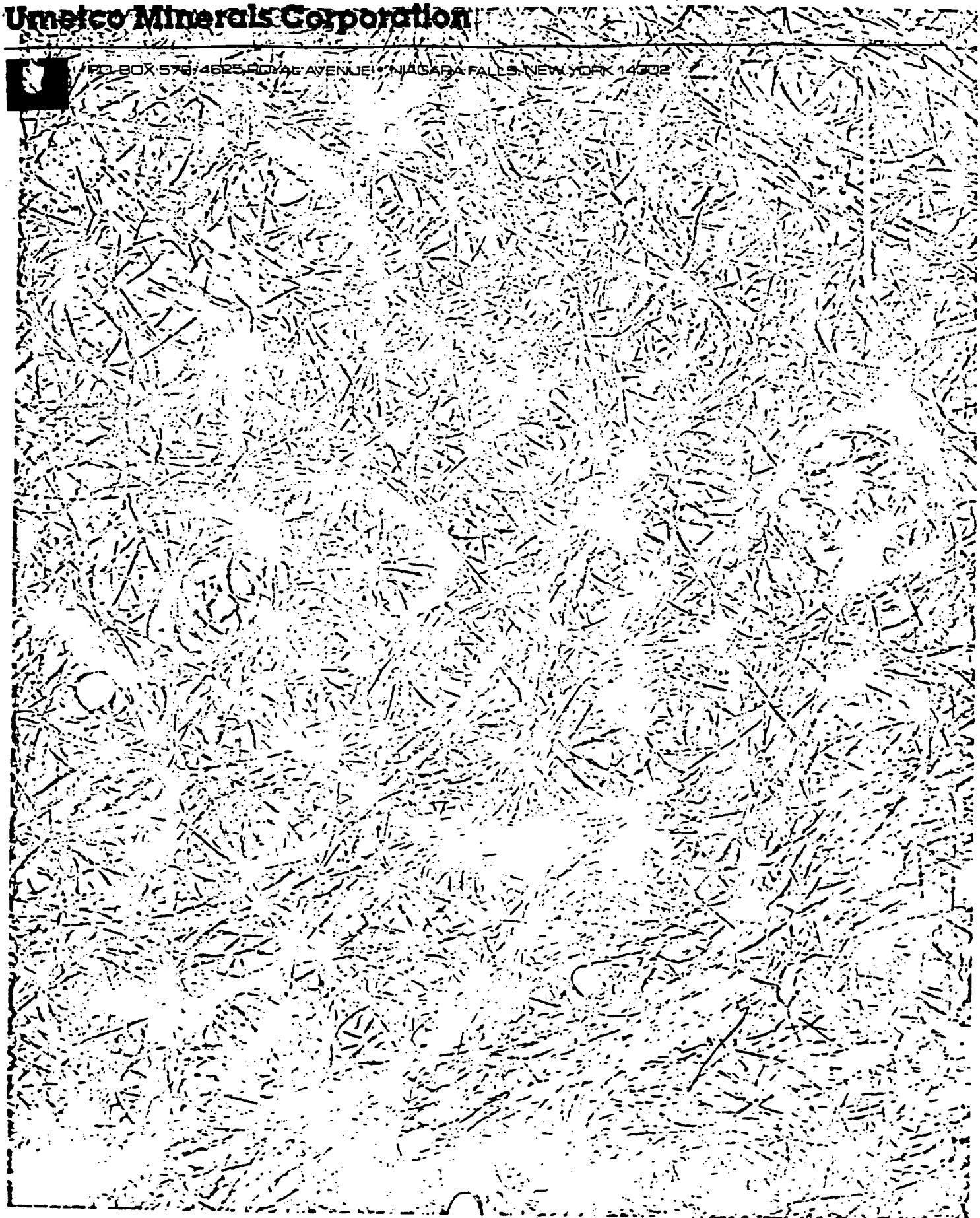


Electron Micro[illegible] structure.

A10941 Electron Micrograph of typical cross-fiber chrysotile showing the tubular structure

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Electron Micrograph of typical Canadian asbestos fibers

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showing the morphology of a fibrous chrysotile from the

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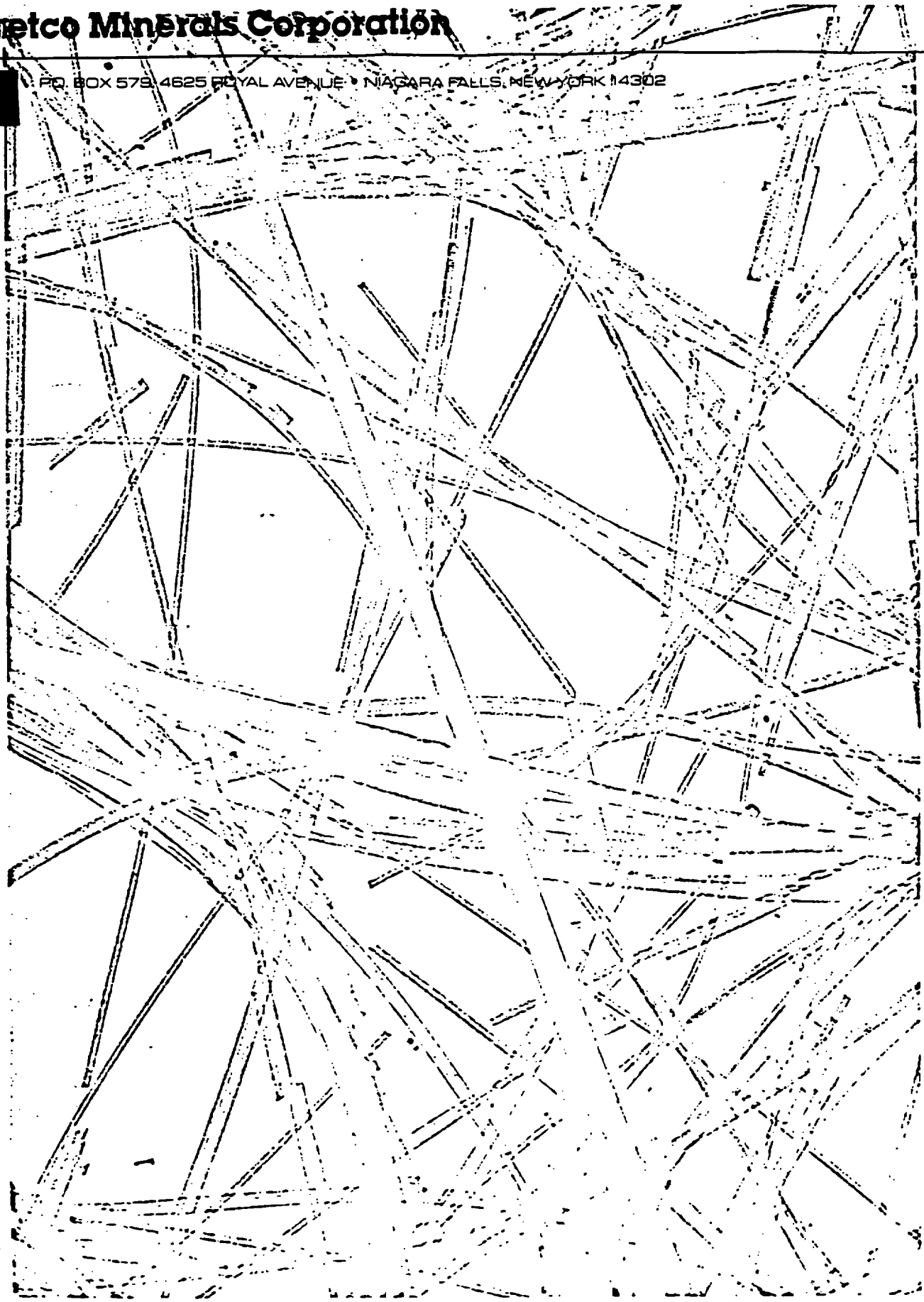
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A 1 0 3 Electron Micrograph of dry processed asbestos fibers

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Electron Micrograph of wet processed [illegible] asbestos fibrils

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