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Asbestos Minerals in Modern Technology

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Asbestos is a generic term for a variety of hydrated silicate minerals which have one common attribute, namely, the ability to be separated into relatively soft, silky fibers. Although the name is ordinarily associated with those varieties which have technologic importance, it is applicable to all minerals which fit the above description. The term "asbestiform minerals" is perhaps most descriptive.

The known varieties of asbestiform minerals can be divided into two main classes on the basis of their crystal structures: serpentine and amphiboles. The sole member of the serpentine class is chrysotile asbestos, which is by far the most common of the asbestiform minerals. It accounts for more than 95% of the asbestos fiber produced today.

There are five recognized asbestiform varieties of amphibole: crocidolite, amosite, anthophyllite, tremolite, and actinolite. Although the amphiboles are common rock-forming minerals, the asbestiform varieties are much less abundant than chrysotile.

The physical and chemical properties of the asbestiform minerals can be directly related to their crystal structure and chemical composition. In turn, the physical and chemical properties are responsible for the commercial importance of asbestos. It is understandable, therefore, that great emphasis has been placed on the elucidation of the structure and composition of these important minerals.

Several comprehensive reviews on the asbestiform minerals have been published in recent years, including Hendry (30), Gaze (25), Hodgson (33), and Deer, Howie, and Zussman (17). The objective of this paper is to bring this information up to date with particular emphasis on recent developments concerning the physics and chemistry of the asbestiform minerals. In addition, the uses of asbestos will be discussed briefly in relation to the properties of the individual species.

OCCURRENCE

The epigenesis and occurrence of the asbestiform minerals have been the subject of considerable geologic and petrologic research. Chrysotile and amphibole fibers are found in entirely different geologic formations. Chrysotile was most probably formed as a result of two separate metamorphic changes in ultrabasic rocks of volcanic origin. The first stage involved the formation of serpentine by the hydrothermal alteration of the original rock. At some later time the chrysotile was formed in cracks and fissures in the rock by recrystallization of the serpentine, again by an aqueous solution and reprecipitation proc-

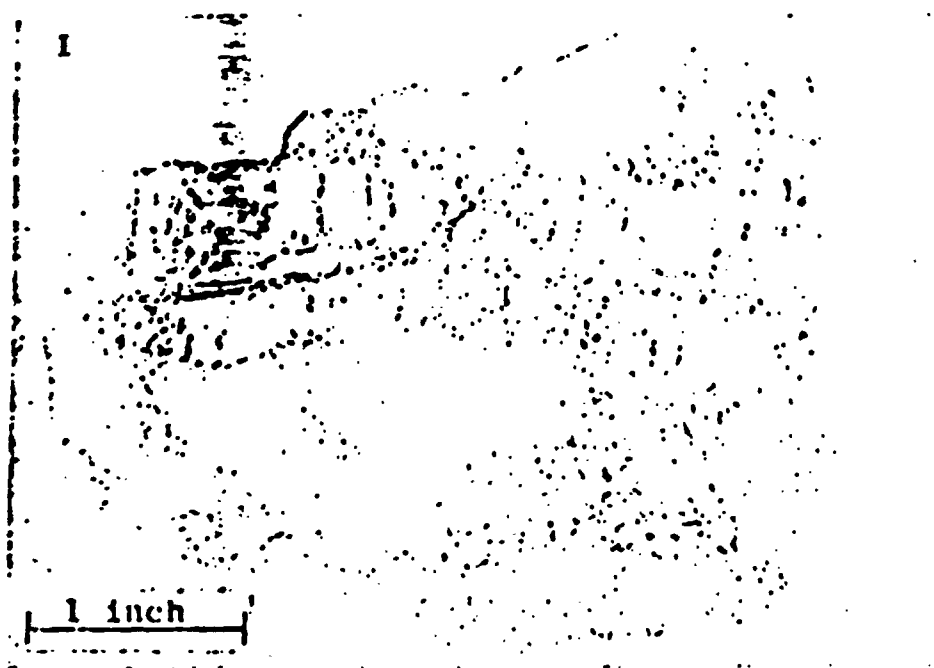


FIG. 1. Cross vein fiber chrysotile.

ess. In most cases, chrysotile occurs as "cross fibers" which are oriented in a parallel array across the veins in the serpentine rock as shown in Fig. 1. Occasional occurrences of "slip fiber" are found in which the fiber is oriented parallel to the vein as shown in Fig. 2.

A notable exception to the normal mode of occurrence of chrysotile is the fiber found in the New Idria serpentinite of Western California and at Stragari, Yugoslavia (15). The New Idria fiber is generally referred to as Coalinga fiber. The great bulk of this deposit consists of soft powdery pellet-like agglomerates of chrysotile as shown in Fig. 3. The material may be the result of intensive

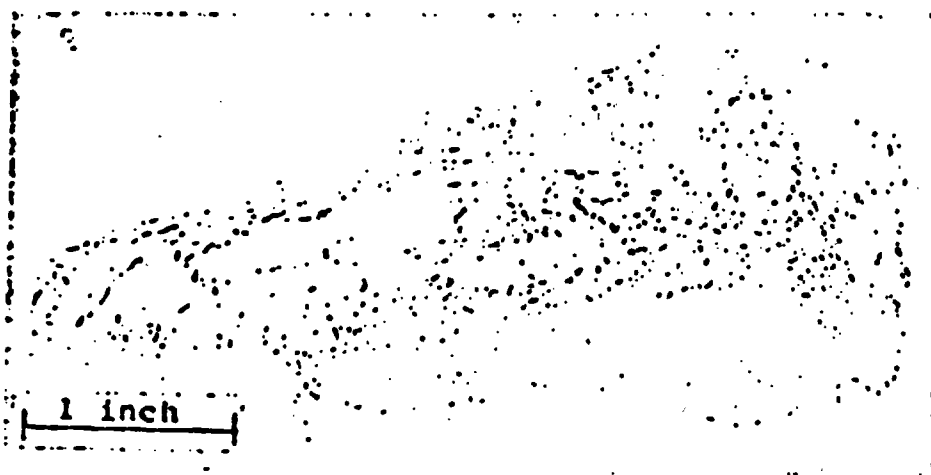


FIG. 2. Slip fiber chrysotile.

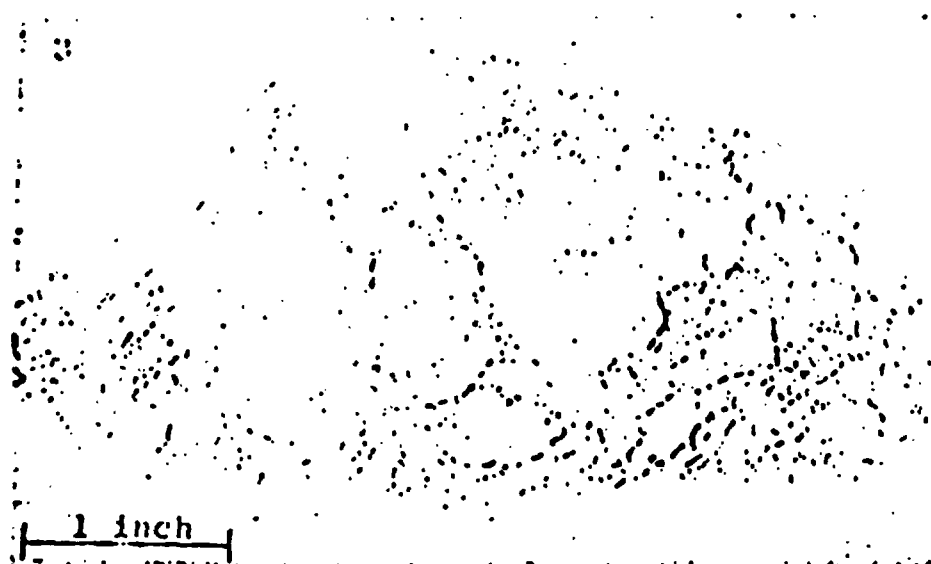


FIG. 3. Nodules of coalinga chrysotile.

crushing and pulverization during or after serpentinization. In addition to its unusual mode of occurrence, Coalinga chrysotile is also unusual from the standpoint of its physical structure. This feature will be discussed in the appropriate section of this paper.

The genesis of the amphibole fibers is not as clear-cut as that of chrysotile. Their name, taken from the Greek word *am, hiholos*, meaning ambiguous, is a very apt choice. Figure 4 is a typical example of the mode of occurrence for crocidolite which is found in the banded ironstones of the Transvaal system of



FIG. 4. Crocidolite in banded ironstones.

South Africa. They are metamorphosed rocks of sedimentary origin, which accounts for the variability in composition of the host rocks and consequently of the fiber. The only significant occurrence of amphibole is also found in this area. Crocidolite is found in other areas, including Bolivia and Western Australia.

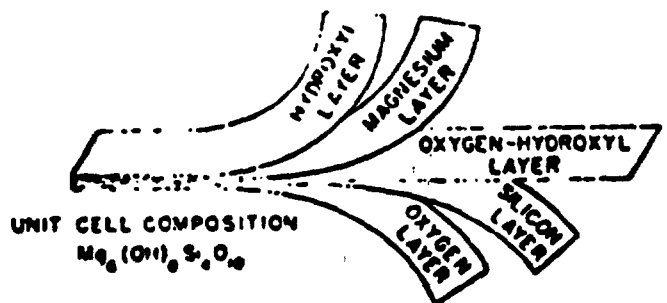
Asbestiform anthophyllite is found in many places throughout the world, but there are only a few deposits of commercial importance in Finland and the United States. Tremolite and actinolite are the result of metamorphism of carbonate rocks. They are widely distributed in nature, but of little commercial significance. Tremolite is a very common contaminant of commercial talc.

CRYSTAL STRUCTURE

Chrysotile

The crystal structure of chrysotile asbestos was first determined by Warren and Bragg (72) and later elucidated by Warren and Herring (69). These investigators determined that the mineral has a layered-type structure similar to the minerals of the kaolinite group. The basis of the structure is an infinite silica sheet (Si_2O_5)_n in which all the silica tetrahedra are pointing in the same direction. Attached to one side of this sheet is a brucite $\text{Mg}(\text{OH})_2$ layer in which two out of every three hydroxyls are replaced by the apical oxygens of the silica tetrahedra. The result is a double sheet as shown in Fig. 5. The mismatch in the dimensions of the silica and brucite sheets introduces a strain in the structure. Better matching of the layers and relief of the strain can be accomplished in three ways.

1. Substitution of larger ions in the silica sheet or smaller ions in the brucite sheet.
2. Distortion of the octahedral brucite network or of the tetrahedral silica network.
3. Curvature of the sheet with the brucite layer on the outer surface.



BUILD-UP OF SHEETS INTO FUNDAMENTAL FIBRILS

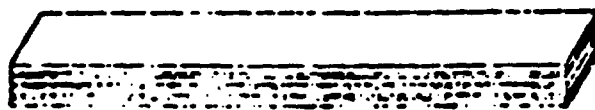


FIG. 5. Fundamental sheet of chrysotile.

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Ever since the first electron micrographs were published showing the apparent tubular structure of chrysotile (7, 50, 70), there has been considerable controversy over the morphology of the fibers. Whittaker (70), by means of careful X-ray diffraction studies, demonstrated that the lattice was definitely curved.

Although he was unable to show whether the structure was a cylindrical arc, a closed circular cylinder, or a cylindrical spiral, he favored a spiral structure. The tubular concept was supported further when Maser, Rice, and Klug (44) published the electron micrograph of Fig. 6 showing an end-on view of a chrysotile fiber bundle. The fibrils were definitely cylindrical and included many which appeared to be pairs of concentric cylinders.



FIG. 6. Electron micrograph of chrysotile cross section. $\times 195,000$. Reprinted with permission from *American Mineralogist* 43, 650 (1960).

A recent paper by Yada (51) has furnished what appears to be the final answer to the structure of chrysotile fibrils. By means of high resolution electron microscopy, he was able to observe the actual crystal lattice planes both parallel and perpendicular to the fiber axis. These pictures, Figs. 7 and 8, show that most of the fibers have a hollow cylindrical form. The lattice planes have a multispiral arrangement confirming the prediction of Whittaker (70). Also apparent in several of Yada's pictures is the presence of crystallographic dislocations which strongly suggest that the basic structural unit consists of a single magnesia-silica sheet, rather than a double sheet as previously postulated by most authors. Yada's observations also confirm Whittaker's hypothesis that the basic spiral element consists of five silica magnesia units with approximately 10 silica-magnesia units forming the 70 Å wall of a single fibril.

Occasional fibers were observed which were solid rather than hollow. At

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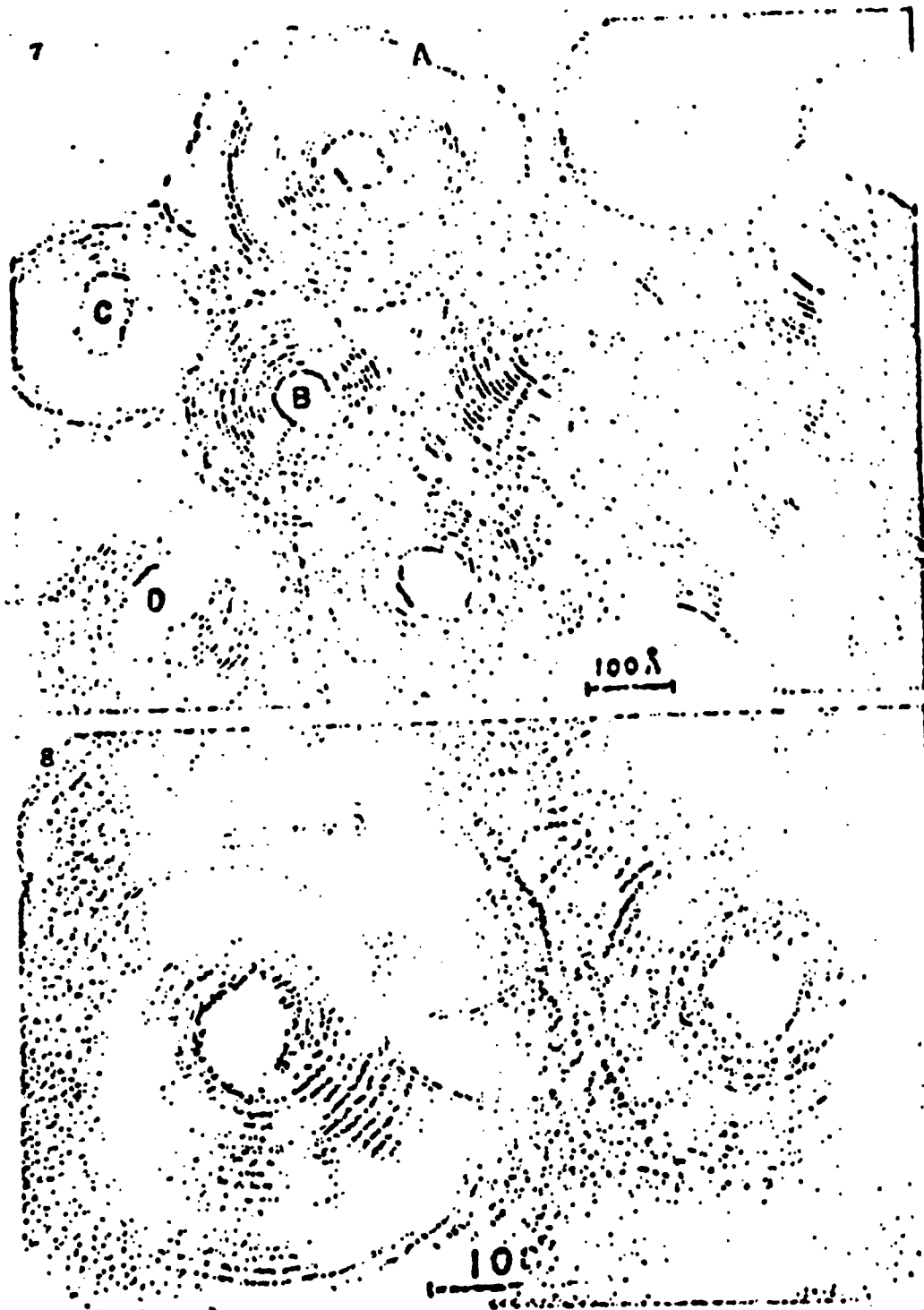


FIG. 7 and FIG. 8. High resolution electron micrographs of chrysotile. Reprinted with permission from *Acta Cryst.* 23, 701 (1967).

TABLE I
CHEMICAL COMPOSITION OF CHRYSOTILES*

	Chrysotiles					Lizardite	Antigorite
	Jeffrey Mine (59) Adirondack, Quebec	New Idria, California (Coolings) (59)	Arizona (32)	Africa (32) Transvaal	Russland (18)	Aboutville, New York (32)	Cecil County, Maryland (32)
SiO ₂	44.1	38.4	41.07	41.83	42.59	41.80	44.50
MgO	41.6	29.9	42.35	41.39	41.48	42.67	41.36
FeO	0.92	1.1	0.42	1.29	4.01	0.93	0.09
CaO	0.80	2.4	9.14	0.08	—	0.06	0.33
Al ₂ O ₃	0.34	0.44	0.55	0.39	0.79	0.19	1.41
Cr ₂ O ₃	0.019	0.31	0.03	—	—	0.008	0.06
Na ₂ O	0.010	0.15	tr	—	—	0.02	0.10
Mn ₂ O ₃	0.03	0.10	0.07	0.04	—	0.04	0.09
CaO	0.04	0.59	1.02	tr	—	0.19	0.02
FeO	0.01	0.05	0.01	0.02	—	0.10	0.00
K ₂ O	0.04	0.04	tr	—	—	0.02	0.00
Na ₂ O	0.04	0.04	0.03	—	—	0.01	0.00
H ₂ O	13.2	14.0	13.97	13.09	12.9	13.88	12.36

* Theoretical chrysotile composition: 43.4% SiO₂, 43.5% MgO, 13.1% H₂O.

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though these fibers are relatively common in the samples, they are not enough to account for the discrepancy between the measured and calculated densities reported by Pandisack (55).

One final point should be made about the Yada micrographs. The outside surface of most of the fibers shows the presence of highly disorganized or amorphous material. This is the result of damage to the outer layer of fibrils by the electron beam under the conditions of observation.

There are two other serpentine materials found in chrysotile-bearing rocks: lizardite and antigorite (20). They both have the same chemical composition and the same fundamental sheet structure as chrysotile. The differences between these minerals reflects the way the strain in the crystal lattice has been relieved. Lizardite, which is the principal constituent of massive serpentine, generally has an extremely fine grained, platy morphology, visible only under the electron microscope in most specimens. Its structure has not yet been elucidated, but X-ray diffraction patterns indicate flat rather than curved sheets. Antigorite, on the other hand, does show evidence of curved sheets. Two of its unit cell dimensions are equal to chrysotile, but the third is much larger and variable. This third (b) dimension can vary from 18.5 Å to as large as 100 Å, compared to the 9.2 Å value for chrysotile. It is believed that the structure consists of undulating sheets the periodicity of which corresponds to the variable unit cell dimension.

Amphiboles

The basic crystal form of the amphibole minerals is less complicated than that of the serpentines. The basic structural unit is a double silica chain (Si_2O_{11}). As in the chrysotile sheets, all of the silica tetrahedra point in one direction. These chains are paired, "back-to-back," with a layer of hydrated cations in between to satisfy the negative charges of the silica chains. The final structure is formed by the stacking of these sandwich ribbons in an ordered array. A pictorial concept of this structure is shown in Fig. 9. The various minerals in the amphibole groups are characterized by the cations which occur in the structure. The principal cations are magnesium, iron, calcium, and sodium. Since the bonding between these ribbons is rather weak, the crystals are easily cleaved parallel to the ribbons along A-A. If the cleavage is very facile, the result is an asbestiform mineral.

For each variety of asbestiform amphibole, there is a corresponding massive form with a different mineral name. Normally the asbestiform varieties are not found along with the massive counterparts. Undoubtedly, the local geochemical conditions extant at the time of formation contributed to the relative ease of cleavage of any specific deposit and, therefore, to its commercial utility. The massive and asbestiform varieties have the same chemical compositions and X-ray crystal structures. They can be distinguished by their physical properties and by petrographic examination.

CHEMICAL COMPOSITION

The chemical composition of commercially available chrysotiles from various locations are shown in Table I. For comparison, analyses of lizardite and anti-

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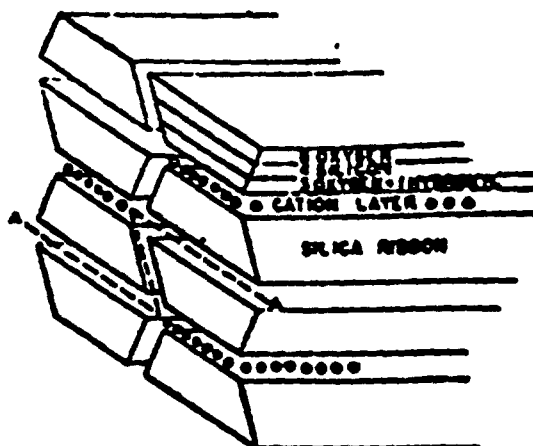


FIG. 9. Amphibole structure.

gorite are included. In all cases, it is apparent that the composition differs very little from the idealized composition of $Mg_3(Si_4O_{10})(OH)_2$. The impurities which are present may be part of the crystal structure or due to associated minerals. The most common impurity is iron. This can be in the form of ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions. It is generally assumed that the Fe^{2+} can be substituted for silicon in the silica sheets, and the Fe^{3+} can be substituted for the magnesium in the brucite layer. The next most common impurity in chrysotile is aluminum. Since aluminum can assume either tetrahedral or octahedral coordination it can be substituted in either the silica or brucite layers. Other impurities, generally found to be associated with chrysotile in lesser amounts than iron or aluminum, are calcium, chromium, nickel, manganese, sodium, and potassium.

The ionic radii of the ions commonly associated with chrysotile are given in Table II. Since these ions vary considerably in size, they can have an effect on the strains which exist in the chrysotile lattice. Ions which are larger than silicon and smaller than magnesium will tend to relieve the strain when substituted in the respective layers. Aluminum fits this requirement for the silica layer, since it is intermediate in size between silicon and magnesium. Ferric iron is larger than silicon so it will help relieve the strain when substituted in the silica layer. Ferrous iron in the brucite layer will increase the strain because of

TABLE II
IONIC RADII FOR ELEMENTS ASSOCIATED WITH CHRYSOTILE

Element	λ
Mg^{2+}	0.41
Mg^{2+}	0.65
Al^{3+}	0.50
Fe^{2+}	0.76
Fe^{3+}	0.64
Ni^{2+}	0.73
Co^{2+}	0.72
Co^{3+}	0.57
Mn^{2+}	0.83
Ca^{2+}	0.99

its larger size. Finally, it is improbable that the very large ions, such as the alkali or alkaline earths, can truly be substituted to any significant extent in the brucite layer, and when present in appreciable quantities may exist as "inter-layer" cations between the primary layers. Various authors have "normalized" chemical analyses of chrysotile, indicating the probable location of the impurity ions in the crystal structure.

The chemical composition of the asbestiform amphiboles is more complex than that of chrysotile. The idealized chemical formulas for the various species are given below. In these formulas, when cations are written in parentheses without subscripts, a variable composition is indicated with the most abundant species first.

Crocidolite..... $(\text{Na}, \text{Fe}^{2+}, \text{Fe}^{3+})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
 Amosite..... $(\text{Fe}^{2+}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
 Anthophyllite..... $(\text{Mg}, \text{Fe}^{2+})_2\text{Si}_4\text{O}_{10}(\text{OH})_2$
 Tremolite..... $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
 Actinolite..... $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

The range of chemical analyses for these varieties of amphiboles are listed in Table III. Detailed analyses can be found in various publications (17, 23, 33).

TABLE III
CHEMICAL COMPOSITION OF ASBESTIFORM AMPHIBOLES^a

Asbestiform amphibole (range %)					
	Crocidolite	Amosite	Anthophyllite	Actinolite	Tremolite
SiO_2	49-53	49-53	56-58	51-56	55-60
MgO	0-8	1-7	75-84	13-20	21-26
FeO	13-20	24-44	3-12	3-15	0-4
Fe_2O_3	17-30	—	—	0-3	0-0.6
Al_2O_3	0-0.2	—	0.5-1.5	1.5-3	0-2.5
CaO	0.3-2.7	—	—	10-13	11-13
K_2O	0-0.4	0-0.4	—	0-0.8	0-0.6
Na_2O	4.0-8.5	1r	—	0.5-1.5	0-1.5
H_2O	2.5-4.5	2.5-4.5	1.0-6.0	1.5-2.5	0.5-2.5

The considerable variation in composition which can occur is readily noted. The actual identification of a particular amphibole species may depend on which of the idealized compositions the sample in question most closely represents. This variability in composition is a direct consequence of the fact that the structure can accommodate many different ions in the space between the silica ribbons, and the variable nature of the host rocks can contribute different ions to this structure.

Accessory Minerals

The analysis of asbestiform minerals is often complicated by the fact that the samples may contain fragments of the host rock and its associated minerals, and also that other minerals may be intimately intergrown in the fiber bundles.

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Contamination due to host rock fragments is common in commercial fibers. In the case of chrysotile asbestos, the most common contaminants are the other serpentine minerals—lizardite and antigorite. While these species have similar over-all compositions, the trace element analyses could be influenced by their presence. Other minerals which are found in serpentine masses, and which could be found in commercial chrysotile fibers, are: magnetite, brucite, chromite, calcite, magnesite, olivine, pyroxene, tremolite, actinolite, chlorite, talc, and chalcodan. The proportions of these minerals will vary considerably with the location and nature of the deposit. For a specific commercial mine, the nature and content of the impurities in the ore will be relatively constant. Neighboring deposits in the same serpentine belt may differ considerably in their impurities. Several good publications are available (19, 27, 45) which describe the geology and mineralogy of the various chrysotile producing areas.

Other than lizardite and antigorite, the most common minerals associated with chrysotile are magnetite and brucite. Both of these species often are found ~~within the fibers~~. In many occurrences, the ends of the fiber bundles are ~~in a magnetite-rich layer of rock~~. A mineralogic curiosity which is found in some chrysotile deposits including the Jeffrey mine at Asbestos, Quebec, is a form of magnesium hydroxide which has been given the name ~~brucite~~ (9). These fibers usually occur in bundles which are often several feet long.

Reimschuessel (20) studied the association of chromium and nickel with carefully separated components of ore from the Jeffrey mine at Asbestos, Quebec. Using a combination of chemical dispersion and magnetic separation, the asbestos was divided into fibrillar chrysotile, serpentine, and magnetic concentrates.

All of the chromium was found to be associated with the magnetite phase, most probably as an isomorphous substitute for ferric iron. When chromium appeared in the chrysotile or serpentine fractions, it was associated with the last traces of magnetite which were impossible to remove.

Most of the nickel in the ore is also found in the magnetic fraction. A small amount may be associated with the magnetite, but the majority occurs as a separate phase. This phase is the iron-nickel alloy, awaruite, whose composition ranges from FeNi_2 to FeNi . It can be separated by a differential solution method proposed by Nickel (49). Finally, a small amount of nickel, about 0.005%, is found to be present in the chrysotile lattice, most probably as a substitute for magnesium.

Organic Impurities

The association of benzo(a)pyrene and other organic impurities with asbestos-form minerals from various sources was investigated by Reimschuessel (20). The total amount of extractable organic matter was determined by long-term Soxhlet extraction with cyclohexane. After drying and weighing, the organic residue was analyzed for benzo(a)pyrene by thin-layer chromatographic techniques.

The fibers examined included North American and African chrysotiles, crocidolite, amosite, and anthophyllite. All samples contained measurable amounts

of extractable organic matter, ranging from 10 to 300 ppm. There was, however, no correlation between the amount of organic matter and the amount of benzo(a)pyrene present. The Canadian and United States fibers (11 chrysotiles and one anthophyllite) contained no detectable benzo(a)pyrene. The detection limit varied with the amount and complexity of composition of the extracted organic matter. It was as low as 0.02 parts per billion and generally below 5 ppb. All of the fibers from Africa and Finland, on the other hand, did contain benzo(a)pyrene. The highest concentration (150 parts per billion) was found in crocidolite from the Cape Province, South Africa. Crocidolite and amosite from the Transvaal Province contained 12-18 ppb; Rhodesian chrysotile and Finnish anthophyllite contained less than 10 ppb.

These results are in general agreement with those reported by Harington (28) except that Harington found no benzo(a)pyrene in African chrysotiles. The explanation of this difference may lie in the fact that Harington used virgin samples collected in the field, whereas Reimschuessel analyzed typical commercial products. This could mean that at least some of the benzo(a)pyrene is introduced during the processing or shipping of the fiber.

SURFACE CHARACTERISTICS

The surface characteristics of the asbestiform minerals are very important in relation to their commercial uses and to their interaction with whatever environment they may be exposed to. Most of the discussion relates to chrysotile because the surface characteristics of the asbestiform amphibole minerals have received much less attention.

The external surface of chrysotile fibers consists of magnesium hydroxide and, therefore, it is not surprising that the fibers behave in some respects as though they were magnesium hydroxide. For example, Pundsack (53) determined that the pII of a suspension of chrysotile in carbon dioxide-free distilled water is 10.33. This compares to a value of 10.37 for a magnesium hydroxide suspension under the same conditions. Pundsack and Reimschuessel also determined the "solubility product constants" for various chrysotile fibers (56). The values ranged from 1.0×10^{-11} to 3×10^{-11} and correspond quite closely to a value of 1.0×10^{-11} reported for magnesium hydroxide (64).

Surface Charges

The electrokinetic behavior of chrysotile is another manifestation of the magnesium hydroxide surface. Martinez and Zucker (42) studied the effect of pII on the surface charge, or zeta potential, of asbestos ore body minerals by the streaming potential method. Figure 10 shows the complete pII vs zeta potential curve obtained by these authors. They found the isoelectric point of chrysotile to be 11.8. At lower pII values, the surface charge is positive; above the isoelectric point, the charge becomes negative. They attributed the sharp increase in potential which was obtained as the pII was lowered from 7 to 3 to removal of hydroxyl groups from the surface and resultant exposure of the magnesium ions. Below pII 3, the magnesium ions are removed and the silica surface exposed, accounting for the decrease in zeta potential in this range.

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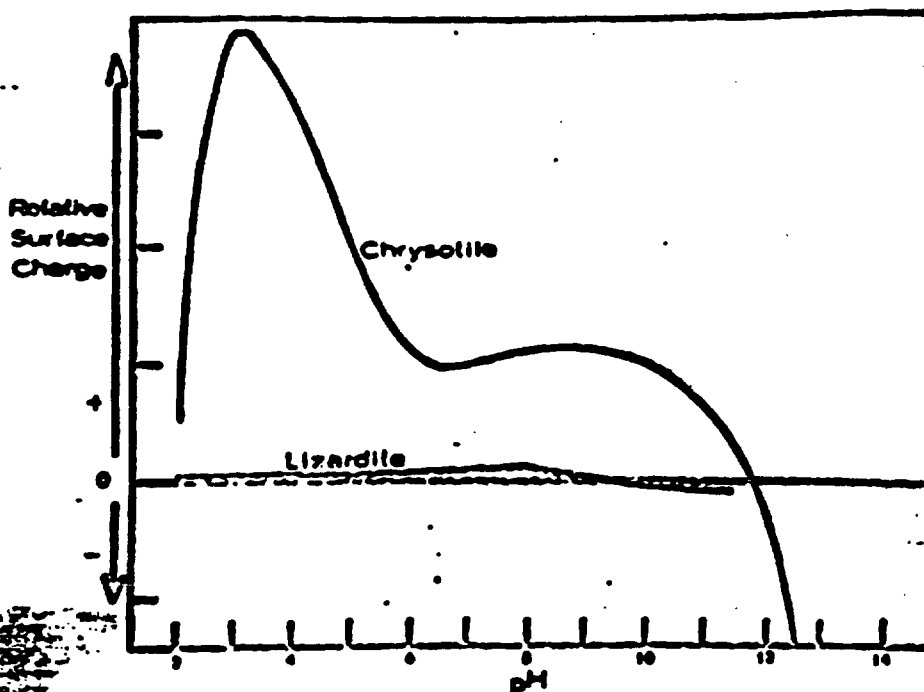


FIG. 10. Surface charges on serpentine minerals.

The electrokinetic behavior of lizardite, also shown in Fig. 10, is significantly different from that of chrysotile. It has an isoelectric point of 9.7 with a much smaller charge than chrysotile. Furthermore, the sharp rise in potential, between pH 7 and 3, is not found. This would be in accord with the proposed undulating structure in which both silica and magnesium hydroxide surfaces are exposed.

Chemically, the surface of the amphiboles is similar to that of silica. It is polar in nature, but not as highly polar as chrysotile. The electrokinetic charge is negative and smaller in magnitude than the positive charge of chrysotile. Isoelectric points have not been well established, although it is presumed that the charge would become positive at very low pH.

Most materials have a negative surface charge in aqueous systems. Since chrysotile has a positive charge, it will attract or be attracted to most dispersed materials. This characteristic of chrysotile manifests itself in many of the commercial applications. In addition, the highly reactive surface causes many interesting surface reactions to take place which are intermediate between simple adsorption and true chemical reaction. For the sake of better continuity, these interactions will be discussed along with the chemical properties of the fibers.

Surface Area

The specific surface area of chrysotile asbestos as determined by gas adsorption measurements has been found to vary considerably with the physical condition of the fibers. For example, Pundack (31) reported that pulling fibers from a block of crude Jeffrey chrysotile fiber with tweezers gave products with surface areas, as determined by nitrogen adsorption, ranging from 4 to 12 m²/g.

depending on how thoroughly the fibers were pulled apart. When the fibers were opened further in a Willy Mill, the comparable surface area was more than 30 m²/g. Values in excess of 30 m²/g were obtained when the fibers were soaked in an Aerosol OT solution to separate individual fibrils.

Neumann and Dreher (48) studied the surface areas of various chrysotiles in more detail. They also found a considerable variation in surface area with the degree of fiber opening for most fibers. The two exceptions were the chrysotiles from New Idria (Coalinga) and Stragari. In these cases, there was very little variation with the degree of opening. Theoretical surface areas of the chemically dispersed fibers calculated from measurements of fibril diameter distributions were in good agreement with the measured values, as shown below:

Fibers from	Observed SA	Calculated SA	Average Fibril diameter
Canadian Grade 7R	50 m ² /g	55 m ² /g	375 Å
New Idria	78 m ² /g	76 m ² /g	375 Å

The authors proposed, that for those fibers whose surface areas are sensitive to the degree of opening, the voids between fibers are partially filled with solid material, and therefore not accessible to nitrogen or other gases. In the case of the New Idria fibers, these interfibril voids are available for adsorption. In either case, the intrafibril voids are not available.

Several workers (18, 48, 54) have attempted measurements of the pore-size distribution of various asbestos fibers, including chrysotile and amphiboles. The methods have included water vapor adsorption, nitrogen adsorption, and mercury penetration. Most nitrogen adsorption results show a peak in the vicinity of 20 Å which has been interpreted as a measure of the radius of the pores within the fibrils. Harris (29), however, pointed out that this may be an artifact of the measuring method and is open to serious questions.

The surface area of amphibole asbestos is considerably lower than chrysotile. It does not exhibit any unusual porosity. Patterson and Thompson (52) reported that sawn blocks of Wittenoom crocidolite have surface areas around 5 m²/g. This increases to between 7 and 8 on teasing fibers from the block. The fully fibrillized material had a value of 14.8 m²/g.

Adsorption

The adsorption of various materials on the surface of chrysotile has been studied from both the liquid and vapor states. Young and Healy (54) studied the adsorption of several vapors on chrysotile. They found that nitrogen, argon, carbon monoxide, acetylene, n-butane, trimethyl amine, and dimethyl amine all gave surface areas of 9.7 m²/g on grade 7R Canadian fiber. Ammonia and water vapor, however, gave surface areas of 17.8 m²/g for the same sample. The difference could not be explained in terms of chemisorption or other specific interactions because all the isotherms were completely reversible. Their conclusion was that the extremely polar water and ammonia molecules could be adsorbed on portions of the surface which are not available to less polar molecules. They further concluded that some of the pores in chrysotile may be

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plugged with water, and that these plugs are permeable to polar vapors only.

Young and Healy also reported a similar anomalous sorption of water vapor on antigorite, a nonfibrous serpentine. Anthrophyllite and tremolite, the only amphiboles studied, did not exhibit this behavior.

The adsorption of various organic compounds on chrysotile from both the liquid and vapor phases is currently being studied by Weeks and Leinweber (75). The fiber used in this study was specially air cleaned to remove most of the nonfibrous material and extracted with carbon tetrachloride to remove organic contaminants. Ethanol, benzene, and hexane all exhibit normal isotherms on chrysotile. The surface areas, estimated from the isotherms are ethanol, 18.8 m²/g; benzene, 11.2 m²/g; and hexane, 9.0 m²/g. The nitrogen surface area is 21.2 m²/g. The corresponding heats of adsorption are ethanol, 13 kcal/g; benzene, 11 kcal/g; and hexane 9 kcal/g. Zettlemoyer *et al.* (85), reported 16 kcal/g for the heat of adsorption of water on chrysotile.

These adsorption data support the obvious premise that the polar surface of chrysotile has a greater affinity for polar molecules than for nonpolar, in general agreement with the findings of Young and Healy.

Adsorption from solution is complicated by the concurrent adsorption of solute and of solvent, making the interpretation of the isotherms quite difficult. Weeks and Leinweber studied the following binary systems on the same fiber used for the vapor adsorption studies: benzene-ethanol; benzene-tert-butanol; benzene-*n*-butanol; benzene-naphthalene; benzene-anthracene; hexane-naphthalene. Typical adsorption isotherms obtained from these systems are shown in Fig. 11. These isotherms of concentration change are plots of the "apparent" or differential adsorption of the "solute" (the component whose concentration is indicated on the abscissa) vs. concentration. These concentration changes were determined by means of a differential refractometer. The extremes in the type of isotherms obtained are illustrated by the benzene-ethanol system and the

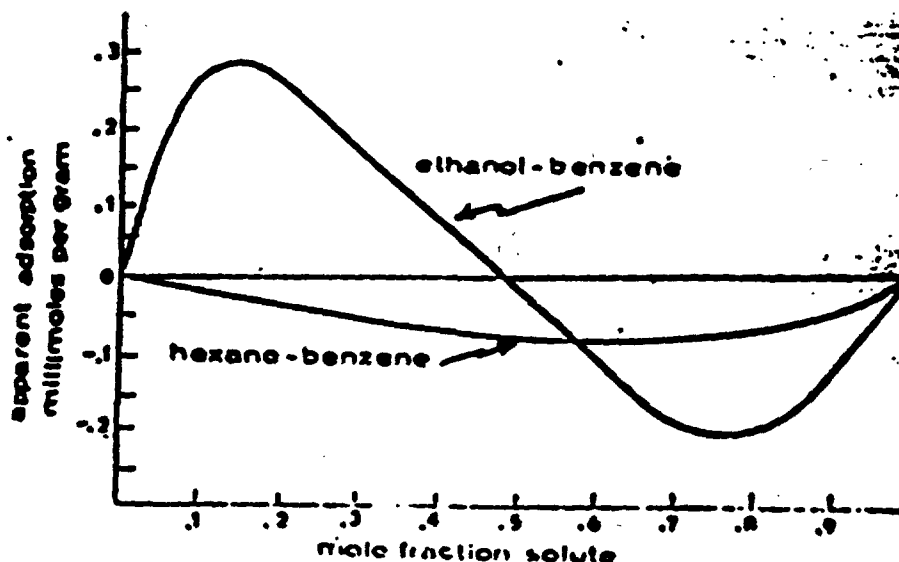


FIG. 11. Sorption of organic liquids on chrysotile.

hexane-toluene system. In the former, the apparent adsorption of ethanol is positive at low concentrations and negative at high concentrations, whereas in the latter system the apparent adsorption of hexane is negative throughout. A qualitative interpretation of these effects is that the affinity of the surface for ethanol and benzene are essentially equal, while benzene is more strongly adsorbed than hexane. The affinity of the surface for the compounds studied can be listed in the following decreasing order:

ethanol = benzene > toluene > naphthalene > anthracene > hexane

Quantitative interpretation of these isotherms by the methods proposed by Kipling and Tait (36) was impossible because sufficient information was not available to be able to extract the individual isotherms.

CHEMICAL CHARACTERISTICS

Asbestos has often been touted as the "indestructible mineral." In reality, this is far from the case. As far back as 1835 (67) the reactivity of chrysotile with acids was recognized and in 1900 Clark and Schneider (16) found that chrysotile was the most susceptible to acid attack of all the serpentine minerals. Nagy and Bates (47) and Nagy (48) confirmed this conclusion with electron microscopic and X-ray diffraction studies on acid-treated chrysotile and antigorite. After treatment with 1N HCl for 1 hour at 100°C, the chrysotile X-ray diffraction pattern completely disappeared while that of antigorite was relatively unchanged. Electron micrographs of the reaction products showed that chrysotile was very severely etched and had lost its tubular morphology. Faust and Nagy (21, 22) studied the differential solubility of chrysotile and serpentine in more detail. They confirmed that chrysotile is almost completely destroyed in 1N HCl for 1 hour at 93°C, while antigorite is almost untouched under the same conditions. The reactivity of lizardite is intermediate between that of chrysotile and antigorite.

Badollet (2, 3) summarized the available information on the stability of asbestiform minerals. Strong acids decompose chrysotile rapidly with the removal of all MgO and a total weight loss of 60%. The residue which remains after acid attack consists of amorphous silica which retains a very fragile fibrous morphology.

In contrast to the sensitivity of chrysotile, the amphibole fibers are much more resistant to acids. There are, however, significant differences between these fibers. The data in Table IV shows that anthophyllite, crocidolite, and tremolite are significantly more resistant to acid attack than amosite and actinolite. Twenty-two days at room temperature had essentially the same effect as the 2-hour reflux exposure. All of the fibers were relatively stable in 25% sodium hydroxide solutions. The high solubility of actinolite was attributed to impurities in the sample.

Hiscock (33) more recently studied the rate of decomposition of asbestiform fibers in boiling 4N hydrochloric acid. He found the following relative order of stability as shown in Fig. 12:

tremolite > anthophyllite > crocidolite > actinolite > amosite > chrysotile

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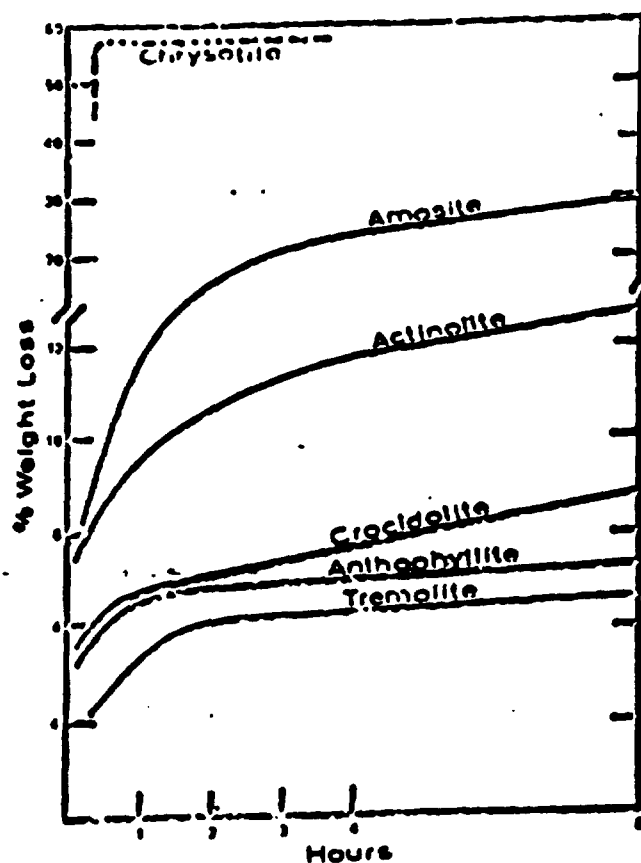


FIG. 12. Acid resistance of asbestos (4N HCl boiling).

After an initial rapid weight loss, the rate of attack decreases radically with tremolite and anthophyllite showing extremely low rates. Recently Weeks (74) studied the rate of decomposition of chrysotile fibers less than 1μ in diameter in 0.12N hydrochloric acid at 37°C . Decomposition was determined by analysis for magnesium which had gone into solution. The decomposition is relatively slow under these conditions as shown in Fig. 13. The straight line indicates that

TABLE IV
SOLUBILITY OF ASBESTOS MINERALS IN 25% ACID OR CAUSTIC*

	Per cent loss in weight, refluxing 2 hours				
	HCl	CH_3COOH	H_2PO_4	H_2SO_4	NaOH
Chrysotile	55.60	23.42	55.18	55.75	0.99
Crocidolite	4.35	0.91	4.37	3.69	1.34
Amosite	12.81	2.63	11.67	11.35	6.97
Anthophyllite	2.66	0.60	3.16	2.73	1.22
Actinolite	20.31	12.28	20.10	20.34	9.25
Tremolite	4.77	1.99	4.99	4.58	1.80

* Reproduced with permission from Canadian Mining and Metallurgical Bulletin, April, 1961.

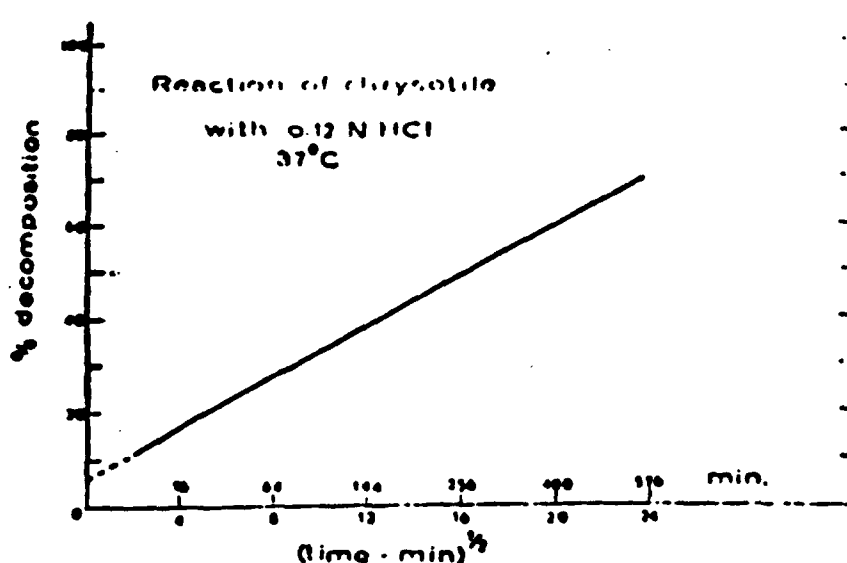


FIG. 13. Reaction of chrysotile with 0.12 N HCl 37°C.

the decomposition is diffusion controlled. This conclusion is justifiable because extraction of the magnesium from the chrysotile structure leaves a residue of silica through which both the acid and magnesium ions must diffuse for the decomposition to continue.

It is also interesting to note that extrapolation to zero time indicates an initial decomposition of approximately 6%. This decomposition probably represents the immediate dissolution of the surface magnesium hydroxide. X-ray diffraction analysis of the 6½-hour reaction product showed no difference from the original material in spite of the fact that it was more than 50% decomposed. The acid apparently attacks the surface of the fibrils leaving an unreacted core which diffracts X-rays the same as chrysotile. This is in accord with the observation that chrysotile fibers can be readily fibrillized by agitation in weak acid. Electron micrographs of the reaction product show an etched surface on typical chrysotile tubes. The residual silica on these partially decomposed fibrils is probably responsible for this etched effect.

The very rapid initial reaction of the surface hydroxyls was also noted by Pundsack (50) during the stepwise titration of chrysotile with 0.5 N hydrochloric acid at 100°C. Ample time was allowed for equilibrium to be attained after each increment of acid. The titration curve, Fig. 14, exhibits several inflection points. The first increments of acid cause a sharp decrease in pH from an initial value of 10 to about 0.8. This point corresponds to the reaction of about 4.5% of the fiber with acid. After the first inflection the curve levels off until about 67% of the fiber is reacted and finally tails off to a pH of 2.3 as the reaction is completed. Pundsack estimated that about 7% of the total hydroxyls exist on the surface, and that 67% decomposition represents reaction of all the structural hydroxyls. The final 33% reaction represents reaction with the silica gel formed by the process.

The chemical reactivity of eriochrolite has been studied in considerable detail

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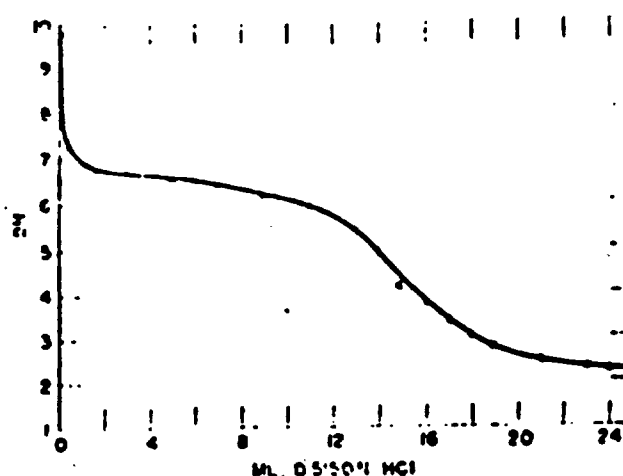


FIG. 14. Titration of chrysotile.

by Thompson (65) using fibers in the diameter range of 0.05 to 0.15 μ . In a Soxhlet extractor, water removed 1% of the silica and 6% of the sodium ions. These values correspond to a depth of attack of 1 and 1½ unit cells, respectively. Similarly, in boiling alkali the attack is limited to the surface layer.

In 5*N* hydrochloric acid at 100°C, 20% of the structure is disrupted within 3 minutes, corresponding to a 57 Å penetration. After 3 minutes, the rate drops rapidly with less than twice the above penetration after 6 hours, agreeing generally with Hiscock's findings (33). Thompson proposed that the formation of a tough coating of polymerized silica protects the crystals from further attack. This hypothesis is supported by the fact that the fibers are again susceptible to acid attack if the silica layer is removed by reaction with alkali.

In the presence of 0.2*N* EDTA at pH 5.5 and 100°C, the rate of decomposition of the fiber appears to be diffusion controlled. In this case at least a portion of the silica becomes dispersed in the reaction medium. Thompson concluded that the amphibole structure is not intrinsically resistant to acid attack. The apparent resistance is a result of the protection afforded by the silica layer. The lesser resistance of amosite to acid attack can possibly be attributed to faults in the structure.

The resistance of the asbestiform minerals to attack by reagents other than acids is generally considered excellent at temperatures up to 100°C, but deteriorates rapidly at higher temperatures. Ball and Taylor (6) studied the reactions of chrysotile with several materials under hydrothermal conditions.

Recent studies by Yang (53) indicate that reaction between chrysotile and calcium hydroxide is detectable in 2 days at 230°C. Similarly Reimschuessel (60) found that chrysotile was completely decomposed in concentrated potassium hydroxide at 200°C within 24 hours. Thompson (61) showed that crocidolite is attacked by potassium hydroxide above 100°C and studied the hydrothermal reaction of other varieties of asbestos minerals.

Under certain conditions, the reaction of chrysotile asbestos with weak acids can be limited to the surface of the fibers. Hiscock and Brown (33) and

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demonstrated that fatty acids and other weak organic acids when dissolved in nonaqueous solvents react with the fiber surface to form a monomolecular "chemisorbed" layer. The amount of chemisorbed acid is affected by the presence of sorbed water on the fiber. This is illustrated below.

CHEMISORPTION OF OLEIC ACID FROM BENZENE BY CHRYSOTILE

	Fiber conditioned for 48 hours at		
	15°C	25% RH	100% RH
Mg acid sorbed/g. fiber	10.8	7.4	0.5

Equilibrium in these reactions is established very rapidly, probably within seconds. It was also noted that above a concentration of 0.005 moles of oleic acid/kg of benzene, the amount of acid chemisorbed by the fiber is constant and has a value of about 1% by weight of the fiber. This value could vary with the exposed surface area of the fiber. Even after 15 extractions with hot benzene, 80% or more of the original oleic acid remains fixed on the fiber surface. Fiber which contains chemisorbed fatty acid is somewhat hydrophobic and markedly organophillic. The hydrophobic character of the fiber is of a limited nature, since the fiber can be wet by vigorous stirring in water.

In general, organic compositions possessing acidic functional groups dissolved in nonpolar or slightly polar solvents, such as benzene and methyl ethyl ketone, exhibit a strong tendency either to chemisorb or to slowly react with chrysotile. Long-chain aliphatic acids, such as stearic acid, oleic acid, and palmitic acid, are chemisorbed by dry fiber. Aromatic-type acids, such as benzoic acid and related compounds, are also chemisorbed as are dibasic aliphatic acids, such as adipic acid. Although the unsaturated six-carbon sorbic acid appears to be chemisorbed by chrysotile, the related shorter carbon chain acrylic, crotonic acids show some evidence of slow reaction with the dry chrysotile even in nonpolar solvents and there is a tendency for the adsorbed layer to show an affinity for water. Maleic acid reacts with the bulk fiber.

If the fiber contains adsorbed water, the interaction of an organic acid in benzene or MEK solutions differs markedly from that with the dry fiber. The long chain aliphatic acids, e.g., stearic, oleic, when dissolved in nonpolar or slightly polar solvents, show little or no tendency to sorb on fibers containing adsorbed water. Acids such as adipic, benzoic or sorbic, which have some slight affinity for water, react with the bulk fiber structure instead of chemisorbing as they do on dry fibers.

The reaction of chrysotile with certain anionic wetting agents, such as Aerosol OT, is peculiar in that they cause the fiber bundles to separate into ultimate fibrils. This reaction is accompanied by strong chemisorption of the agents with permanent modification of the surface (51).

When chrysotile fiber is decomposed by strong hydrochloric acid in the presence of chlorotrimethyl silane (24) a very interesting reaction occurs. Normally, the decomposition by acid leaves a residue of amorphous silica which polymer-

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izes in the shape of the original fiber. The chlorotrimethyl silane, however, reacts with the silica sheet as the magnesium is removed and prevents further polymerization of the silica. The final product of the reaction is in effect an organic silica polymer in sheet form. The sheets are rolled into hollow tubular forms which exhibit typical chrysotile morphology under the electron microscope. They show a 15 Å spacing between the layers by X-ray diffraction. In organic solvents the polymer swells and the X-ray diffraction pattern disappears indicating that the tubular sheets have unrolled. This product is interesting because the basic chrysotile structure is a spiral rather than a closed concentric cylinder.

Reaction with Water

In addition to being vulnerable to attack by acids, and, under certain circumstances alkalis, asbestos fibers are also subject to attack by water. Froese's study of chrysotile with water has been studied by Holt and Clark (1962). They found that chrysotile was attacked by water and that the solution contained both magnesium and orthosilicic acid. They suggested that the chrysotile decomposed by loss of magnesium ions to form a colloidal silica. He also suggested that the colloidal silica is hydrolyzed to orthosilicic acid.

Froese's results confirm that chrysotile is decomposed by water. He found that the concentration of magnesium in the extract was relatively constant during the first 3-4 hours of Soxhlet extraction and then began to decrease. The decrease in magnesium concentration was accompanied by the formation of a precipitate of amorphous magnesium silicate. After the initial rapid decrease in magnesium and silica are removed in amounts proportional to the chrysotile composition. Whether the removal of silica proceeds by way of solution or the formation of colloidal silica is yet to be determined. There is, however, that chrysotile is slowly "soluble" in water under these conditions.

For crocidolite, Thompson (63) reported that it is attacked by water and that sodium are removed by Soxhlet extraction with water. He found that the rate of attack was equivalent to that of alkalis at corresponding temperatures.

SYNTHESIS

Chrysotile

Numerous investigators have studied the synthesis of chrysotile and other serpentine minerals. These studies were motivated either by the desire to grow large synthetic crystals or by the desire to grow large synthetic crystals. It is quite probable that chrysotile was synthesized as early as 1927 (34) but before the advent of electron microscopy and sophisticated X-ray diffraction techniques, it was not possible to distinguish among the minerals of the serpentine group. The micrographs of the chemical analysis of the reaction products matched that of serpentine and not be considered distinctly diagnostic for chrysotile.

Chrysotile has been synthesized only under hydrothermal conditions. Turekian and Turekian (10) demonstrated that chrysotile is formed at temperatures between 200°C and 300°C.

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pressures up to 40,000 atm. for the synthesis of chrysotile at temperatures as low as 115°C. Since a lower hydrostatic pressure stability for chrysotile has not been established, it is conceivable that the conditions for the synthesis of this system with the correct composition, under ambient conditions, particularly within geologic time periods, may be established. This is a very interesting question, particularly in view of the fact that the synthesis of chrysotile has been achieved in the laboratory, which has been the subject of considerable controversy. The method has been described in the literature, and the synthesis of chrysotile which occurs in nature is also described. The synthesis of chrysotile is a complex process, and the evidence of sheets in the process of rolling is also described.

Roy and Roy (63) carried out an extensive study of the synthesis of serpentine minerals with magnesium and silicon substituted wholly or partially by other ions. Replacement of magnesium by similar-sized nickel ions yielded a product which was either platy or tubular depending on other factors, such as the presence of sodium chloride in the reaction mixture. Increasing the size of the tetrahedral layer by substituting silicon with germanium resulted in a serpentine mineral which formed large platy, hexagonal crystals. Similarly, partial substitution of aluminum in both layers yielded platy "aluminum-bearing" $(Mg,Al)(AlSi_3O_{10})(OH)_2$. Another serpentine phase was also synthesized from nickel and germanium $Ni_3Ge_2O_{10}(OH)_2$, which also had a platy structure. It was not possible to produce serpentine-type phases substituting manganese, zinc, cobalt, iron, chromium, or gallium for magnesium. This, however, does not preclude the possibility of trace amounts of these ions being present in natural or synthetic materials. The authors concluded that the tubular structure of chrysotile is not only a consequence of the ion sizes, but other external influences as well.

Amphiboles

The amphibole minerals can be synthesized by either pyrogenic or hydrothermal methods. Recent studies at the Institute for Silicate Chemistry, Leningrad, are probably the most comprehensive in this field. Amphiboles containing fluorine substituted for hydroxyl were produced by heating a mixture of oxides and fluorides to 900-1100°C in tightly closed platinum or ceramic vessels (25). The mineral phase and the morphologic characteristics of the products depend on the composition of the initial mixtures, the fluorine content, and the temperature. The isomorphous series of fibrous fluoro-amphiboles included a wide variety of cations comprising a mixture of Na or other monovalent ions plus either Mg^{2+} , Fe^{2+} , Cr^{3+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , or Al^{3+} . Within the reaction mix, crystals of 0.5-1.0 mm in length, and 0.1-2.0 μ in diameter were formed with crystals as long as 20 mm on the surface of the reaction mass. The physical properties of the synthetic fluoroamphiboles were stated to be superior to the best natural varieties with tensile strength of 20,000-40,000 kg/cm². Thermal decomposition did not occur until the temperature exceeded 900°C.

Hydroxy amphiboles containing combinations of Na or Ca plus either Mg^{2+} ,

Fe^{2+} or Ni^{2+} were formed under hydrothermal conditions (39). Typical reaction conditions were 350–600°C with pressures ranging from 300–2000 atm. After reaction times of 6 hours to 3 days, fibers as long as 4 mm were obtained with diameters ranging from 0.1–1.0 μ . The hydrothermal fibers were too small to measure their mechanical properties. Their thermal stability was of the same order of magnitude as the natural materials.

PHYSICAL PROPERTIES

Tensile Strength

Asbestos is used primarily as a reinforcing fiber. Its tensile strength is, therefore, of prime significance. The measurement of tensile properties is complicated by the combination of short length and small diameters resulting in a wide range of values from the same type of fiber as reported by Badollet (2). Zukowski and Cavo (88) showed a strong dependence of strength on fiber length with maximum values of 81,000 kg/cm² and 58,000 kg/cm² for crocidolite and chrysotile, respectively, with a fiber length of approximately 2 mm. Motion pictures showed that fiber failure normally occurred by rupture of weak interfiber bonds, rather than true tensile failure of a fiber. Using a newly developed microtensile machine, comparable data were obtained by Burman on a variety of asbestos fibers 4 mm long and 10–20 μ in diameter (33). Crocidolite and chrysotile had the greatest strength, followed closely by amosite, with the other amphiboles significantly weaker. More recent work by Burman (13) in Table

TABLE V
PHYSICAL PROPERTIES OF AMPHIBOLIFORM MINERALS

Ore samples	Tensile strength ($\times 10^4$ kg/cm ²)	Young's modulus ($\times 10^4$ kg/cm ²)	Average cross-sectional area fibers tested ($\times 10^{-4}$ cm ²)
Chrysotile, Arizona, U.S.A.	38.8	1.48	2.07
Chrysotile, Thetford, Canada	37.1	1.49	2.13
Crocidolite, Koppa, Cape Province	29.0	1.80	1.66
Crocidolite, Koppa, Cape Province	31.8	1.84	1.88
Crocidolite, Pumfret, Cape Province	47.8	1.72	1.94
Crocidolite, Pumfret, Cape Province	36.2	1.78	1.81
Crocidolite, Cochabamba, Bolivia	14.7	1.73	2.43
Amosite, Penge, Transvaal	20.3	1.66	2.71
Amosite, Penge, Transvaal	20.2	1.46	1.83
Anthophyllite, Hankila, Finland	25.0	1.89	0.98

casts doubt on the validity of assigning specific tensile strength values to an asbestiform mineral, although the same relative order is maintained. All appear to have strengths less than the theoretical value of over 100,000 kg/cm² attributable to silicate chain structures. The fact that chrysotile and some of the amphiboles give so nearly the same values has led Whittaker (77) to suggest that the fiber strength is affected more by the crystal imperfections introduced during fiber formation rather than by the atomic arrangement or structure.

This is consistent with the hypothesis that amphibole fibers are built up of crystallites held together by II—O—II coordinate linkages or other intercrystallite forces. Chrysotile fibers, on the other hand, are bundles of fundamental units of relatively constant diameter, but varying length. The difference between these two types of chrysotiles is best exemplified by Coalunga fiber (Fig. 15) which consists of overlapping fibrils approximately 0.5-2 μ long compared with the long, and Jeffrey chrysotile which has long individual fibrils (Fig. 16).

This type of structure can also explain the gradual time-dependent loss in strength



FIG. 15. Electron micrograph of coalunga chrysotile. $\times 0000$.



FIG. 10. Electron micrograph of Jeffrey chrysotile. X40000.

of asbestos fibers with increasing temperature below the decomposition temperature of the crystal. Small losses of water in the early stages of dehydration for both chrysotile and amphiboles are probably associated with reduced edge-wise bonding between the fibrils or crystallites comprising the asbestos fibers, resulting in reduced "tensile strength" of the fiber.

Hardness

The term "hardness" is related to the flexural modulus of the asbestiform fibers. The high modulus of the fibers is generally high and relatively stiff

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even in the finest fibers shown in the electron micrograph of Fig. 17. Although most chrysotile fibers are soft, semiharsh fibers are also commercially available. Harsh chrysotile is not usually commercially significant. The difference in the appearance of fiber masses is well illustrated by the photomicrographs of Figs. 18 and 19.

Harsh fibers yield an open, bulky, fast-filtering mass. Flexible soft fibers form stringy, dense masses with slow filtration characteristics. This specific at-



Fig. 17. Electron micrograph of chrysotile. X4500.

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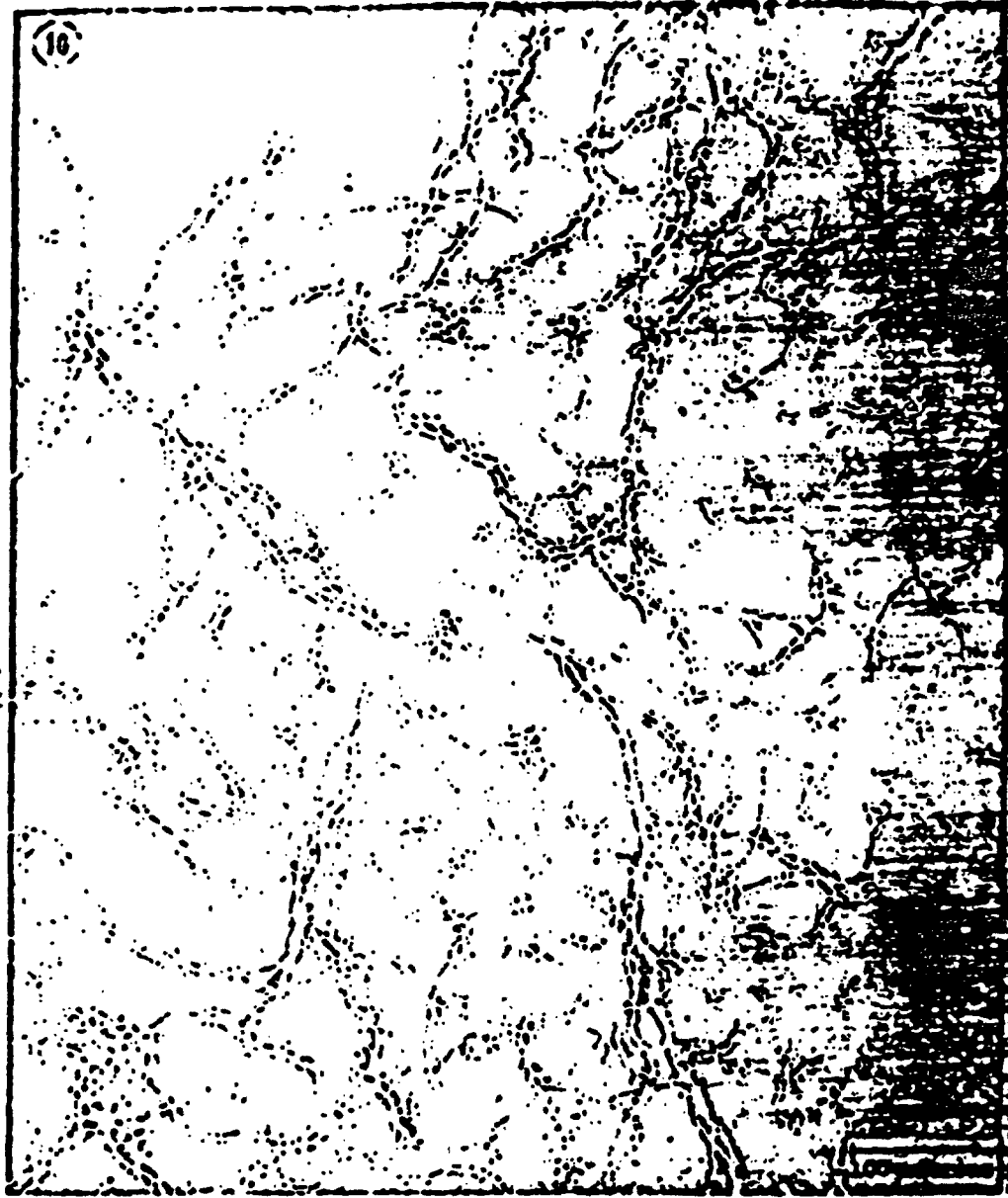


FIG. 18. Soft chrysotile. X150.

tribute of soft chrysotile is often a serious disadvantage in the processes and techniques employed in the manufacture of asbestos-cement products. Soft chrysotile fibers, when economically available, or crocidolite can partially replace soft chrysotile to improve filtration. Chemical techniques may also be used to accomplish the same objective either by adding polyelectrolytes (1) or by treating the fiber with sodium silicate (58).

Considerable research has been devoted to correlate harshness with fundamental physical or chemical factors. Woodroffe (59) has indicated a relationship with the water content of the fiber. In line with this, Backofet and Scott

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(1) have patented a technique for increasing the hardness of chrysotile by flash calcining in the range of 500°C to drive off part of the chemically combined water. More recently, Langer and Kerr (37) have indicated a correlation with fine mineral intergrowths in the bundles of fibrils comprising chrysotile. Another hypothesis is that hardness is related to the relative contents of the two crystallographic forms, clino-chrysotile and ortho chrysotile in the fiber from a specific source (Whittaker and Zarsman (77)).

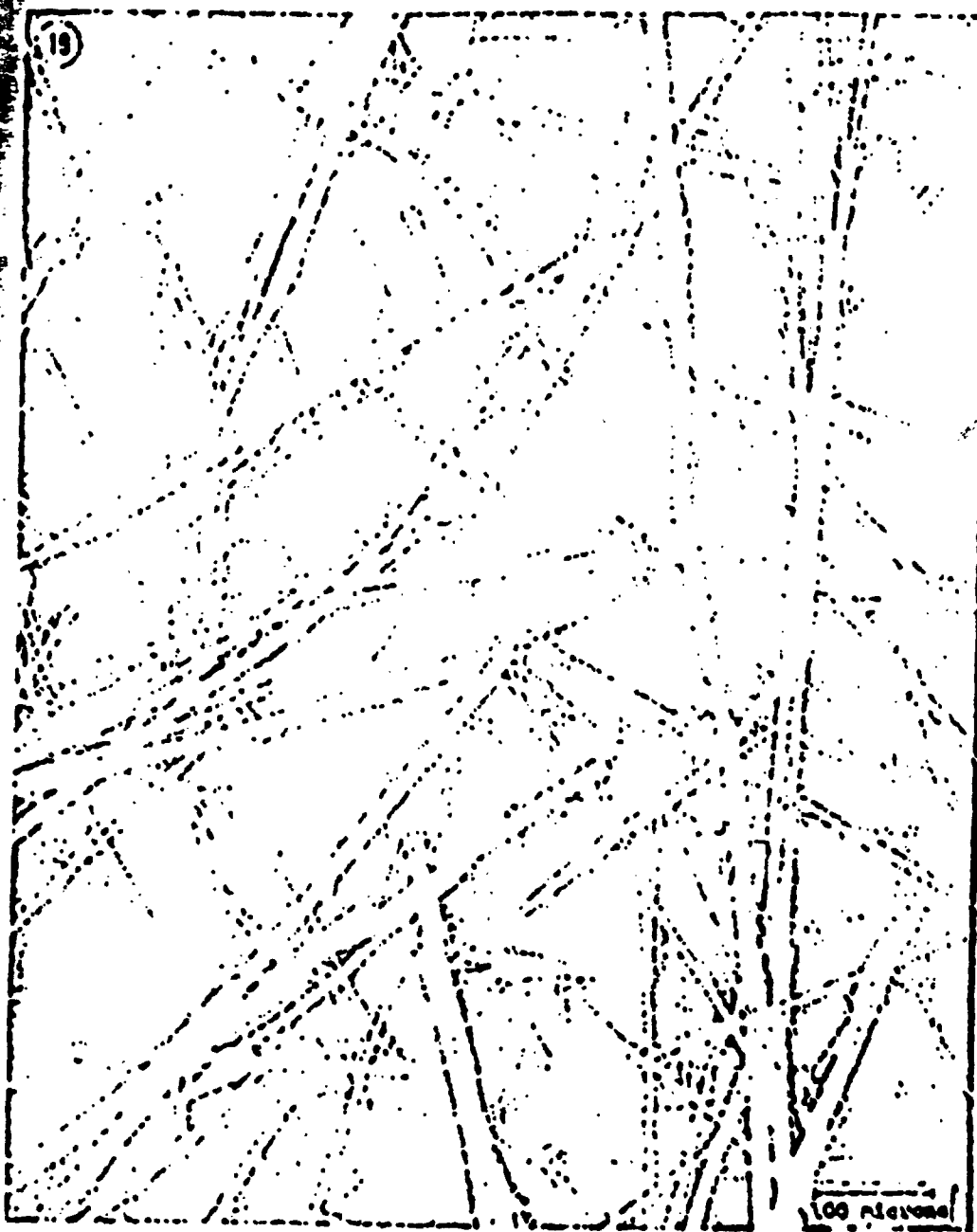


FIG. 19. Hard chrysotile. $\times 1000$.

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Thermal Decomposition

Asbestos minerals, despite their relatively high fusion temperature, are completely decomposed at temperatures of 1000°C or lower, depending on the mineral species.

The course of the thermal decomposition can be followed by three different but interrelated techniques: differential thermal analysis (DTA), thermogravimetric analysis (TGA), and static dehydration.

The actual decomposition phenomena in amphiboles are extremely complicated and depend on the type of atmosphere and particularly on the specific amphibole involved. Typical curves for the behavior of crocidolite in air are given in Fig. 20 from Hodgson (33). The first chemical change, corresponding

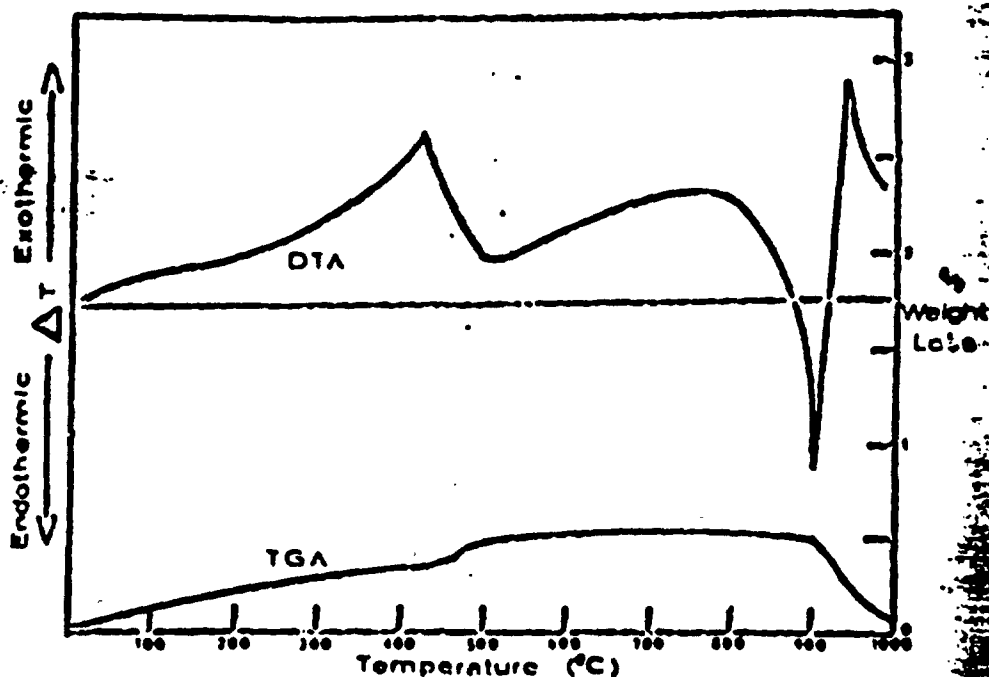


FIG. 20. Thermal analyses of crocidolite in oxygen.

to an apparent loss of water, occurs at 420°C with the final decomposition of the amphibole into a pyroxene mineral, cristobalite, and iron oxide occurring at 900°C. This water is formed by migration of protons which are oxidized at the surface by oxygen in the air.

The other amphiboles lose water primarily by condensation of hydroxyl groups. Oxidation of divalent iron has a profound effect on the thermal behavior of these minerals and this becomes very evident by comparing the reactions in air and in an inert atmosphere. Both the dehydroxylation temperature and decomposition temperature appear to increase with increased MgO content in the different amphibole species. Hodgson (32) gave a detailed experimental and theoretical review of these phenomena, which include loss of physically combined water, loss of chemically combined water, and breakdown into ultimate decomposition products. These thermal analysis techniques have proved

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Finally, in categorizing amphibole samples from different locales. For example, crocidolite exhibits characteristics of both anthophyllite and crocidolite. The Transvaal species is often an intimate mixture of crocidolite and anthophyllite.

The decomposition of chrysotile is much simpler and independent of atmospheric or dynamic heating conditions (DTA), dehydration occurs at approximately 50°C with formation of forsterite and silica, about 810°C, as in static dehydration experiments, the initial water loss below

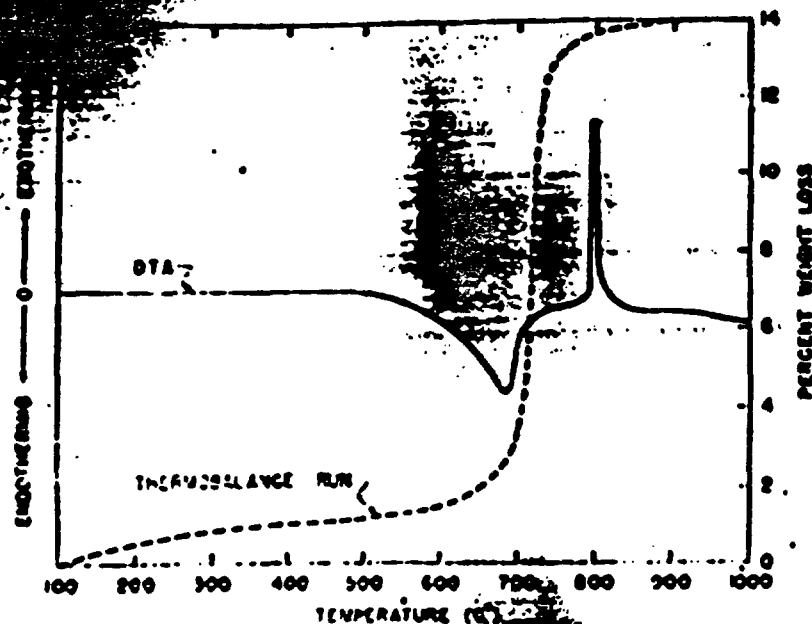


FIG. 21. Thermal analysis of chrysotile.

500°C is time-dependent with no detectable change in the X-ray diffraction pattern (12, 50). Martinez (11) has summarized the various theories for the atomic rearrangement during the dehydration and formation of forsterite. The simplest approach to describing the decomposition above 500°C (static) is to consider it as a three-step process: the solid residue of the first step (<600°C) is a slightly hydrated amorphous magnesium silicate with a minor amount of poorly crystallized forsterite. This is followed by the formation of well-crystallized forsterite with some residual amorphous material at 600–1000°C.

Finally, heating above 1100°C yields a mixture of enstatite and forsterite. This generalized scheme has been confirmed by comparisons of infrared spectra of heated chrysotile with those of mixtures of pure synthetic minerals (61).

Many investigators have studied the thermal decomposition of chrysotile from a wide variety of sources, and all have been found to yield essentially the same DTA curves. Recent studies with an extremely sensitive duPont Differential Thermal Analyzer have disclosed significant differences between fiber from different sources. For many chrysotiles, the 670° dehydration peak is really a doublet (35). This doublet phenomenon was first observed by Mar-

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finer (40) in a mixture of two samples of the same fiber which had been subjected to different degrees of intensive grinding. The dependence of dehydration temperature on particle size in the analogous mineral kaolinite was reported by Spiel (23). It has not yet been determined whether these observed doublet peaks in specific chrysotiles correspond to two fiber distributions or to some other phenomenon.

Mechanical Disintegration

For effective reinforcement, the asbestiform mineral should be fibrous to the degree required by the specific application. Mechanical milling is the basic method of fiberizing asbestos minerals. Ideally, the fiber should be opened without reducing the fiber length. In practice, the fiber is shortened to a degree controlled not only by the severity of the mechanical action, but even more, by the brittleness or harshness of the mineral. The chrysotiles show minimum length disintegration during opening while, under the same mechanical attrition, the semiharsh and harsh chrysotiles are shortened significantly. Amphiboles are even more susceptible to length attrition under mechanical impact, and are usually given their final opening by the consumer, often in the actual mixing or processing operations.

Normally as the fibers become more open, the additional energy required for further opening increases rapidly, imposing a practical limit on the degree of subdivision attainable in commercial milled products. Recently, laboratory grinding tests with an intensive dry grinder¹ showed that it is possible to destroy the structure of chrysotile so that it is no longer identifiable by X-ray diffraction or by the electron micrograph of Fig. 22 (20). Jeffrey chrysotile heated to 700°C for 1 hour yields an amorphous material with exactly the same appearance when viewed by the electron microscope. This suggests that the changes observed with intensive grinding were actually caused by localized temperature surges in a fibril as it absorbed the tremendous energy. To substantiate this hypothesis, chrysotile was subjected to prolonged dry ball milling which yielded a similar appearing amorphous mass. Work is in progress which precluded the possibility of attaining localized high temperatures. Indeed short ultimate fibrils which maintained their crystalline form were easily identifiable as chrysotile.

These observations have been used to explain the results of controlled wear tests performed at the Johns-Manville Research and Engineering Center (23). Wear dust was collected from passenger car brake linings subjected to a series of stops simulating normal traffic and highway driving. Airborne dust and debris in the brake drums were collected separately and analyzed compositionally. The composition of the inorganic fraction of these residues matched that of the original brake lining which contained a total of 70% chrysotile. No chrysotile was observable in the wear dust by either X-ray or optical microscopy. An electron micrograph of the dust is shown in Fig. 23. The resemblance between the dust and chrysotile, which had been mechanically (and, presumably, thermally) destroyed, is evident.

¹Spec. Mixer/Mill, manufactured by Spec. Industries, Inc., 3900 Park Avenue, New Jersey 08812.

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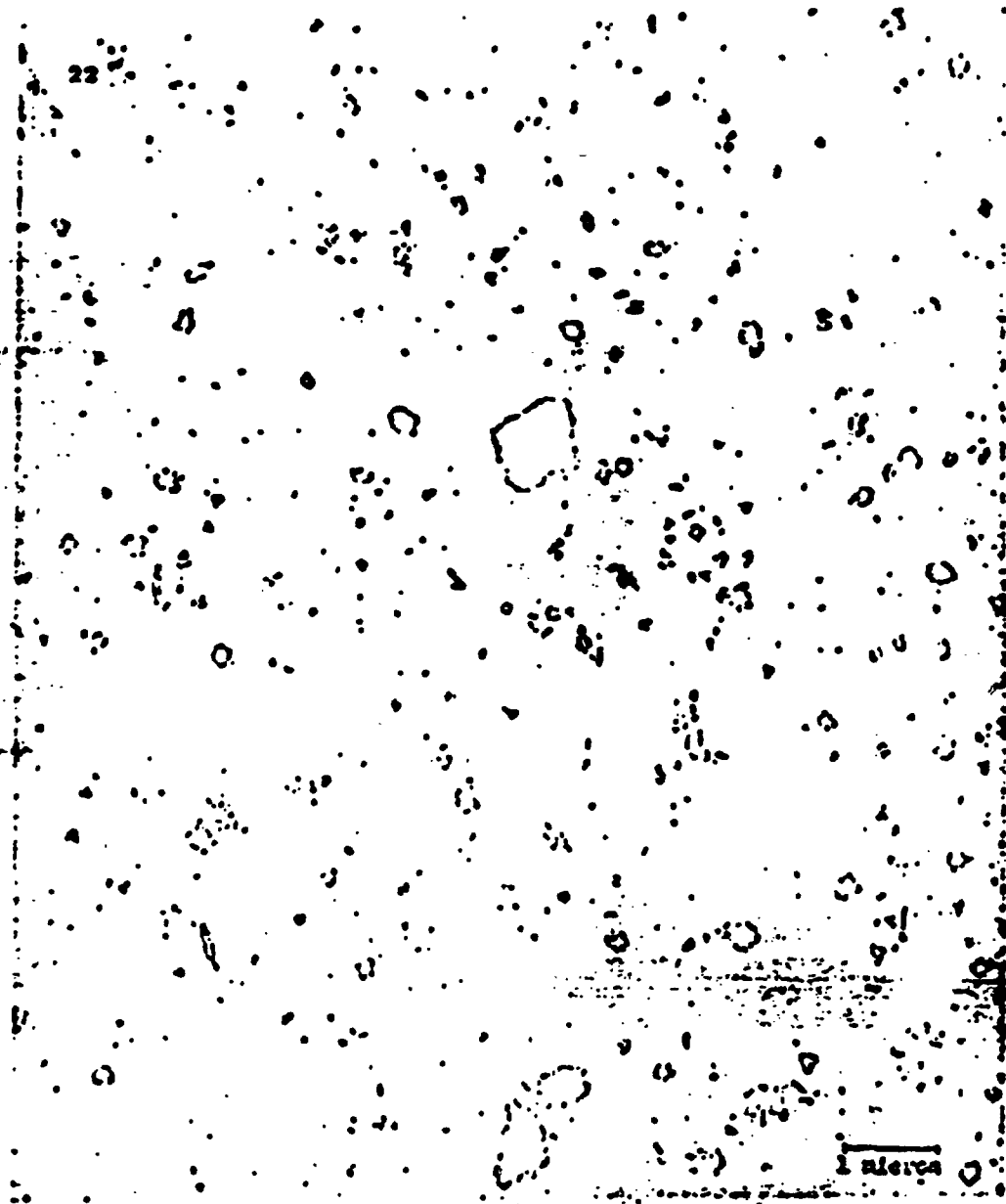


FIG. 22. Electron micrograph of Spec-milled chrysotile. X11,250.

decomposed, is apparent. Despite the fact that thermocouple measurements of the brake drum temperature did not exceed 275°C , theoretical calculations indicated that the temperatures at localized points of contact exceeded 1000°C . Minute fragments of chrysotile fibrils could be observed in some of the electron micrographs and a modified point count technique was devised to determine the chrysotile content. Conservative estimates of the chrysotile content by this method showed that more than 99% of the chrysotile is destroyed during normal brake usage. Similar studies by the U.S. Public Health Service substantiated these results for normal driving conditions (33).

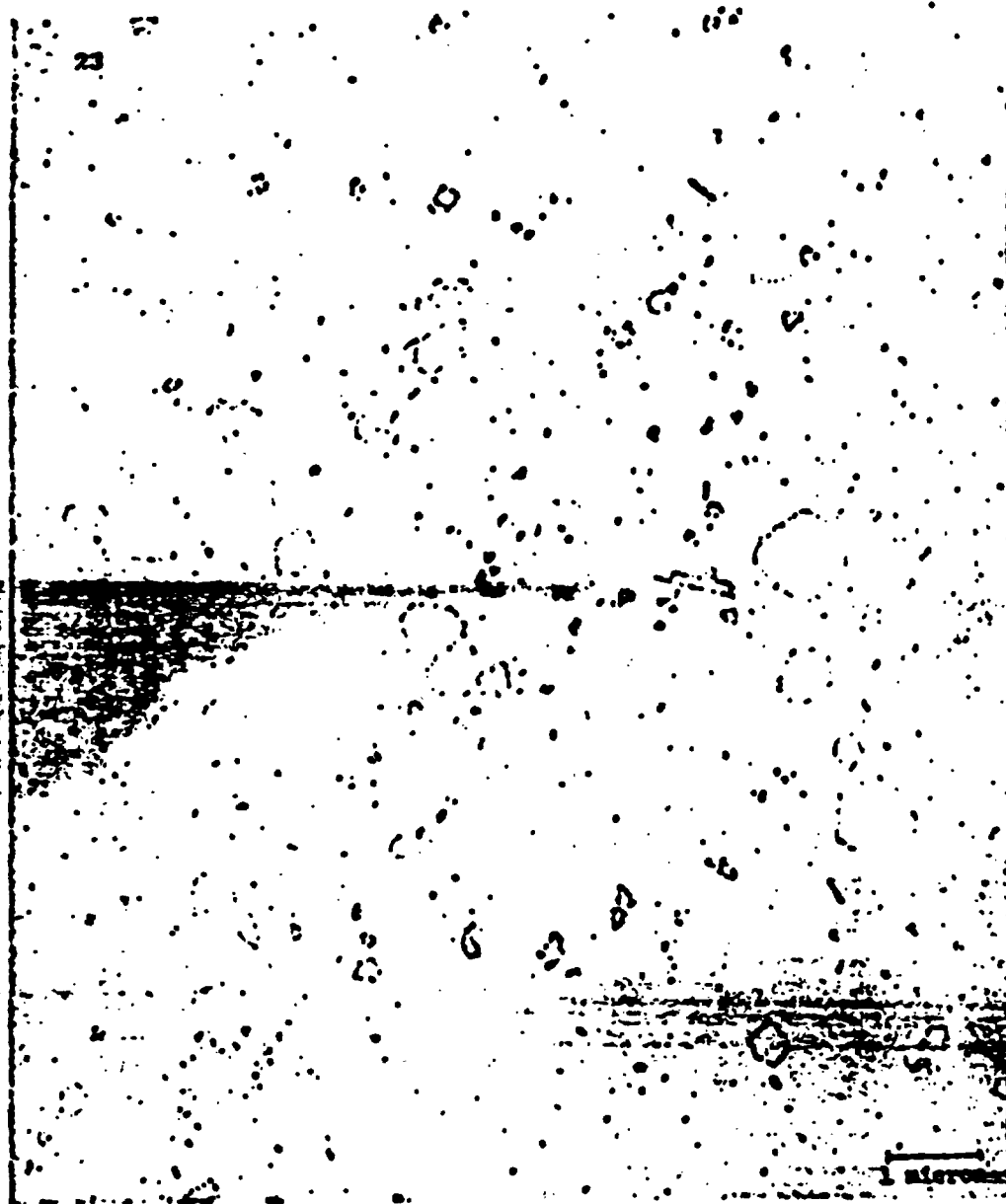


FIG. 23. Electron micrograph of brake lining dust. X11,500.

IDENTIFICATION

The positive identification of the asbestos-form minerals is highly dependent upon such factors as the physical form, the presence of contaminants, prior mechanical, thermal or chemical treatment. The variable nature of the amphiboles makes it necessary to classify a particular sample as "most closely resembling" a specific mineral species.

It is obvious that, even if sufficient material is available, simple chemical analysis is not sufficient to characterize an asbestos-form mineral because all asbestos-form minerals have massive counterparts with the same chemical composition.

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One must, therefore, rely on a combination of methods. The methods most frequently used are chemical analysis, petrographic microscopy, X-ray diffraction, electron microscopy, electron diffraction, and differential thermal analysis.

Perhaps the most reliable method of identification for particles down to a few microns in diameter is petrographic microscopy. Using this technique, the fibrous nature of the species is evident and the optical properties can be used to determine which species is present. Among the amphiboles, however, the variable composition may also effect the optical properties, so that again positive identification may be difficult. In such cases, X-ray diffraction and chemical analysis or DTA can be used for confirmation.

If the size is below the practical working limit for optical microscopy, the electron microscope is the proper tool. This instrument will only give information about the size and shape so that positive identification is not usually possible for specific amphiboles. The tubular appearance of chrysotile under the electron microscope is specific. When electron diffraction is used in conjunction with electron microscopy a better, but still not conclusive, identification of amphiboles is possible.

The electron microprobe is a relatively recent development which is proving of great value for the characterization of small amounts of material. With this instrument it is possible to obtain a complete chemical analysis on a particle as small as 1 μ . It is also possible to study the same particles with both the electron microprobe and the electron microscope, thus making a more complete characterization possible.

Table VI is a listing of the properties of the asbestiform minerals used for their characterization.

SOURCES OF FIBER

Hendry (30) at the 1953 Conference on Biologic Effects of Asbestos summarized the pertinent aspects of the occurrence, production, and commercial applications of asbestos fiber.

Table VII presents the world production of asbestos in 1953 (43). Production has increased with few changes in the relative standing of the producing countries.

The major difference is the great increase in Russian production which now outranks Canada as the major producer. The increased production in the United States over the past few years is due to the recent development of the Coalinga fiber deposits in California. One important change since 1900 is the closing of the Australian crocidolite mines and the elimination of this source from the market. Thus, South Africa remains as the one significant area producing crocidolite and amosite.

Chrysotile accounts for approximately 95% of commercial asbestos. Chrysotile asbestos from Quebec is available in more than 50 standard or specialized grades to meet specific requirements. Some of the larger asbestos mills, such as that of the Jeffrey mine in Asbestos, Quebec, produce many of these grades simultaneously by a complex system of continuous crushing, screening, and aspiration from the same mill feed material.

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TABLE VI
PHYSICAL PROPERTIES USED FOR CHARACTERIZATION OF AMPHIBIOUS MINERALS

	Chrysotile	Crocidolite	Anisite	Anthophyllite	Actinolite, Tremolite
Density	2.54	3.02-3.42	3.10-3.60	2.83-3.37	3.02-3.44
Refraction (M ₂)	21	3	5-6	51-6	5-6
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Unit cell dimensions— <i>a</i>	5.30 ± 0.002 Å	9.75 Å	9.6 Å	14.5 Å	9.83 Å
<i>b</i>	9.10 ± 0.05	18.0	18.3	18.0	14.1
<i>c</i>	7.32 ± 0.02	5.3	5.3	5.3	5.3
<i>γ</i>	98°	103°	105° 30'	—	104° 50'
Refraction indices	1.522-1.540	1.654-1.701	1.635-1.656	1.500-1.604	1.503-1.604
<i>n_α</i>	—	1.624-1.711	1.675-1.700	1.605-1.710	1.612-1.657
<i>n_β</i>	1.544-1.546	1.638-1.717	1.688-1.729	1.613-1.728	1.622-1.708

TABLE VII
PRODUCTION OF ASBESTOS IN 1966

Country	No. of short tons
North America	
Canada (sales)	1,479,281
United States (shipments)	126,923
South America	
Argentina	240*
Bolivia (exports)	4
Brazil	1320
Europe	
Austria	—
Bulgaria	1430*
Finland	13,250
France	7720*
Greece	85*
Italy	90,101
Portugal	10
U.S.S.R.	1,972,000*
Yugoslavia	8111
Africa	
Botswana	530*
Kenya	73
Mozambique	—
Rhodesia, Southern	175,000*
South Africa, Republic of	276,307
Swaziland	26,112
United Arab Republic (Egypt)	2057
Asia	
China	140,000*
Cyprus	21,119
India	7616
Japan	17,067
Korea, South	657
Philippines	—
Taiwan	731
Turkey	1238
Oceania	
Australia	18,473
New Zealand	—
World Total ^b	4,297,010

* Estimates.

^b Unpublished data considered to be reliable (not from Minerals Yearbook).

All fibers from Quebec are classified by a standardized system which, with some modifications, forms the basis for other classification systems in use throughout the world. The longest fibers are Groups 1 and 2, with fiber lengths of over 3 in. and from 3 to 3 in., respectively. These consist of hand-selected cross-void fiber and are termed "crude" asbestos grades since they are normally given final preparation by the ultimate user. Groups 3 through 7 are classified as "milled" fiber with decreasing fiber length, as measured by the Quebec Standard Screen Test (57). Each group is further subdivided into a number of sub-

grades according to their "crudiness," content of grit, bulking, chemical and absorption properties. Subgroups fibres from different sources are not necessarily interchangeable for specific end applications. In the asbestos industry, "crudy" fiber is one which contains a large number of unopened fibrils. Those fiber subgrades in which the fibers have been well fiberized or split are known as "opened" grades.

Table VIII gives the approximate distribution by grades of chrysotile produced in Canada and the United States, as compared to that produced in the USSR in 1968.

TABLE VIII
APPROXIMATE PRODUCTION OF CHRYSOTILE FIBERS BY GRADES IN 1968

Grade	U.S.S.R.	U. S. and Canada
No. 1 Grade		200,000
No. 2 Grade	18,000	
3	130,000	45,000
4	180,000	200,000
5	650,000	200,000
6	380,000	230,000
7	130,000	620,000

Applications

The commercial applications of asbestos are so numerous that this can do no better than refer the reader to the many excellent texts which quite fully cover this subject (8, 92). The uses range from asbestos-cement or floor tile, which consume hundreds of thousands of tons, to specialty applications which may consume only several tons annually. Asbestos is a great variety of products a combination of properties which are attained by using other materials. Its strong fibrous form reinforces such as plastics or cement, or controls viscosity of many systems; its nature is important for resistance to heat and chemical or environmental. Its fine size contributes filtration efficiency and insulating efficiency. Its low cost and low cost are significant factors in promoting commercial applications.

On the basis of relative abundance alone, chrysotile will be used wherever possible in preference to other forms of asbestos. Where a combination of bulking characteristics plus low water content and high temperature resistance are desirable, e.g., thermal insulation, amosite has usually been preferred. Applications requiring resistance to acids usually take advantage of the relatively good acid resistance of crocidolite. Textile products require a silky, longer grade of chrysotile although crocidolite has also been used in acid-resistant textile forms. Geographic considerations may exert economic influence to increase the usage of specific amphiboles, such as anthophyllite in Finland or the crocidolites in South Africa. Anthophyllite has shown some advantages over other asbestiform minerals in reinforcing polypropylene fibers and is used extensively for this purpose.

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In general, specific grades of chrysotile have been developed by the asbestos industry for each market. Although the longer fibers are considered to be of better quality, it would be just as impractical to use relatively long 4-grade fiber in floor tile as it would be to attempt to make satisfactory asbestos paper or asbestos-cement products with 7-grade fibers. In fact, some applications may even require the presence of a considerable amount of the nonfibrous, fine-grained particulate serpentine which is contained in some of the 7-grade subgroups. Normally, the consumer selects the least expensive grade of fiber which will meet his needs.



FIG. 24. Electron micrograph of commercial talc. $\times 2250$.

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Production and applications of asbestos fibers are usually considered to be the only significant sources of asbestos fibers entering the environment. However, on closer examination it becomes evident that we should also consider the question of impurities in asbestos, but also the fact that asbestos fibers are an ubiquitous impurity in many deposits of minerals. Valuable nonmetallic minerals as mica, talc, etc., are often found in association with asbestos. In fact, talc is a mineral product which is often found in commercial asbestos.

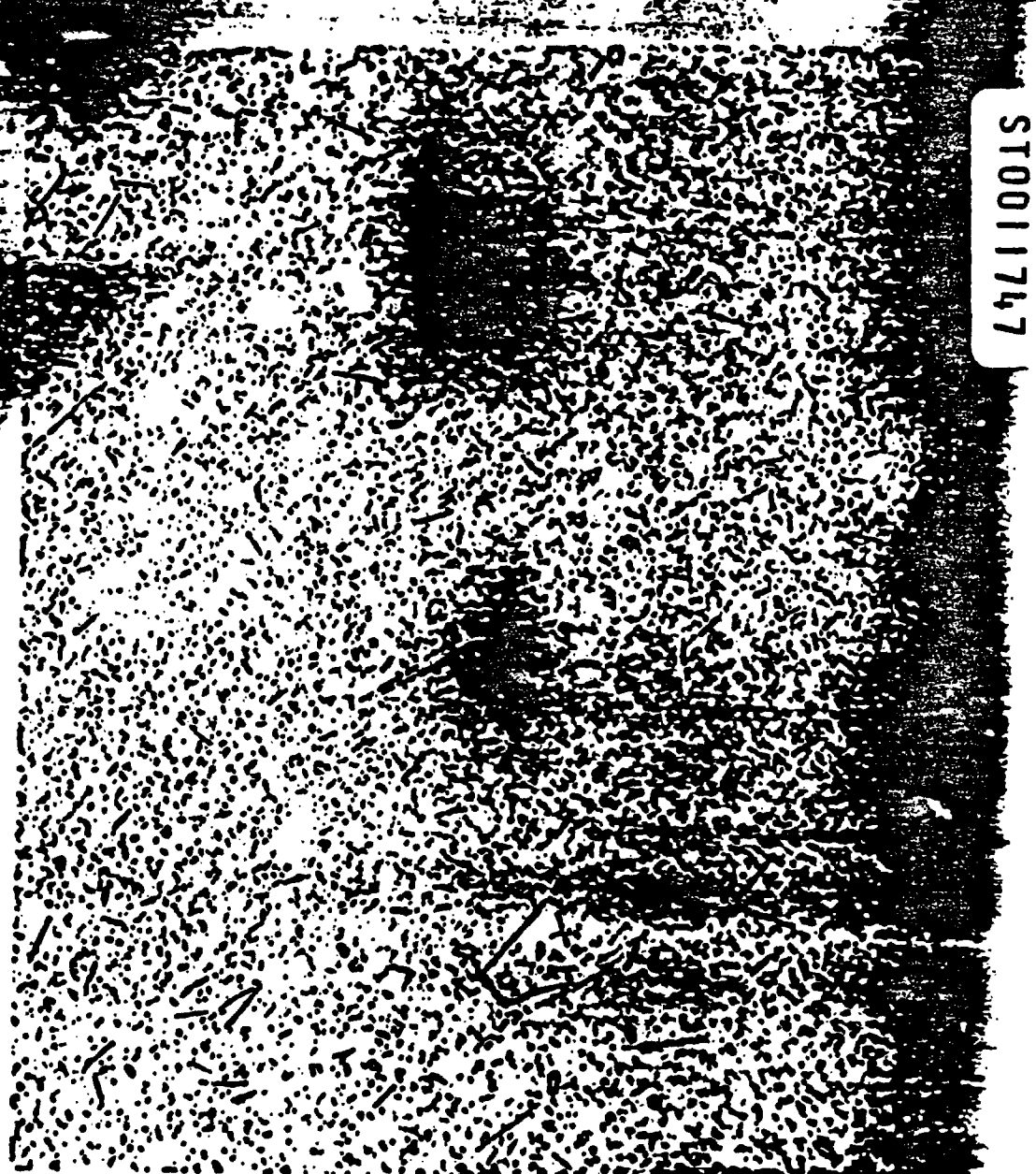


FIG. 21. Electron micrograph of Warren County, New York, asperity. X1000.

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cosmetic applications. Figure 24, an electronmicrograph of a typical lens-faciated industrial talc, reveals the presence of considerable fibrous tremolite. Approximately 3000 tons of talc are used annually as a carrier for pesticides (71). Winslow *et al.* (79) investigated the distribution of talc in the atmosphere and in glacier and snow samples to study the migration of pesticides. Their samples covered a world-wide geographic distribution. In practically every sample, amphiboles were detected along with the talc, as might be anticipated from the common occurrence of amphiboles in talc.

Cralley (14) *et al.* have recently investigated 22 cosmetic talcum products. All had significant fiber contents ranging from 5 to 30% by count of the total talc particulates, and averaging 19%. The fibrous talc included tremolite, anthophyllite, and chrysotile. They made special note of the fact that cosmetic talcum products should be included as a source of fibers from which may be derived ferruginous bodies observed in the lungs of humans.

In another investigation by the U.S. Public Health Service of the source and identification of respirable fibers, Cralley (15) noted that there are more than 100 different natural minerals with some degree of fibrous structure which may occur in respirable sizes. In addition to the asbestos minerals, these included fuller's earth, zeolite, vermiculite, calcium carbonate, gypsum, pyrophyllite, talc, kyanite, hornblende, mica, magnesite, and many others.

Pure serpentine is considered to be composed of nonfibrous antigorite or lizardite based on petrographic and X-ray examination. However, electron microscopy reveals the fact that all serpentine rocks contain significant amounts of chrysotile. Figure 25 is an electron micrograph of a practically translucent "museum grade" serpentine specimen from Warren County, New York, obtained through Wards Natural Science Establishment. Despite its apparent content of approximately 20% of fibers, optical microscopy showed no chrysotile whatsoever.

Examination of many other authenticated samples of "pure serpentine" has revealed the presence of chrysotile. Serpentine rock deposits are widespread throughout the world. In the United States they form the Franciscan serpentine belt along the entire length of California, just as they form much of the Appalachian range on the East Coast. They are used as the basis for many large-scale applications, such as ballast, mud construction, aggregate, building stone. During grinding and preparation for such commercial usage, there could be opportunity for escape of fibrous material.

CONCLUSIONS

It is important for the medical investigator of the biologic effects of asbestos-form minerals to properly understand the wide diversity between the several individual asbestos minerals, the ubiquitous nature of their occurrence, both in commercially valuable form and as impurities in other materials, and the widespread existence of many other minerals with fibrous form. It is only by relating experimental biologic evidence with the variations in physical size and form, in physical strength attributes, in physicochemical surface reactions, in chemical reactivity, and in associated impurities, that we can ultimately arrive at valid medical conclusions.

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COMMONWEALTH OF PENNSYLVANIA
DEPARTMENT OF HEALTH
DIVISION OF OCCUPATIONAL HEALTH

HYGIENIC INFORMATION GUIDE NO. 7

ASBESTOS

K28126

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PROPERTIES:

Asbestos is composed of a number of different minerals which are allicates of various compositions, but basically are of a form of hydrous magnesium silicate. Their chief characteristic is a structure composed of long, parallel, flexible fibers, capable of repeated longitudinal subdivision. Many varieties are sufficiently flexible to be spun into yarn or woven on modified textile machinery. Manufacturing processes can cause this mineral to break up into many minute particles.

THRESHOLD LIMIT VALUE (acceptable atmospheric concentration for 8-hour work period):

5 million particles per cubic foot of air.

MEDICAL ASPECTS:

Long continued inhalation of asbestos dust may result in a form of pneumoconiosis known as asbestosis. The primary effect of such inhalation is a condition of pulmonary fibrosis. A characteristic finding of asbestosis is the presence of "bodies" in the lungs and sputum. Complete roentgenologic study of the chest and histopathological findings are necessary to establish the presence of this disease. Recent studies indicate a definite relationship between inhalation of asbestos and cancer of the lung. In addition pleural and peritoneal mesothelioma have been associated with inhalation of asbestos.

PREVENTION:

- Preplacement:** Occupational history is a necessity. A complete physical examination, including a chest x-ray, should be emphasized.
- Periodic Examination:** A physical examination, together with a 14 x 17 inch chest x-ray film, should be given annually. Cases where pathologic lung changes have occurred should be removed from employment in dusty occupations and medically evaluated periodically.

EXPOSURE CONTROL:

- All dust-producing operations should be equipped with local exhaust ventilation. Where possible, isolation or segregation of the operation should be observed, together with the use of wet methods.
- Housekeeping should be maintained with a view to preventing any accumulation of deposited dust. Vacuum methods of cleaning are preferred, and should be performed "off-shift" or when least exposure to plant personnel would occur.
- Where other methods of control are not feasible, dust respirators, of a type approved by the U.S. Bureau of Mines for protection against pneumoconiosis-producing dusts, should be supplied to those employees subjected to the dusty atmosphere.
- A periodic determination of the dust levels of the plant atmosphere should be made to ascertain the efficiency of the control measures in use.

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