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PROPERTIES OF ASBESTOS SUITABLE FOR USE IN CELLULOSIC PAPER

A. W. Naumann*

ABSTRACT

Chrysotile asbestos is now available in a highly-purified, grit-free form, non-abrasive to Fourdrinier wire and printing plates. Its chemical and physical structure and properties are described relative to the geometry of cellulose pulp fibers. The electrostatic charge properties and surface chemistry of chrysotile in water systems are also discussed in relation to other materials found in paper furnishes.

*Union Carbide Corporation, Mining and Metals Division, Tuxedo, New York, 10987

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Asbestos is a class name for several naturally occurring fibrous minerals. The most common, and the one that is finding increasing use as a paper additive, is chrysotile, $Mg_3(OH)_8Si_4O_{10}$. The purpose of this paper is to compare chrysotile properties with those of other commonly used additives.

CRYSTAL STRUCTURE AND PARTICLE MORPHOLOGY

Chrysotile has a structure like that of the kaolinite minerals (1) in that the structure consists of an alternate series of layers of tetrahedrally coordinated silica and octahedrally coordinated magnesium joined into a composite sheet, with the tips of the silica tetrahedra and one of the surfaces of the octahedral layer lying in a common plane. The silica layer is in an oxide form. The magnesium layer is in a hydroxide form, giving this layer a resemblance to the mineral brucite, $[Mg(OH)_2]$. Figure 1 is a representation of the structure, the "a" dimension having been exaggerated to show the details of the structure.

Pauling (2) predicted, before the layer structure of chrysotile was recognized, that a magnesium analog of the kaolinite minerals would have to exist as curved sheets because of a mismatch in the repeat distances of the individual layers. The normal repeat distance for the silica layers (8.9A), as found in kaolin, is smaller than the corresponding repeat distance of an octahedral magnesia sheet (9.4A), as found in the meneral, brucite (3). Pauling's prediction has been abundantly verified by x-ray diffraction studies and by electron

microscopy (1,4,5). The layers of chrysotile curve and close to form cylinders of extreme length-to-diameter ratio. It is partially this filament-like form of chrysotile asbestos that makes it useful as an additive to a paper furnish. An electron micrograph of typical chrysotile fibrils is given in Figure 2.

As is shown by the calibration marks, the individual chrysotile fibrils are extremely small; many thousands being needed to make up the asbestos filaments visible to the naked eye. Fibril lengths vary from a few microns to many tens of microns. Diameters vary much less, and usually are in the range 250 to 350A. As the following data illustrate, this is a size considerably below that of many materials normally considered to be of small dimensions.

Material	Typical Diameter (microns)
Rock Wool	1-20
Synthetic Organic Fibers	10-40
Human Hair	approx. 40
Paper Pulp Fibers	10-30
Kaolin	0.2-10
TiO_2	0.2-2
Chrysotile	0.025-0.035

The usual mode of occurrence of chrysotile is a "cross-fiber" configuration in which filaments of chrysotile (i.e. bundles of fibers) are closely packed together and set at right angles to the walls of cracks and fissures that extend through the host rock of the ore body (6). Liberation of this material is accomplished by repeated crushing and classification operations (6). The resultant products, particularly the less expensive grades, contained up to several percent by weight of rock fragments and other abrasive constituents; and, for this reason, are not well suited to use on the high-speed machinery used in the paper industry.

In 1959, an unusual deposit of chrysotile asbestos, with properties and mode of occurrence that differ from those of cross-fiber material, was discovered in central California (7). The ore of this deposit, instead of occurring in veins, occurs in randomly-oriented, matte-like flakes and agglomerates that are not associated with the hard, consolidated rock masses characteristic of cross-fiber deposits. The ore is of high grade and is therefore amenable to different processing procedures than are usually used with conventional chrysotile ores. Specifically, wet-processing procedures have been developed that give rise to high-purity asbestos products, essentially grit-free and of high brightness.

ABRASIVENESS OF CHRYSOTILE PRODUCTS

The measure of abrasiveness commonly used in the paper industry is the Valley Abrasion Test. Essentially, the method consists of rubbing a section of Fourdrinier wire with a Micarta block in the presence of a slurry of the material under test. The slurry is introduced at the interface between block and wire. It then flows through the wire to a receiving vessel from which it is recirculated to the interface. The results of the test are reported as the "Valley Abrasion Value", corresponding to the weight lost by the wire in milligrams. Unfortunately, the Valley Abrasion Test does not work well with fibrous materials, since fibers are retained on the Fourdrinier wire and do not recirculate freely. A radiometric-tracer method was developed to circumvent this problem. The details of this method have been given elsewhere (8); but, basically, it consists of measuring the amount of radioactivity transferred to the particles of a suspension, from an irradiated Waring-Blendor impeller, during a prescribed blending period.

A comparison of the abrasiveness of wet-processed and conventional dry-processed chrysotile products, along with data for bleached-sulfite paper stock, is given in Figure 3. The data points of this figure, which establish the correlation between the Valley and the radiometric methods, are for a group of nonfibrous samples for which Valley Abrasion Values were available. Count-rate ranges observed for samples of the

fibrous materials are superimposed on this correlation curve, and the Valley abrasion values inferred. The actual count-rate ranges for materials of the different types were:

	Count Rate (counts/min)
Wet-Processed Chrysotile Products	500 to 1,500
Bleached Sulfite Paper Stock	2,000 to 2,700
Dry-Processed Chrysotile Products	24,000 to 78,000

The wet-processed materials were clearly much less abrasive than the conventional products, and, in fact, were less abrasive than paper pulp. The wet-processed materials, therefore, would not be expected to cause excessive wear to metal surfaces such as those of Fourdrinier wires, trimming knives, printing plates, etc.

CHEMICAL AND PHYSICAL PROPERTIES

It will be shown in the following paper that chrysotile is an unusually versatile paper additive. The properties that make this possible are:

1. electro-positive surface charge in the pH range where most papermaking circuits operate
2. highly anisodimensional particle shape
3. high surface area

Chrysotile fibrils are of colloidal dimensions by virtue of their small diameters; and, when suspended in water, behave according to the classical electrokinetic rules of hydrophobic colloids. That is, the fibrils

develop a surface charge when suspended in aqueous solutions as a result of an adsorption of "potential-determining" ions from the suspending medium. With chrysotile and other oxygen-containing materials (metal silicates, oxides, hydroxides, etc.), the potential-determining ions are H^+ and OH^-. For a given material, adsorption favors hydrogen or hydroxide, depending upon pH. Chrysotile, by virtue of the magnesium hydroxide layer exposed at the surface, has a strong preference for the adsorption of hydrogen ions. Chrysotile surfaces retain hydrogen and display a positive charge in the range of pH 10 to 12 (9,10). Most materials (including cellulose and the mineral fillers commonly used in the paper industry) carry a negative charge in neutral or acidic solutions. Typical values for the electrophoretic mobility of cellulose and of representative fillers are given in Table I. The significance of the charge of chrysotile fibrils, from the standpoint of the retention of fillers and cellulose fines, is obvious. Having a mutually coagulating system of oppositely charged particles is clearly desirable.

Electrostatic attraction, however, is but one of the factors that influence the effectiveness of chrysotile as a retention aid. The cylindrical shape of chrysotile particles is equally important. Collision and coagulation rate in suspensions of solids follow an expression of the form (11).

$$\frac{dn}{dt} = K D R n^2$$

where D = particle diffusion constant

R = particle radius of influence

n = particle concentration

To a first approximation, R (the collision radius of an anisodimensional particle) varies as the longest dimension of the particle; while D (the diffusion constant) varies as the mean particle dimension (11). The net result, for the rod-like particles of chrysotile, is a large effective collision radius and a large diffusion constant. It has also been established that coagulation in polydisperse systems (i.e., systems containing particles of differing size) proceeds more rapidly than in monodisperse suspensions (11). These factors combine to give a high probability for collisions, not only between chrysotile fibrils, but also between the fibrils and other particulate matter. Thus, in a paper furnish, chrysotile simultaneously acts as an effective "getter" for small particles such as pigments or cellulose fines; and is collected itself, either by the fibers of the paper pulp or as tenuous asbestos flocs. With either mode of collection, macroscopically uniform distribution of chrysotile, and of materials collected by the chrysotile, is obtained. The electron micrographs of Figure 4, which are of surface replicas of handsheets prepared with and without fillers, show the distribution of asbestos and TiO_2 on the surface of a pulp fiber.

The electron micrographs of Figure 4 are of further interest with regard to the mechanical properties of paper. The strength of paper is attributable to the combined effects of four factors: (1) the strength of the pulp fibers, (2) the strength of fiber-to-fiber bonds, (3) the fraction of the fiber areas involved in bonding, and (4) the over-all distribution of bonds as determined by sheet formation (13). The adsorp-

tion of chrysotile fibrils onto pulp fiber surfaces will have little influence on the strength of the fibers, but may have considerable influence on the bonding between fibers. It is now generally agreed that bonding in paper is due to the formation of hydrogen bonds at fiber-fiber contacts, and to secondary valence forces of the London-van der Waal's type. Both types of bonding are of short range nature. London-van der Waal's forces decrease as some multiple power of distance. Even for interactions between large particles, where the additivity of forces extend their operative range, the forces fall off rapidly in the first few angstroms and are practically non-existent beyond 100A (14). Typical hydrogen bond distances are 1 to 2A (15). The diameters of chrysotile fibrils (approximately 300A) are long compared to these bond distances. This is not to say that the fibrils act as inert spacers, separating pulp fibers by 300A; for chrysotile fibrils have OH outer surfaces that can enter into hydrogen bonding. Also, pulp fibers are pliable and deformable to a degree, and can expand to fill in the spaces between chrysotile fibrils. But the net effect is to reduce the total attraction between pulp fibers. It has been found, for example, that chrysotile additions to paper result in lower tensile and burst values, and correspondingly improved tear factor and softness. Practical applications of this effect--to improve the softness of tissue and towel products--will be discussed in the paper that follows.

As would be expected from geometric considerations, chrysotile has a relatively high surface area. BET nitrogen values for wet-processed asbestos suitable for the paper industry fall in range 50 to 60 m^2/g. As-

is evidenced by the rather extensive use of chrysotile as a reinforcing filler for plastic and resin systems, chrysotile surfaces have an affinity for organic materials. Use can be made of this property to adsorb soluble organic matter. Adsorption occurs not only for negatively charged molecules (anionic dyes, organic acids, etc.), where electrostatic attraction can be used to account for adsorption, but under favorable conditions can also occur with cationic species. The adsorption of methylene blue from an aqueous solution is given in Figure 5. Dye concentration in solution was extremely low until surface saturation was reached, indicating an extremely favorable distribution between the surface and solution even though a positive ion and a positive surface were involved. In the paper that follows, examples will be given where the adsorption properties of chrysotile have been used for specific applications such as dye retention, improved printability, and pitch control.

Another property of chrysotile that may be of interest for paper applications is its chemical reactivity. Chrysotile is inherently a basic (alkaline) material because of the brucite-like layers that are exposed at fibril surfaces. It has been shown that the solubility and reactivity of chrysotile suspensions are, to a first approximation, similar to those of magnesium hydroxide slurries (16). It is also known that acid gases in the atmosphere and the acid nature of some of the constituents of paper (alum and chloride residues from bleaching) shorten the useful life of paper. It is reasonable to expect that chrysotile would provide a reserve of alkali which would adsorb and neutralize these acids, and thus would contribute to paper's permanence and durability.

In summary, the shape and composition of chrysotile fibrils give rise to a unique combination of chemical and physical properties that should make chrysotile an unusually versatile paper additive. Non-abrasive chrysotile products are now available in quantity, permitting their evaluation for specific applications.

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ACKNOWLEDGMENTS

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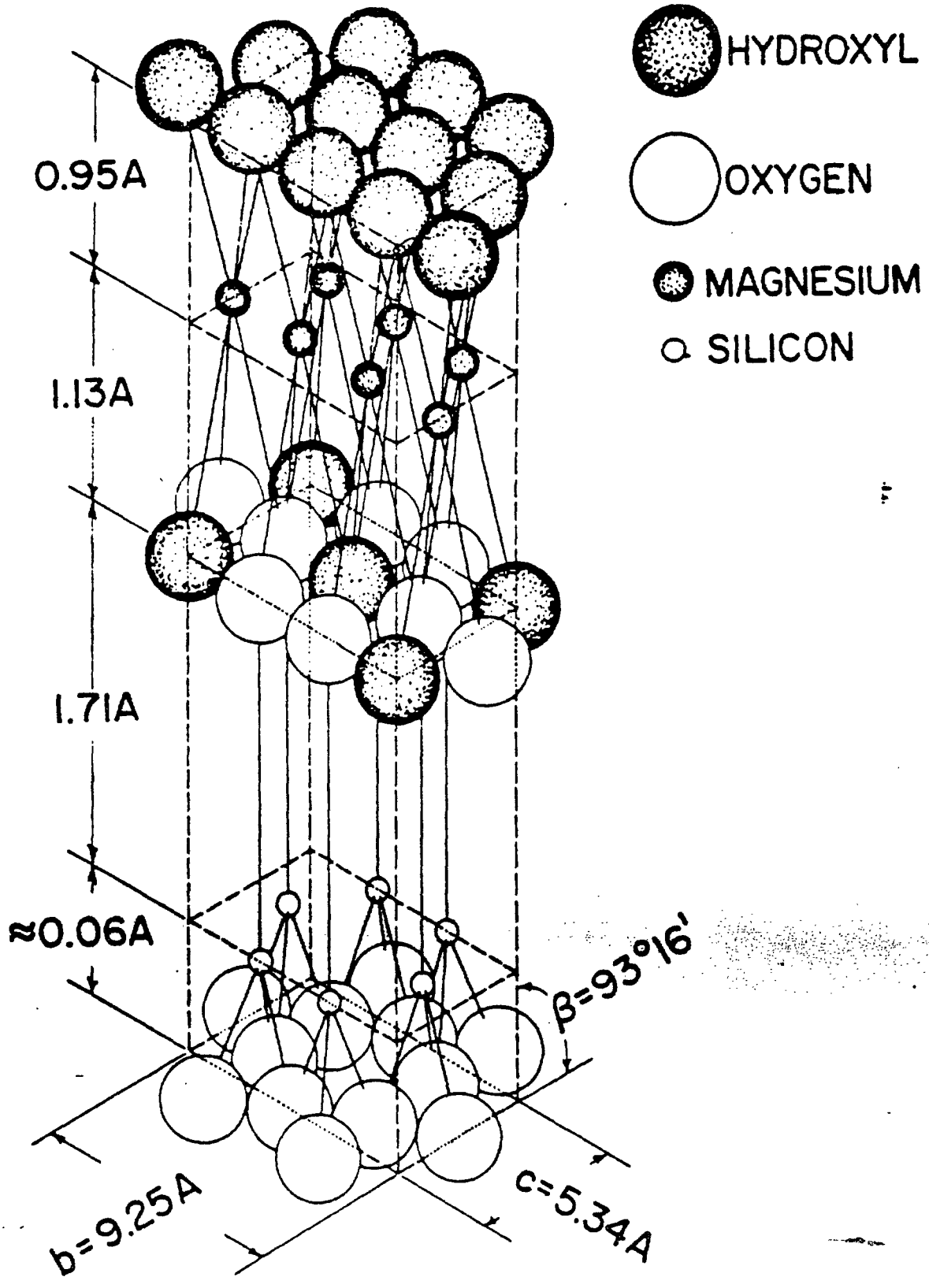


FIGURE 1: Chrysotile structure (after Whittaker).



FIGURE 2: Electron micrograph of chrysotile fibrils (15,900X).

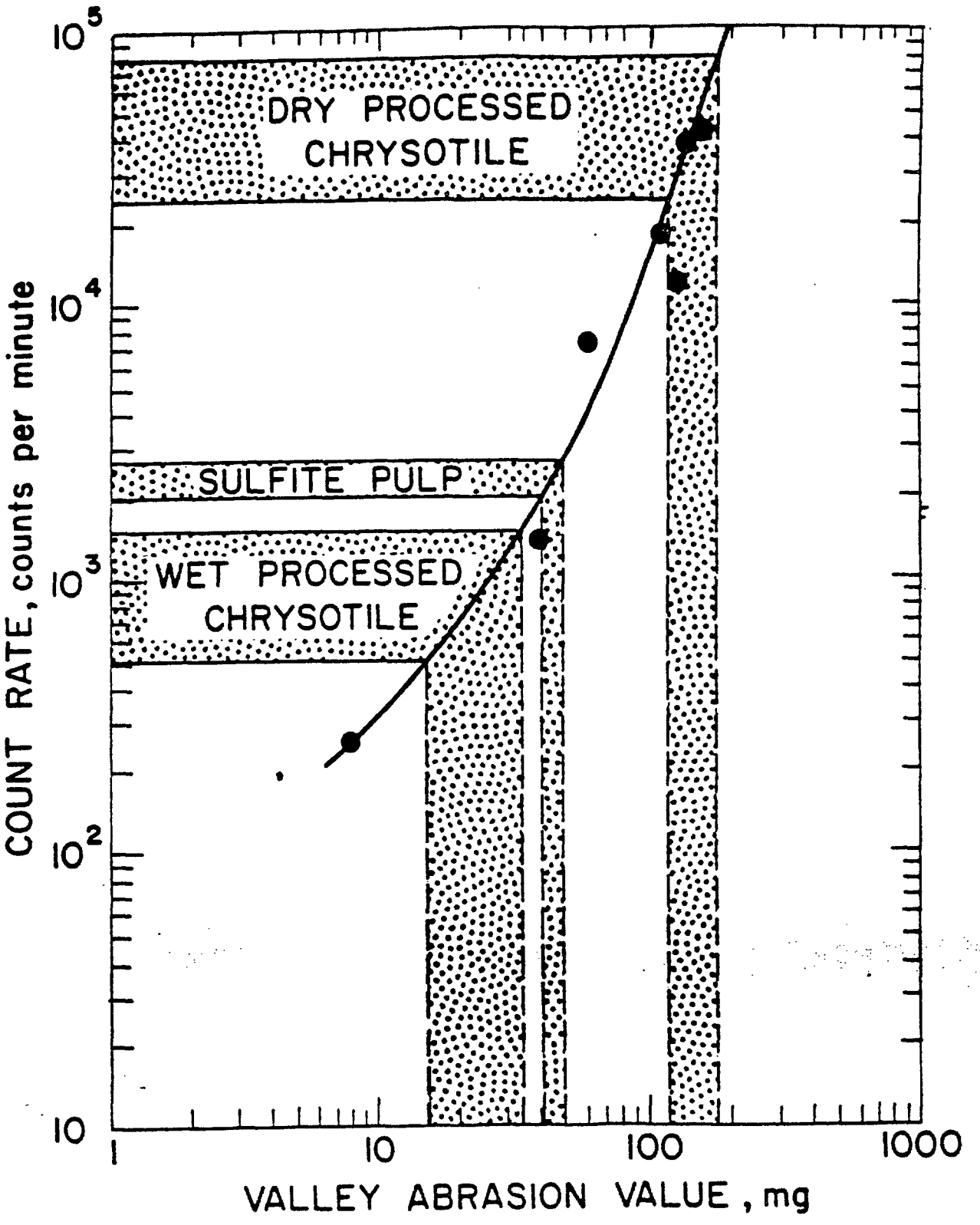
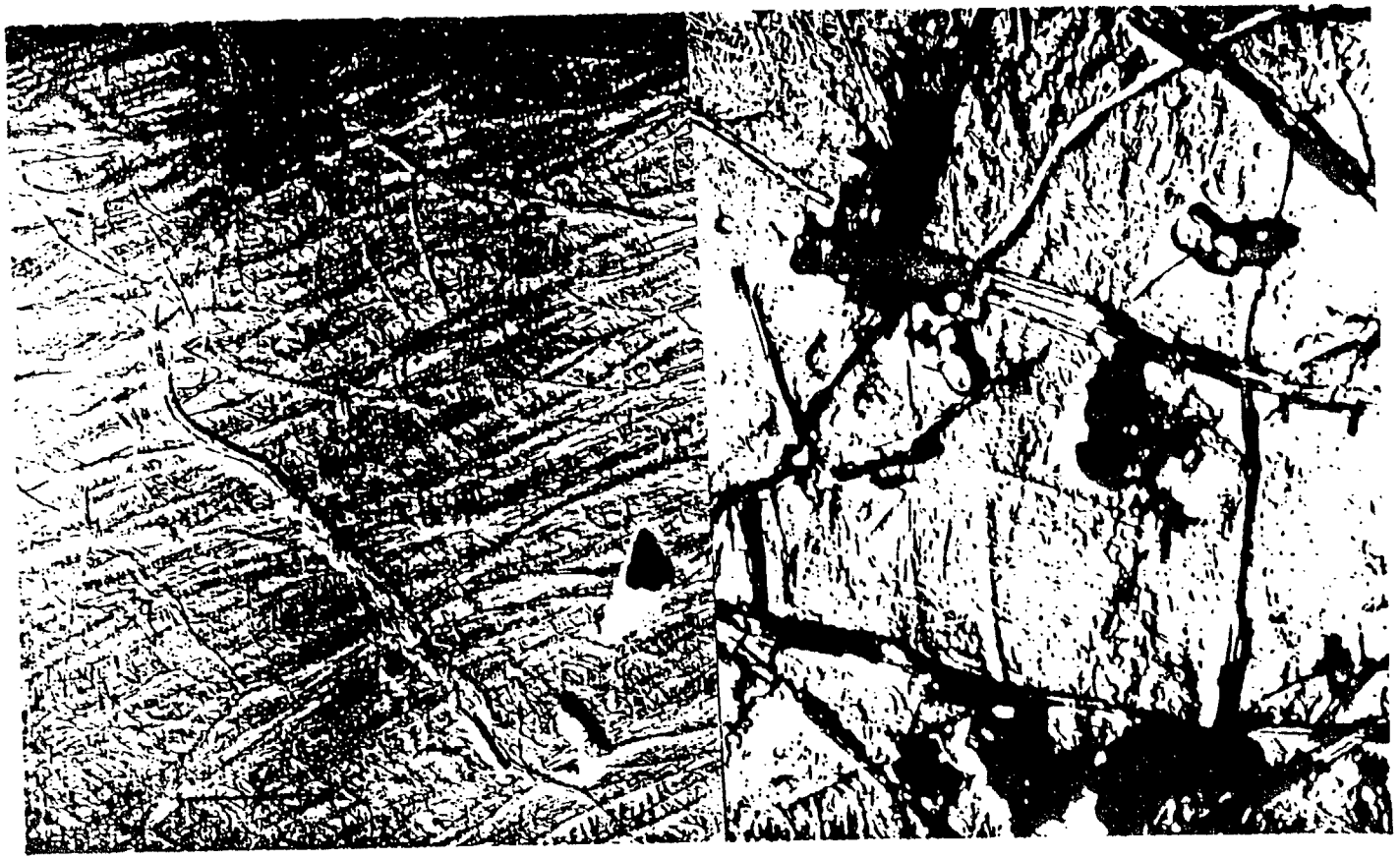


FIGURE 3: Abrasiveness of chrysotile products.



UNFILLED HANDSHEET

FILLED HANDSHEET

FIGURE 4: Electron micrographs (19,950) of surface replicas of handsheets.

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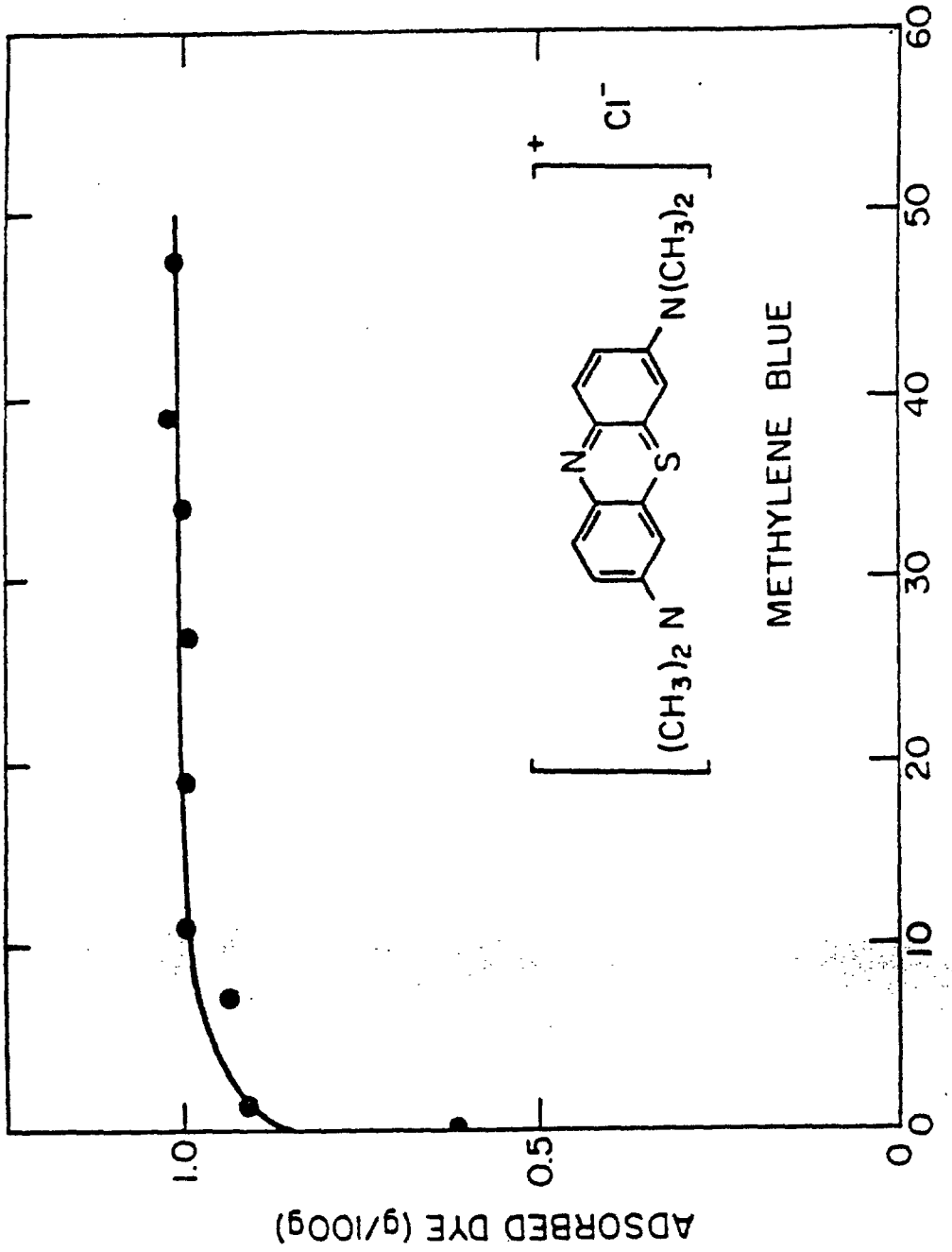

FIGURE 5: Adsorption isotherms of chrysotile with methylene blue.

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TABLE I

ELECTROPHORETIC MOBILITY DATA FOR MINERAL FILLERS*

Material	pH	Mobility micron/sec per volt/cm
Kaolin (Hydrite UF)	6.2	-1.4
Talc (Mistron Frost)	6.6	-1.1
Titanium Dioxide (Titanox AWD)	6.1	-1.1
Bleached Sulfite Paper Pulp	6.4	-1.0
Chrysotile	6.2	+3.1

*Data were obtained by the micro-electrophoresis technique described by Riddick (12).