RESEARCH REPORT NO. 61

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PLAINTIFF'S EXHIBIT

UC-3046

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PHYSICAL PROPERTIES OF COALINGA ASBESTOS.
I. MORPHOLOGY AS INFERRED FROM NITROGEN
ADSORPTION DATA

UNION CARBIDE

UNION CARBIDE CORPORATION

NUCLEAR DIVISION

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RESEARCH REPORT NO. 61

PHYSICAL PROPERTIES OF COALINGA ASBESTOS. I. MORPHOLOGY AS INFERRED FROM NITROGEN ADSORPTION DATA

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Issued: June 26, 1964

UCC 001898

TABLE OF CONTENTS

		Page
I.	SUMMARY AND CONCLUSIONS	1
II.	INTRODUCTION	3
III.	BACKGROUND	5
IV.	EXPERIMENTAL PROCEDURES	13
V.	EXPERIMENTAL RESULTS	15
	A. Reference Chrysotiles	15
	B. Coalinga Specimens	18
	1. Flake chrysotile	19
	2. Bladed chrysotile	21
	3. Serpentinite	22
	4. Products	23
	5. Cross-fiber	24
	C. Stragari Chrysotile	25
	D. Texture Studies	25
VI.	REFERENCES	29

UCC 001899

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ACL Doc 17890 · Page 3 of 32 asbestosclaims.law/library/17890/3

I. SUMMARY AND CONCLUSIONS

Surface area measurements have been made on samples that are representative of the mineral forms that make up the Coalinga asbestos ore body, and these data have been compared with data for chrysotile specimens from other sources. In general, the samples from the Coalinga deposit were of higher surface area than is usually found for natural chrysotile. Coalinga material was also less subject to variation with activation temperature and with wet or dry opening treatments than is usually observed. Surface area values for Coalinga samples ranged from approximately 20 m^2/g for a hard, dense, probably non-fibrous form of serpentine, to 80 m^2/g for thin, leathery flakes of pure chrysotile. Refined and semi-refined asbestos products derived from the Coalinga deposit had areas in the range 50 to 60 m^2/g.

In a comparison study, a specimen of chrysotile from Stragari, Serbia, Yugoslavia, was found to have physical appearances and adsorptive properties similar to those of "Coalinga flake". The results of similar examinations made on specimens of four Canadian materials were more in line with values reported in the literature to be typical for chrysotile. The apparent surface area of the Canadian specimens was a function of activation temperature, and was increased by wet or dry mechanical opening treatments. After chemical dispersion treatment these Canadian specimens had areas approaching those of Coalinga materials, and the surface area was also independent of activation temperature.

The adsorption properties of the Canadian specimens were interpreted as reflecting a structure consisting of a closely packed array of tubular chrysotile fibrils with extra-fibril solid matter cementing the assemblage together. A solid made up in this way would have a well-defined pore structure and would have, as available surface, something less than the total surface of the individual fibrils. Thus, various types of opening processes tear fibrils from the matrix in which they are imbedded and expose their true surface area. Chemical dispersion of the opened material allows a nearly pure fraction of fibrils to be obtained. The adsorptive properties of the Coalinga and Stragari chrysotile specimens were indicative of a much looser structure with essentially all fibril surfaces available for adsorption, and with voids between fibrils sufficiently large so

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ACL Doc 17890 · Page 4 of 32 asbestosclaims.law/library/17890/4

as to prevent capillary condensation of water between fibrils. The adsorption data indicate further that the central pores of the fibrils from both the Coalinga and the Canadian specimens studied in the present investigation were not available for adsorption, and that the pore structures observed with the Canadian specimens were associated entirely with voids between fibrils, and not within fibrils.

The similarities between the Coalinga materials and the Serbian chrysotile indicate that while Coalinga asbestos differs from most other chrysotile asbestos, it is not truly unique.

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ACL Doc 17890 · Page 5 of 32 asbestosclaims.law/library/17890/5

II. INTRODUCTION

Very soon after the first samples of asbestos were received from the Union Carbide deposit near Coalinga, California, it was realized that this was an unusual and perhaps a unique material. In all mineralogical and chemical examinations the material was without a doubt the mineral chrysotile - the most commonly occurring asbestiform mineral. The mode of its occurrence and some of its physical properties indicated, however, that there were differences between this material and the material mined in Canada and elsewhere. In spite of these outward differences, the microscopic particles, as observed in the electron microscope, and the crystal structure, as observed using x-ray diffraction, indicated that structurally these two materials were identical.

The mode of occurrence of the material in the deposit misled many people, including asbestos experts, for many years. Even though there are small deposits of conventional cross-fiber chrysotile in the vicinity of the Coalinga deposit which, at various times, have been mined on a small scale, the main ore body was completely ignored because of its unusual appearance. The ore, instead of occurring in veins with the fiber oriented perpendicular to the plane of the vein, occurs in randomly oriented matte-like flakes and agglomerates in a "slip" orientation. The ore is so high grade and so friable that the deposit can be mined non-selectively with a bulldozer.

Early physical tests and application amenability studies indicated that there were differences between Coalinga chrysotile fiber and Canadian chrysotile fiber. When asbestos is to be used in organic polymer matrices, such as in vinyl-asbestos tile, the oil absorbency of the fiber is a critical factor. Comparative tests run on Coalinga dry-processed material and Canadian dry-processed material showed that nearly twice as much di-octyl phthalate could be absorbed by Coalinga asbestos as could be absorbed by Canadian asbestos. Similarly, Coalinga products showed a substantially higher kerosene absorption factor than did the comparable Canadian Group 7 grade fiber. Specific surface areas, as determined by nitrogen adsorption, were invariably higher for Coalinga fiber than for Canadian materials. Early tests of the amenability of Coalinga asbestos to vinyl-asbestos tile

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ACL Doc 17890 · Page 6 of 32 asbestosclaims.law/library/17890/6

production indicated the need for significant changes of the tile formulation and manufacturing procedure if this material was to be used. The need for these changes was quickly correlated with the high specific surface of Coalinga asbestos. Independently, Johns-Manville personnel discovered that between one-third and one-half the amount of asbestos would be required in vinyl-asbestos tile formulations if Coalinga fiber were to be used in place of Canadian fiber. The balance of the formulation could then be made up by less expensive fillers.

In view of the similarities and yet obvious differences between Coalinga chrysotile asbestos and chrysotile asbestos from other sources, fundamental studies were undertaken to explain the apparently anomalous behavior of the Coalinga asbestos.

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ACL Doc 17890 · Page 7 of 32 asbestosclaims.law/library/17890/7

III. BACKGROUND

The mineral chrysotile, $Mg_6(OH)_8 Si_4O_{10}$, has a layer structure like that of the kaolinite minerals[1,2]. The structure consists of a tetrahedral silica layer and an octahedral magnesium hydroxide layer joined together into a composite sheet in which the tips of the silica tetrahedra and one of the surfaces of the octahedral layer lie in a common plane. Figure 1 is a representation of the structure. In this diagram the "a" dimension has been exaggerated in order to show the details of the structure.

Pauling[3] 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 miss-match in the natural repeat distances of the individual layers. The normal repeat distance for the silica layers, 8.9 Å, as found in kaolin, is smaller than the equivalent repeat distance of an octahedral magnesia sheet, 9.4 Å, as found in the mineral, brucite[4]. Pauling's prediction has been abundantly verified by x-ray diffraction studies and by electron microscopy[2, 5-10]. The layers of chrysotile curve and close to form cylinders of extreme length to diameter ratio. The electron micrographs of Figure 2 are typical of the chrysotile crystals or fibrils that are formed in this way.

Figure 2 illustrates another peculiarity of chrysotile fibrils, namely, in electron micrographs they appear hollow along some segments of their length. It was once suspected that this was an artifact resulting from changes that occurred during sample preparation or under the influence of electron beams[2,11], but later work, particularly the end-view electron micrographs of Maser, Rice, and Klug[10], leaves little doubt about the tubular morphology of chrysotile. This permits a characterization of the fibrils in terms of an inner and an outer diameter.

The length of chrysotile fibrils range from a few microns to many tens of microns. Tube diameters are subject to much less variation. Dimensional data that have been obtained for chrysotile specimens from various sources are summarized in Table I. A narrow range of inner and outer diameters is to be expected, for the lattice miss-match that causes curvature and tube formation gives rise to a strain-free configuration at only one unique radius of curvature. There will be strain for larger or smaller

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ACL Doc 17890 · Page 8 of 32 asbestosclaims.law/library/17890/8

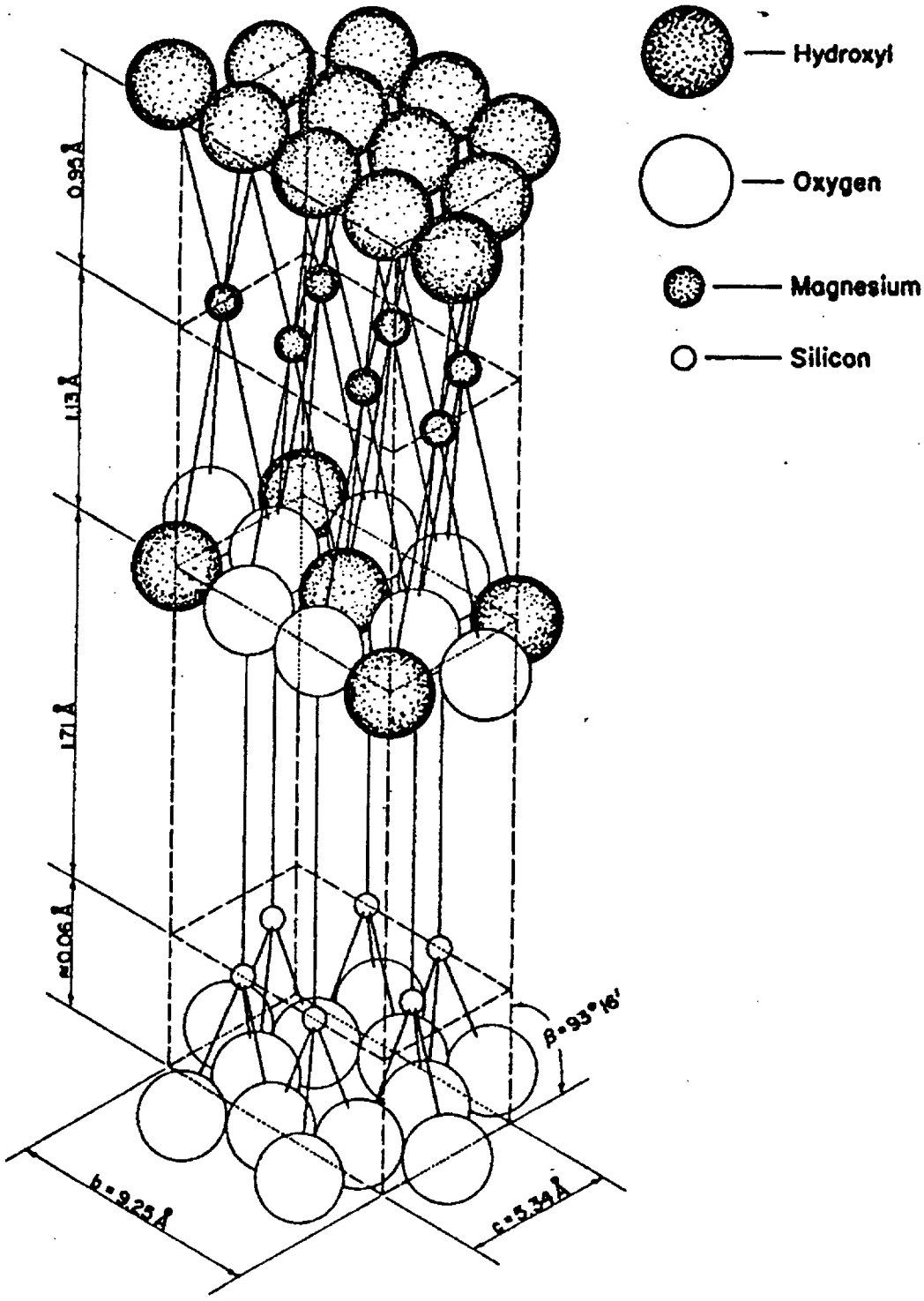
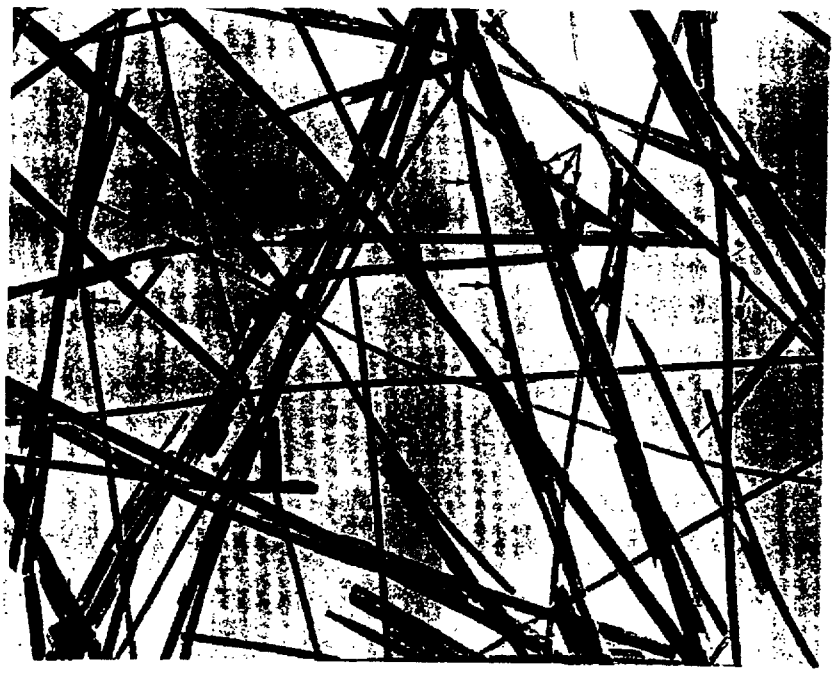
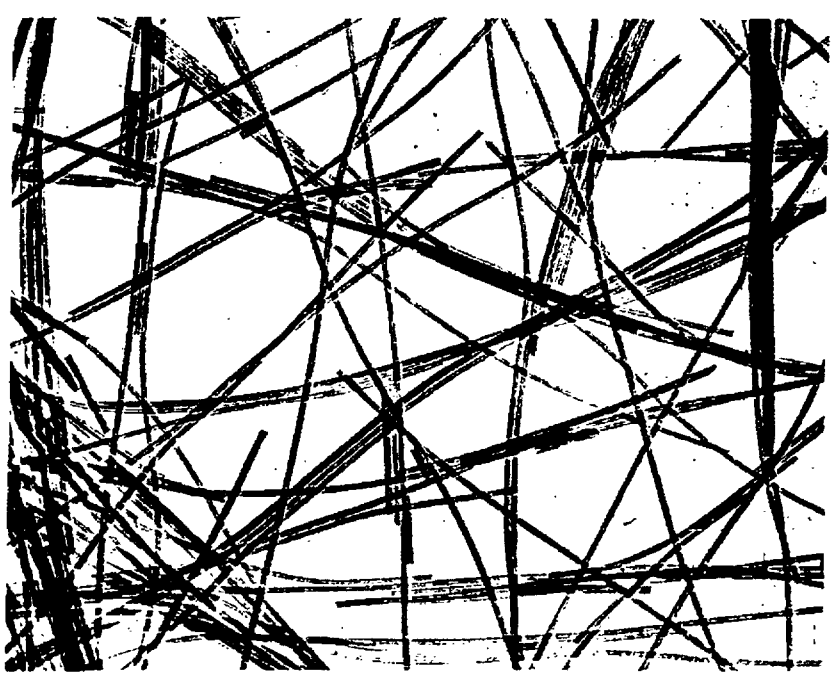


FIGURE I : CHRYSOTILE STRUCTURE (after Whittaker)

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a. Dispersed Grade 7R Asbestos



b. Dispersed Coalinga Flake Chrysotile

FIG. 2 : ELECTRON MICROGRAPHS OF CHRYSOTILE.

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radii which will increase with increasing departure from the ideal radius. This limits the number of layers that can be built-up into a stable cylindrical wall, and thus it controls average fibril dimensions and the distribution of sizes around the average. Whittaker's average values of 260 Å and 110 Å for outer and inner diameters, for example, correspond to a wall 10 layers thick[2].

TABLE I

DIMENSIONAL DATA FOR CHRYSOTILE ASBESTOS

Reference	Inside Diameter, Å		Outside Diameter, Å	
	Range	Average	Range	Average
Fankuchen and Schneider[12]				195-250
Noll and Kircher[7]			120-300	
Jagodzinski and Bagchi[13]		130		260
Young and Healey[14]		150		350
Whittaker[2]	50-75	110	175-350	260
Kalousek and Muttart[15]			100-500	340
Bates and Comer[16]	20-190	68	114-850	250
Maser, Rice, and Klug[10]			200-500	340
Jagodzinski[17]		350		500
Pundsack[18]		20-50		200-500

In view of the strain considerations, one might expect fibril diameter to be restricted to an even narrower range than is observed. It is known, however, that composition varies somewhat for chrysotile from different sources and, as discussed by Roy and Roy[19], the kind and degree of isomorphous substitution influences the morphology of serpentines. Also, some variation in fibril diameters can arise through strain relief by the formation of structures more complex than simple cylinders. The "tube-within-tube" structures observed by Maser, Rice, and Klug[10] may be cited as an example.

A simple packing of fibrils to form the filaments characteristic of chrysotile should, from simple geometric considerations, lead to a material

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ACL Doc 17890 · Page 11 of 32 asbestosclaims.law/library/17890/11

of high surface area and high porosity. For example, a packing of hollow cylinders as depicted in Figure 3a, with outer diameters of 300 Å, inner diameters of 150 Å, and a specific gravity of 2.56 g/cc for tube walls would lead to the following bulk properties:

Surface Area:	69	m^2/g for external fibril surfaces
	35	mm^2/g for internal fibril surfaces
	104	m^2/g Total
Pore Volume:	23%	for internal voids
	9%	for voids between fibrils
	32%	Total

The observed bulk properties of chrysotile seldom approach these indicated values, as is illustrated by the data of Table II.

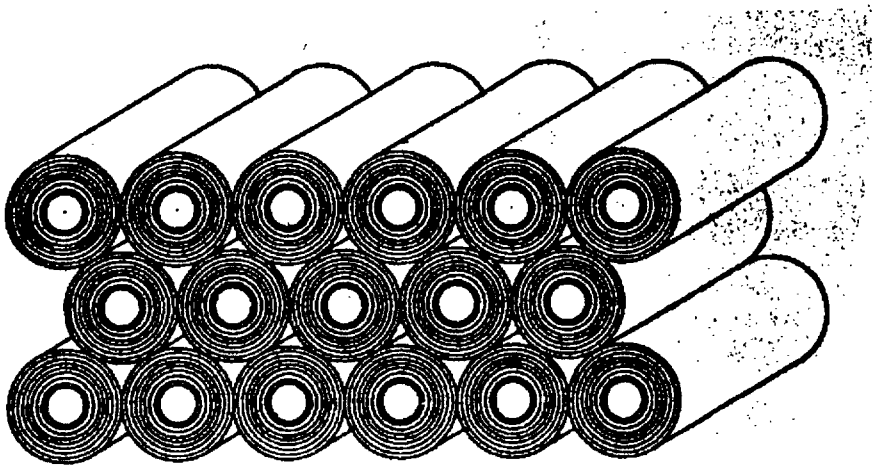
TABLE II

BULK PROPERTIES OF CHRYSOTILE ASBESTOS

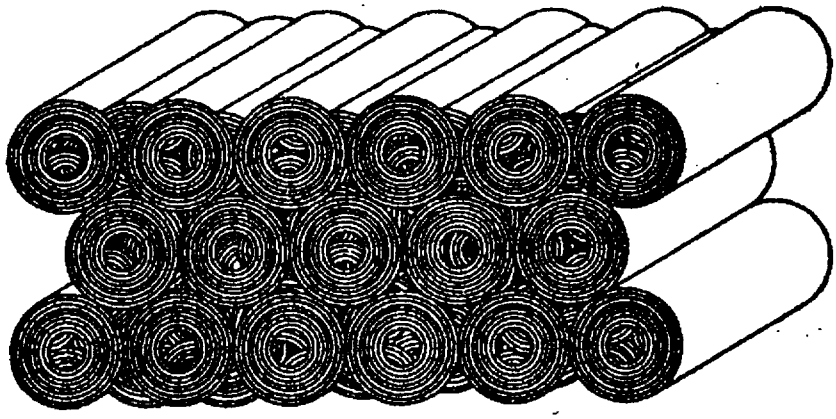
	Specific Surface, m^2/g	Pore Volume, %
Bugge, Kerlogue, and Westwick[20]	14	
Nagy and Bates[21]	7	
Young and Healey[14]	10-20	
Pundsack (1955)[22]		
Bulk specimens	4-12	
Product of dry mechanical opening	≈ 30	
Product of chemical opening (Novak Process)[23]	> 50	
Kalousek and Muttart[15]	-	1-12
Noll, Kircher, and Sybertz[24]	10-60	
Pundsack (1961)[18]	17-21	4-5

The rather wide range of values observed for specific surface and pore volume is not due to an inability to measure these properties, for, in general, the measurements have been made with high precision. Rather, a range of values

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a. Idealized open structure



b. Idealized closed structure (after Whittaker)

FIG. 3: REPRESENTATIONS OF FIBER PACKING.

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ACL Doc 17890 · Page 13 of 32 **asbestosclaims.law/library/17890/13**

is observed because variations occur with the source, state of subdivision, and prior treatment of the materials studied.

The most reasonable interpretation for the discrepancies between potential and observed bulk properties is that at least a portion of the potential void spaces are not empty. As shown in Figure 3a, there are at least two types of void spaces in a compaction of asbestos fibrils - the intra-fibril or axial void and the inter-fibril void. Several investigators have considered the filling of these voids with condensed water or with a solid material. Evidence for a capillary condensation of water into pore spaces within chrysotile fibril compactions has been given by Pundsack[18] and by Young and Healey[14]. The presence of condensed water has been used to account for the variation of specific surface with temperature that is often observed with chrysotile. The question of the existence of solid material filling pore spaces must be divided into the filling of inter-fibril pores and the filling of intra-fibril pores. Convincing evidence has been obtained for the presence of solid matter between fibrils. Particularly noteworthy in this regard are the electron microscope replicas of Bates and Comer[16] which show that troughs with sharp cusps between them appear on fracture surfaces. These may be identified as regions where asbestos fibrils have been pulled from a solid matrix. The question of the presence or absence of solid materials in the central pores of chrysotile fibrils is less well resolved, but the preponderance of evidence points to at least a partial filling of the fibril centers. Electron micrographs show that the centers of fibrils are, for the most part, of lower electron density than the fibril walls, but they also indicate that density is greater in some regions than in others. The differences may reflect regions that contain a solid filling and others where none is present. Alternatively, the fibrils may be completely filled and the differences result because of variations in the density of the filling. Density data for massive chrysotile specimens favor the latter[11,15]. With either interpretation, at least a partial blocking of the central pores is indicated.

Aside from the evidence for its existence, little can be said about the nature or structure of the solid materials within and between fibrils. Presumably, it can range from amorphous phases as favored by some authors[10,16,25], to crystalline cylindrical segments of chrysotile arranged as suggested by Whittaker[2] (Figure 3b). There can also be a

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ACL Doc 17890 · Page 14 of 32 asbestosclaims.law/library/17890/14

variation in the amount of extra-fibril solid matter present. The illustrations of Figure 3 are idealizations to represent the extremes that are possible. Natural chrysotiles, in principle, can have structures anywhere between these extremes.

It is the purpose of this report to show that chrysotile from the Coalinga asbestos ore body resembles the loose structure of Figure 3a more closely than does chrysotile from most other sources. These data will deal with the magnitude of the surface area of chrysotile specimens, as determined by nitrogen adsorption. Particular emphasis will be on the manner in which surface area varies with activation temperature, with wet and dry mechanical opening, and with chemical dispersion, and on the structural implications that can be inferred from these variations.

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ACL Doc 17890 · Page 15 of 32
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IV. EXPERIMENTAL PROCEDURES

Nitrogen adsorption data were obtained using a Perkin-Elmer-Shell Model 212B Sorptometer. A discussion of the principle upon which this instrument operates and of the experimental procedures employed has been given by Nelson and Eggertsen[26]. Specific surface areas were calculated from adsorption data using the conventional BET treatment[27]. The surface areas of two sets of referenced samples were measured to check the validity of the method.

Data for the referenced adsorbents were as follows:

National Bureau of Standards Reference Adsorbents

Adsorbent	NBS Value	This Laboratory
No.2 - Anatase	10.3 m^2/g	10.8 m^2/g
No.6 - Bone Char	69 m^2/g	73 m^2/g
No.8 - Silica-Alumina Catalyst	550 m^2/g	550±25* m^2/g

*Difficulties were encountered with the activation of this sample. The material was extremely fine-grained, and contained approximately 20% by weight volatiles.

Reference Samples from Tonawanda Laboratories, Linde Company

Adsorbent	Linde Value	This Laboratory
Cabot P-4 Wollastonite	2.5 m^2/g	2.7 m^2/g
UCCND Coalinga Asbestos	53	59
Silica adsorbent produced by acid leaching of Coalinga asbestos	515	467
Davison Grade 03 silica gel	740	730

Samples were outgassed by heating overnight in a vacuum. Temperatures for activation were those suggested by the suppliers for the two sets of adsorbents. A temperature of 200°C was used for the Linde samples, and 350°C for the NBS materials. Absolute agreement was within approximately 5% of the stated values for the NBS adsorbents, and approximately 10% for the Linde samples. Reproducibility for a given sample was better than 5%.

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ACL Doc 17890 · Page 16 of 32 asbestosclaims.law/library/17890/16

Surface area data were obtained for chrysotile specimens in their natural state, i.e., the form in which they were received, and, in most cases for portions of the samples that had been given additional mechanical opening and chemical dispersion treatments. The chemical dispersion treatment consisted of mechanically thrashing the samples in a Waring Blendor with a solution of an appropriate dispersing reagent such as acetic acid, aluminum chloride, or a combination of sodium aluminate and acetic acid. The resultant suspensions were centrifuged for 5 minutes at 1000 rpm. in an International Model SBV centrifuge to remove gangue particles and partially opened fiber bundles. The materials remaining in suspension were collected and dried for surface area measurements. The purpose of this treatment was to provide a source of completely defibrillated, monofilament chrysotile for examination. Purely mechanical opening was achieved either by thrashing a suspension of the materials in a Waring Blendor without dispersdng reagents, or by dry grinding in a high intensity ball mill.

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V. EXPERIMENTAL RESULTS

A. Reference Chrysotile Samples

Nitrogen adsorption data for four Canadian chrysotile specimens were consistent with literature values for chrysotile with regard to magnitude, and also with regard to the manner in which apparent surface area varied with activation temperature[14], with mechanical opening, and with chemical opening treatments[22].

TABLE I

APPARENT SURFACE AREA FOR CANADIAN CHRYSOTILES

Material	Activation Temperature 100°C	200°C	425°C
Quebec Long Fiber - Untreated	15	18	22
Cassiar AC - untreated	19	20	22
Mechanically opened, dry	34	36	38
Mechanically opened, wet	43	43	-
Dispersed chemically	51	50	49
Grade 7R3 - untreated	31	30	44
Dispersed chemically	52	52	50
Grade 7TF - untreated	20	25	30
Dispersed chemically	45	45	44

The first two materials were essentially pure chrysotile. The first was a longer fiber asbestos from the Thetford, Quebec, area supplied by Wards Natural Science Establishment. The adsorption data were obtained for filaments pulled from a cross-fiber block specimen. The second material was a mechanically purified product from the Cassiar, British Columbia, mine of Cassiar Asbestos Corp., Ltd. This was also a long fiber material, and was in the form of tangled filaments. The material designated "Mechanically opened, dry" consisted of filaments that had been ground to -200 mesh in a Pitchford Grinder - a high intensity vibrating ball mill. "Mechanically opened, wet"

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ACL Doc 17890 · Page 18 of 32 asbestosclaims.law/library/17890/18

refers to material that was thrashed with water in a Waring Blendor. The third and fourth asbestos types were powdery, commercial asbestos products prepared by conventional dry processing methods. The probable source of these materials was the Thetford, Quebec, area. Both contained appreciable amounts of brucite and magnetite, and lesser amounts of other impurities. Of the two, 7TF had the greater gangue content.

A BET plot of the data for untreated Cassiar AC is given in Figure 4 to give a feel for the sensitivity and resolution of the surface area method. The change in area with activation temperature for this sample was real and measurable, even though the changes were small. The data points for each temperature fall on a straight line in accordance with BET theory.

The adsorption data for the Canadian materials were in line with the generally accepted view of the morphology of natural chrysotile, namely, a closely packed array of tubular asbestos fibrils with extra-fibril solid matter cementing the assemblage together. A solid made up in this way would have a well defined capilliary pore structure, and because of the extra-fibril filling, would have something less than the total surface of the individual fibrils as available surface.

In terms of this close-packed structure, the Canadian materials had a relatively low surface area when activated at 100°C. because a large portion of the fibril surfaces are made unavailable by extra-fibril solid materials and by water condensed in capillary pores. Apparent surface area was larger at higher activation temperatures because of the removal of the capillary water. An additional variation with activation temperature occurs when accessory minerals that decompose to yield products of high surface area are present. As mentioned previously, both Grade 7R and 7TF contained brucite which dehydrates to MgO at 350° to 400°C. This contributed to the increase in apparent surface between 200°C. and 425°C. for both materials. The increase in surface area with wet or dry mechanical opening is due to a liberation of individual fibrils. The effects of dry mechanical opening is shown directly by the samples of Cassiar AC where an increase in surface area was brought about by grinding. The effect is shown indirectly by the magnitudes of the areas of the four starting materials. The Quebec long fiber sample, which had received the least mechanical work, had the smallest area; while the commercial grades 7R3 and 7TF, whose powdery appearance were indicative of drastic mechanical treatments, had the largest areas.

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ACL Doc 17890 · Page 19 of 32 asbestosclaims.law/library/17890/19

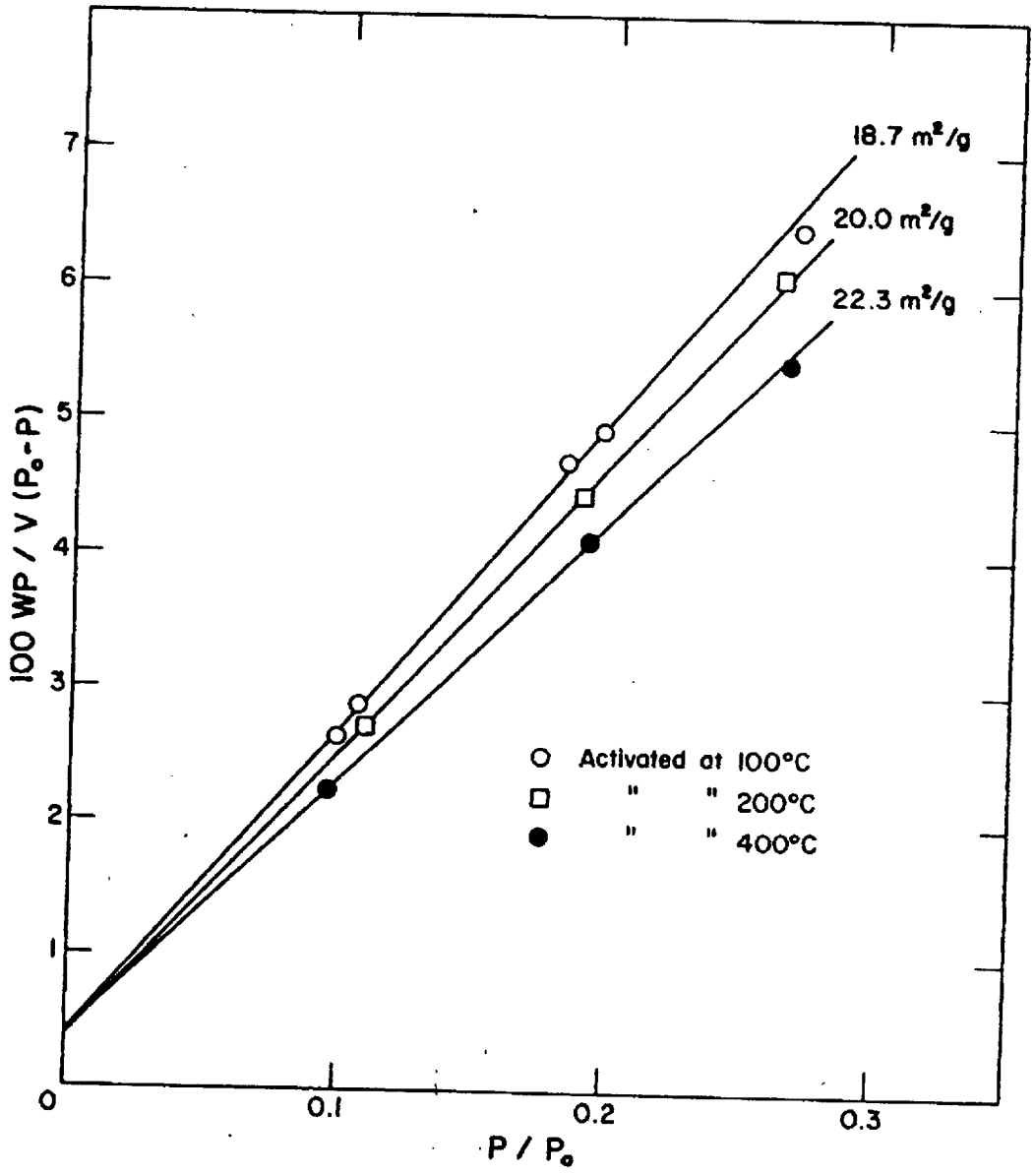


FIG. 4: BET plot for Cassiar chrysotile.

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ACL Doc 17890 · Page 20 of 32
asbestosclaims.law/library/17890/20

The products of the wet mechanical opening treatments, especially those produced in the presence of chemical dispersants, had the highest surface areas. This is to be expected, for with the latter procedure liberated chrysotile fibrils were separated from gangue and partially opened fibril agglomerates by centrifugation. Disaggregation reached the state where essentially all fibrils were separated from each other, and surface areas approached values which correspond to all fibril surfaces available for adsorption.

B. Coalinga Specimens

F. A. Mumpton and C. S. Thompson of this laboratory have shown that the Coalinga asbestos ore deposit and the serpentinite body in which it lies are composed of minerals of the serpentine group along with minor quantities of brucite and magnetite, with traces of chromite, calcite, and uvaravite garnet. They have shown further that the asbestos ore itself can be considered to be a mixture of four physically distinct types of material if allowances are made for gradations between types. The basic types are: (1) thin, tough, leathery sheets of matted chrysotile; (2) brittle, plate-like and bladed fragments of green chrysotile varying in size from fractions of an inch to several inches, and also varying somewhat in color, hardness, and in brittleness; (3) hard, dense, dark colored fragments of the massive serpentinite; and (4) small, soft, flexible, pellet-like agglomerates of fibrous chrysotile varying in size from about 1/4" to 1" in diameter. The bulk of the chrysotile exists in this latter form. The agglomerates generally contain appreciable quantities of both the green-bladed material and fragments of the hard, serpentinite rock. In addition to the four basic types, which occur throughout the ore body, there is at least one area of limited size where typical cross-fiber chrysotile is found.

In the discussion which follows, material of Type 1 will be referred to as Coalinga flake chrysotile; material of Type 2 as Coalinga bladed chrysotile; and material of Type 3 as Coalinga serpentinite. Surface area determinations were made for selected specimens of each of these types, for Coalinga cross-fiber chrysotile, and for a variety of products derived from the Coalinga ore body.

The materials of Types 1, 2, and the Coalinga cross-fiber, occurred as large pieces and it was possible to select specimens that were essentially

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ACL Doc 17890 · Page 21 of 32 asbestosclaims.law/library/17890/21

pure chrysotile. The Coalinga serpentinite, while not pure serpentine, also occurred in massive form and could be sampled readily. This was not true of the agglomerates of Type 4. The variable composition, heterogeneity, and finely divided nature of Type 4 material made it impractical for study as a specific type. However, since the bulk of the ore exists in this form, and since processing removes most of the gangue minerals of the aggregates, the properties of the fibrous chrysotile of the agglomerates can be inferred from measurements made on gross asbestos products.

1. Flake chrysotile: Nitrogen adsorption data for the Coalinga materials differed considerably from the pattern normally found for chrysotile. This was particularly true for specimens of Coalinga flake which were of considerably higher surface areas than has been reported for any natural chrysotile.

The results for four samples selected at different times from pilot plant materials were as follows:

Samples	Specific Surface
1	78 m^2/g
2	81 m^2/g
3	74 m^2/g
4	77 m^2/g

The apparent surface area of Coalinga flake was independent of activation temperature:

Activation Temperature	Apparent Surface Area
100°C	79 m^2/g
200°C	80 m^2/g
470°C	76 m^2/g

Also, apparent surface area was not increased by mechanical opening and chemical dispersion treatments. Figure 5 is a BET plot for portions of Sample 1 above. The plot includes data for untreated flake and for flake that had been pulped and opened in a Waring Blendor, both with and without chemical dispersants. Three separate methods of chemical dispersion were used. The

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ACL Doc 17890 · Page 22 of 32 asbestosclaims.law/library/17890/22

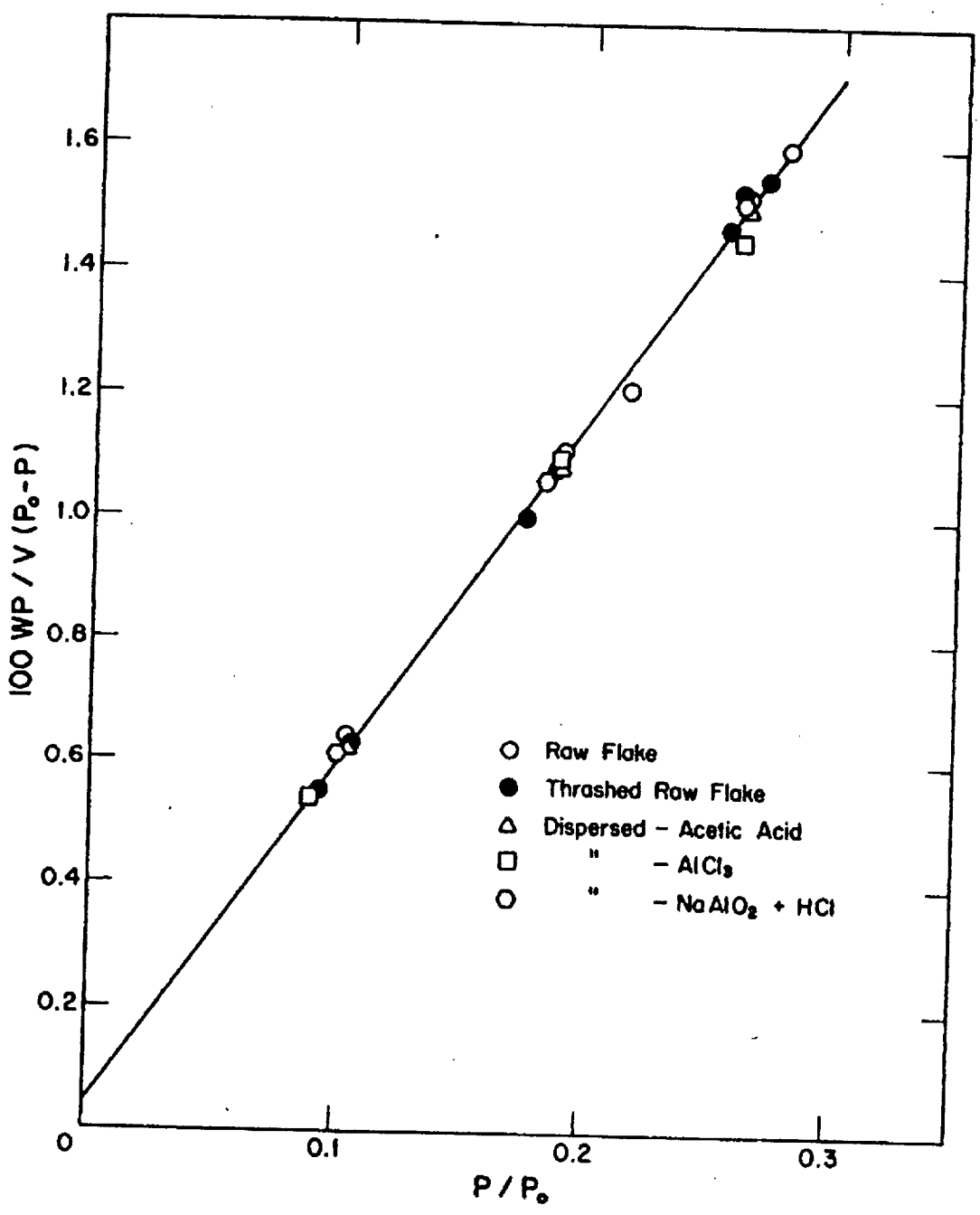


FIG. 5: BET plot for Coalinga flake chrysotile.

Union Carbide trial exhibit UC-3046: A. W. Naumann and W. H. Dresher, Research Report No. 61: Physical Prope…
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ACL Doc 17890 · Page 23 of 32
asbestosclaims.law/library/17890/23

data points for the products of the various treatments fell on a single straight line corresponding to 78 m^2/g. The values for the individual samples were as follows:

Sample	Apparent Surface Area
Strips of flake, untreated	78 m^2/g
Mechanically opened flake, wet process	79 m^2/g
Dispersed fiber, acetic acid as dispersant	79 m^2/g
Dispersed fiber, aluminum chloride as dispersant	77 m^2/g
Dispersed fiber, sodium aluminate and hydrochloric acid as dispersant	79 m^2/g

These results suggest a very open structure in the natural state, with essentially all fiber surfaces available for adsorption, and with inter-fibril pores sufficiently large that capillary condensation of water does not occur. No additional surfaces were made available for adsorption by mechanical treatments nor was material of higher surface area separated as individual fibrils by any of the chemical dispersion processes. The apparent surface areas of approximately 80 m^2/g for Coalinga flake as compared to approximately 50 m^2/g for purified Canadian chrysotile fibrils is indicative of a somewhat smaller average fibril diameter in the Coalinga sample.

2. Bladed chrysotile. The surface area of Coalinga bladed chrysotile was lower than that of Coalinga flake, but was high compared to most non-Coalinga chrysotile specimens. Surface area of individual samples of bladed chrysotile was also more variable than for Coalinga flake. Values ranged from 25 to 40 m^2/g.

Sample	Particle Size	Activation Temperature	
		Room Temp.	400°C
401-36-1	16x20 mesh	30 m^2/g	29 m^2/g
401-36-2	16x20 mesh	37 m^2/g	39 m^2/g
401-36-3	16x20 mesh	30 m^2/g	32 m^2/g
367-38-1	60/80 mesh	26 m^2/g	27 m^2/g
367-44-1A	+200 mesh	24 m^2/g	-

As mentioned previously, the bladed chrysotile varies somewhat in color, hardness, and brittleness between samples. Too few samples were examined to

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ACL Doc 17890 · Page 24 of 32 asbestosclaims.law/library/17890/24

establish a firm correlation between physical properties and surface area, but there were indications that surface area was less for the harder, more brittle materials.

The apparent surface area of Coalinga bladed chrysotile, like that of Coalinga flake, was independent of activation temperature. Chemical dispersion treatments, however, increased surface area appreciably. Sample 401-36-3, which had an area of 30 m^2/g when sized to 16 x 20 mesh, gave an area of 58 m^2/g after dispersion. Similar results were obtained with other samples. These results indicate the presence of an open structure with inter-fibril voids too large for condensation in the material, but with some extra-fibril solid material present like that of the Canadian samples to block a portion of the surfaces.

3. Serpentinite. Coalinga serpentinite was of low surface area compared to Coalinga flake or bladed chrysotile.

Activation Temperature	Apparent Surface Area
100° C.	20 m^2/g
200° C.	24 m^2/g
400° C.	55 m^2/g

These data were obtained for material sized to 20 x 60 mesh. The specimen was hard, brittle, and a dark blue-gray in color. X-ray diffraction showed the presence of serpentinite and brucite. Chemical analyses were as follows:

SiO_2	32.1%
MgO	42.2%
Fe_2O_3	8.3%

This composition corresponds roughly to 75 per cent serpentine, 15 per cent brucite, and 10 per cent magnetite.

The serpentinite did not respond to chemical dispersion treatments. Thrashing in a Waring Blendor reduced the particle size but, unlike Coalinga flake and bladed chrysotiles, these treatments did not yield a suspension of colloidally-sized particles. It is probable that the Coalinga serpentinite specimen consisted chiefly of a non-fibrous form of serpentine. This is indicated by the failure of the material to respond to chemical dispersion

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ACL Doc 17890 · Page 25 of 32 asbestosclaims.law/library/17890/25

treatments. Electron micrographs of surface replicas provided more direct evidence in this regard. The replicas, which were obtained for freshly fractured surfaces, showed a layer structure like that found with clay minerals as the dominant feature. There were occasional regions showing highly disordered tubes or lathes embedded in a solid matrix, but these made up only a small portion of the total surface.

The slight increase in apparent surface area between 100° and 200° is indicative of a pore network within the serpentinite. The large increase between 200° and 400° was probably due to the dehydration of the brucite of the specimen.

4. Products. Surface area data were obtained as part of the present investigation and on a service basis for a variety of pilot plant products from the Coalinga ore body. Values fell in the range 50 to 60 m^2/g. The following may be considered as typical:

Products by Wet Processing	
UCN pilot plant "JT101"	56, 59, 57, 60 m^2/g
UCN pilot plant "Jig Flake"	53, 53, 56
UCN pilot plant "CMS"	61
Products by Dry Processing	
UCN pilot plant "L-1"	55 m^2/g
Johns-Manville "Red Label"	59
Johns-Manville "Blue Label"	54, 56

The apparent surface area of the products increased by 10 to 20 m^2/g with dispersion treatments. It is difficult to estimate how much of this increase, if any, was due to changes in the chrysotile, however. The products were chiefly chrysotile, but they contained lesser amounts of other minerals such as brucite, magnetite, and the massive serpentinite. Chemical dispersion treatments remove the bulk of these gangue materials, and this alone will cause some increase in surface area.

The surface area of Coalinga products will vary with activation temperature when decomposable accessory minerals such as brucite are present, but in general the concentrations of these minerals are small and the dependence of surface area on activation temperature is also small. This is shown by the following data which were obtained for the pilot plant JT-101.

Union Carbide trial exhibit UC-3046: A. W. Naumann and W. H. Dresher, Research Report No. 61: Physical Prope... Published by AsbestosClaims.Law
ACL Doc 17890 · Page 26 of 32 asbestosclaims.law/library/17890/26

Activation Temperature	Apparent Surface Area
100° C.	60 m^2/g
200° C.	62 m^2/g
400° C.	66 m^2/g

As mentioned previously, asbestos products prepared from the Coalinga ore body are derived chiefly from the heterogeneous chrysotile agglomerates that make up the bulk of the ore and, because of this, the properties of the agglomerates can be inferred from those of the products. With this as a basis, the properties of the agglomerates would be classified as being intermediate between those of the Coalinga flake and bladed types. Pertinent properties for the three types are summarized as follows:

	Flake Chrysotile	Bladed Chrysotile	Chrysotile Agglomerates (inferred from Asbestos Products)
Apparent Surface Area	70-80 m^2/g	20-40 m^2/g	50-60 m^2/g
Variation of Area with Activation Temperature	No variation	No variation	Little, if any, variation
Variation of Area with Dispersion Treatments	No variation	Area increased	Probably increased some, but not as much as for bladed chrysotile

These results suggest that the chrysotile agglomerates may not be a distinct mineral form, but rather may be a mixture of the flake and bladed types with particle sizes so small they do not appear as such.

5. Cross-fiber. The following results were obtained for a specimen of Coalinga cross-fiber chrysotile:

Activation Temperature	Apparent Surface Area
100° C.	41 m^2/g
200° C.	43 m^2/g
380° C.	41 m^2/g

Union Carbide trial exhibit UC-3046: A. W. Naumann and W. H. Dresher, Research Report No. 61: Physical Prope... Published by AsbestosClaims.Law
ACL Doc 17890 · Page 27 of 32 asbestosclaims.law/library/17890/27

These data were obtained for filaments approximately 1 cm. long pulled from a solid block. Again, surface area was high compared to reported values for non-Coalinga cross-fiber chrysotile, and again apparent area was not a function of activation temperature. An open structure like that of the other Coalinga chrysotiles is indicated. Thus, it appears that the open structure of Coalinga slip fiber is associated more with the locality than with the mode of occurrence of the fiber.

C. Stragari Chrysotile

A sample of chrysotile from Stragari, Serbia, Yugoslavia, having a physical appearance very similar to Coalinga flake was obtained through the American Museum of Natural History. Surface area data for this material were as follows:

Material	Activation Temperature	Surface Area
Untreated flakes	100° C.	78 m^2/g
	200° C.	78 m^2/g
	400° C.	80 m^2/g
Chemically dispersed flakes	100° C.	88 m^2/g

The apparent surface area of the untreated flakes was not a function of activation temperature. Some increase in area occurred with chemical dispersion, but the increase was small (10-15%) compared to Canadian chrysotiles where area is increased by a factor of two or more.

It has been pointed out in the open literature that the physical appearance of Stragari chrysotile is similar to Coalinga asbestos(28). The results above indicate that the material is also similar in regard to adsorption properties, and presumably also in regard to structure and morphology. Thus, while Coalinga asbestos differs from most chrysotiles, it is not truly unique.

D. Texture Studies

In the discussion of the experimental observations, the Canadian chrysotile samples were described in terms of a relatively tight packing of individual fibrils with additional solid matter in interstices between fibers.

Union Carbide trial exhibit UC-3046: A. W. Naumann and W. H. Dresher, Research Report No. 61: Physical Prope... Published by AsbestosClaims.Law
ACL Doc 17890 · Page 28 of 32 asbestosclaims.law/library/17890/28

Coalinga materials, particularly Coalinga flake, were described in terms of a much looser structure with essentially all fibril surfaces available for adsorption, and with voids between fibrils sufficiently large so as to prevent capillary condensation of water. Differences in the magnitude of surface area between dispersed Canadian samples and Coalinga flake were attributed to differing average fibril diameters. Thus, the structural interpretation for the differences between Coalinga and Canadian chrysotiles hinge on two factors: (a) the presence of extra-fibril solid matter in Canadian chrysotile, and the absence of such material in Coalinga fiber; and (b) a smaller average fiber diameter for Coalinga chrysotile. A series of electron micrographs of dispersed Canadian Grade 7R3 and dispersed Coalinga flake were prepared and the external diameters of a statistical sampling of the fibrils appearing on each photographic plate were measured precisely using an optical microscope with filiar eyepiece. The results of these measurements are shown graphically in Figure 6. The fibers of the Canadian specimen were of larger average diameters and had a greater variation in fiber size than those of the Coalinga chrysotile. Average diameter for the Canadian sample was 375 Å with a standard deviation between fibers of 76 Å. For Coalinga flake, these values were 275 Å and 26 Å, respectively. Diameter did not vary significantly along a given fiber of either material, but the greater variation was with the Canadian sample. Surface areas calculated from the fibril dimensions were in satisfactory agreement with the nitrogen adsorption values.

The fibrils of the Coalinga sample were characteristically smooth and regular along their entire length as would be expected for a material that contained no extra-fibril solids. The fibrils of 7R3 appeared rough and "lumpy" along some segments, and had bits of particulate matter adhering to them at others. The general appearance was consistent with the view that the fibrils had been broken from a solid matrix. These differences were by no means subtle, as is shown by the prints of Figure 2. Both are prints of plates used in the fibril dimension analysis, and are at the same total magnification. Figure 2b is of the Coalinga sample, and Figure 2a of dispersed 7R3. Areas showing particulate matter adhering to the fibrils of 7R3 are indicated by the arrows.

A pertinent question that remains is the location and nature of the pores that give rise to the variation of apparent surface area with activation temperature. Young and Healey[14] took the view that the pores

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ACL Doc 17890 · Page 29 of 32 asbestosclaims.law/library/17890/29

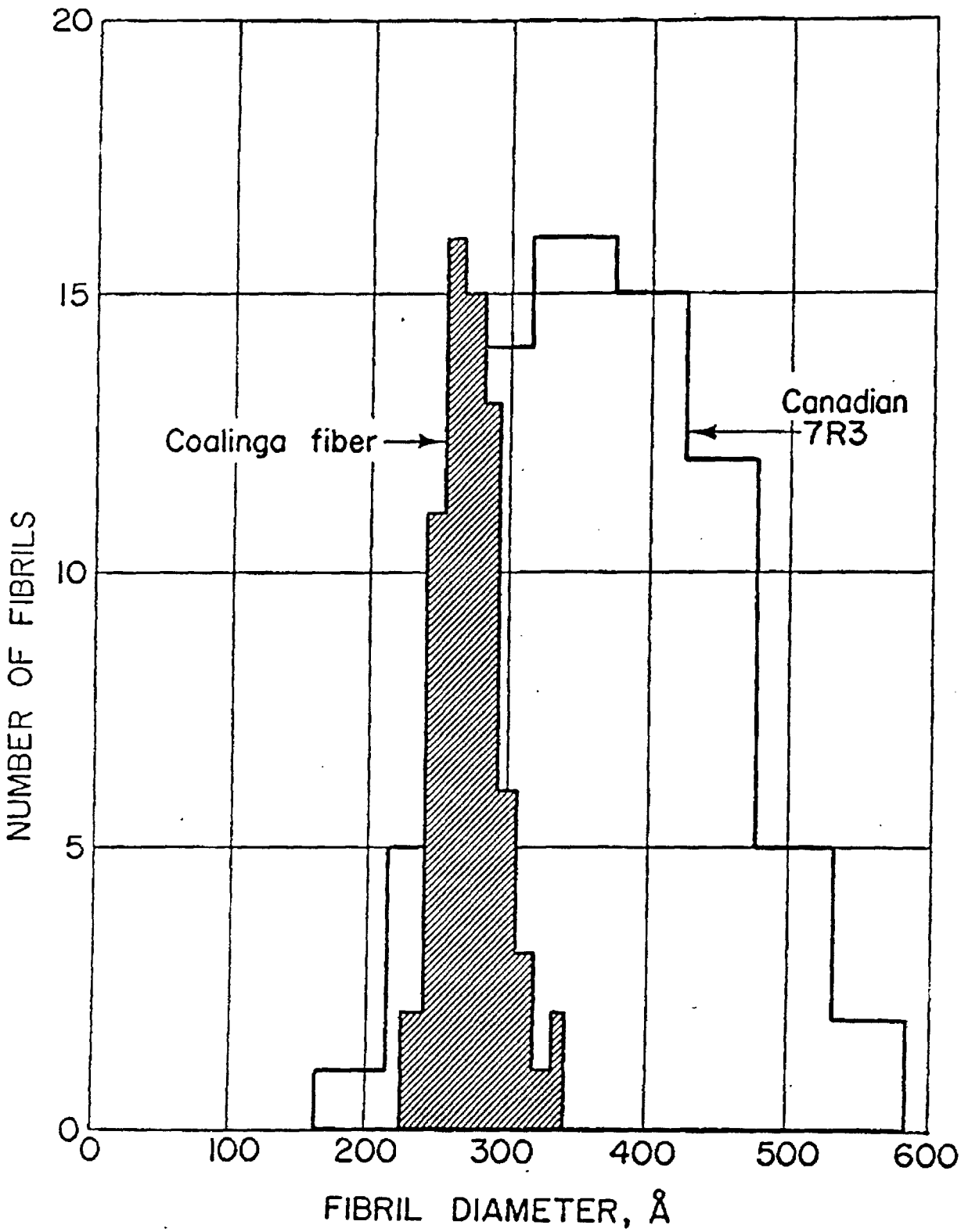


FIG. 6 : Histogram of fibril diameter distribution.

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were within the individual fibrils, and probably could be identified with the apparent hollow tubular structure of chrysotile as seen on electron micrographs. Pundsack[18] interpreted water adsorption data in terms of pores of two types - one, the hollow tubes within fibrils and, the other, pores between fibers. The results of the present investigation cannot be reconciled with these interpretations. If pores within fibrils were involved, a variation of surface area with activation temperature would be expected with all chrysotile specimens. None was observed with the Coalinga flake or bladed types. It might be argued that this was because the pores of Coalinga fiber are closed, while those of most chrysotile specimens are open, but this argument would not apply for the results obtained with the Canadian chrysotile specimens which were given the chemical dispersion treatment. These materials showed a variation in the natural state. If internal voids were responsible, a variation would also be observed after chemical dispersion treatments, since state of aggregation would have no effect on condensation in voids within individual fibrils. No variation was observed for dispersed products. The adsorption data indicate, therefore, that the central pores of the specimens studied in the present investigation were not available for adsorption, and that the pore structure observed for the Canadian materials was associated with voids between fibrils rather than within fibrils.

Union Carbide trial exhibit UC-3046: A. W. Naumann and W. H. Dresher, Research Report No. 61: Physical Prope...
Published by AsbestosClaims.Law
ACL Doc 17890 · Page 31 of 32
asbestosclaims.law/library/17890/31

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ACL Doc 17890 · Page 32 of 32 asbestosclaims.law/library/17890/32