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THE EFFECT OF CHRYSOTILE ASBESTOS ADDITIONS TO CELLULOSIC PAPER

I. INTRODUCTION

In the previous paper the properties of a highly refined chrysotile asbestos product were discussed. The three principal characteristics of this product that apply to paper applications are:

1. The surface charge - cationic
2. Particle shape - fibrous
3. Surface characteristics -
   (a) organic adsorption
   (b) chemical reactivity

These properties differ sufficiently from those of the more conventional paper additives to indicate a promising potential for use in the paper industry. In addition, refined asbestos is a material of low cost and is available in sufficient quantity to supply a consumer as large as the paper industry. Advances in processing techniques have insured a uniform product that can be supplied within quite rigid specifications. With respect to abrasiveness, radiometric determinations have shown that the purified asbestos is considerably less abrasive than ordinary fillers or bleached sulfite pulp. The properties imparted to paper by addition of purified chrysotile asbestos, as well as paper-machine behavior, were determined by experimental work both in the laboratory and in full scale mill trials. These results are discussed in this paper.

II. LABORATORY DATA

The laboratory results, as reported herein, were obtained in our own laboratories at Tuxedo, New York, and through the efforts of Professors L. C. Jenness and A. J. Chase of the University of Maine, who have acted as our consultants during this program. The tests were conducted principally in the laboratory Noble and Wood handsheet machine and, unless otherwise specified, used a bleached sulfite stock beaten to a Canadian Standard Freeness of 300 ± 10 ml. Handsheets were made at the standard basis weight of 60 grams per square meter and tested, wherever applicable, according to the TAPPI standard procedures.

1. Effects on Retention - The effects of incorporating a highly defibrillated chrysotile fiber in cellulose paper were found to be unique among inorganic additives. Because of its electropositive surface charge, the self retention of the asbestos fiber is very high when compared with clay or titanium dioxide pigment. As shown in Figure 1, this improved retention is significant on a single pass retention system or in one where white water recirculation is employed. On the basis of single pass retention, the asbestos showed almost 80% retention compared with only 40% for either clay or titanium dioxide.

It can be postulated that any method of introducing a positively charged material into a paper furnish should tend to improve retention of all components. A summary of the relative surface charges of paper-making constituents (as calculated from laboratory measurements of individual mobilities) were determined to be:

	ζ, mv	pH
Bleached Sulfite Cellulose	-14	6.4
	- 9	5.0
Titanium Dioxide (RA-50)	-19	10
	None	6
Talc	-15	6.6
Purified Chrysotile Asbestos	+38	6.6
	+45	5.0

Accordingly, the chrysotile asbestos should coflocculate with any and all of the furnish constituents. That this is so is shown when asbestos and TiO_2 pigment are agitated together to form what appears to be a fibrous titanium dioxide pigment. Titanium dioxide dispersed in water produces a milky liquor that tends to remain cloudy for long periods of time. When coflocculation is achieved, the water at the interstices of the flocs is clear. Thus, all of the TiO_2 is being held by the asbestos. Electron micrographs of the combined product (Figure 2) show that the pigment is still in the dispersed state and is held by the asbestos. Most important is the fact that these flocs are formed without agglomeration of the pigment. This should allow maximum efficiency in obtaining its optical properties.

The advantages of asbestos over conventional flocculants, either

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ABSTRACT

EFFECTS OF CHRYSOTILE ASBESTOS ADDITIONS TO CELLULOSIC PAPER

Robert G. Woolery*

The effects of incorporating a new, highly purified, grit-free chrysotile asbestos fiber in cellulose paper are discussed. Data are presented from both laboratory handsheet tests and paper mill trials on the effect of the fiber on both operational factors and on sheet properties. Effects discussed include retention of cellulose fines and fillers such as TiO_2, freeness, drying rate, pitch control, brightness and opacity, softness, strength, porosity, printability, and dye retention. Savings possibilities and other economic factors are also discussed.

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KIRBY A. KENNEDY
COURT REPORTER

* Group Leader - Product Development and Technical Services
Union Carbide Corporation
Mining and Metals Division
P. O. Box 324
Tuxedo, New York 10987

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inorganic or organic, are two-fold: (1) retention without agglomeration, and (2) floc stability. Experience has shown that no degradation of the floc occurs even after repeated agitation. Once formed, these flocs are stable even under prolonged high-shear agitation of a Waring Blendor. Laboratory studies have shown asbestos to be compatible with all types of organic and polymeric flocculants. In a furnish of high filler content, particularly, the combination of asbestos and coagulant is especially effective. Usually the net effect is greater than can be achieved by either alone.

Data from laboratory tests run on handsheets to demonstrate the retention properties of chrysotile fiber are shown in Figures 3 and 4. The control series for this evaluation were made with 4% clay. Where asbestos was employed, it was substituted on a pound-for-pound basis for clay, so that at equivalent retention the ash and opacity values would be comparable. The level of TiO_2 addition was then varied from no TiO_2 to 10% added based on the stock. It is apparent that the retention of the additives is greatly improved with as little as 2% asbestos. Clay retention is also greatly affected. Because these data are based on single pass retention values, the values are quite low as can be seen in Figure 4. Since this is probably the most difficult retention condition, the effectiveness of the purified fiber is clearly demonstrated.

In another series of tests, run under similar conditions but with high levels of clay, the results were equally encouraging. The ash values for levels of clay additions ranging from 25% to 50% show that the retention of the filler is increased with increasing asbestos additions up to 6% asbestos (Figure 5). The effects of white water recirculation on the ash content of the sheet were also determined and are shown in Figure 6. Whereas the average ash retention only reached about 47% with a one pass circuit, with recirculation the average retention was increased to 70%. There is also evidence that equilibrium was reached in the recirculation system at 3% asbestos whereas it required about 5% for the single pass system.

2. Effects on Opacity - Inasmuch as chrysotile asbestos has an index of refraction of 1.52 - 1.55 that is similar to that of kaolin, it could be expected to have equivalent opacifying power. On the basis of the amount added, asbestos-filled sheets showed higher opacities; however, as is shown in Figure 7, the opacities are essentially identical at corresponding filler weights in the sheet. In the series where asbestos was substituted for 2% clay

in a titanium dioxide filled sheet, the resulting opacities associated with the asbestos were invariably higher. In Figure 8, the average opacity increase is from 2 to 3 points. This is attributed to the increased retention of all components through the cationic charge of the chrysotile asbestos.

3. Effects on Tear and Tensile - The comparative tear values for the addition of either clay or asbestos are similar. For both minerals, small quantities are beneficial whereas larger quantities prove to be detrimental. Figure 9 shows that small quantities (< 5%) of asbestos resulted in better tear factors. Above 5% asbestos additions the tear factor decreases below that for clay-filled paper. This effect is probably due to the geometry of the fiber as well as to its smaller particle size. Asbestos is more efficient at disrupting the hydrogen bonding of the cellulose fiber than are non-fibrous minerals. An even better example of the geometry effect can be seen in Figure 10, where the tensile values are shown for corresponding filler content of the sheet. Once 3% filler in the sheet is exceeded, the effect on tensile strength is influenced considerably more by the asbestos than by either clay or TiO_2.

4. Effects on Softness - While the strength of the sheet is reduced by asbestos content, a corresponding softening effect is also achieved. This relationship is shown in Figure 11. In a light-weight tissue sheet a 9% asbestos content resulted in doubling the softness values obtained on a Clark Softness-Stiffness tester. Various furnishes were investigated and all types appeared to respond in a manner similar to the light weight sulfite furnish.

5. Effects on Pulp Freeness - As might be expected from the use of a small sized, fibrous filler, the freeness of the furnish is affected. The degree to which the asbestos slows up the furnish drainage appears to be dependent on the original freeness of the stock. For example, the data in Figure 12 show that the lower the freeness of the stock the less it is affected by asbestos. At the low levels of asbestos additional normally used in paper this has not been a problem in the mill.

6. Effects on Porosity - With the incorporation of the highly refined asbestos the sheet porosity invariably has a tendency to decrease with increasing asbestos content as shown in Figure 13. The initial high increase in porosity values obtained by the addition of between zero and 2% asbestos is attributed to the retention of fines. This effect normally accompanies the addition of chrysotile asbestos.

7. Effects on Printability - Normally, any time the porosity of the sheet is reduced and the formation of the sheet is improved, the printability is subsequently benefited. Printing evaluations by the Research Institute for the American Newspaper Publishers' Asscciation of samples obtained from the various mill trials verified these conclusions. Where sheet containing asbestos were compared to the control runs on the same grade, improvements in the following properties were noted:

1. Smoothness
2. Opacity
3. Ink Transfer
4. Printability

In most cases, improvements were noted for both the felt and wire sides. Usually the more significant improvements were observed on the wire side thus demonstrating an improvement in two-sidedness.

8. Effects of Stock Type - Some data have been obtained on furnishes employing stocks other than a bleached sulfite stock. For the most part the data obtained were consistent with the results reported so far. The most notable exception was in a typical newsprint furnish of 80% groundwood - 20% bleached sulfite. Under these conditions, as much as 6% asbestos in the sheet caused no appreciable reduction in the tensile strength. This probably can be attributed in part to the inherent weakness of the sheet and, in part, to the retention of the groundwood fines which contribute to the sheet strength.

9. Other Applications - Probably the largest single application for asbestos, in addition to those already described, is as a pitch controlling agent. Laboratory studies have been conducted on a wide variety of pulps, but because of the diversity of pitch problems, no universal data are obtainable. In the majority of the cases, however, asbestos has proven to be more effective than other commercially available products. The total reduction in pitch is generally only slightly lower than competitive products but the amount of asbestos necessary to reach this level is usually significantly less.

Considerable laboratory effort has also gone into the retention of beater-additive latices. Since most of the commercially available latices are anionic, they have proven to be compatible with the cationic chrysotile. It has been found advantageous to blend the asbestos with the cellulose first in order to put the asbestos on the cellulose in a dispersed state. Thus, when the latex

is added, it is deposited uniformly throughout the furnish and minimizes the tendency to form the latex agglomerates which are undesirable in the finished sheet. The overall asbestos retention is almost universally improved and the resulting physical properties have been found to be enhanced (particularly wet tensile and fold) to a higher degree than can be attributed to the improved latex retention.

Studies in dye retention have shown that 2% asbestos addition will generally improve the retention and greatly reduce the two-sideness. This is particularly true with acid and pigment dyes. It has also been possible to pre-dye the asbestos which in turn can be added directly to the furnish and results in a close control of color and shade.

A rather unique application was also discovered in the field of conductive paper. Its function in this area is to improve the sheet formation and to provide a more uniform distribution of the conductive media through flocculation. Again, the asbestos addition levels required for this application are found to be in the 2-3% range.

III. MILL TRIAL DATA

Since the beginning of this program, something in excess of 200 mill trials have been conducted. In the majority of these trials the purified asbestos has performed as predicted from the laboratory studies. In addition, on machines where mineral additions are commonplace, no serious problems have developed due to the addition of asbestos. These trials have been conducted on a wide variety of paper grades as well as in paper board. A review of some of these trials demonstrates the versatility and advantages obtained with the chrysotile fiber.

1. Retention - In a machine trial on a 40 lb. opaque printing paper, 3% asbestos substituted for 3% clay resulted in a reduction of the TiO_2 requirement from 165 lbs/ton to 120 lbs/ton and eliminated the glue previously used as a retention aid. This was accomplished without departing from the specifications of the sheet and without machine problems. A summary of these results is as follows:

Condition	% Clay	% Asbestos	% TiO_2	% Glue	Opacity
1 (control)	4		8.25	0.25	89.5
2	1	3	7.0	0.25	92.5
3	1	3	6.0	0.25	91.
4	1	3	6.0	-	91.

In another trial, on a 37 lb bond paper, 2% asbestos was used for a corresponding amount of clay. Titanium dioxide amounting to 2.5% of the furnish was also going into this sheet for opacity. A summary of these results follows:

PAPER ANALYSIS

Condition	Opacity	% TiO_2	% Ash	% TiO_2 Retention
Pre-trial	82.5	1.64	12.0	65.5
2% Asbestos Added	83.5	2.20	13.9	88.
Post Trial	82.0	1.75	12.2	70.

These data show an improvement in TiO_2 retention from about 68% to 88% with a 2% asbestos addition.

In addition, the saveall effluent was monitored during both the control and trial periods. The average solids content during the pre-trial and post-trial period was 2.3 pounds per 1000 gallons. During the trial the solids content was reduced to 1.5 lbs per 1000 gallons. Due to the improved efficiency resulting from the asbestos, a 35% reduction in solids loss was realized.

It is not unusual to expect saveall efficiencies improvement during these trials. In one trial, particular attention was paid to the saveall unit since it had been operating under a heavy load with a low efficiency. In this instance both the influent and effluent were monitored. A summary of these data follows:

Condition	Saveall - (lbs solids/1000 gal.) Influent	Effluent	Saveall Efficiency
Pre-trial	17.9	4.36	
During Trial (2% asbestos)			
1.0 hr.	14.3	1.15	
2.0 hr.	13.2	0.90	
3.0 hr.	11.0	0.71	
Post Trial	21.4	6.00	
Average:			
Without Asbestos	19.64	5.18	74%
With Asbestos	12.83	0.92	93%
Reduction in Solids resulting from the use of Asbestos	35%	82%	

2. Softness - A natural application for the highly refined chrysotile fiber is in the tissue and towel grades. This mineral is unique as an inorganic softening agent. Numerous mill trials have demonstrated its ability to impart both softness and a velvety handfeel to both tissue and towels. A typical relationship between asbestos content and Handle-O-Meter values on a 40 pound towel is shown in Figure 14. The levels illustrated, up to 5% asbestos, are typical of the levels used for this purpose. For this grade a 5% asbestos addition reduced the Handle-O-Meter values from a control of 27 to 17.

In a machine trial on a 13.25 lb tissue, 4% asbestos was added to improve softness and handfeel. The furnish consisted of 25% Pine, 60% Hardwood, and 15% Broke. The effects on Handle-O-Meter values were as follows:

Condition	HANDLE-O-METER VALUES MD	CD
Control	15 *	22.5 *
Trial	9 **	11.5 *

* Average of 6 reels
** Average of 8 reels

Not only was a significant improvement in softness realized, but the level of difference between machine direction and cross-machine direction was reduced by nearly 50%. This is probably due to the improved sheet formation.

In addition to these improvements the improved drying rate of the asbestos-filled tissue resulted in a lower steam requirement to the Yankee Dryer.

By virtue of the inherent physical properties of chrysotile asbestos a wide variety of applications to the tissue and towel grades have been explored. Its largest single application at this time is as a tool to achieve quality in a wide variety of furnish components. In mills where the use of coarser and harsher cellulose stocks (or even waste paper) is limited, the incorporation of asbestos has permitted a higher percentage of these cheaper and coarser pulps without a loss in quality and at a significantly reduced furnish cost. For still another mill, where the drying chain controlled the machine speed, as much as 30 to 50 feet per minute increase in machine speed was achieved with a 2% asbestos addition, a situation considerably more economical than the standard furnish at the slower rates.

3. Pitch Control - The most universal application to date is in pitch control. In mills where this use has been investigated it has been found to be more effective than other commercially available products. Where asbestos is currently being used it has replaced talc, at the ratio of 2 lbs. of asbestos per 3 lbs. of the competitive product.

IV. CONCLUSION

These studies have shown purified chrysotile asbestos to be unique as an inorganic additive to cellulosic paper. Unlike other paper components this material is cationically-charged and, as such, performs as a retention aid to all constituents in the furnish. Its uniformity, small particle size and fibrous geometry contribute to the softness of the sheet and improve two-sided effects. The high surface area and its adsorption of organics aid in dye adsorption and printability. Its performance on the paper machine has been most satisfactory and, as a rule, has caused no problem in the subsequent processing of the paper. Where care has been used to employ a sufficient quantity of asbestos to be effective, yet not so much that the strength of the paper is degraded beyond reasonable limits, the results have been quite successful.

Because of this versatility we believe that purified chrysotile asbestos will continue to grow in its present application to the paper industry and that new areas will develop where the unique properties of this material will be advantageous.

ACKNOWLEDGMENTS

I am greatly indebted to Professors L.C.Jenness and A.J.Chase, of the University of Maine, for their collaboration, guidance, and laboratory data throughout all stages of this project. Thanks are also due to Messrs. B.L.Ingalls and G.L.Dickson, of the Union Carbide Corporation, Mining and Metals Division Research Center, for their assistance in obtaining the data that have been used in this paper; to Dr. S.Chwastiak for the electrophoretic mobility data; and to the many members of the laboratory staff who have helped through their advice and encouragement.

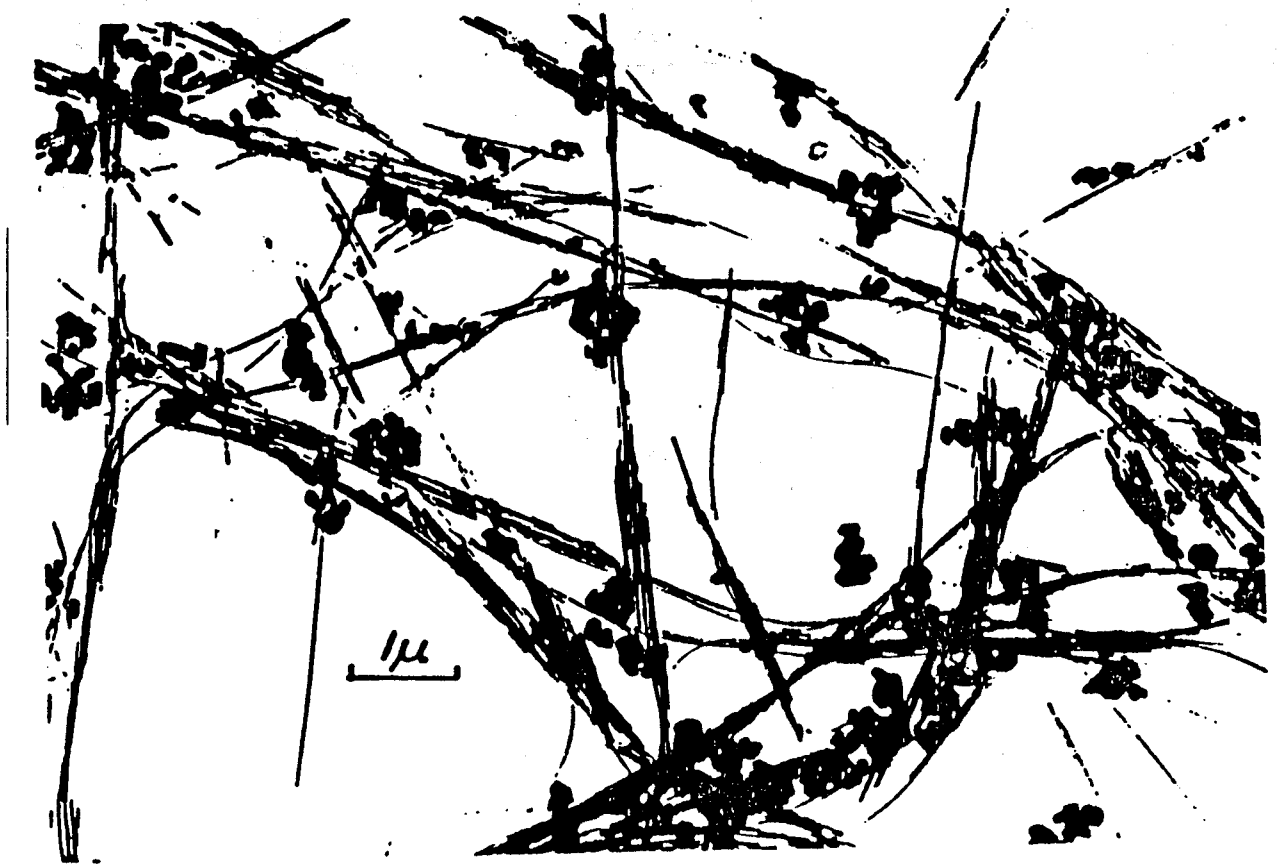


FIGURE 2: Co-flocculation of purified chrysotile asbestos and titanium dioxide (electron photomicrograph, magnification = 15,900X).

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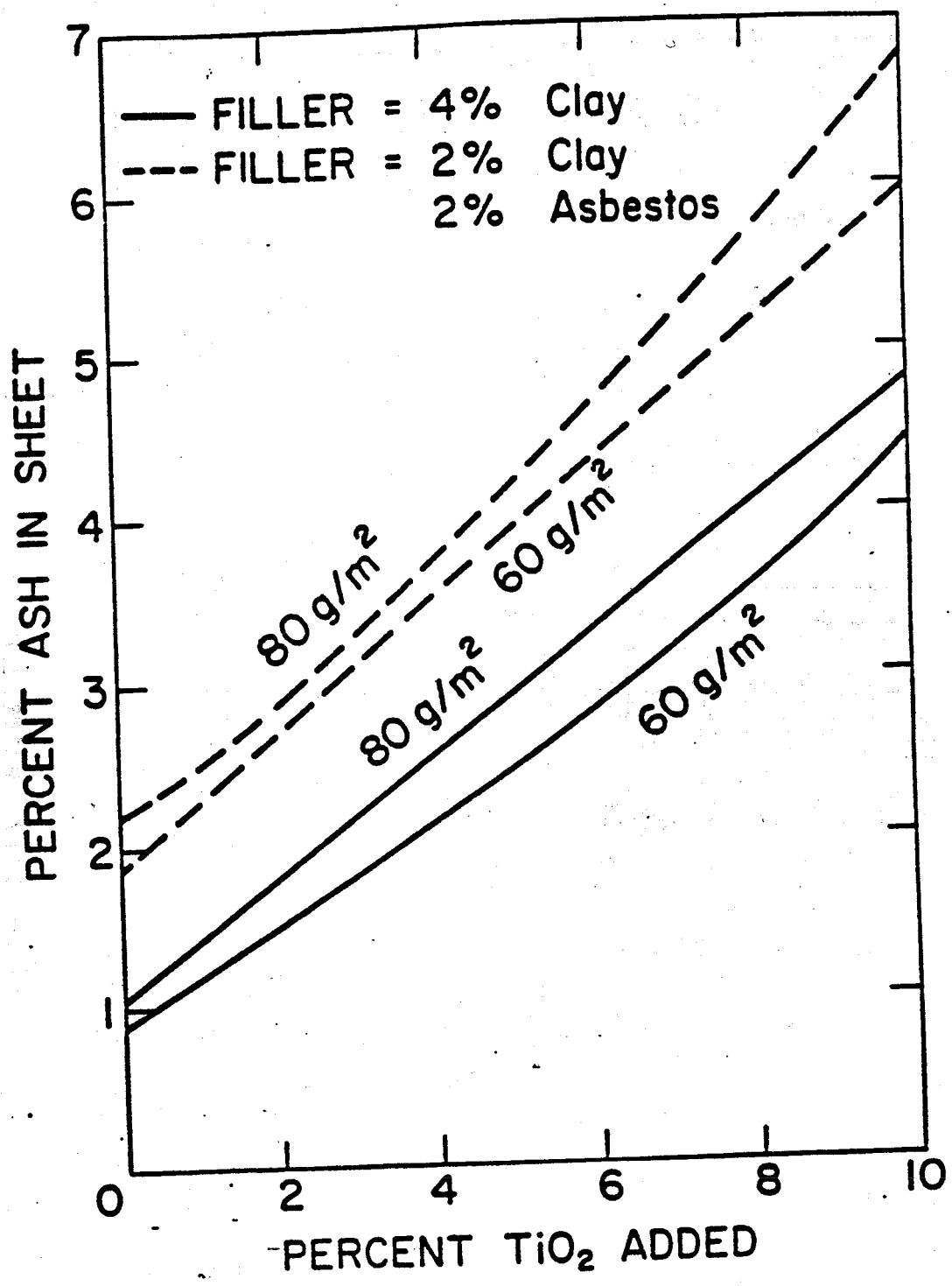


FIGURE 3: Ash content vs. percent TiO_2 added, with and without asbestos.

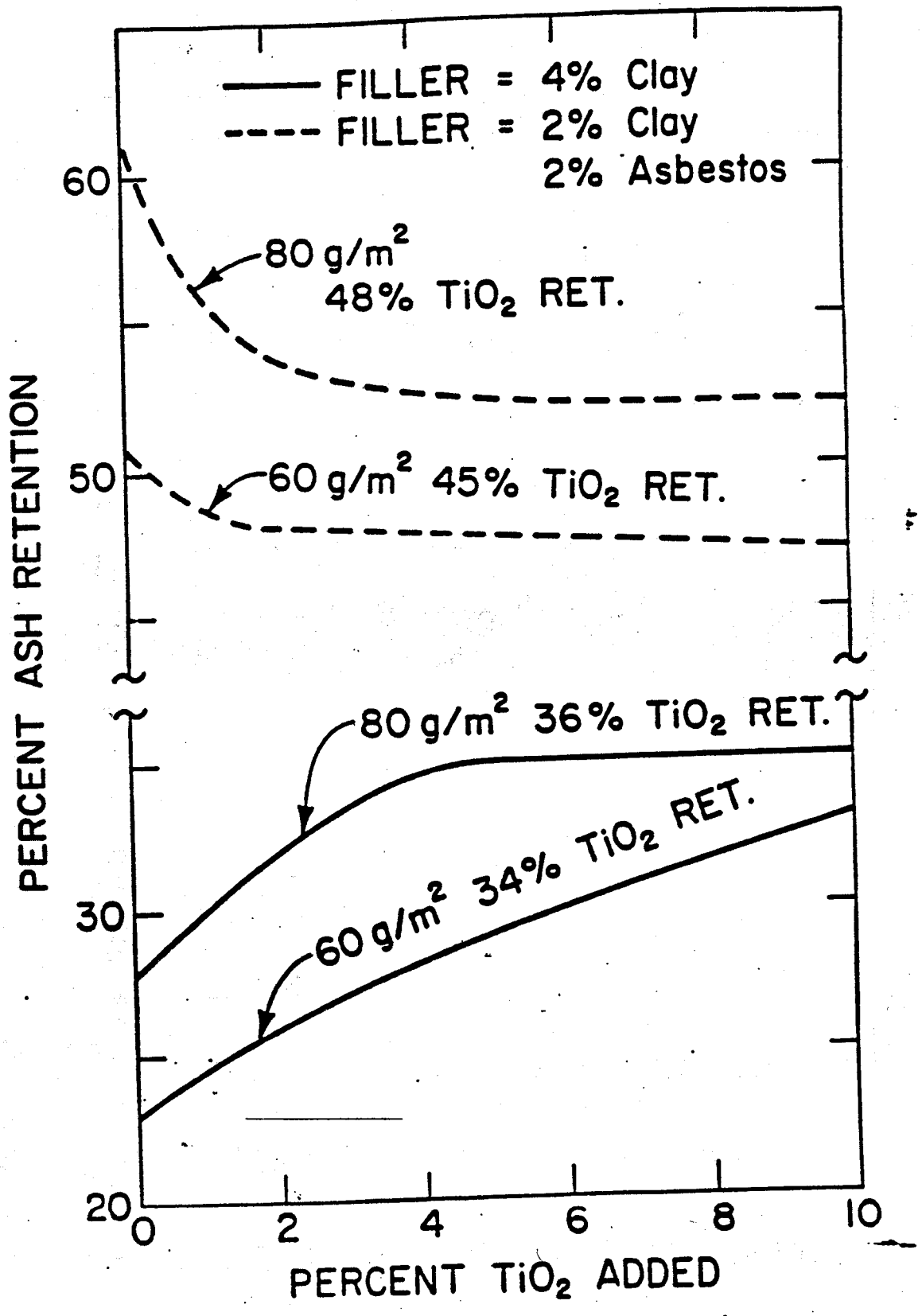


FIGURE 4: Effect of basis weight and percent TiO_2 additions on ash retention with and with-

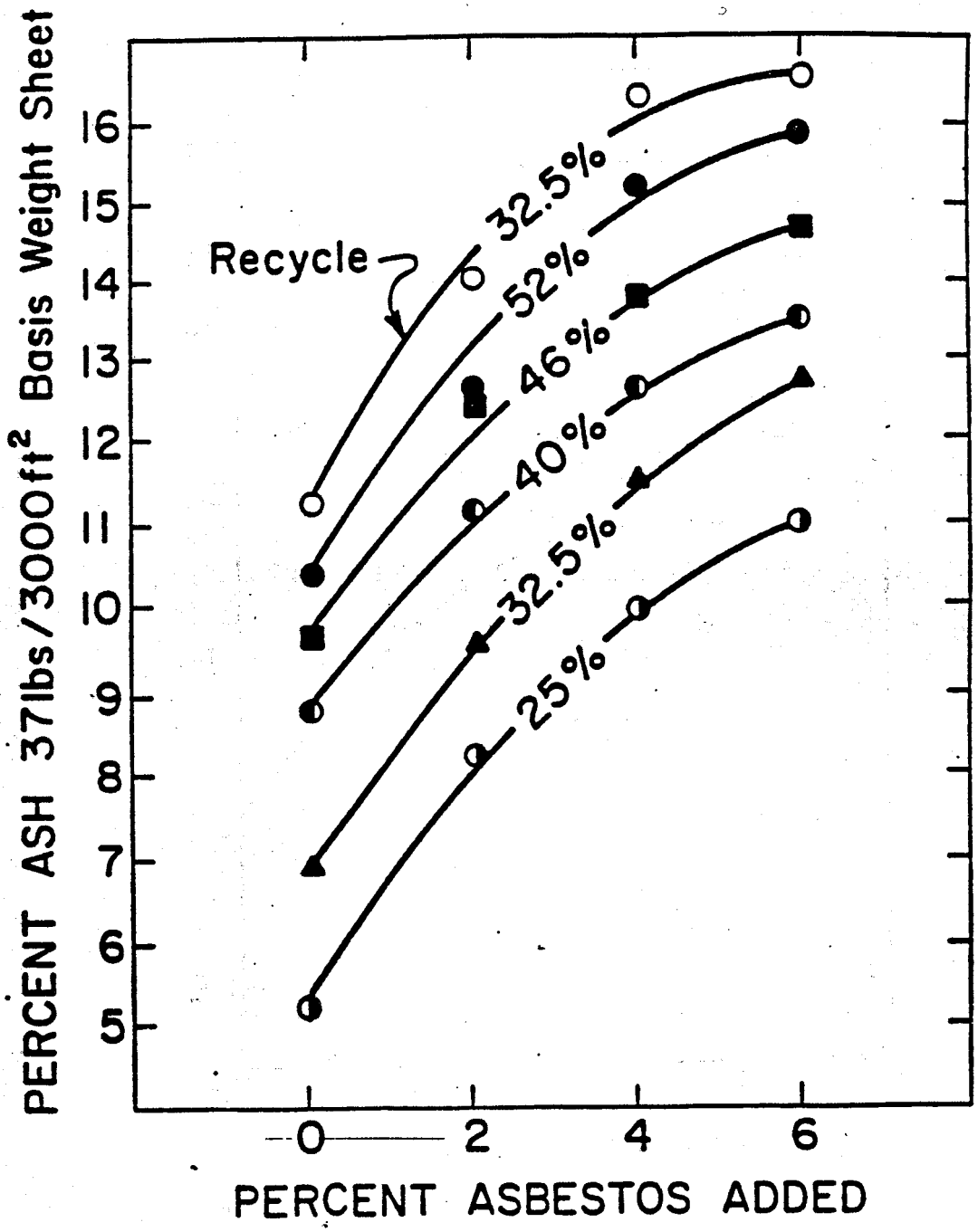


FIGURE 5: Effect of asbestos additions on ash content in highly filled handsheets.

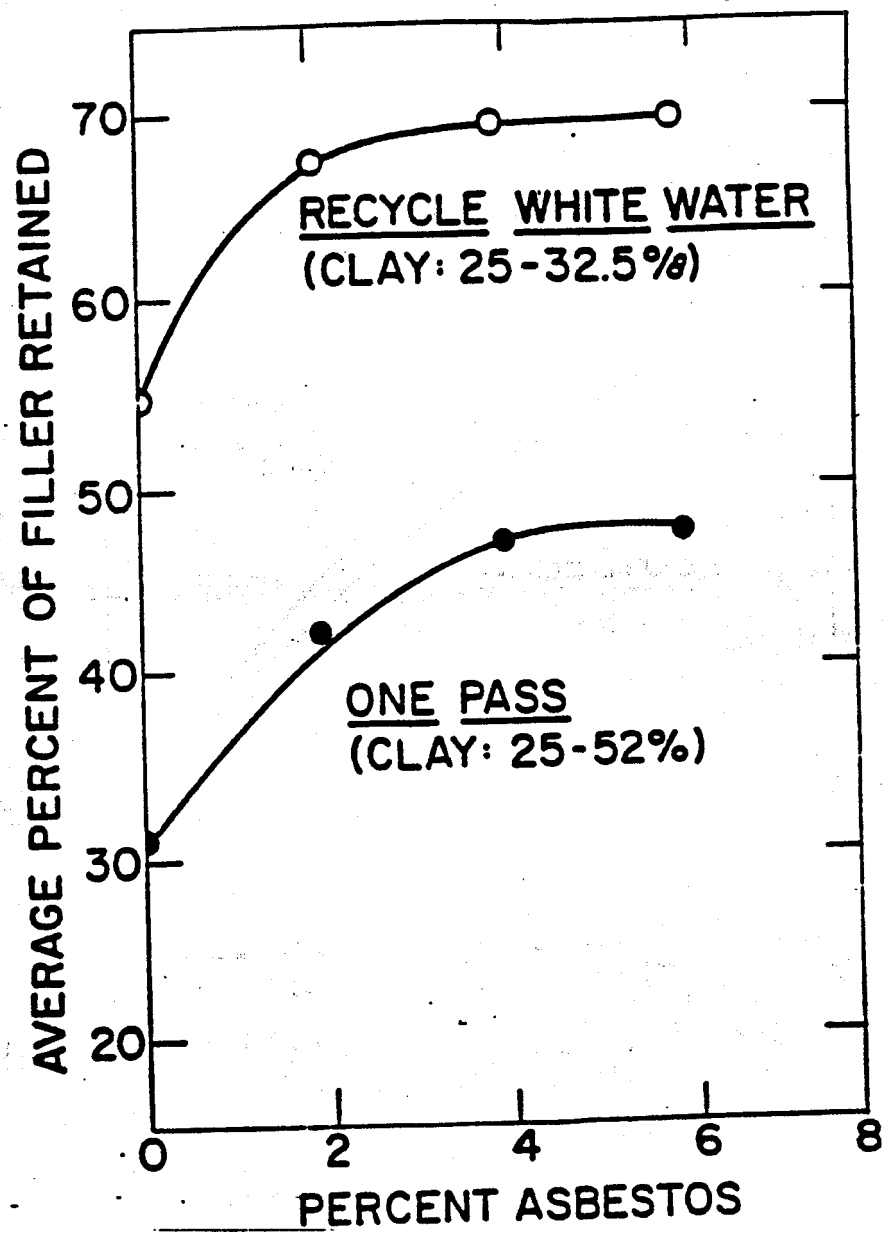


FIGURE 6: Average filler retention vs. asbestos additions.

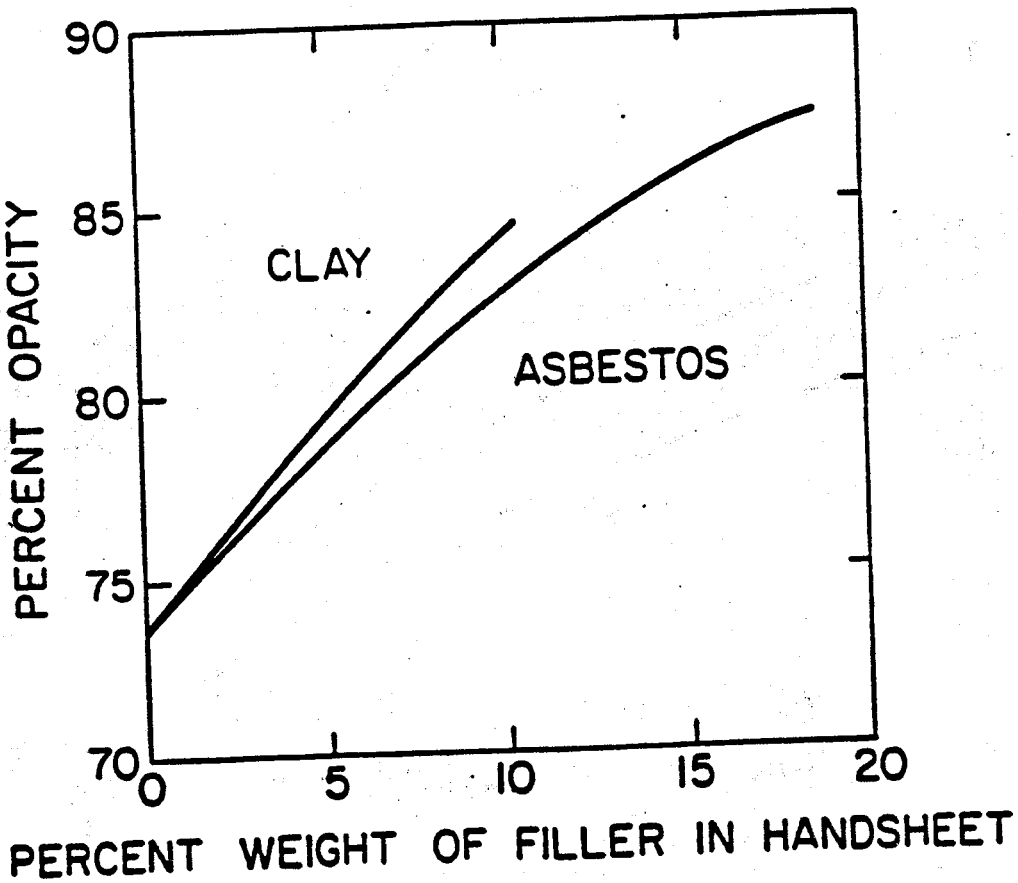


FIGURE 7: Handsheet opacity vs. filler content.

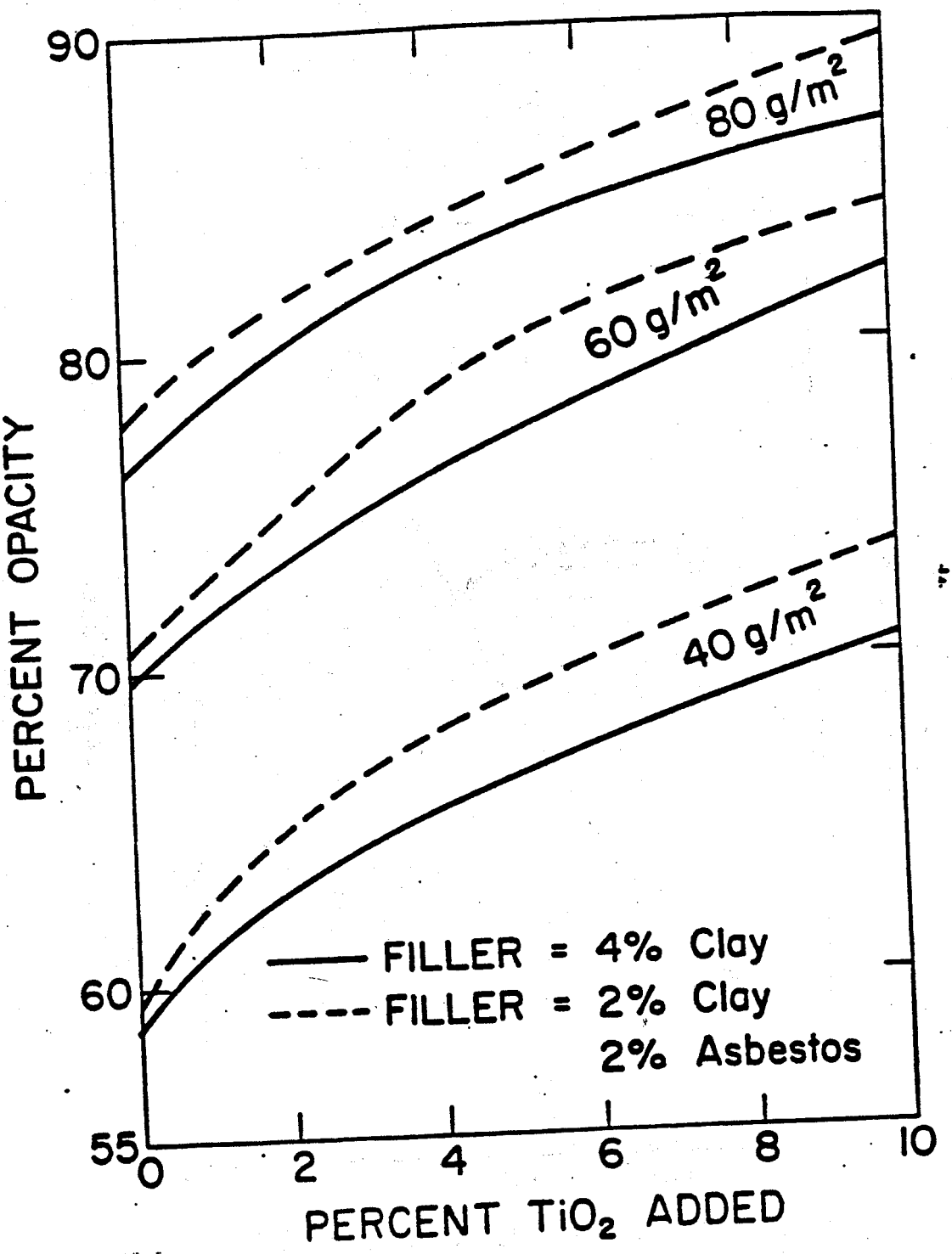


FIGURE 8: Opacity gain vs. percent TiO_2 added, with and without asbestos.

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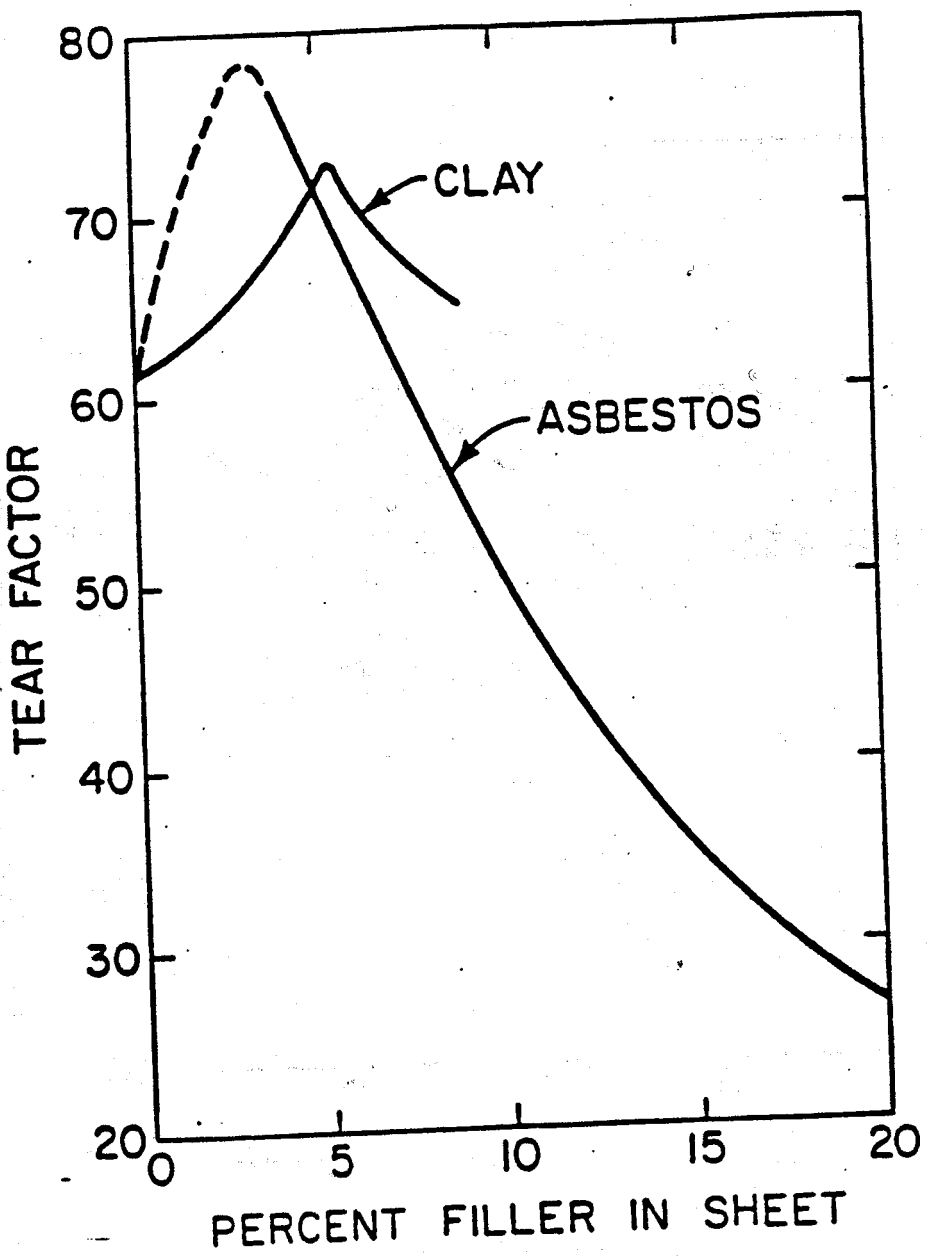


FIGURE 9: Tear factor vs. filler content.

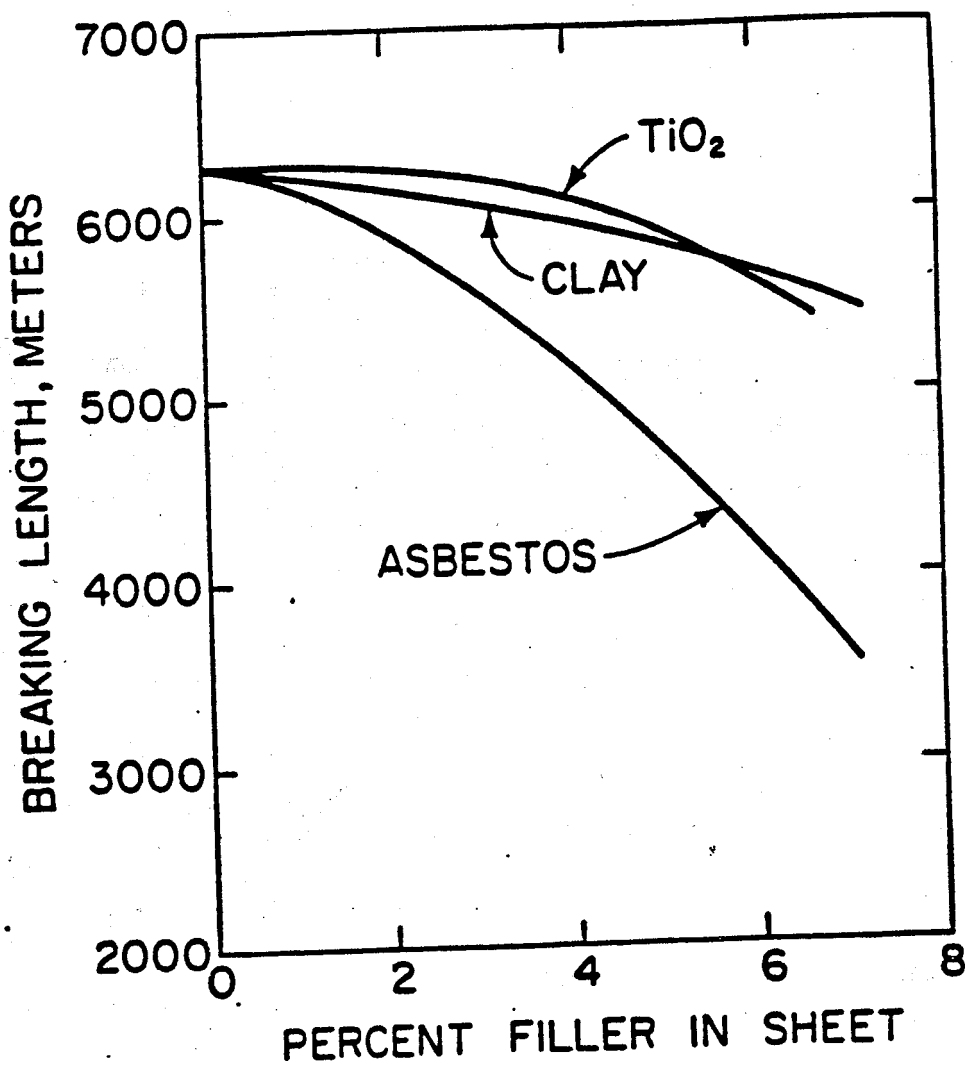


FIGURE 10: Handsheet tensile strength vs. filler content.

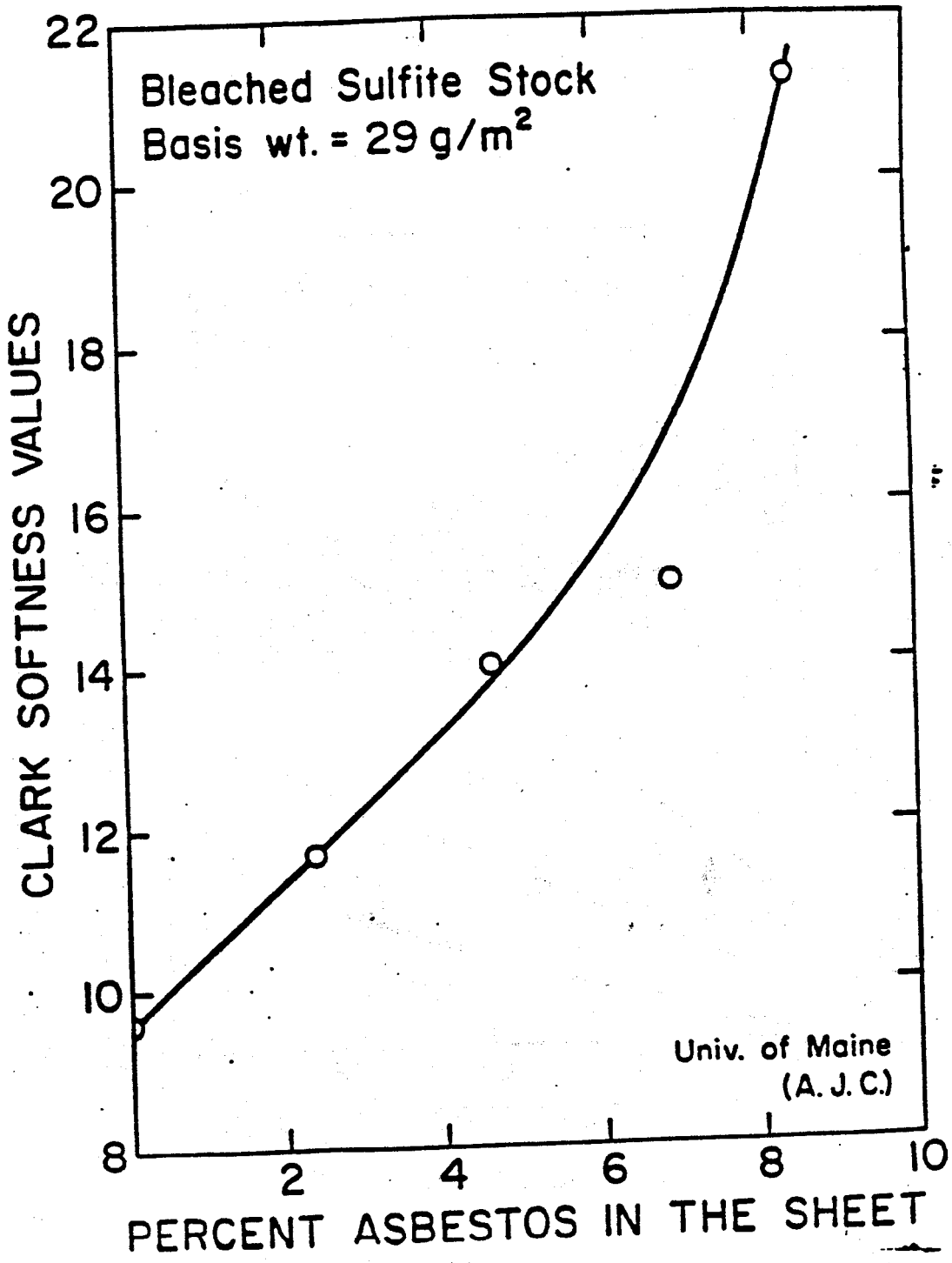


FIGURE 11: Handsheet softness vs. asbestos content.

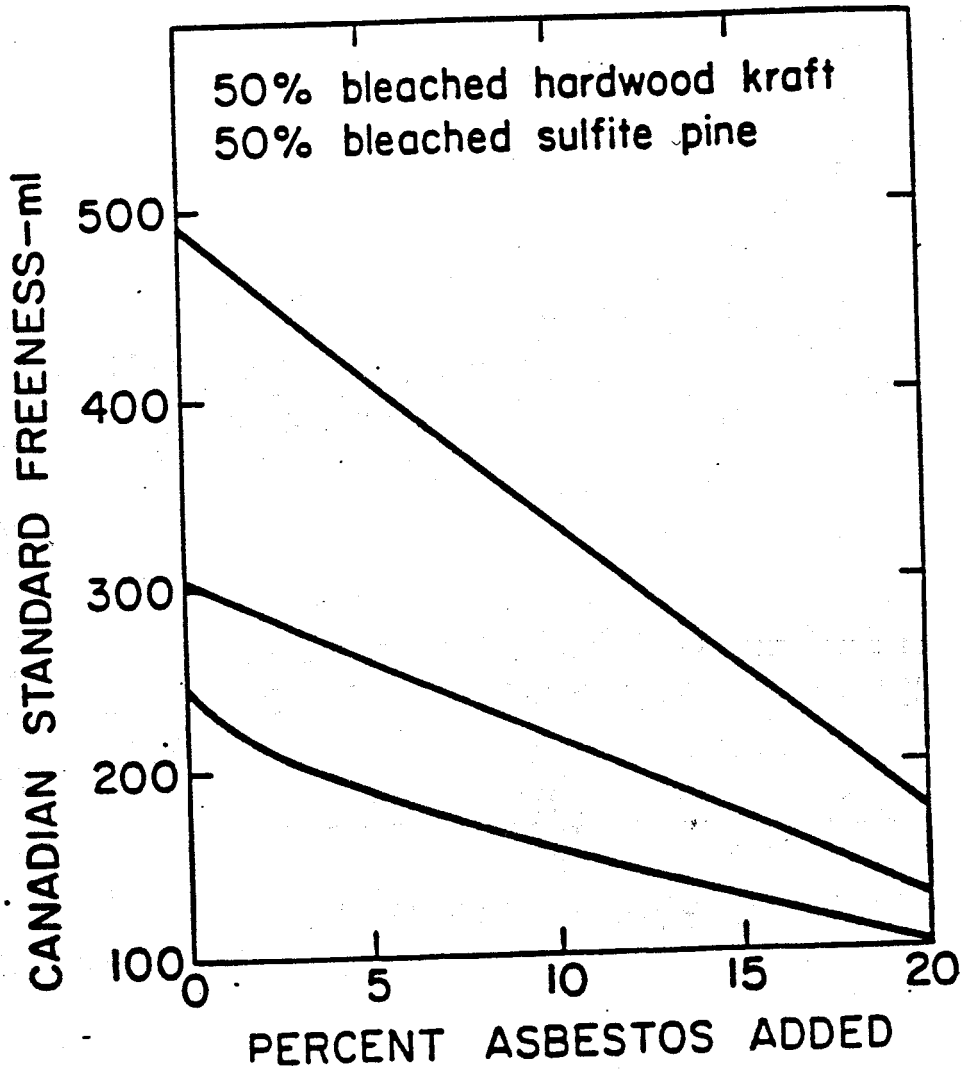


FIGURE 12: Furnish freeness vs. asbestos content.

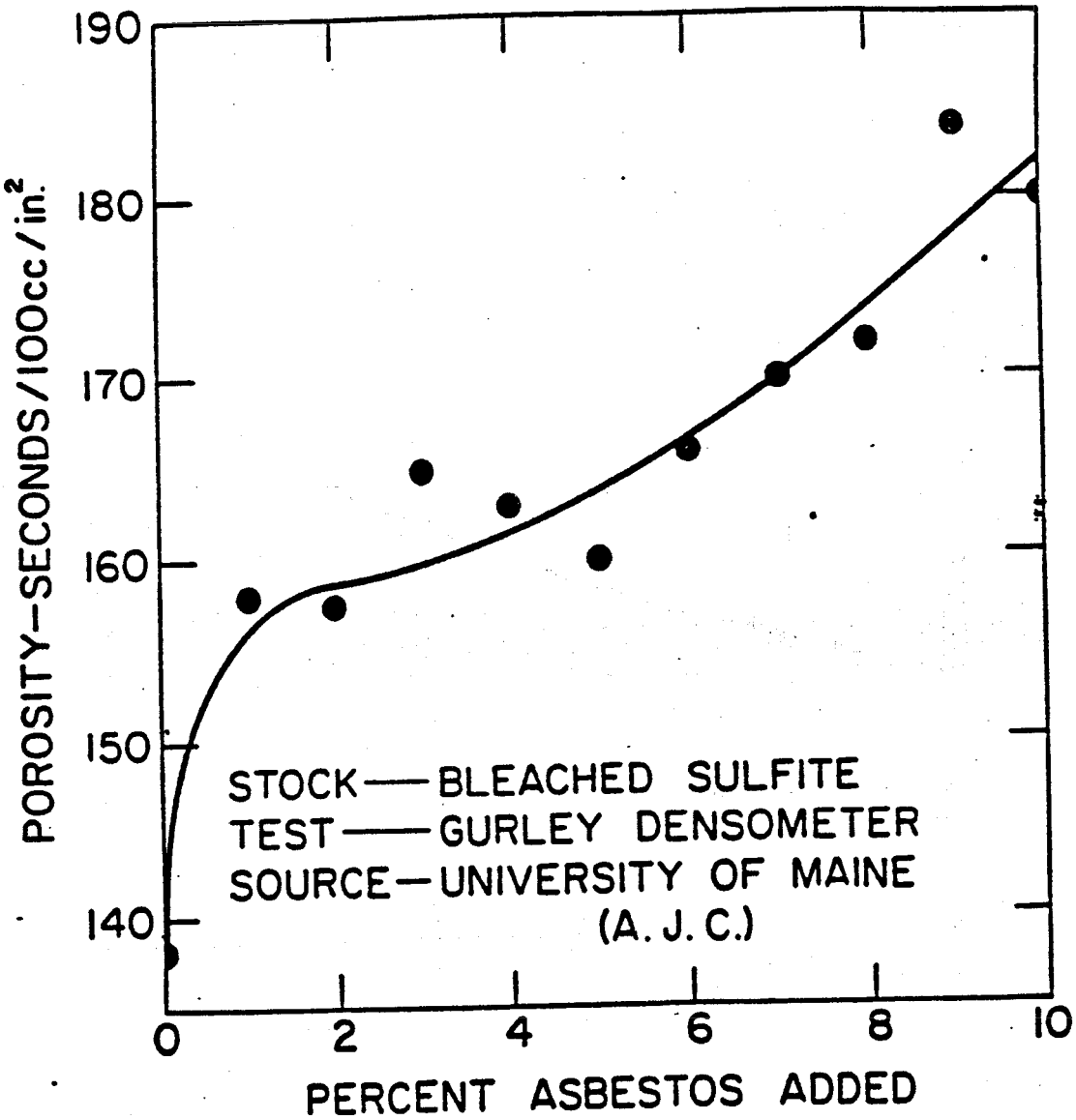


FIGURE 13: Handsheet porosity vs. asbestos content.

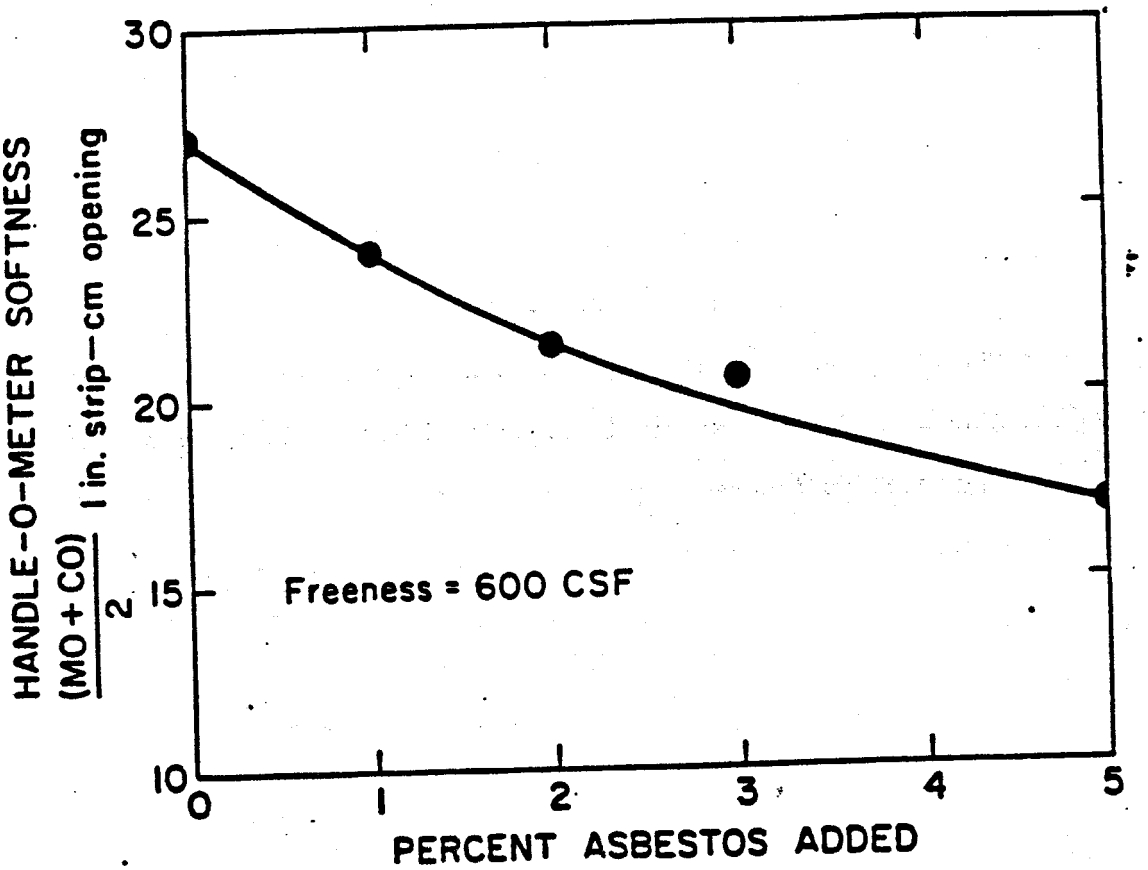


FIGURE 14: Towel softness vs. asbestos content.

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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, $Mg_6(OH)_8Si_4O_{10}$. 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).

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

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.

ACKNOWLEDGMENTS

The author wishes to thank Mr. Wolbert Roettgers for the preparation of the electron micrographs of this communication.

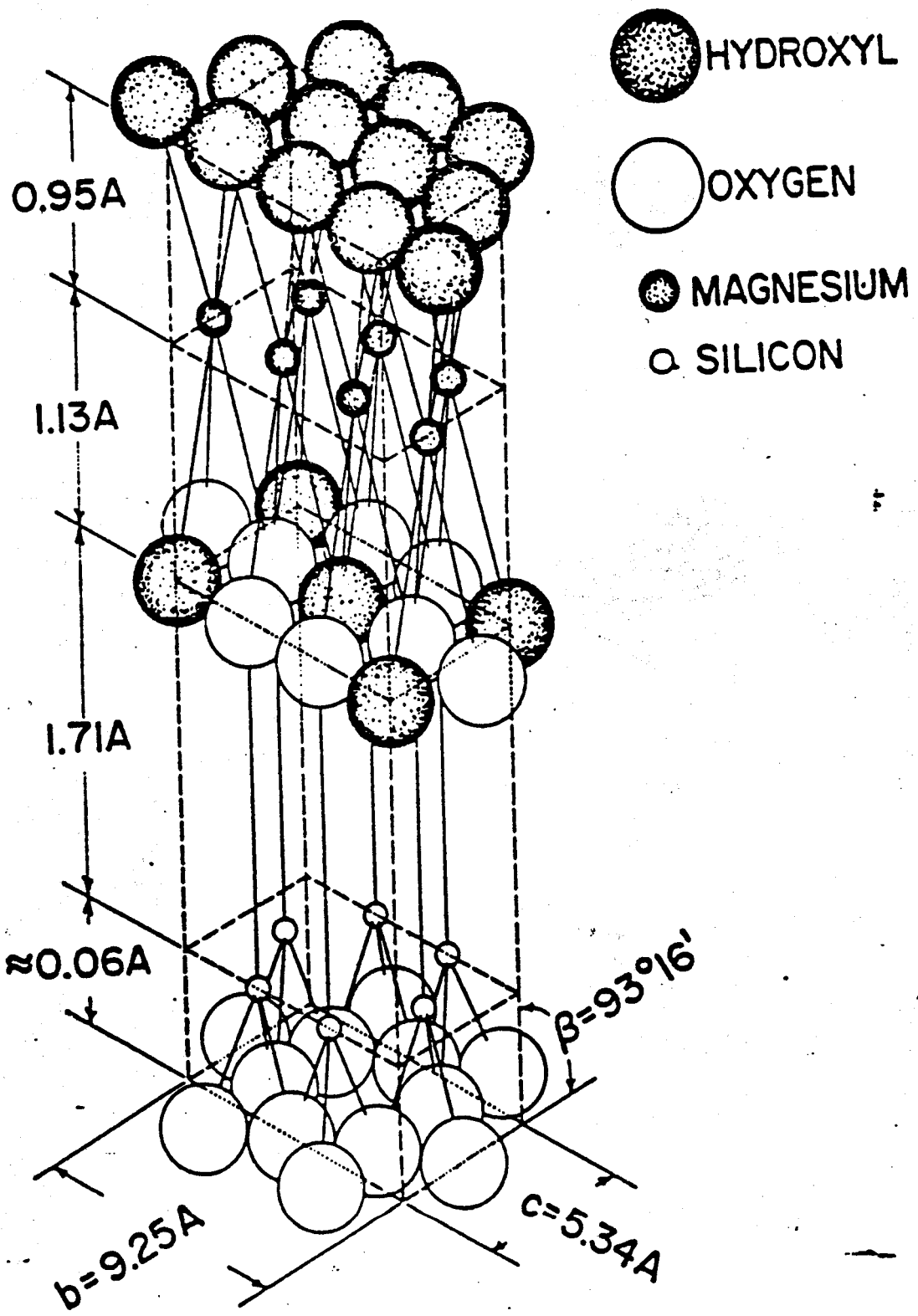


FIGURE 1: Chrysotile structure (after Whittaker).



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

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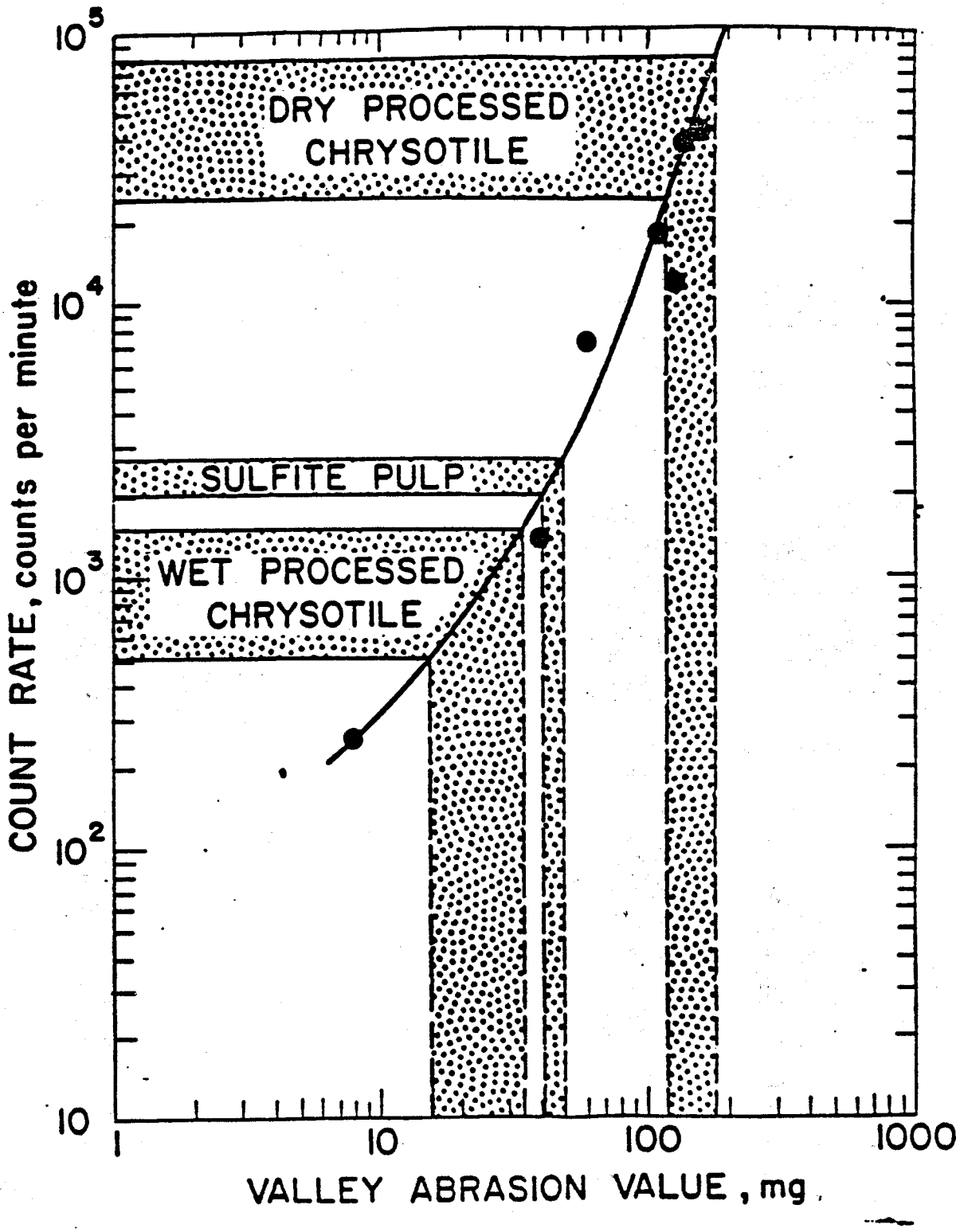
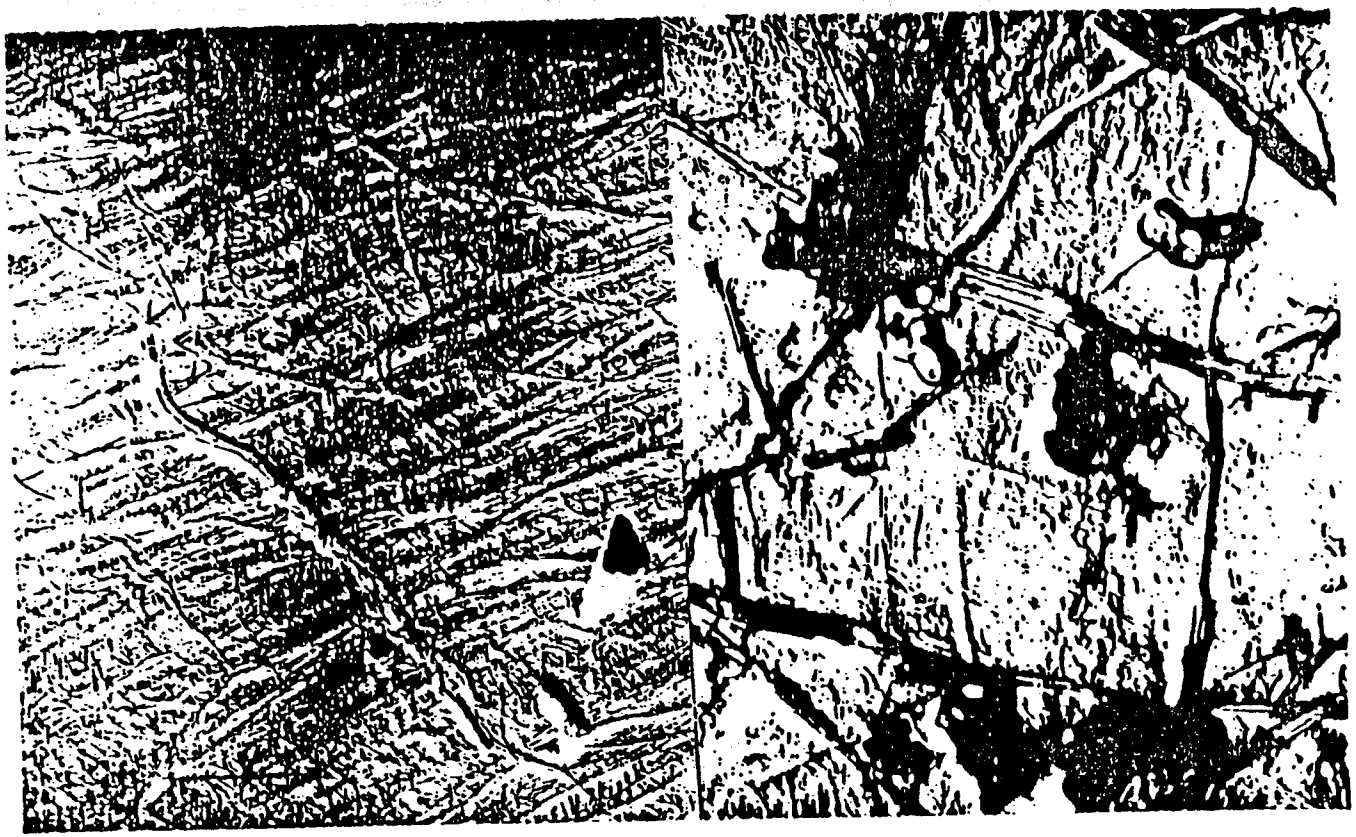


FIGURE 3: Abrasiveness of chrysotile products.



UNFILLED HANDSHEET

FILLED HANDSHEET

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

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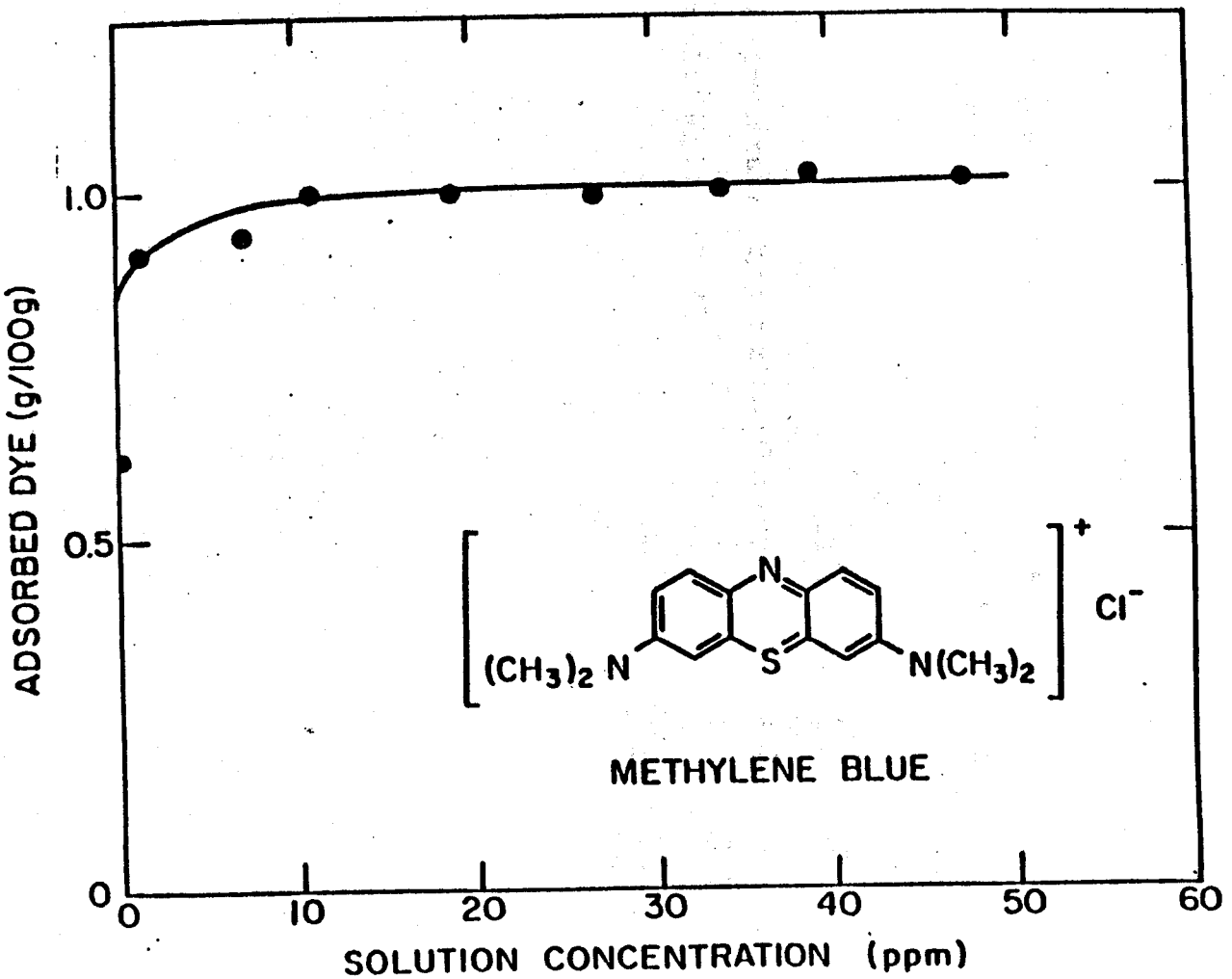


FIGURE 5: Adsorption isotherms of chrysotile with methylene blue.

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).

UNION CARBIDE U.K. LIMITED

076839

Asbestos as a Health Hazard in the United Kingdom

by

I. C. Savers

Vernehl DEPO. EXH. 5
3/10/89
KIRSY A. KENNEDY
COURT REPORTER

Myers DEPO. EXH. 7
1/6/89
KIRSY A. KENNEDY
COURT REPORTER

ALLOYS DIVISION
METALS PRODUCTS DEPARTMENT

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SUMMARY

This report has been written to show the concern on to: grounds of those people involved with asbestos in the l

Descriptions are given of the attitudes of the various approached. Action taken by Union Carbide U.K. person recorded. Up to date information is presented, and it are discussed.

Attention is brought to a formal request made by the P Research Unit, Penarth, S.Wales, for assistance with t programme. The recommendation is made that Union Carb offer its facilities for trace element analysis of the Samples, assembled under the auspices of the U.I.C.C.

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ASBESTOS AS A HEALTH HAZARD IN THE UNITED KINGDOM

1.0 INTRODUCTION

Union Carbide U.K. Limited has been promoting the sale of Coalinga asbestos for just over two years. During this time, the public has become increasingly aware of the considerable health risks associated with the use of this material. This has come about with a mixture of both good and misleading press articles, and in January, interest was accelerated by a provocative television programme in which Blue asbestos was spectacularly condemned.

So far, over 20 potential customers have raised the issue, and have requested an assurance that Carbide's material will not be a source of danger to their employees. Some have even refused to consider a laboratory evaluation until the matter becomes satisfactorily resolved. It is felt that an intensification of activity by the Factory Health Inspectors as well as potential Union objections are the prime reasons for the reluctance.

Carbide's replies have been based upon the two communications sent from New York Office on March 22nd, 1966, and October 7th, 1966, as well as Dr. Dernehl's "Asbestos Toxicology Report". These have gone part-way in alleviating some of the anxiety. However, there is a growing feeling that the quoted "Threshold Limit Value" is no longer tenable. This, coupled with the overall lack of positive knowledge, still makes the whole situation manifestly unsatisfactory. With this in mind, it was thought opportune to review the action taken to date by Union Carbide U.K., and present a survey of the information gleaned from several sources.

2.0 HISTORICAL SUMMARY

2.1 General

It is possible that public interest was initiated in Great Britain by an article in the Sunday Times (31st October, 1965) which summarised the work of Newhouse and Thompson at the London Hospital. These two workers had conducted an epidemiological survey on 83 patients admitted to the hospital over approximately 50 years. Each patient (41 male and 42 female) had positively diagnosed diffuse pleural or peritoneal mesothelioma. Evidence of exposure to asbestos was obtained in 40 of the 76 cases whose background histories could be accurately traced.

It was also in this article that the description was given of a docker's wife who died of mesothelioma, and whose only contact with asbestos had resulted from washing her husband's overalls. This example has become a cliché, and is now cited by all opponents of asbestos usage.

Factories in the U.K. are at present governed by outmoded Asbestos Regulations promulgated in 1931. Realisation that they are not entirely effective was

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of new cases of most types of pneumoconiosis, but for asbestosis the trend is still upward. Shown below are the number of diagnosed asbestosis cases over the years 1960-64.

	1960	1961	1962	1963	1964
Number of Cases	29	43	52	67	83

The Ministry of Labour is now actively engaged in formulating a new code of regulations, which this time will be more stringent and will include pipe laggers and dockers, both of whom were excluded in 1931.

To date, about 500 cases of cancer of the lung and mesothelioma are known to have occurred among people exposed to asbestos dust in the U.K. This may seem surprisingly small when it is realised that 25,000 cases of carcinoma of the lung - largely due to smoking - are diagnosed in this country every year. It is pointed out, however, that it is only recently that close attention has been paid to the problem. It is therefore inevitable that an unknown number of cases has escaped detection.

2.2 Paper

Only 3 or 4 mills in the U.K. are bona fide asbestos users. Probably with these mills specifically in mind, the Paper and Board Makers Federation sent a circular to its members last year. This stated that the Minister of Social Security had made regulations (invoked in 1966) which allowed for compensation to be granted to persons suffering from a number of prescribed diseases. One of these was "diffuse mesothelioma".

This publication caused a number of questions and doubts by several mills engaged in the evaluation of High Purity asbestos. The following examples exhibit the approach to the problem taken by some of the British mills.

2.2.1. Southalls. - makers of cellulose wadding for sanitary applications. This was the first mill to challenge our material from a toxicological standpoint. They ran a 2-day trial at the end of 1965, and showed some technical advantages. They refused, however, to proceed further as they calculated that there would be at least 2 lbs. of airborne asbestos produced each day at the creping doctor.

2.2.2. Charles Turner. - rival of Southalls. Also worried by dust hazard at creping doctor and cutters.

2.2.3. Tullis Russell. - the laboratory personnel were advised to wear masks when evaluating High Purity asbestos. Nevertheless, failure to run a trial so far is probably attributable to indecisive experimental work rather than trepidation as to toxic hazards.

2.2.4. Dartford Paper. - ran a trial a few days after the damning television broadcast. The mill safety officer was present, and asked several (mainly unanswerable) questions, as did a number of the operatives. Present mill policy is to run the next trial when the subject has been 'forgotten'.

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2.2.5. Reed Group. - showed concern 9 months ago. Their Medic consulted the Chemical Health Officer and sent a letter t mill, who were intending to use asbestos. He stated that opinion, the amount of asbestos used (less than 2% in the was too small to be a hazard to health.

2.3 Other Applications

Market development in fields such as caulks, sealants, mastics, and polyesters is still in its infancy, and is currently very ac these applications it has been necessary to offer the open grade because few manufacturers have sufficiently high shear devices t the compacted pellets.

All manufacturers are aware of the probable toxic hazards, espec already utilising asbestos in some of their products. Reaction it would seem that more objections and refusals to go further ha obtained from the larger firms. This is most likely due to a gr frequency of visits by the Health authorities, and also to more union activity.

I.C.I. are tightening up their procedures concerning asbestos. laboratory personnel have been instructed to wear masks when de the material.

The technical section of Dunlop Chemicals is very worried by th proposal that all asbestos should be eradicated from their work

British Paints report that the factory inspectors have recommen eventually insist on, costly extraction equipment for those dep dealing with asbestos. The technical personnel have stated tha no substitute for the fibrous material, and they envisage that will have to be made.

2.4 Dockers

Until the last few months, asbestos was imported into the U.K. bags. Probably as a result of the television programme, the L are now refusing to handle asbestos until the consignments are packed in indestructible containers. This attitude has now sp ports. For example, less than three weeks ago, a dispute aros docks over a cargo of asbestos.. 900 men were involved, and ev employers had offered to supply masks and overalls, together w pay rates, the dockers refused to work the cargo until it was packed. It is believed that only three ports are now open to th the material. They are Bristol, Hull and Manchester.

3.0 ACTION TAKEN BY UNION CARBIDE

3.1 Visits

... since September, 1

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3.1.1. Chemical Inspector of Health, Baynards House, 1-13 Chepstow Place, Westbourne Grove, London. Contact: Mr. R. Walpole.

This is the headquarters and reference centre for the regional factory inspectors. The outcome of the meeting was a confirmation that the 5,000,000 particles per cubic foot threshold limit is currently adhered to in Great Britain. It is expressed over here as 176 particles per c.c.

3.1.2. Asbestosis Research Council, P.O. Box No. 40, Rochdale, Lancashire. Contact: Dr. S. Holmes.

This is a body set up by the three biggest asbestos companies in Great Britain. It is primarily concerned with minimizing the asbestos dust atmospheres in their factories. Their ambitions seem to have been almost fulfilled. Turners of Rochdale claim to have had only 3 deaths attributed to asbestos since 1881. They believe that these were the result of the last war when their operators were working long hours under blackout conditions, and when a quantity of Crocidolite was used. This material had not been used before the war, nor has it been used since.

Dr. Holmes mentioned an item of great interest. Apparently, some types of masks used to protect workers from asbestos and other dusts, do themselves contain Crocidolite as the filter medium. Turners have experimented with them, and have found that it is possible to inhale an extremely high concentration of asbestos in a short space of time.

3.1.3. Pneumoconiosis Research Unit, Llandough Hospital, Penarth, Glamorgan. Contacts: Dr. V. Timbrell, Dr. A. Walters.

This unit is a branch of the Medical Research Council. It was originated initially to study the effects of coal dust in the lung. It is also associated with the U.I.C.C. (Union Internationale Contre Cancer).

The group consists of about 12 competent men, among whom Drs. Gilson, Wagner and Timbrell are world authorities. They are currently attempting to seek a solution to the problem of the aetiology of mesothelioma, and also to discover whether only one type of asbestos is responsible for the development of these tumours.

3.2 Dockers

Three courses of action have so far been taken:

3.2.1. Meeting with the Shipowners and Dock Labour Committee, Union Carbide being represented by Messrs. Cheston, Sayers and Sly. The purpose was to acquaint the dockers with our pelletised product, and to learn what form of packing was most acceptable to them. The outcome of this meeting has already been described in a report by Mr. P. R. Cheston on 16th February, 1967.

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3.2.2. Messrs. Chesten and Sly were present at the unloading of 50 tons of Union Carbide High Purity pellets from the s.s. Bolinas. A description of the consignment's condition and the subsequent difficulty encountered in persuading the dockers to work it have already been reported by Mr. Sly.

3.2.3. Designs of a new and stronger pallet have been sent to New York and King City. Negotiations have also been conducted with several shipping lines who specialise in container transport. One particular company has offered favourable rates which should enable material to be delivered to London docks at a viable cost and in a manner which will be completely acceptable to the dockers.

3.3 Literature Surveys

These are made from time to time on the subject of toxicology, and a number of the more important articles have been collected.

4.0 INFORMATION ACCRUED

4.1 Diseases Associated with Asbestos

Three diseases are believed to be caused by the inhalation of asbestos into the lungs. They are:

4.1.1. Asbestosis.

4.1.2. Bronchial carcinoma.

4.1.3. Mesothelioma of the pleura and peritoneum.

Evidence is now growing to indicate that there is also an increased incidence of cancers of the gastro-intestinal tract. It has been suggested that asbestos fibres may migrate from the lung, but there is also the possibility that they may be swallowed direct (ingestion of bronchial secretions). Support for the migration theory has been strengthened by the discovery of asbestos fibres in the liver and spleen.

4.2 Asbestosis

4.2.1. Nature of Disease: This disease, which appears to result from long exposure to asbestos dust, is similar to the well defined complaint, silicosis. The dust particles stimulate the proliferation of fibroblasts, which produce a slow, insidious, low grade, progressive fibrosis, which commences in the region of the bronchioles. This causes a thickening of the bronchiole wall and the pleura, but in its early stages, the lesion is not obstructive. As fibrosis develops, however, the whole lung becomes scarred, so that the oxygen/carbon dioxide interchange between the air and the blood is impeded. This causes an extra burden on the heart, which may prematurely fail under the strain.

The final stage of asbestosis is the formation of the 'asbestos body', which is believed to be a Ferritin envelope (Ferritin is

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the asbestos fibre. This is laid down in concentric rings. The Ferritin material is a normal body constituent, and the iron component is believed not to be derived from the iron present in asbestos.

4.2.2. Mortality Rates: Examination of the figures covering the two periods 1931-46 and 1957-64 reveals that there has been no striking change in the years of exposure or duration of illness in the deaths from asbestosis. There has, however, been a marked change in the average age at death - a rise of nearly 10 years in men and 20 in women. (This increase has been attributed to a virtual elimination of tuberculosis in the U.K. in recent years.) In 1964, the average age at death was 57 years, but even so, subjects who had been under heavy exposure to asbestos were dying in their 30's and 40's.

4.2.3. Experimental Work: Quantitive inhalation experiments on animals are now being carried out by Wagner et al. They have already shown that Chrysotile produces less fibrosis than Amosite or Crocidolite for the same dose by inhalation. This appears to be due to a more rapid elimination of the Chrysotile, probably due to a solubility effect. Figure 1 shows the results of giving equal doses of Chrysotile, Crocidolite, Amosite and finely powdered glass to rats by inhalation. Each point on the graph is the mean of 8 rats, (equal numbers of male and female).

The importance of particle length in the development of fibrosis is still not solved. Wagner has shown that in several animal species, fibrosis of the lungs is produced by fine particles or very short fibres. It is believed that long fibres may still be more fibrogenic for a given mass than short ones.

4.3 Bronchial Carcinoma

4.3.1. Nature of Disease: This is the same type of cancer as that produced by cigarettes, and it is now accepted that asbestos also predisposes to this condition.

4.3.2. Mortality Rates: The proportion of asbestosis death certificates which also record a thoracic tumour (lung cancer), has risen in both sexes disproportionately to the number of uncomplicated cases of asbestosis. Currently, over 50% of males dying with asbestosis also have a neoplasm. Even when viewed against the steadily rising incidence of lung cancer in the population as a whole, there seems little doubt that the increase is a real one. Evidence of this is shown below in Table 1:

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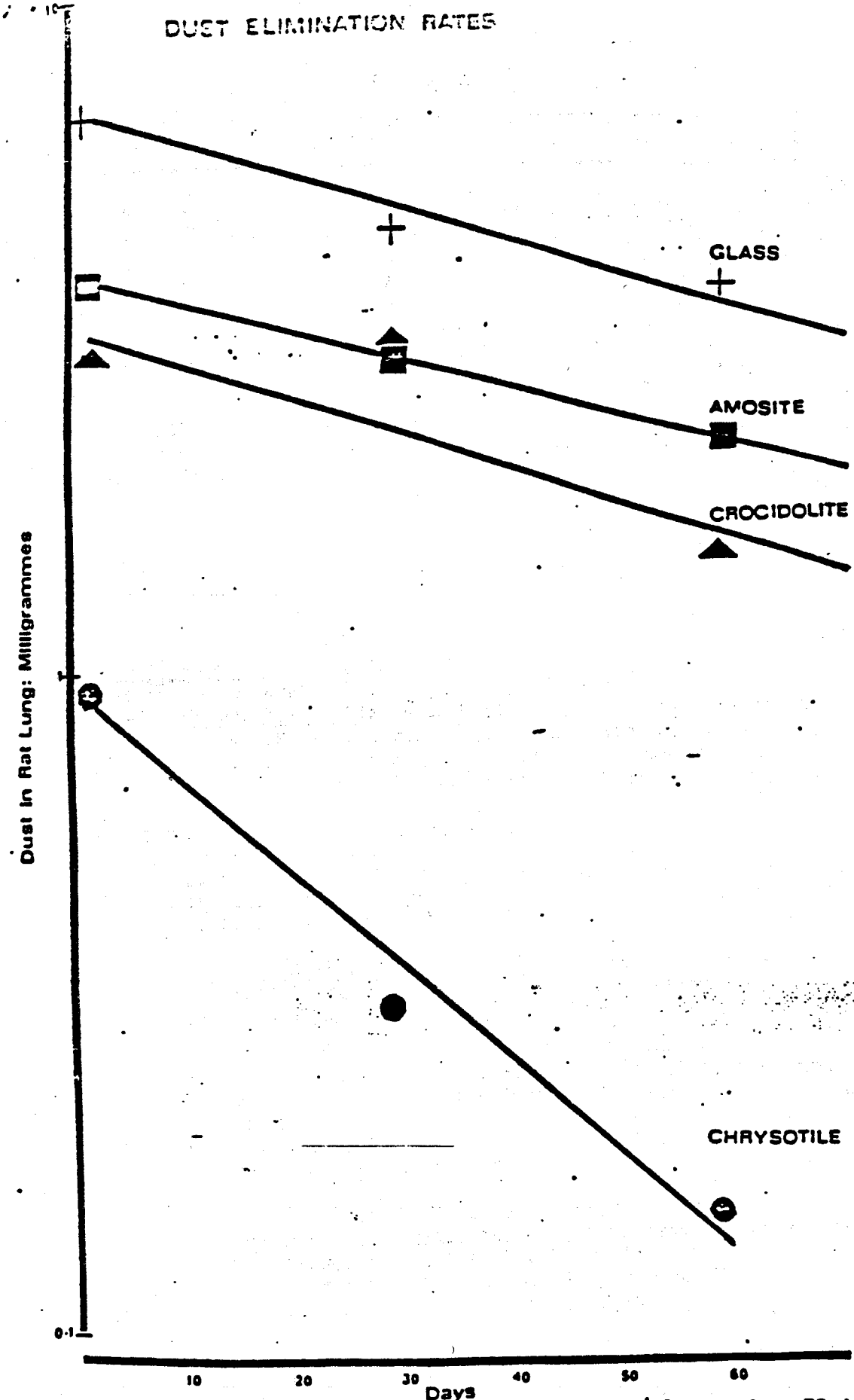


Fig.1: The weight of asbestos dust and powdered glass in rats' lungs after 30 days' exposure t

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Period	MALES			FEMALES		
	Asbestosis all deaths	Asbestosis with lung cancer	% with cancer of lung	Asbestosis all deaths	Asbestosis with lung cancer	% with cancer of lung
1924-30	13	-	NIL	7	-	NIL
1931-40	66	13	19.7	82	5	6.1
1941-50	92	21	22.8	45	5	11.1
1951-60	144	45	31.3	40	11	27.5
1961-64	113	62	54.7	26	7	26.9
1924-64	428	141	32.9	200	28	14.0

Table 1

4.4 Mesothelioma

4.4.1. Occurrence of Disease: Mesothelioma is the most disturbing of the three diseases attributable to asbestos for two reasons. Firstly, in contrast to bronchial carcinoma, it can occur in people with minimal fibrosis, i.e. only after a brief exposure, which may be as little as three months. Some authorities even believe that a single brief exposure might be sufficient.

Secondly, there is a very long time lag between the original exposure and the clinical appearance of the cancer. Thirty years is estimated to be an average time.

4.4.2. Cause of Disease: The most up to date information on the likely agent responsible for this type of pleural neoplasm was presented in a press hand-out issued by Dr. Wagner in February of this year. He wrote:

> "On current evidence from South Africa, Australia and Britain, it would appear that Crocidolite is mainly implicated in the development of mesotheliomas. However, cases have occurred in the U.S. (16 in number between 1963 and 1965) Canada (6 in number, 1952-1964) and a few in Britain, in which people concerned appear to have only been exposed to Chrysotile."

At present in South Africa a continuous search is being made to detect any cases of mesothelial tumour coming from the Amosite and Chrysotile mining areas; so far, none has been discovered. This search has also been carried out in Czechoslovakia where only Russian Chrysotile is in use; again, no diagnosis of mesothelial tumours is reported.

Dr. Gilson, Research Director of the M.R.C. Pneumoconiosis Research Unit, and his colleague, Dr. Wagner, have both stated in a number of papers that their major task at present is to "establish whether only one type of asbestos is responsible for the development of these

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4.4.3. Experimental Work: Wagner at the Pneumoconiosis Research Unit has shown (1964) that under animal experimental conditions, asbestos appears to be a powerful carcinogen. Twenty mg. of asbestos injected into the pleura of specific pathogen-free strains of rats has produced mesothelial tumours in a high proportion of animals. This is so for Chrysotile, Amosite and Crocidolite, both natural and after extraction of its natural oil by a single solvent. The investigation, a survival experiment, is not yet complete, thus, it is not yet known whether there are significant differences in the number of tumours produced by different types of fibres. So far, Amosite has produced the least.

Studies on the organic components of asbestos are being carried out by Harington of the Chester Beatty Research Institute. No hydrocarbons have been isolated from Chrysotile, but Crocidolite, which was mined in an area of South Africa with a high incidence of mesothelioma, contained 3,4 benzopyrene in relatively high amounts. Harington (1965) has also shown that during a storage period of 6 months, asbestos absorbs 70-85% of the jute oil present in jute sacks. It is not yet clear whether these oils are of any biological or medical importance.

The suggestion has been made that asbestos carcinogenicity may be related to the metals or metal complexes contained in asbestos fibres; Chrysotile contains nickel (0.5%) and chromium (0.1%), while Amosite has manganese (0.7%). Serum can elute small amounts of nickel, chromium, magnesium and manganese from Chrysotile, iron and manganese from Crocidolite and Amosite. Wagner's animal experiments tend to make the significance of iron unlikely, as the proportion of this element in Chrysotile is only about one tenth of that of Crocidolite or Amosite.

4.5 Aerodynamic Behaviour of Asbestos Fibres

4.5.1. Influence of Fibre Dimensions: Dr. V. Timbrell of the Pneumoconiosis Research Unit has been engaged for the past few years in examining the size parameters of fibres which influence their respirability. His investigations have explained the observation which puzzled earlier workers in this field, namely, the presence of fibres of 100 microns or longer in the lungs of men or experimentally exposed animals.

The explanation is that the particle-free falling speed is the most important parameter influencing its entry into the lung. This falling speed is predominantly determined by fibre diameter, and shows very little sensitivity to length, especially when the aspect ratio (length:diameter) is high. If, therefore, a fibre has a sufficiently small diameter, the falling speed can be low enough for the fibre to escape deposition by settlement and inertial precipitation mechanisms in the upper part of the respiratory tract. Hence, deep penetration to the pulmonary air spaces is possible. This has been shown to occur if the fibre diameter is less than about 3.5 microns.

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4.5.2. Influence of Aspect Ratio: It would seem that the longer the fibre, the more probability there is of it being intercepted by the nasal hairs. However, examination of asbestos particle lengths in the lung has shown them to be of the same order of magnitude as the distances between the nasal hairs. The possibility thus arises that the fibres in airways, in which the airflow is laminar, may align themselves with the streamlines. Hence if the fibres are fine enough, they can be expected to show a capacity for wending their way through fine airways.

There is no direct evidence available on whether fibres do tend to align themselves with the air streamlines. Dr. Timbrell has assumed that the conditions in an aerosol spectrometer prevail in the lung airway. Consequently, he has measured the orientations of fibres in the particle deposits in this instrument. Figure 2 shows histograms in which percentage of fibres is plotted against angle to airstream in the aerosol spectrometer for glass, Amosite and Crocidolite fibres with aspect ratios <5. A similar histogram for fibres with an aspect ratio >5 is plotted in Figure 3.

It is seen from Figure 2, when the aspect ratios are <5, there is no preferred orientation for any of the four fibres. However, for fibres with aspect ratio >5 (see Figure 3) there is a definite tendency for the fibres of all four materials to align themselves with the direction of airflow.

Furthermore, it appears from Figure 3 that there is a more marked tendency for alignment of the glass fibres than for the fibres of the three types of asbestos. It is suggested that this is due to the highly symmetrical character of these synthetic fibres, whereas the asbestos fibres, although highly selected groups, exhibit slight asymmetry.

4.6 Standard Samples

At the International Conference on the Biological Effects of Asbestos in November 1964, one of the conclusions was as follows:

> "There are large differences both in morbidity and mortality of asbestos in the surveys in different parts of the world. These discrepancies may be explained by the different chemical nature of the minerals, but there is at the same time an urgent need to standardise radiological findings and histology."

The U.I.C.C. working party on asbestos and cancer also realised this problem, and suggested that international samples of the four main commercial types of asbestos be made available.

Dr. Timbrell supervised the production of such samples in Johannesburg at the end of July, 1966. The five samples produced were: Amosite (S.Africa), Crocidolite (S.Africa), Chrysotile (Rhodesia), Chrysotile (Canada) and Anthophyllite (Finland). The Canadian fibre consists of components from eight mines, and the most difficult problem experienced was mixing them so that any portion of the standard sample as small as a match head would be representative.

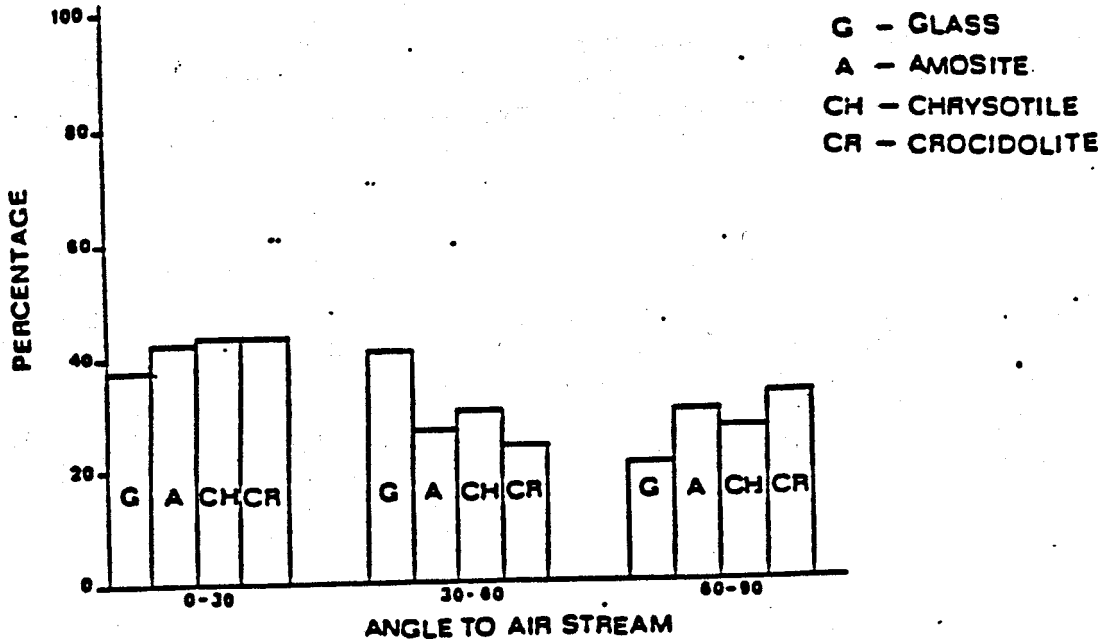


Figure 2: Frequency histograms in which percentage of fibres is plotted against angle to the airstream (axis of duct) in the aerosol spectrometer, for glass, amosite, chrysotile and crocidolite fibres with aspect ratios ≤ 5.

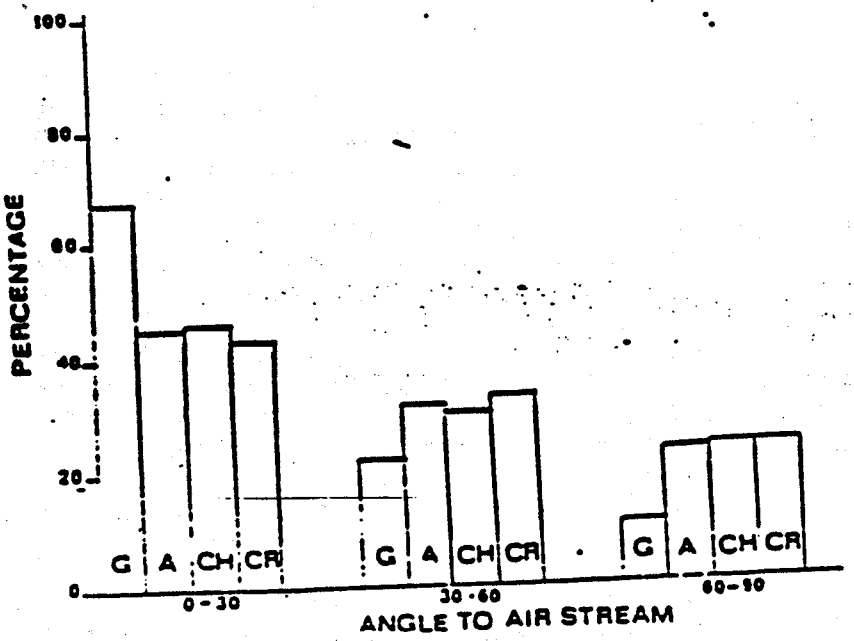


Figure 3: Frequency histograms in which percentage of fibres is plotted against angle to the airstream (axis of duct) in the aerosol spectrometer, for glass, amosite, chrysotile and crocidolite fibres with aspect ratios > 5.

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The prepared asbestos has been packaged into small samples, which are now available for distribution. Studies of a wide range of physical and chemical properties of the samples are being made at a number of world research centres.

5.0 REQUEST FOR ANALYTICAL ASSISTANCE

It is understood that all the major asbestos producers in the U.K. have proffered their assistance in conducting research work on the International Samples. Dr. Timbrell asked Union Carbide U.K. whether the Corporation would be prepared to assist in a similar manner. He requested that we should carry out trace analyses of the five samples. Apparently, they have no adequate facilities at Llandough Hospital for doing this. Dr. Timbrell has also requested that we should examine identical aliquots of the Canadian Chrysotile sample to determine whether uniform mixing was achieved in Johannesburg.

It was explained to Dr. Timbrell that it was impossible to give an immediate answer to his requests. He was, however, promised a reply at the conference on the physics and chemistry of asbestos minerals to be held in Oxford on July 19th. Dr. Timbrell, and hopefully, Drs. Gilson and Wagner, are scheduled to be at this symposium, and arrangements have already been made for them to meet Dr. T. J. Hall and Mr. F. Mumpton of the Union Carbide Corporation.

6.0 DISCUSSION

6.1 Moral Issues

6.1.1. There seems little doubt that the toxic effects of our Coalinga product are still largely unknown. There is a general inference that Crocidolite is more liable to produce mesothelioma. Exoneration of Chrysotile has not been made, however. A discussion with Dr. W. Taylor of the Department of Social Medicine, Queens College, Dundee, two days ago, revealed that concern over asbestosis is still increasing, and that Chrysotile is definitely implicated along with the other types of asbestos.

It therefore seems that on the basis of present evidence, we are not entitled under any circumstances to state that our material is not a health hazard. What is more, if it is believed that a potential customer would use our material 'dangerously', and that he is unaware of the toxicity question, then it must surely be our duty to caution him and point out means whereby he can hold the asbestos air float concentration to a minimum.

6.1.2. There has been a general recognition that Union Carbide has shown a praiseworthy responsibility in offering a pelletised product. Undoubtedly, this has contributed considerably to the continuance of negotiations with a number of papermaking firms, where dust extraction equipment to deal with an open product is inadequate.

On the other hand, the Resin Grade (open) and High Purity open materials do not possess this benefit, and the moral question is

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brought to the fore because sales of both are foreseen in the near future. Carbide's responsibilities are somewhat lessened, however, as the customers will mostly be firms already experienced in the use of asbestos, and those who are always under the watchful eye of the Factory Inspector.

6.2 Expected Rise in Asbestos Diseases

In Figure 4, a diagram has been presented relating the history of the development of the asbestos industry and associated health hazards. It is seen that the world production has increased tremendously since the war. With the knowledge that mesothelial tumours can take up to 40 years to develop, it is expected that there will be a dramatic rise in the next two decades in the number of cases discovered. If this hypothesis is proved correct, then it is certain that asbestos will receive increasingly more adverse publicity. As a result, sales resistance to our product may be expected to strengthen. It is therefore imperative that we keep abreast of current research work and publications, in order that we may combat both informed and exaggerated criticisms.

6.3 Threshold Limit Value

It is understood that the maximum dust level of 5 million particles per cubic foot (still adhered to by the U.K. Factory Inspectorate) was proposed by an engineer in 1938 as an interim guide. This figure was an arbitrary choice, and had no experimental foundation.

Dr. Taylor in his report of the International Conference on the Biological Effects of Asbestos, 1964, says:

> "The M.A.C. (Maximum Allowable Concentration) of 5 million particles per cubic foot is not now acceptable. Industry should aim at 1 million particles, and accept this figure with reservations until our knowledge in this field is extended."

Dr. Taylor reiterated this again two days ago, but he did admit that practically 2 million particles per cubic foot might have to suffice for quite a while to come.

It thus appears that the sentence in Dr. Dernehl's Asbestos Toxicology Report:

> "It is now generally accepted that a man can work a 40-hour week for a lifetime without developing asbestosis, if the asbestos dust particle count is kept at or below 5 million particles per cubic foot of air"

is now no longer held to be true by a number of informed people. An indication of the present opinion on this matter held by Union Carbide's Toxicology department would be most welcome.

6.4 Similarities Between Different Chrysotiles

At the moment, there are signs that Chrysotile may be less responsible than Crocidolite for the development of mesothelial tumours. Should it be proven, either on statistical grounds or histochemically, that this indication is

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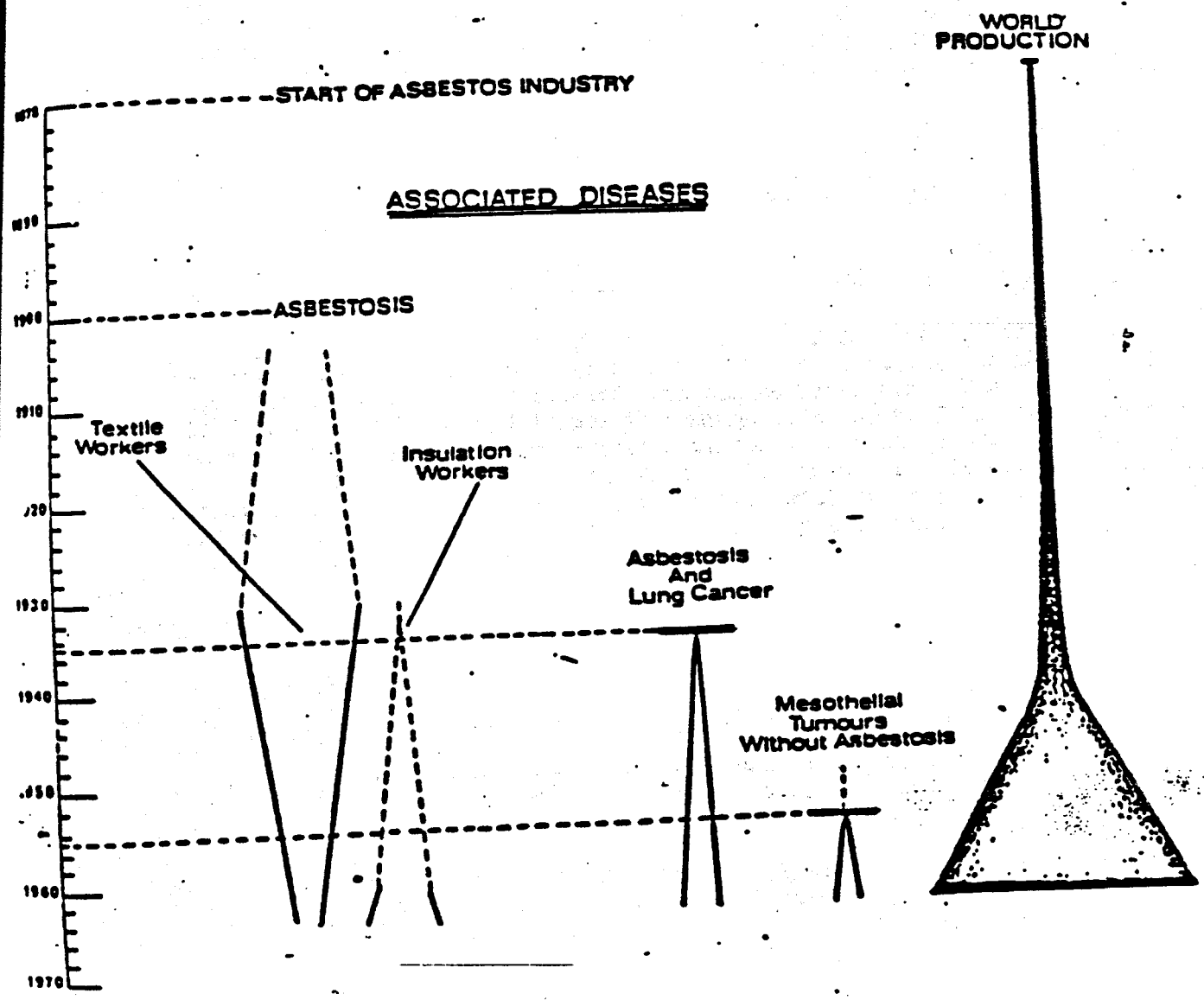


Figure 4: Diagram relating the history of the development of the asbestos industry and associated health hazards.

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to that variety of Chrysotile which has been vindicated. The case could arise, for example, that only one of the two Standard Chrysotile samples (Canadian and S.African) is given a total clearance.

6.5 Fibre Aerodynamics -

One of the obvious differences between Chrysotile from the Coalinga deposit and that from other sources is its inherently small fibre dimensions. This, together with the unique wet refining method employed, has meant that there is a great abundance of very small liberated fibres available for inhalation into the lung.

The diameter of a single Coalinga fibre is less than 300 A°. It has already been shown in 4.5.1. that fibres stand a good chance of deeply penetrating the lung if their diameters are about 3.5 microns or less. With a diameter at least 100 times smaller, there is no doubt that the Coalinga fibre is capable of reaching the innermost portions of the lung. This argument will apply to the fibre bundles contained in a bag of open material as well.

It may be seen from electron photomicrographs of Coalinga asbestos that the aspect ratio is usually much greater than 5, and that the fibrils are highly symmetrical, and are unassociated with gangue materials. Thus there is the likelihood that they will behave in a manner similar to fibreglass in Figure 3. As a result, they will have a greater tendency to align themselves with the direction of air flow. Assuming laminar flow in the bodily air passages, which in fact is probably not the case, the fibres will avoid contact with the nasal hairs, and so will be capable of passing into the depths of the lung.

7.0 RECOMMENDATIONS

7.1 Dust Counts

7.1.1. Bags: Dr. Dernehl in the Toxicology Report states:

> "In paper manufacturing, it would be desirable to know the dust concentrations where the asbestos is dumped from bags into the pulp slurry."

Dr. Taylor states recently that he believes there is more dust produced in opening a paper or plastic bag of asbestos than there is with a conventional hessian sack. He was questioned on his reason for this, but no satisfactory answer was forthcoming.

The author has himself witnessed a dust cloud in the vicinity of bags of both pelletised and open materials when making up customer sample bags after dark. A large number of suspended particles were visible in a torch beam.

It is recommended that a dust count be made in the region of a freshly opened bag of pelletised and open products. The readings obtained will be independent of the site of opening.

7.1.2. Cutters and Crêping Doctor: It is appreciated that dust conditions [illegible] a rough guide as to the amount of atmos-

doctor would nevertheless be very useful. The asbestos concentration would then be a small proportion of this. Dr. Taylor has suggested the use of the Royco instrument for a period of, say, 8 hours.

7.2 Analytical Assistance

It is recommended that Union Carbide offer to assist the Pneumoconiosis Research Council in trace element analysis of the Standard samples, for three reasons:

7.2.1. This unit is held in high esteem in the U.K. Carbide's aid would enable us to maintain close contact with the unit, and so enable us to keep up to date with current research work and ideas. Drs. Gilson Wagner and Timbrell are leaders in the field in Great Britain. It wa noticeable too that "at the New York Academy of Sciences Symposium on the Biological Effects of Asbestos held last Autumn, about half the contributions were from the U.K."

7.2.2. Dr. Timbrell has shown great interest in our material, mainly because of the symmetry and uniformity of the fibre structure. He has statec his intention of doing some animal inhalation experiments with it. We therefore stand a good chance of having the Coalinga material, at least in part, evaluated alongside the Standard samples.

7.2.3. The fact that we would be assisting research would make a good selli point. It is felt that if customers see that the company has recog- nised a problem, has tried to define it, and is subsequently offerin assistance towards a solution, then they cannot refuse to buy solely on toxicological grounds.

T. C. Savers

ICS:ik

Deposition Exh. 4
3/10/89

UNION CARBIDE CORPORATION

Legal

ASBESTOS TOXICOLOGY REPORT

It has been known for many years that some persons working in asbestos production were prone to develop a disabling lung disease. In time, this condition became known as asbestosis and was related to exposure to high concentrations of asbestos dust. With further experience, it was found that men could work with asbestos without development of lung disease if dust concentrations were kept below a certain level. It is now generally accepted that a man can work a 40-hour week for a lifetime without developing asbestosis if the asbestos dust particle count is kept at or below 5 million particles per cubic foot of air. This dust concentration of 5 million particles per cubic foot of air is the Threshold Limit Value for asbestos, and no cases of asbestosis are known to have occurred when exposures have been maintained at or below this level, despite large-scale utilization (now approaching one million tons per year in the U.S.A.). This concentration of dust is generally not visible in the average work area unless a beam of light causing a Tyndall effect is present. Usually the dust concentration must be from 8-10 million particles per cubic foot before its presence is visible in average lighting conditions.

Several years ago, it was reported that there was an increase in the incidence of cancerous tumors, especially of the lung, associated with asbestosis. Recently there have been reports of some cancers occurring in individuals exposed to asbestos dust, but who have not developed clinical asbestosis. It is believed by most authorities that these cases have been associated with exposures significantly exceeding the Threshold Limit Value. A major manufacturer of asbestos products who also mines asbestos has not been able to show an increase in cancerous growths in men working where dust concentrations were maintained at the Threshold Limit Value.

Control of asbestos dust exposure is therefore necessary. The control methods are the standard ones applicable to a variety of dusty operations. They include closed flow systems, wet processes where possible, and adequate exhaust ventilation where openings in the system are necessary. Pelletization is sometimes used to improve the handling characteristics of otherwise dusty materials. Where satisfactory containment to stay within the Threshold Limit Value is impractical or impossible, efficient and reliable respirators are available for the protection of the employee. A program of environmental monitoring is highly desirable to determine that Threshold Limit Values are not being exceeded. In paper manufacturing, it would be desirable to know the dust concentrations where the asbestos is dumped from bags into the pulp slurry. Concentrations should also be determined where dusting occurs in finishing products. While initial dust determinations should be made at frequent intervals, once the level has been established as satisfactory, the frequency may be extended to occasional tests to assure continuation of a satisfactory condition.

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Hall DEPO EXH. 23
1/10/89

You should have this statement available for any questions which might arise from your customers. If appropriate in your judgment, perhaps it should be discussed with certain customers who have not yet raised the subject. I do not feel we should make a big issue of it thereby drawing unnecessary attention to the subject since the conclusions are still questionable.

If you have any questions, please discuss them with me.

Very truly yours,

Thomas J. Hall

T.J.Hall/dk

enc.

AU313

Confidential

Report 29-55

R: 7-8-66

7-12-66

12 pages

MELLON INSTITUTE

Special Report

DEPO. EXH. 18
7/10/89
KIRBY A. KENNEDY
COURT REPORTER

The Fibrogenic Potential of Asbestos Products via Intraperitoneal Injection in Guinea Pigs, Rats and Rabbits and by the Intratracheal Route in the Rat

Chemicals Division, Union Carbide Corporation Industrial Fellowship 274-29

Summary

The results of intraperitoneal administration indicate that the asbestos products studied produced fibrotic lesions of the visceral organs in rats and guinea pigs regardless of fiber length. Of the three products, CMS-100 (refined fiber), produces the most severe reaction. JT-100 (standard fiber) and JM-3K (Johns Manville screened fiber) produced similar but less severe reactions. The results on rabbits were inconclusive.

Both JT-100 and CMS-100 produced specific lesions in rats by the intratracheal route but with JT-100 they were more severe. No lesions were found in the rats which received JM-3K fibers.

These results indicate that these three asbestos fibers may be fibrogenic by either route. No specific lesions were observed in the lungs of the JM-3K intratracheal rats, but only two rats survived to be examined.

Samples

The following samples were shipped to Mellon Institute at the request of Mr. Paul W. McDaniel who furnished the descriptive information.

Designation of Asbestos Product	Source	Quantity	Date Received	M. I. Sample Number
*CTS-100 Fiber (same as JT-100 Fiber) "Standard Fiber" containing impurities in the form of clay and magnetite. A short fiber.	Sterling Forest	8 oz.	8-14-63	26-220
*CMS-100 Fiber "Refined Fiber" with lesser impurities than JT-100. A short fiber.	Sterling Forest	8 oz.	8-14-63	26-219

* The individual fibers for most part had lengths of 0.9 to 10 microns, but there were some as long as 30 microns and some that were less than 0.5 micron. The diameters of the fiber were generally 0.3 to 1.2 microns, but there were smaller sizes noted. The clay-magnetite particles were

Designation of Asbestos Product	Source	Quantity	Date Received	M. I. Sample Number
JM-3K Fiber. "Long Fiber". (Brushed through screen to reduce fiber length to 1 mm. or less before injecting.)	Manville, N.J.	8 oz.	8-26-63	26-227

Intraperitoneal Injections

Methods

The JM-3K asbestos was brushed through a 1 mm. screen to reduce its fiber length to < 1000 micra (1.0 mm.) in order to facilitate dosing. The CMS-100 and JT-100 asbestos samples were used as received. Each asbestos product was prepared as a 2.5% (W/V) suspension in 0.85% saline. All needles, syringes and suspensions were sterilized prior to use. The animals were divided into three groups--each consisting of eleven male albino guinea pigs (P), six male albino rats (R), and two male albino New Zealand rabbits (H). The guinea pigs and rabbits received intraperitoneal injections of 2 ml. (50 mg.) and the rats, 1 ml. (25 mg.) of the respective asbestos suspensions. Eleven guinea pigs and six rats received control intraperitoneal injections of saline. There were no rabbit controls. All injections were made in the lower right quadrant of the abdomen. Tables 29-92 through 29-95 contain the results on individual animals.

Results

CMS-100 produced the most severe reaction in the form of granulomas with giant cells in six of the seven guinea pigs examined micropathologically. Typical granulomas with giant cells were observed in three of four rats and the one rabbit.

JT-100 asbestos fiber produced a granulomatous reaction in all of the 8 guinea pigs as well as the one rat subjected to micropathological examination. The rabbits had incidental lesions unrelated to the asbestos fibers.

The JM-3K asbestos fibers produced granulomas with fibers visible in five of the five guinea pigs examined. One of two rats had granuloma formation which was visible on gross examination.

Intratracheal Injections

Methods

One per cent (W/V) suspensions of JT-100, CMS-100 JM-3K and a 0.5% suspension of CMS-100 were prepared in 0.85% saline as for the intraperitoneal injections.

Female albino rats weighing in excess of 200 grams were given 1 ml. of the respective asbestos suspensions by intratracheal injection. The rats were anesthetized with saturated vapor of anhydrous diethyl ether. The trachea was exposed by blunt dissection and the injection was made directly and the incision closed with a Michael Wound Clamp.

Eight rats were injected with 1 ml. of a 1% JT-100 suspension (10 mg. asbestos). Eight rats were injected with 1 ml. of a 1% JM-3K suspension (10 mg. asbestos). Because of the flocculent properties of CMS-100, only three rats were dosed with 1 ml. of a 1% suspension (10 mg. asbestos). Eight rats were injected with 1 ml. of a 1% CMS-100 suspension (5 mg. asbestos). Six rats injected with physiological saline served as controls. Tables 29-96 through 29-99 contain results on individual animals.

Results

Specific lesions were found in most of the rats given CMS-100 and JT-100 that consisted of marked granuloma formation with bluish foreign body material present (magnetite?). Marked bronchiolitis obliterans was noted in most rats, also with bluish foreign body material within the lesions. The JT-100 rats had a more severe fibrotic reaction to this foreign material. Multinucleate giant cells were a common feature with the granulomas of the JT-100 rats but were conspicuously absent in the lungs of the rats given CMS-100. Micropathology was performed on only two rats receiving JM-3K asbestos. Neither of these animals had lesions similar to JT-100 or CMS-100.

Edwin R. Kinkead

Edwin R. Kinkead, B.S.
Research Associate

Urbano C. Pozzani

Urbano C. Pozzani, M.S.
Senior Fellow

Approved:

Charles P. Carpenter

Charles P. Carpenter, Ph.D.
Assistant Administrative Fellow

Acknowledgments:

Technical Assistance
Pathological Examination
Data in Book 868, pp. 63 to 90
and 99-109.

Charles C. Haun, B.S., Junior Fellow
John M. King, Ph.D., DVM, Fellow

Typed: July 11, 1966 - ald

Intraperitoneal Injections of Asbestos CMS-100

Dose of Asbestos	Animal Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
50 mg. (2 ml. of 2.5% suspension)	P. 96813	20 D	Peritonitis; asbestos scattered throughout abdominal cavity.	Not examined.
	P. 96803	75 D	Peritonitis; adhesions of intestines to liver.	Not examined.
	P. 96815	240 D	Autolyzed.	Not examined.
	P. 96806	270 D	No asbestos in abdominal cavity.	Not examined.
	P. 96802	286 S	Multiple small adhesions of the omentum to the mesentery.	Several small, well marked granulomas with giant cells on the serosal surface of colon.
	P. 96807	286 S	Adhesions of liver to stomach. Deposits scattered in the intestinal mesentery.	Liver--marked granulomatous reaction on the surface. Granulomas--serosal wall.
	P. 96810	286 S	Omentumal adhesions to liver with deposits in the omentum.	Liver--well marked granulomas. Marked chronic granulomas in the intestine and diaphragm.
	P. 96811	286 S	Intestinal adhesions to midline and seminal vessels.	Intestinal, liver, skeletal muscle--adhesions to each other. Areas of giant cell formation.
	P. 96812	286 S	Areas of fibrosis in most of left liver lobes.	Colon--large cystic masses filled with debris. Lined by columnar epithelium.
	P. 96814	286 S	Adhesions--liver to stomach and intestines.	Liver--fibrosis and granuloma formation. Foreign body granulomas on abdominal wall.
	P. 96821	286 S	Adhesions of abdominal wall to liver, stomach and omentum with deposits.	Granulomatous lesions of the stomach, liver and skeletal muscle.
	H. 96737	60 D	Numerous deposits of asbestos adherred to intestines.	Not examined.
	H. 96574	270 S	Multiple adhesions, ventral colon and urinary bladder.	Multiple well encapsulated granulomas present with innumerable giant cells.

(Continued)

Table 29-9

(Continued)

e of Asbestos	Animal Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
ag. e ml. of 2.5% pension)	R. 4571	20 D	Congested lungs and liver; asbestos scattered throughout abdominal cavity.	Not examined.
	R. 4678	170 D	Asbestos deposits throughout abdominal area.	Not examined.
	R. 4629	258 S	Nodules of white material in mesentery, ventral and abdominal wall.	Scattered granulomas in intestine and skeletal muscle.
	R. 4631	258 S	Deposits in the mesentery and ligaments of the testicle.	Multiple granulomas with giant cells and asbestos deposits.
	R. 4634	258 S	Chronic abscess pneumonia.	Chronic bronchopneumonia.
	R. 4660	258 S	Scattered deposits in mesentery and wall of small intestines. Adhesion of testes to intestines.	Large granulomas, well encapsulated.

Table

Intraperitoneal Injections of Asbestos JT-100

ose of Asbestos	Animal Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
0 mg. 2 ml. of 2.5% uspension)	P. 96844	11 D	Peritonitis, asbestos scattered throughout abdominal cavity.	Not examined.
	P. 96851	150 D	Entire gut adherred together. Liver adherred to ventral wall and diaphragm.	Not examined.
	P. 96849	185 D	Multiple visceral adhesions of the asbestos to the ventral abdominal wall.	Not examined.
	P. 96834	286 S	Gray deposits in the ventral abdominal wall.	Scattered foreign body granulomas with slightly elongated fibers of asbestos in them.
	P. 96835	286 S	Severe multiple adhesions with pus incorporated.	Typical granulomas.
	P. 96837	286 S	Multiple intestinal adhesions. Gray deposits in the abdominal wall.	Adherred masses with many granulomas on the serosal surface.
	P. 96839	286 S	Omental adhesions to the liver with tiny deposits in this mesentery.	Typical connective tissue granulomas.
	P. 96840	286 S	Spleen adherred to ventral wall, stomach to diaphragm.	Typical connective tissue granulomas.
	P. 96841	286 S	Multiple tiny deposits on left liver lobes and left abdominal wall.	Numerous granulomas with foreign bodies present in them.
	P. 96847	286 S	Omental adhesions to the ventral tips of the liver.	Typical granulomas with foreign bodies, giant cells, fibrosis present.
	P. 96848	286 S	Deposits on the intestinal mesentery and abdominal wall with omental adhesions.	Typical connective tissue granulas.
	H. 96729	270 S	Heart covered by chronic connective tissue.	Essentially normal.
	H. 96734	270 S	Multiple serosal deposits scattered primarily on the colon and ventral wall.	Essentially normal.

(Continued)

Table 29-93

(Continued)

ose of Asbestos	Animal Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
5 mg.	R. 4576	36 D	Cannibalized.	Not examined.
One ml. of 2.5%	R. 4536	160 D	Autolyzed.	Not examined.
uspension)	R. 4534	200 D	Peritonitis, pleuritis, some fibrosis in pleural cavity.	Not examined.
	R. 4617	242 D	Pneumonia. Asbestos particles scattered throughout entire abdominal cavity.	Not examined.
	R. 4596	258 S	Slight deposits in the mesentery and omentum.	Intestine--typical granulomas with foreign bodies.

Table 29-95

Intraperitoneal Injections of Saline Control

ose of Saline	Animal Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
ml.	P. 96857	88 D	Pneumonia.	Not examined.
	P. 96856	156 D	Pneumonia.	Not examined.
	P. 96853	170 D	Pneumonia.	Not examined.
	P. 96858	207 D	Pneumonia.	Not examined.
	P. 96852	286 S	Essentially normal.	Essentially normal.
	P. 96859	286 S	Essentially normal.	Scattered areas of interstitial pneumonia.
	P. 96860	286 S	Emaciated. Liver massively reduced in size.	Liver necrosed and abscessed
	P. 96861	286 S	Essentially normal.	Essentially normal.
	P. 96862	286 S	Essentially normal.	Essentially normal
	P. 96863	286 S	Chronic nephritis in both kidneys.	Chronic interstitial nephritis.
	P. 96864	286 S	Essentially normal.	Essentially normal.
e ml.	R. 4484	12 D	Pneumonia.	Not examined.
	R. 4483	258 S	Chronic abscessed pneumonia.	Massive abscessed pneumonia.
	R. 4531	258 S	Essentially normal.	Essentially normal.
	R. 4540	258 S	Essentially normal.	Essentially normal.
	R. 4542	258 S	Essentially normal.	Essentially normal.
	R. 4557	258 S	Essentially normal.	Essentially normal.

Table 29-96

Intratracheal Injections of Asbestos CMS-100 to Rats

Dose of Asbestos	Rat Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
10 mg. (One ml. of 1% suspension)	84636	30 S	Pneumonia.	Pneumonia, numerous granulomas scattered throughout lung.
	84645	90 S	Pneumonia.	Pneumonia, lesions of bronchiolitis obliterans in several bronchi and bronchioles.
	84702	180 S	Chronic pneumonia.	Scattered granulomas; lesions of bronchiolitis obliterans with foreign material and thrombotic-like areas.
5 mg. (One ml. of 0.5% suspension)	72531	12 D	Cannibalized.	Not examined.
	81427	30 S	Lung--appeared normal.	Multiple granulomas; bluish material present in all granulomas.
	81433	90 S	No lesions.	Scattered small granulomas. Some bronchiolitis obliterans also apparent.
	81440	90 S	Chronic pneumonia.	Pneumonia; scattered granulomas; bronchiolitis obliterans.
	72528	180 S	Not recorded.	Scattered small granulomas.
	77679	180 S	Lipid foci in lungs.	Bronchiolitis obliterans. Chronic granulomas sans giant cells.
	77680	180 S	Gray foci in lungs.	Numerous scattered granulomas.
	81600	180 S	Pneumonia.	Multiple granulomas scattered throughout lung. Bronchiolitis obliterans.

Table .. 7

Intratracheal Injections of Asbestos JT-100 to Rats

ose of Asbestos	Rat Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
) mg. ine ml. of 1% spension)	84629	60 D	Large white areas on lung; atelectasis of the right lung.	Bronchiectasis. Areas of acute bronchopneumonia.
	84672	123 D	Pneumonia.	Not examined.
	84669	151 D	Pasturella Pneumonia.	Not examined.
	84633	30 S	Chronic pneumonia.	Multiple granulomas and bronchiolitis obliterans.
	84659	30 S	Chronic pneumonia.	Pneumonia; granulomas, large lesions of bronchiolitis obliterans.
	84674	90 S	Pneumonia.	Numerous granulomas, well marked bronchiolitis obliterans.
	84676	90 S	Chronic abscessed pneumonia.	Scattered granulomas.
	84631	180 S	Not recorded.	Granulomas, some bronchiolitis obliterans.

Table 29-98

Intratracheal Injections of Asbestos JM-3K to Rats

se of Asbestos	Rat Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
mg. ne ml. of 1% spension)	84695	10 D	Entire lung was dark red.	Not examined.
	84635	13 D	Chronic pneumonia.	Not examined.
	81214	15 D	Pneumonia and emphysema.	Not examined.
	81171	50 D	Chronic pneumonia; bronchial lymph nodes, enlarged and gray.	Not examined.
	81161	30 S	Chronic pneumonia.	Chronic bronchopneumonia.
	84660	180 S	Chronic pneumonia and enlarged lymph nodes.	Chronic bronchopneumonia, a few scattered granulomas.

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Table 29-99

Intratracheal Injections of Saline to Rats

ose of Saline	Rat Number	Days to Death or Sacrifice	Gross Pathology	Micropathology
ne ml.	78253	30 S	Essentially normal.	Essentially normal.
	78273	30 S	Essentially normal.	Essentially normal.
	78302	90 S	Essentially normal.	Essentially normal.
	78717	90 S	Azygous Cbscessed.	Few areas of chronic pneumonia.
	84639	180 S	Essentially normal.	Essentially normal.
	84646	180 S	Essentially normal.	Essentially normal.
	84651	180 S	Essentially normal.	Essentially normal.
	84677	180 S	Essentially normal.	Essentially normal.

MAILING LIST

Medical Departments

4 - C. U. Dernehl
1 - E. Q. Hull
1 - R. E. Joyner
1 - R. J. Sexton
1 - F. E. Medford

2 - R & D Department Library
S. Charleston, W. Va.

10 - P. McDaniel
1 - N. H. Ketcham

Material Safety Data

September 1, 1972
UNION CARBIDE CORPORATION • 4625 ROYAL AVENUE • NIAGARA FALLS, NEW YORK • 14302
TELEPHONE: (716) 285-3311 EXT. 8567

0703-3

076913.

PRODUCT: Chrysotile Asbestos CHEMICAL FORMULA: $Mg_6(OH)_8Si_4O_{10}$

TRADE NAMES: "Calidria" Asbestos

I. PHYSICAL DATA

BOILING POINT AND MELTING POINT: Not Pertinent

SPECIFIC GRAVITY ($H_2O = 1$): 2.45

VOLATILE CONTENT: Absorbed Water 1 – 4% By Weight. Structural Water Approximately 13% by Weight.

APPEARANCE: Pellets or Fine White Powder. No odor. Very Slight Solubility in Water.

II. HAZARDOUS INGREDIENTS

Not Applicable.

III. FIRE AND EXPLOSION HAZARD DATA

Material is not Combustible. No Fire or Explosion Hazard.

IV. REACTIVITY DATA

INERT MATERIAL: No Decomposition or Polymerization Conditions.

V. HEALTH HAZARD DATA

PERMISSIBLE EXPOSURE TO AIRBORNE CONCENTRATION:

The current standard of the Occupational Safety and Health Act of 1970 contains the following exposure limits:

"The 8-hour time-weighted average airborne concentration of asbestos fibers to which employees are exposed shall not exceed 5 fibers per milliliter greater than 5 microns in length, as determined by the membrane filter method at 400-450X magnification (4 millimeter objective) phase contrast illumination. No employee shall be exposed at any time to airborne concentrations of asbestos fibers in excess of 10 fibers per milliliter, longer than 5 microns." (Federal Register – Vol. 37, June 7, 1972, page 11320).

EFFECTS OF OVER EXPOSURE: Prolonged over exposure may result in lung damage.

EMERGENCY AND FIRST AID PROCEDURES: Not applicable. Material has no acute toxicity.

Denied DEPO. EXH. 9
3/10/81
KIRBY A. KENNECY

VI. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED: Avoid inhalation of dust. Remove spilled material by vacuum cleaner or by water wash.

WASTE DISPOSAL METHOD:

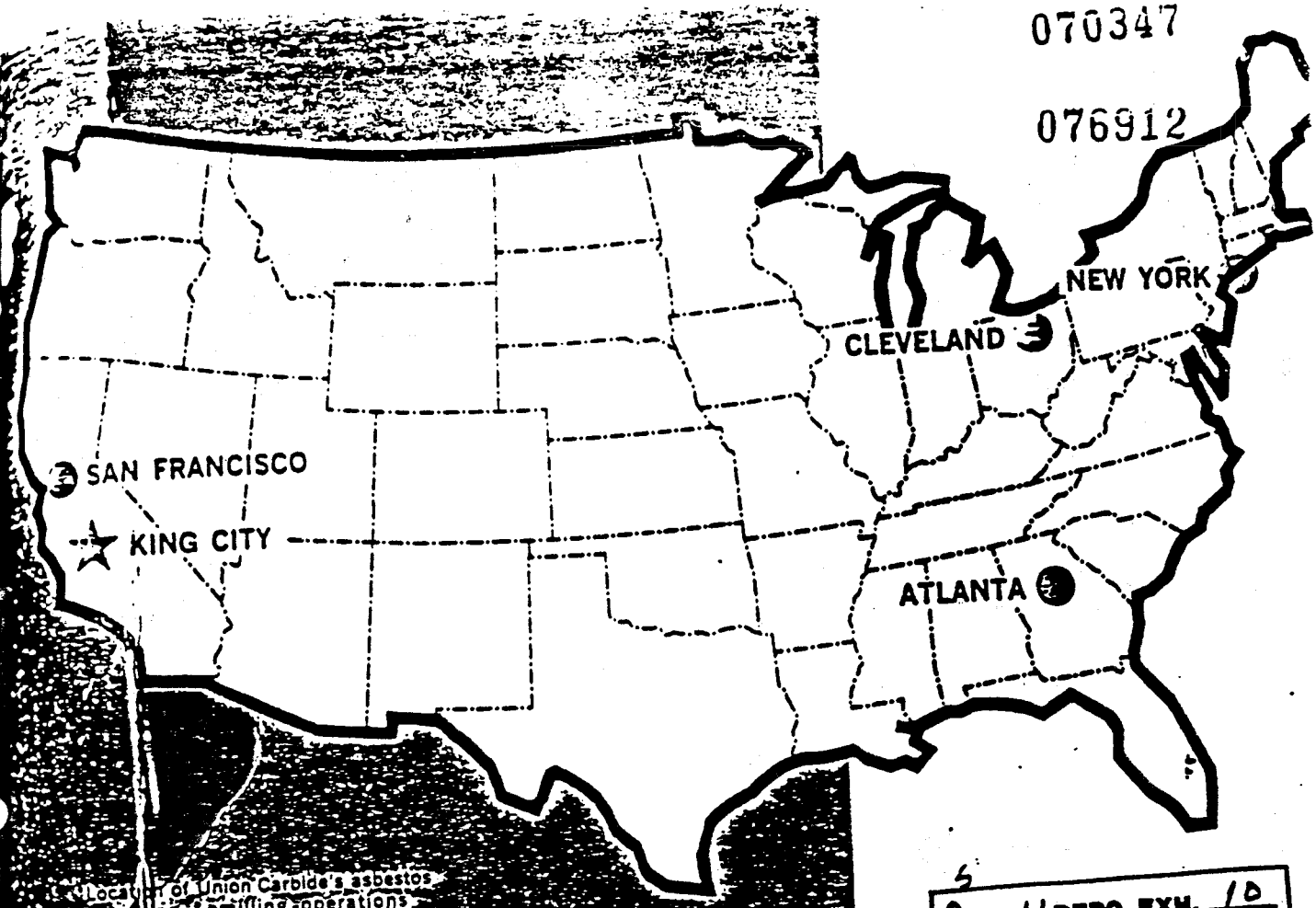
If reasonably foreseeable handling will not produce airborne concentrations in excess of exposure limits, no special procedures are required. When limits are likely to be exceeded, waste and scrap shall be collected and disposed of in impermeable sealed bags or other closed, impermeable containers, suitably labelled.

DEPO. EXH. 21
3/10/81
KIRBY A. KENNEDY

Union Carbide Corporation assumes no responsibility and makes no warranty, expressed or implied, representation, promise, or statement as to completeness, accuracy, or currency of any data provided.

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DEPO. EXH. 10
3/15/89
KIRBY A. KENNEDY
COURT REPORTER

SALES OFFICES FOR UNION CARBIDE ASBESTOS

Northeastern Region
270 Park Avenue
New York, N. Y. 10017
212 551-4420

Southern Region
1371 Peachtree St. N. E.
Atlanta, Ga. 30309
404 873-4966

Midwest Region
1300 Lakeside Avenue
Cleveland, Ohio 44114
216 621-4202

Western Region
22 Battery Street
San Francisco, Calif. 94106
415 982-1360, Ext. 16

UNION CARBIDE

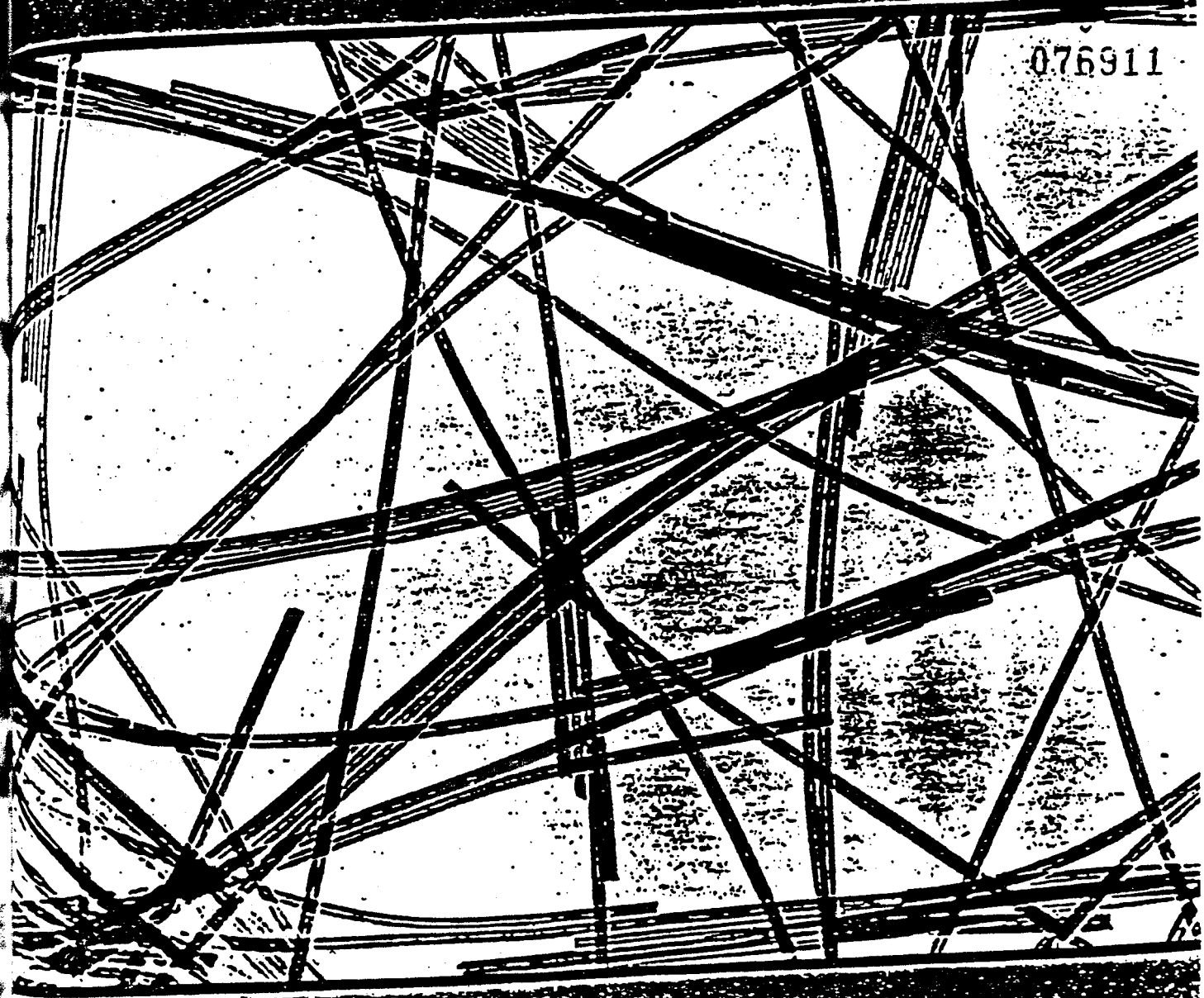
UNION CARBIDE CORPORATION
Mining and Metals Division
270 Park Avenue, New York, N.Y. 10017

DEPO. EXH. 16
KIRBY A. KENNEDY
COURT REPORTER

REFINED CHRYSOTILE ASBESTOS

- PRODUCT SPECIFICATIONS
- DESCRIPTIONS
- USES

076911



UNION CARBIDE

UNION CARBIDE CORPORATION
Minerals and Metals Division
270 Park Avenue, New York, N.Y. 10017

Material Safety Data

September 1, 1972

UNION CARBIDE CORPORATION • 4625 ROYAL AVENUE • NIAGARA FALLS, NEW YORK • 14302
TELEPHONE: (716) 285-3311 EXT. 6567

076913.

PRODUCT: Chrysotile Asbestos **CHEMICAL FORMULA:** $Mg_6(OH)_8Si_4O_{10}$

TRADE NAMES: "Calidria" Asbestos

I. PHYSICAL DATA

BOILING POINT AND MELTING POINT: Not Pertinent

SPECIFIC GRAVITY (H_2O = 1): 2.45

VOLATILE CONTENT: Absorbed Water 1 – 4% By Weight. Structural Water Approximately 13% by Weight.

APPEARANCE: Pellets or Fine White Powder. No odor. Very Slight Solubility in Water.

II. HAZARDOUS INGREDIENTS

Not Applicable.

III. FIRE AND EXPLOSION HAZARD DATA

Material is not Combustible. No Fire or Explosion Hazard.

IV. REACTIVITY DATA

INERT MATERIAL: No Decomposition or Polymerization Conditions.

V. HEALTH HAZARD DATA

PERMISSIBLE EXPOSURE TO AIRBORNE CONCENTRATION:

The current standard of the Occupational Safety and Health Act of 1970 contains the following exposure limits:

"The 8-hour time-weighted average airborne concentration of asbestos fibers to which employees are exposed shall not exceed 5 fibers per milliliter greater than 5 microns in length, as determined by the membrane filter method at 400-450X magnification (4 millimeter objective) phase contrast illumination. No employee shall be exposed at any time to airborne concentrations of asbestos fibers in excess of 10 fibers per milliliter, longer than 5 microns." (Federal Register – Vol. 37, June 7, 1972, page 11320).

EFFECTS OF OVER EXPOSURE: Prolonged over exposure may result in lung damage.

EMERGENCY AND FIRST AID PROCEDURES: Not applicable. Material has no acute toxicity.

VI. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED: Avoid inhalation of dust. Remove spilled material by vacuum cleaner or by water wash.

WASTE DISPOSAL METHOD:

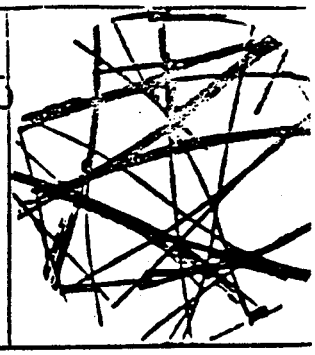
If reasonably foreseeable handling will not produce airborne concentrations in excess of exposure limits, no special procedures are required. When limits are likely to be exceeded, waste and scrap shall be collected and disposed of in impermeable sealed bags or other closed, impermeable containers, suitably labelled.

Union Carbide Corporation assumes no responsibility and makes no warranty, expressed or implied, representation, promise, or statement as to completeness, accuracy, or currency of any data provided.

ASBESTOS

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PRODUCT INFORMATION BULLETIN



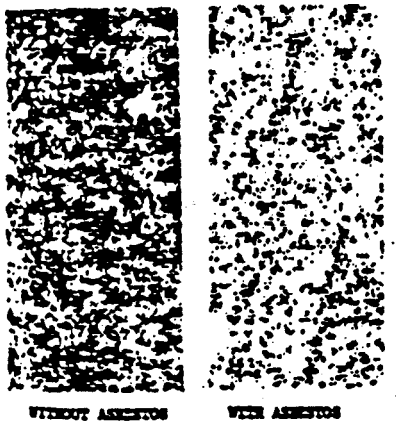
UNION CARBIDE HIGH-PURITY ASBESTOS

A NEW WHITE FIBROUS FILLER AND RETENTION AID

FOR PRINTING PAPERS

IT PROVIDES:

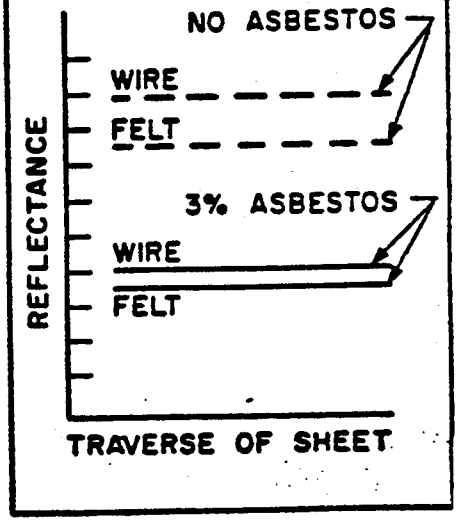
IMPROVED SHEET FORMATION



IMPROVED TiO_2 RETENTION



INCREASE DYE RETENTION



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PLUS

- Opacity
- Brightness
- Reduced Show-Through
- Cellulose Fines Retention
- Printability Improvements
- Reduced Static Electricity Buildup

DEPO. EXH. 4
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COURT REPORTER

SEE ATTACHED MILL TRIAL DATA

RETENTION OF TITANIUM DIOXIDE IN BOND PAPER

076666

Purpose of Trial: Improve Titanium Dioxide Retention to effect either material cost savings or improve the opacity of 37 lb. Bond produced by this paper company.

Type of Paper Machine: Open Fourdrinier — 126" Trim — machine speed 700 ft./min.

Production rate: 70 tons per day.

Furnish (in use):	Furnish Change During Trial:
18% Hardwood-Sulfite	no change
26% Softwood-Sulfite	no change
56% Softwood-Kraft	no change
	2.4% Asbestos
Additives*	
1.6% Talc	no change
13.0% Clay	to 10.6% Clay
0.4% Emulsified Wax	no change
3.0% Titanium Dioxide	to 2.4% (Post trial retention data indicated that 1% TiO_2 could have been removed without a loss in opacity).

Savings Resulting From Improved TiO_2 Retention:

Reduction of TiO_2: 1% of 70 tons of paper per day = $350/day savings.

Cost of 2.4% asbestos (3¢/lb. due to 2¢/lb. clay reduction) $100/day

Net savings per day due to asbestos retention of TiO_2 ..... $250 or $3.60/ton paper

Annual Savings $37,800

These savings are for this one grade being produced 150 days per year. Actually this company has other grades where the same results may be obtained.

Other Gains associated with this mill evaluation:

1. Saveall Effluent was improved in clarity. This unit was handling an estimated one million gallons of excess white water per day and the use of 2.4% asbestos allowed a 35% reduction of solids passing to the sewer. This amounts to reduced stream polution and more tons of paper per 100 tons of stock.
2. Closure or more uniform formation was indicated by porosity readings.
3. Opacity values increased during the use of asbestos even though clay and TiO_2 quantities were reduced as shown above.
4. Smoothness values were improved.

Physical Characteristics of the Bond Paper produced:

Percentage Asbestos:	0%	1%	2.4%
Basis Weight (lbs./300 Ft^2)	38.3	37.0	38.0
Machine Direction Tensile	12.6	13.0	13.8
Cross Direction Tensile	8.3	8.0	6.5
Mullen	20.6	20.8	22.0
Tear	32/33	30/33	34/36
Smoothness (Gain)	53	32	31
Opacity (Gain)	82.5	83	84-84.5
Brightness	83	82-83	82
Wax Pick	18/16	18/18	18/18
Caliper	3.23	3.09	3.10
% Ash in the Bond Paper (gain)	10.2	11.3	12.4

076667

APPLICATION

RETENTION AID IN PAPER MILL SAVEALL OPERATION

OBJECT: REDUCE SOLIDS LOSSES AND REDUCE RIVER POLLUTION

TYPE OF SAVEALL: OLIVER DRUM TYPE FILTER WITH STAINLESS 60/40 MESH WIRE USING FRESH CELLULOSE PULP AS A FILTER AID.

MATERIAL TO BE RECLAIMED FROM EXCESS WHITE WATER RETURNED FROM THE PAPER MACHINE

1. Titanium Dioxide
2. Clay
3. Cellulose fines
4. Starch
5. Dye particles

Data for the operation:

Production rate of Paper Machine: 60 tons/day

Machine Speed: 800 fpm Wire mesh — 75x58

Total Filler Content: 6.25% (1.25% TiO_2; 2.5% clay; 2.5% starch)

Furnish: 50% Magnifite Hardwood
30% Softwood Draft-Spruce
20% Broke

pH 5.0 with Alum

REDUCTION OF SOLIDS LOSSES USING HIGH PURITY ASBESTOS:

% Asbestos	0	2½
Flow Rate (GPH)	1,000,000	1,000,000
Average Solids in lbs./1000 gals.	3.25	0.55
Number of days/year for this particular condition	200	200
Value of Material $/ton	100	100

ANNUAL SAVINGS RESULTING FROM THE USE OF ASBESTOS: $27,000

076003

APPLICATION—RETENTION OF FILLERS

Novel Paper No. 22 for Color Books

Purpose: Improving Retention of Fillers for Improved Opacity, and for Material Savings.

Type Paper Machine: Open-Fourdrinier
Production Rate: 150 tons per day
Systems pH: 4.5 - 5.0
Basis Weight: 32 lb./1000 ft.²

} Machine Trim: 132"
Machine Speed: 804 F.P.M.

Furnish:

Prior to use of Asbestos	with 2% Asbestos
80% Groundwood	80%
20% Unbleached sulfite	20%
5% Georgia clay	5%
0.3% Tetrasodium Polyphosphate	0.3%
0.4% Zinc Hydrosulfite	0.4%
0.3% Alum	0.3%
2.8% Zeolex	0%
0% Asbestos	2.2% — added

Other additives to the headbox: Kymene 557 — 1.7%.

Retention Results:

	0	2.2%	
% Asbestos	24	39	
% Clay	30	43	
% Total ash		62%	} 52.5% ave.
% Increase due to asbestos (clay retention)		43	
% Increase due to asbestos (total ash)			

Paper Tests with and without Asbestos:

	0% Asbestos	2.2% Asbestos
Basis Weight (lbs./3000 ft.²)	32	32
% Ash	4.4	6.5
% Opacity	92.9	93.6
Two-sidedness	1 pt.	0 - 0.5 pts.

Economic Gain and Quality Improvements:

1. High Purity Asbestos (2.2%) replaced 2.8% Zeolex with an immediate cost advantage. With a production rate of 140 ton/day, Zeolex was being used at a cost of $548/day while its replacement, High-Purity Asbestos, cost $308/day, yielding a savings of $240/day. The asbestos also caused an increase in clay retention; a 0.7 pt. opacity gain was achieved allowing either improved quality, or an additional estimated savings of $390/day if normal specifications are held. Final result was a total daily savings of $680/day.

2. Reduced two-sidedness during the use of High-Purity Asbestos also gave an improved paper product.

INTERNAL CORRESPONDENCE

UNION CARBIDE CHEMICALS COMPANY • INSTITUTE PLANT P. O. BOX 8361, CHARLESTON, WEST VIRGINIA

To (Name) Mr. G. J. Ratcliffe
Company: Industrial Relations

Date: 20 July 1962

Originating Dept.: Medical Department - Plant 512

Answering letter date:

Subject: Insulation Block Dust Survey
Construction Insulation Shop
Plant 511

Copy to:
Mr. L. N. Dickinson
Mr. G. H. Daniels
Mr. N. S. Eastman
Mr. R. A. Huber
Mr. B. F. King
Mr. F. B. Snyder
Dr. C. U. Dernehl
Dr. E. M. Best
Mr. E. G. Heinz
Mr. P. E. Henry
Mr. R. A. Neal
Mr. D. R. Matheny
Mr. N. H. Ketcham

Enclosed is an industrial hygiene report by Mr. R. E. Peele on the potential hazardousness of "new and improved" "Thermobestos" insulation blocks submitted by the manufacturer for evaluation by band saw processing in the Construction Department's Insulation Shop. The report points out that the three "new and improved" sample blocks, subjected to test conditions identical with those in use and reported upon in March of this year, are an improvement somewhat, but these blocks too, release quantities of asbestos dust particles into the working environment considerably above the acceptable safe limits (i.e., the T.L.V.). Therefore, definitely, the processing of "new and improved" blocks also constitute a hazard to health.

Mr. Peele recommends that "Thermobestos" blocks not be processed in the Construction Department Insulation Shop until they meet acceptable standards and I concur fully.

Very truly yours,

R. J. Sexton, M.D.
Plant Medical Director

RJS:gl

Enclosure

Deposition DEPO. EXH. 24
2/10/69
KIRBY A. KENNEDY
COURT REPORTER

INTERNAL CORRESPONDENCE

UNION CARBIDE CHEMICALS COMPANY • INSTITUTE PLANT P. O. BOX 2231, CHARLESTON, WEST VIRGINIA

(Name) R. J. Sexton, M.D.

Company

Dept. Medical Department

Copy to

Date 3 December 1962

Originating Dept. Industrial Hygiene - Plant 512

Answering letter date

Subject Johns Manville "Thermobestos"

On 21 March 1962, an Industrial Hygiene Report, i.e., 62-IH-1-6-1, identified the existence of a hazard to health in the Construction Insulation Shop during such times as when insulation blocks manufactured by the Johns Manville Company are being fabricated with exhausted band saws. It was recommended at that time that 18" x 36" x 4" "Thermobestos" insulation blocks* should not be fabricated with the existing equipment unless --

(a) The atmospheric dust problem could be reduced to below 20 mppcf of air through the use of ventilation, etc., or

(b) The producer of this product begins manufacturing an insulation block which will not release upon fabrication with a band saw, dust concentrations in excess of 20 mppcf of air.

In accordance with these recommendations, the Construction Insulation Shop discontinued almost immediately the purchase of "Thermobestos" insulation blocks.

On 20 July 1962, a second Industrial Hygiene Report, i.e., 62-IH-2-G-1, was submitted subsequent to an evaluation of three new insulation materials supplied by the Johns Manville Company. This report concluded that these materials were improved over the original. However, the dust concentrations produced upon fabrication of these insulation blocks were substantially in excess of the recommended safe concentrations of 20 mppcf of air. Therefore, the recommendations contained in this report remained exactly as those stated in the initial report of March, 1962.

On 20 November 1962 the author was contacted by Mr. D. R. Matheny, General Foreman of the Insulation Shop, who stated that three Johns Manville representatives, i.e., Messers. F. E. Saxer, N. Gordon, and H. E. Kaufman, were present and had requested a meeting with the Plant Industrial Hygienist. This meeting was held in the lobby of Building 2, at which time Mr. Saxer produced the accompanying copy of portions of a report submitted by the Johns Manville Industrial Hygiene Laboratory located at Manville, N.J. Mr. Saxer stated that, in accordance with this report, they were not able to produce results which agreed with those contained in the reports submitted by this department. Therefore, they were concerned and interested in learning if their methods of reproducing

*The Johns Manville trade name for their insulation blocks

Darnell DEPO. EXH. 25
3/10/89
KIRBY A. KENNEDY
COURT REPORTER

our environmental conditions, sampling and evaluating the dust concentrations contained therein were subject to question. At this point he stated also that this conclusion was promoted on the basis of their analysis of the atmospheric dust conditions produced by their competitors product, (i.e., Kaylo or Item # 5AT in the report) which in no way agreed with the data submitted in the Industrial Hygiene Report - IH-62-I-G-I.

It was explained at this point, that this department's interest in this problem is always confined solely to the environmental conditions as they effect the health of our workers, and that no part of the investigation should be construed as an attempt to arbitrarily promote the use of one company's product over that of another.

Upon completion of this statement, Mr. Saxer proposed that Mr. D. R. Matheny and the Plant's Industrial Hygienist make a trip to Manville, New Jersey, at Johns Manville's expense and at a time selected by Union Carbide. This visit would be for the specific purpose of observing, scrutinizing and comparing their method of atmospheric dust evaluation with that as utilitized by the Institute Plant's Industrial Hugiene Department. It was Mr. Saxer's opinion that such a visit would permit a more positive approach to the problem and remove the possibility of misunderstandings, etc., that results from written correspondence. At this point, Mr. Saxer was assured that there would be no personal objection on my part to the performance of such a service. However, a proposal of this nature would have to be submitted to the Plant Manager, Mr. L. N. Dickinson, through appropriate channels before a final decision could be made.

In conclusion, it should be stated that a phone call was received from Mr. F. G. Comerford of Design and Construction on the morning of 21 November 1962, who requested that he be brought up to date on this specific problem. This request was immediately satisified both by verbal explanation and by the promise that copies of both reports, i.e., 62-IH-I-G-I and 62-IH-2-G-1, would be mailed to him immediately. Mr. Comerford further stated that we should not back down on our requirements, but that it probably might be wise to consider their proposal in light of the many ramifications of the problem as it affects the whole company structure, i.e., purchasing, sales, manufacturing, etc.

Very truly yours,

Robert E. Peele

Robert E. Peele
Industrial Hygienist

REP:gh

Enclosure

UNION CARBIDE

INTERNAL CORRESPONDENCE

UNION CARBIDE CHEMICALS COMPANY • INSTITUTE PLANT P. O. BOX [illegible], CHARLESTON, WEST VIRGINIA

(Name) Mr. S. C. Giambruno
Dept. Industrial Relations

Date 4 December 1962
Originating Dept. Medical Department - Plant 512
Answering letter date

Subject: Insulation Block Dust Survey
Construction Insulation Shop
Plant 511

cc to
Mr. L. N. Dickinson
Mr. G. H. Daniels
Mr. N. S. Eastman
Mr. R. A. Huber
Mr. B. F. King
Mr. F. B. Snyder
Dr. E. M. Best, Jr.
Mr. E. G. Heinz
Mr. P. E. Henry
Mr. R. A. Neal
Mr. D. R. Matheny
Mr. N. H. Ketcham
Dr. C. U. Dernehl

Two reports by Mr. R. E. Peele have been issued on this subject (21 March 1962 and 20 July 1962) and sent out under my signature. On 16 May 1962, a copy of a letter from Doctor Nale to the UCC Central Purchasing Department in New York pertaining to this subject was sent to some of the people on the above distribution list. Undoubtedly, Johns Manville is extremely interested in having our Construction Department use their "Thermobestos" blocks. However, I believe that possibly unnecessary pressure is being applied to us from several sources.

The enclosed report by Mr. Peele includes information on an invitation for Mr. Peele to visit Manville, New Jersey, at Johns Manville's expense to evaluate their industrial hygiene studies. Mr. Peele points out in this report also that he has been contacted recently by the Design and Construction Department at the Technical Center who have implied that Mr. Peele should comply with Johns Manville's proposal.

It is my opinion that we should continue to do surveys, with limitations, on samples of "thermobestos" blocks that are of a new formula and are submitted to our Construction Insulation Shop at the Institute Plant for evaluation. However, I am not in favor of Mr. Peele accepting Johns Manville's invitation and would appreciate approval or disapproval for this trip from my supervision so that Mr. Peele can be informed accordingly.

Very truly yours,

R. J. Sexton

R. J. Sexton, M.D.
Plant Medical Director

RJS:gh
Enclosure

Dernehl DEPO. EXH. 26
3/10/89
KIRBY A. KENNEDY
COURT REPORTER

P.C. V.3
10 7 8 11.C

UNION CARBIDE

INTERNAL CORRESPONDENCE

UNION CARBIDE CHEMICALS COMPANY • INSTITUTE PLANT P. O. BOX 2231, CHARLESTON, WEST VIRGINIA

To Mr. S. C. Giambruno

Industrial Relations

Date 23 October 1963

Originating Dept. Medical Department - Plant 512

Answering letter date

Subject Insulation Block Dust Survey
Construction Insulation Shop
Plant 511

Copy to
Mr. L. M. Dickinson
Mr. N. S. Eastman
Mr. R. A. Huber
Mr. B. F. King
Dr. E. M. Best
Dr. C. U. Dernehl
Mr. J. W. Perry
Mr. P. E. Henry
Mr. R. A. Neal
Mr. D. R. Matheny
Mr. N. H. Ketcham
Mr. L. B. Weddell - Safety Dept.

Enclosed is a very excellent and very complete Industrial Hygiene report on the potential hazardousness of "Thermobestos", "Kaylo" and "Carey-Temp" insulation blocks which have been processed in the Construction Department's Insulation Shop. The report points out definitely that "Thermobestos" and "Carey-Temp" insulation blocks cannot be fabricated safely with existing equipment, but that "Kaylo" insulation blocks can be fabricated safely. Mr. Peele's recommendations are quite definite and I am sure that you will wish to comply with them. I believe this particular project should be considered completed.

If there are any comments, suggestions or criticism, please direct these to me.

Very truly yours,

R. J. Sexton, M.D.
Plant Medical Director

RJS:hl

Enclosures

Arnold DEPO. EXH. 27
7/10/89
KIREY A. KENNEDY
COURT REPORTER



UNION CARBIDE CORPORATION
Nuclear Division

New York, N. Y.

W. T. Cohen
J. A. Riddle
E. W. Haskins
L. F. Crow
G. C. Brice
D. S. Kemeny
K. West
G. Vessels
Shifters

MEMORANDUM

January 12, 1965
File JAR

To: Messrs. T. Dougherty
R. A. Miller
R. Stobaeus
T. R. van Fleet

cc: Messrs. K. W. Lentz
A. E. Pufahl

G. S. Jordan
H. F. Reichard
N. J. Setter
R. G. Woolery

J. A. Riddle

Dr. C. U. Darnehl

Subject: ASBESTOS TOXICOLOGY REPORT

Gentlemen:

Recently several reports were given at technical meetings and summaries of them carried by the national wire services concerning possible carcinogenic properties of asbestos. Some of you may have received questions from your customers on this subject.

In order to counteract any serious problems or worries before they get out of hand, we have asked Dr. C. U. Darnehl, Director of Toxicology, Union Carbide Corporation, to formulate a statement for us. A copy of his statement is enclosed. Additional copies can be obtained from me or you may make your own copies if you wish to pass them on to interested customers. You will note that, in essence, the report states that good housekeeping -- such as would be required in any dust-producing operation -- should be sufficient to prevent any problem with asbestosis. You will also note that he mentions use in a wet system -- which certainly applies to the paper mill -- and a pellet form -- one of the strong points of our asbestos -- as additional means of minimizing any potential problem with the product.

Further, other asbestos producers and those acquainted with the subject feel that the original data upon which the cancer-producing report was based did not take into account any outside influences, such as smoking or corrosive atmospheres, which also might produce cancer. Here, it should be noted that much asbestos usage considered in the technical papers is in conjunction with tar and pitch compounds which are known to contain carcinogenic materials.

AU313

Darnell DEPO. EXH. 32
3/10/69
KIRBY A. KENNEDY
COURT REPORTER

Pre-employment and periodic physical examinations of workers are desirable. These should include chest X rays to insure that the worker has no chest condition prior to work with asbestos and to determine that no lung changes are resulting from work with asbestos.

It is believed that the addition of asbestos at the proposed levels during the manufacture of paper products would be harmless to the consumer. Total dusting would have to be well in excess of any levels acceptable to the consumer for the asbestos concentration to approach the Threshold Limit Value.

What's Basis for this statement

In conclusion, while asbestos dust in excess of the Threshold Limit Value is potentially harmful, as are many other dusts encountered in industry, it is as readily controlled as other such dusts and it can be used safely with appropriate precautions.

Carl U. Dernehl, M. D.
Director of Toxicology

K. S. Lane, M. D.
Assistant Director of Toxicology

UNION CARBIDE CORPORATION
270 PARK AVENUE, NEW YORK, N.Y. 10017

MEDICAL
DEPARTMENT

June 7, 1967

Dr. T. J. Hall
Union Carbide Europa A.A.
40, Rue Du Rhone
1211 Geneve 3
Suisse

Dear Tom:

I have reviewed the report, "Asbestos As A Health Hazard In The United Kingdom", prepared by I. C. Sayers, and in general I find that it is reasonably accurate. I do not attach very much importance to the data on the incidence of asbestosis and death from asbestosis and cancer because these are merely tabulations of events and do not take into consideration the numbers of people who were subjected to the possibility of the event occurring.

We had been interested in the possibility that the short fiber Coalinga product might have a greater hazard than the more conventional forms of asbestos because sub-micron silica has been known to cause a rapidly progressive silicosis after exceedingly brief exposure. We were concerned about whether the Coalinga material with its exceedingly fine fibril diameter might have a similar effect in causation of asbestosis. We therefore made some preliminary studies in which the material was injected into the belly cavity of guinea pigs, rats and rabbits and also was injected intratracheally by a method which distributes the asbestos throughout the lungs of rats. The materials injected were the standard fiber, a refined fiber and a long fiber obtained from Johns Manville for purposes of comparison. In the injection study the Coalinga refined fiber produced the most severe reaction in the belly cavity, whereas the

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standard fiber and the Johns Manville fiber were essentially the same and less severe. In the inhalation study in the lung the crude fibers caused a more severe fibrosis, the refined fiber was intermediate and the Johns Manville fiber was least reactive. The only conclusion we can draw from this crude test is that it is possible that our Coalinga product may be more inert than long fiber asbestos in that it may produce less disease, asbestosis, at an early time after exposure.

The question was raised whether the 5 million particles per cubic foot would still be a tenable Threshold Limit Value. I maintain that this value is still useful in terms of preventing the disease, asbestosis. There is no evidence of asbestosis occurring among people who have worked in an environment where the concentration was kept within the Threshold Limit Value. It is probable that the 5 million particles per cubic foot will not be acceptable for the prevention of mesothelioma. I have no idea what concentration will be effective in preventing this disease and I would wonder whether even a limit of 1 million particles per cubic foot would be effective in this regard.

Finally, I would give my unquestionable support to the request of the Pneumoconiosis Research Council for trace element analysis of the standard sample of asbestos. By so doing we would develop techniques which could be applied to our product from King City and which would be useful in making comparisons with the standards.

I hope this will be helpful to you, if you have any further questions please let me know.

Very truly yours,

C. U. Dernehl, M.D.
Associate Medical Director

C. U. Dernehl, M.D.
ed

13 June, 1967

1415 TE/MLF

Mr. Frank Dexter
Union Carbide Corporation
Chemicals & Plastics Division
270, Park Avenue
New York, N.Y. 10017

Re: ASBESTOS TOXICOLOGY

Dear Frank:

I assume that you are aware of the occasional reports concerning possible toxicity and carcinogenic properties of asbestos. Dr. Dernehl of Union Carbide Medical Department has followed this area very closely and has maintained a very close check on the working conditions at the King City plant.

Perhaps the most publicity and "interest" in this problem has been in England. There, only two ports will handle normally bagged asbestos, at the other ports the Union of Dock Workers have refused to handle the shipments of asbestos.

We have been permitted to bring in several shipments with not very favorable results. The last shipment, because of rather poor handling and packing, was in bad shape with many broken bags and much free asbestos. Copies of reports on these shipments have undoubtedly already come to your attention.

Mr. Sayers of the asbestos group in UCL has written a report summarizing the findings and feelings concerning asbestos in the U.K. I assume that you have also seen a copy of this report. I am enclosing with this letter, a copy of the comments Dr. Dernehl made in response to this report from England.

My main purpose in writing this to you is to confirm that at the July asbestos meeting in Oxford we will implement the suggestion made by Mr. Sayers and agreed to by Dr. Dernehl that Union Carbide join in the cooperative standard sample comparisons to the extent of arranging for standard samples to be forwarded to Niagara Falls for trace element analysis. In joining the program to this extent we will be able to keep in close contact with the progress of this study and will also be aware of any adverse findings which may develop.

I assume that this is satisfactory to you. We will, of course, keep you directly advised of any information that may develop over here. If these findings or any others of which we may not be aware cause any change in marketing plans or programs for asbestos, we assume you will immediately advise us.

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[illegible]DY A. KENNEDY

UNION CARBIDE CORPORATION
270 PARK AVENUE, NEW YORK, N.Y. 10017

ASBESTOS TOXICOLOGY REPORT

It has been known for many years that some persons working in asbestos production were prone to develop a disabling lung disease. In time, this condition became known as asbestosis and was related to exposure to high concentrations of asbestos dust. With further experience, it was found that men could work with asbestos without development of lung disease if dust concentrations were kept below a certain level. It is now generally accepted that a man can work a 40-hour week for a lifetime without developing asbestosis if the [illegible] particle count is kept at or below 5 million particles per cubic foot of air. This dust concentration of 5 million particles per cubic foot of air is the Threshold Limit Value for asbestos, and no cases of asbestosis are known to have occurred when exposures have been maintained at or below this level, despite large-scale utilization (now approaching one million tons per year in the U.S.A.). This concentration of dust is generally not visible in the average work area unless a beam of light causing a Tyndall effect is present. Usually the dust concentration must be from 8-10 million particles per cubic foot before its presence is visible in average lighting conditions.

Several years ago, it was reported that there was an increase in the incidence of cancerous tumors, especially of the lung, associated with asbestosis. Recently there have been reports of some cancers occurring in individuals exposed to asbestos dust, but who have not developed clinical asbestosis. It is believed by most authorities that these cases have been associated with exposures significantly exceeding the Threshold Limit Value. A major manufacturer of asbestos products who also mines asbestos has not been able to show an increase in cancerous growths in men working where dust concentrations were maintained at the Threshold Limit Value.

Control of asbestos dust exposure is therefore necessary. The control methods are the standard ones applicable to a variety of dusty operations. They include closed flow systems, wet processes where possible, and adequate exhaust ventilation where openings in the system are necessary. Pelletizing is sometimes used to improve the handling characteristics of otherwise dusty materials. Where satisfactory containment to stay within the Threshold Limit Value is impractical or impossible, efficient and reliable respirators are available for the protection of the employee. A program of environmental monitoring is highly desirable to determine that Threshold Limit Values are not being exceeded. In paper manufacturing, it would be desirable to know the dust concentrations where the asbestos is dumped from bags into the pulp slurry. Concentrations should also be determined where dusting occurs in

finishing products. While initial dust determinations should be made at frequent intervals, once the level has been established as satisfactory, the frequency may be extended to occasional tests to assure continuation of a satisfactory condition.

Pre-employment and periodic physical examinations of workers are desirable. These should include chest X-rays to insure that the worker has no chest condition prior to work with asbestos and to determine that no lung changes are resulting from work with asbestos.

It is believed that the addition of asbestos at the proposed levels during the manufacture of paper products would be harmless to the consumer. Total dusting would have to be well in excess of any levels acceptable to the consumer for the asbestos concentration to approach the Threshold Limit Value.

In conclusion, while asbestos dust in excess of the Threshold Limit Value is potentially harmful, as are many other dusts encountered in industry, it is as readily controlled as other such dusts and it can be used safely with appropriate precautions.

Carl U. Darnehl, M.D.
Director of Toxicology

K. S. Lane, M.D.
Assistant Director of Toxicology

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NIREF. 1415 TJH/MLF

BRUXELLES 6, 1 August, 1957
166, AVENUE LOUISE

RECEIVED
SEP 1 1957
T.F. FRANCIS

Mr. Frank Dexter
Union Carbide Corporation
Chemicals & Plastics Division
270 Park Avenue
New York, N.Y. 10017

Re: ASBESTOS TOXICOLOGY

Dear Frank:

During a recent conference on Physics and Chemistry of Asbestos Minerals at Oxford, England, I met with representatives of the group who are coordinating an analytical program for asbestos samples. These were:

Dr. V. TIMBRELL
Medical Research Council
Pneumoconiosis Research Unit
Llandough Hospital
Penarth, Glamorgan. U.K.

Dr. T.G. MORRIS
M.R.C. Llandough Hospital
Penarth, Glamorgan.

This meeting was to arrange for Union Carbide's cooperation in trace element analyses of standard samples.

Dr. Mumpton, who, incidentally, gave an exceptionally good and well received paper at the meeting, is bringing the samples back to Niagara Falls and is aware of the requirements of the group for analysis. Briefly, they would like to have all possible trace elements analyzed to the highest possible degree of accuracy.

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There are two samples of chrysotile asbestos, one of amosite and, I believe, two of crocidolite. Dr. Timbrell has sizable quantities - close to one ton each of these materials - which have been "thoroughly" blended. In the case of chrysotile he also has samples of the different types from which the standard sample mix was prepared. He asked if we could possibly analyze samples of these original components in order to see if any components were present which might be used as a key to the efficiency of their mixing and blending procedures. Dr. Mumpton agreed to determine the cost of these further analyses to see if we could justify also doing some of them.

We had a lengthy discussion with Dr. Timbrell and Dr. Morris and Dr. Mumpton can fill you in on the details. I believe it is fair to say that there are certainly many questions and problems still unanswered and realistically there is not much evidence yet as to the true "danger" of using asbestos.

I expect to be in New York during the week of August 14 and would like to talk to you more about this and other asbestos subjects.

Very truly yours,

Tom Hall

THOMAS J. HALL

cc: Dr. C. U. Dernehl. M.D.
Mr. F. Frangos - N. Y.
Dr. F. Mumpton - Niagara Falls
Mr. L. D. Polderman - Office
Dr. A. E. Pufahl - New York
Mr. I. C. Sayers - London
Mr. R. G. Woolery - Niagara Falls

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DEC 5 1967
J.F. FRANGOS

BRUXELLES 5, 30 November, 1967
166, AVENUE LOUISE

V. REF.
N. REF. 1415 /TJH/MLF

Mr. F. Dexter
Union Carbide Corporation
New York Office

Dear Frank:

As you know we have been trying to keep close to the asbestos toxicology work in the U.K. Fred Mumpton at Niagara Falls arranged for some work to be carried out on a sample and gave us a report on this. Ian Sayers took the report to the laboratory group in the U.K. which is co-ordinating this work. I am enclosing a copy of his hand written report for your information. When they come back to us for additional analytical work we will pass it on to you. There continues to be a great amount of concern about this subject and we are going to have to learn to live with the problem in the U.K. So far there has been no indication of it being passed on to the continent. — OVER

In this report Ian passes on the request for permission to publish our data and I would like your comments on this. Even if you agree we would try to find out in more detail the conditions under which this data would be presented before agreeing directly with them. Perhaps it would be better to have this sort of publication first approved by Carl Dernehl before we finally agree. Also I will ask Ian to follow directly on obtaining the spectrographic analysis method.

If you or any of the others receiving this letter have any comments I would welcome them.

Best regards,

Very truly yours,

THOMAS J. HALL.

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EXHIBIT "C"

SUMMARY ON SAYER'S REPORT OF VISIT TO PNEUMOCONIOSIS RESEARCH UNIT 7-11-67

GAVE DR. TIMBRELL MUMPTON'S ANALYTICAL DATA.

PRU NOW SAYS THAT CHRYSOTILE FIBERS, BEING CURVED, ARE LESS LIKELY TO GO DEEP INTO LUNGS. INJECTED CHRYSOTILE DOES CAUSE CANCER IN RAT SO THE FACT THAT IN PRACTICE IT IS LESS RESPONSIBLE FOR TUMOR PRODU IS PROBABLY DUE TO ITS GREATER ELIMINATION RATE AS WELL AS ITS GEO

A03157

Mr. D. C. Willard

Building 8-96-2

April 28, 1967

E. Q. Hull, M.D.

Particulate Matter in Air
Asbestos Dust
Project No. IE-PAR-76-67

Dear Don:

As per our telephone conversation today, I am attaching a resume' of our determinations of dust breathed by the employees while cutting and installing "kale" insulation.

We feel that further air sampling is needed to give you more meaningful conclusions as to the best protection for the employees handling this material.

At your convenience, we will be glad to discuss these findings with you. In the meantime, if you would keep us informed of jobs pertaining to cutting, installing and removing "kayle" insulation, it would be helpful in scheduling the air sampling work.

Thanks,

Bert Murray

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KIRBY A. KENNEDY
COURT REPORTER

Union Carbide Corporation
Metals Division
Niagara Falls, New York
September 29, 1975

MEMORANDUM

To: R. E. Byrne, Jr.
B. L. Ingalls
J. L. Myers
M. C. Thurber

From: H. B. Rhodes

Copies: File

Subject: Visit to the 18th International Congress on Occupational Health - Brighton, England, September 14-19, 1975

The writer attended the above noted conference in Brighton. There were 22 papers directly relating to asbestos presented and about another 15 on occupational lung cancer generally attributed to various particular matter such as silica. Talc was covered in several of these. Abstracts of all papers are available and a complete set of papers will be published in some months.

The conference was attended by over 2000 delegates, including most of the big names in the asbestos controversy. I had the opportunity to talk informally with a number of them and their current views on the toxicology situation will be summarized.

In general, the conference produced only one bombshell in the asbestos area, a paper by Dr. M. Wasserman of Israel. It was in a different session on Geography and Occupational Health. He took a detailed look at about 40 mesothelioma deaths that have been recorded in Israel. There were several among small children, they were about equally distributed between men and women, a substantial proportion had no significant traceable occupational exposure, and the highest rates were not in the two regions of Israel where the plants which handle asbestos are located. He drew the conclusion that the cause was non-occupational exposure to asbestos.

The London Times reported this prominately. Both the AIC and Dr. Muriel Newhouse wrote letters of rebuttal which we assume will be published. Bob Hereness will report details via AIA/NA.

Overall, the mesothelioma situation for occupational exposure continues to look discouraging. The McDonalds opened the asbestos session with a survey of the available information on the incidence of this disease in various parts of the world. They found the incidence extremely high in three situations:

1. Among insulators.
2. Among those who work or live in cities with ship yards.
3. Among those who work or live in certain cities with large asbestos plants.

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The evidence for a gradation of effect for the various types of asbestos continues to be conflicting, except for the mining and milling operations. Here a clear pattern from crocidolite, amosite, chrysotile to anthophylite is found. They conclude that this pattern is generally true with some possible exceptions.

The data used in this study went up to 1972. Mr. John Marsh, (Raybestos-Manhattan) mentioned to me that there are a substantial number of new cases reported that could alter the rate of incidence considerably.

The TBA paper updating their mortality studies that followed was almost unbelievable. It was read by Dr. R. Doll who mumbled so fast that nobody understood a word he said. It was backed up by slides containing large tables of unreadably small figures. Bob Mereness is to get a copy of the paper as are a number of others who couldn't understand it.

I had the opportunity to discuss the Rochedale researches with Dr. Lewinsohn. The key controversy with Dr. Selikoff revolves around the reading of the x-rays. A panel of four, including Lewinsohn is now reading them and the results are being correlated. A meeting to discuss the results is scheduled for January. It looks like this will not be ready in time to help in the U.S. OSHA revision.

The discussions with Lewinsohn and his TBA associates brought out clearly another key-point that I do not believe ever really spelled out in the OSHA hearings. This factory that forms the basis for the 2 fiber limit is just now getting their fiber levels down to 2 fibers. All of the mortality data that is being argued over is for exposures well above this.

This point was also emphasized by Dr. Steve Holmes.(Dr. Holmes testified at the OSHA hearings.) The limit is not really 2 fibers but 100 fiber - years based on an assumed 50 year exposure. This is tied to a very critical second condition that concentrations do not exceed 10 fiber/cc measured over a 10-15 minute period. These criteria do not consider mesothelioma.

The TBA paper was followed by Dr. Murial Newhouse with her lastest thinking on her cohort of 3600 asbestos textile workers. She had fitted a distribution function that had worked for other cancers and was predicting a 10-15% death rate from mesothelioma. This was in addition to 20% from lung cancer. This is a very substantial number and the rest of the British experts that I talked to questioned the validity of the extropolation. Interestingly enough, Dr. Selikoff arose and commented that he felt she was high by a factor of about 2. It was interesting to note in all of these discussions that the workers had heavy exposure for a least some period but no real attempt was made to correlate variations in exposure. Dr. Newhouse, however, continues to talk about a dose-response effect in mesothelioma.

Several other papers of particular interest in this seminar related to a cooperative effort to compare asbestos fiber counts by the techniques used in various countries. The general feeling was that the methods left considerable to be desired but in the light of our experiences the comparisons looked pretty good. A key difference found was with the

U.S. PAT samples that everybody but the U.S. laboratory counted very low. We can understand the problem from our own experience and have a real question in our own minds as to whether the PAT samples are really much more than a numbers game.

The Selikoff et. el. paper on TJC was well presented but looked like the same data as was given in Miami. Dr. Fishbein expanded on the short fiber question to the extent that Dr. George Wright got red and climbed all over him after the paper. George insists that there is no evidence that the short fibers are toxic and a great deal of evidence that they are not. Dr. Selikoff himself finally had to come over and smooth things out. As a consequence, I was only able to learn that they do have additional data but could get no details.

The brake lining paper from Mt. Sinai followed the same pattern as TJC with limited data and lots of concern. Dr. Lewinsohn commented privately that the 0/1, 1/0 and 1/1 x-ray changes that the Mt. Sinai group feature so prominently in their statistics are often more in the eye of the reader than in the film. You have to get into the "2" level before there is no question that a change has occurred. The U.K. public response was that dust was controlled in this application in the U.K.

The crocidolite vs other asbestos question was addressed by one paper from South Africa that argued that amosite plus chrysotile caused as much asbestosis as crocidolite. The statistics were based on the number of miners who came back out of the bush to make compensation claims after working for several years in the asbestos mines. There was considerable question regarding the validity of the cohort but it did bring out some background on the crocidolite situation. When the question of regulations came up in England it looked like the blue asbestos from South Africa would be replaced by better amosite and chrysotile from Rhodesia. It was sacrifices much like the spraying of insulation in the U.S.A. and then the Rhodesian sanctions upset the whole picture.

In summary, I get the overall impression that there is a great deal of concern that the mesothelioma and even the asbestosis picture will get worse before it gets better. There is a growing feeling that short, intense exposures which overwhelm the lung clearing mechanisms may be enough to cause serious harm. The question of how short is vague and depends to a considerable extent on the individual susceptibility. The only one I found who would take a firm stand on the 2 fiber limit was Alex Cross of Cape Asbestos and AIC who felt it was safe for mesothelioma as well.

If anyone would like to look at the abstracts, please let me know.

H. B. Rhodes

H. B. Rhodes

HBR:pl

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KIMBERLEY A. KENNEDY
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VARIATION OF PROPERTIES OF CHRYSOTILE ASBESTOS SUBJECTED TO MILLING

A. M. Langer, M. S. Wolff, A. N. Rohl, I. J. Selikoff

Environmental Sciences Laboratory of the Department of Community Medicine, Mount Sinai School of Medicine of the City University of New York, New York, New York

Mechanical milling is commonly used to produce short chrysotile asbestos for experimental purposes. Such manipulation also decreases fiber crystallinity, alters Si-O and Mg-O interlayer bonding, induces coordination changes in the brucite layer, diminishes the ability of fiber to reduce specific free radicals and physisorb organic molecules, and decreases hemolytic potency and antagonist sorption capabilities. The degree of alteration is related to the time of milling. Results of biological experimentation with these materials must be interpreted with caution. Interaction mechanisms in the biological setting are suggested for chrysotile fiber.

INTRODUCTION

The current U.S. federal standard for worker exposure to asbestos dust became effective on July 7, 1972, and established, among other factors, methods and analytical techniques for air analysis. It defined fibers to be enumerated in the work environment as those 5–100 μm in length (*Federal Register*, 1972).

The selection of fibers greater than 5 μm in length was based primarily on methodology evaluation by the U.S. Public Health Service during a study of work environments in the asbestos textile industries in the United States (Lynch et al., 1970). This investigation was indebted to a British study by Addingly (1966), in which the 5 μm fiber was selected as the lower size limit for counting, mostly on a utilitarian basis: the counting procedure, by optical microscopy, was simplified, and the interobserver error for counting was reduced. This latter study was also influenced by an existing theory of pathogenesis of asbestosis, which suggested that disintegration of *large* asbestos bodies, those necessarily nucleated on long

The authors wish to acknowledge support under a Center grant from the National Institute of Environmental Health Sciences, ES 00928. One of use (M.S.W.) wishes to acknowledge support under a postdoctoral fellowship from the NIEHS, ES 02565. The capable technical assistance of A. Tordini and T. Samo is gratefully acknowledged.

Requests for reprints should be sent to A. M. Langer, Environmental Sciences Laboratory of the Department of Community Medicine, Mount Sinai School of Medicine of the City University of New York, Fifth Avenue & 100th Street, New York, New York 10029.

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0098-4108/78/0401-0173$2.25

fibers, was responsible for asbestosis. Malignant tumors were not considered in this size selection.

The use of asbestos in some 3000 applications has been accompanied by increased use of short grades of fiber. These fibers now constitute the major size fraction used throughout the world. The question of the importance of the fibers not counted by the current U.S. standard has recently been raised: in most commercially available asbestos raw materials, small fibers constitute the *numerical preponderance* in all samples examined (Timbrell et al., 1970); small fibers tend to form stable aerosols with greater potential for inhalation; small particles penetrate beyond the terminal bronchioles and come to rest in alveolar spaces through impaction and diffusion mechanisms (Timbrell, 1973); retention of short fibers is marked, as evidenced by their numerical preponderance in human tissues (Pooley et al., 1970; Langer et al., 1971, 1973; Pooley, 1972).

Some controversy has arisen concerning the biological activity of small fibers, mainly because experimental evidence exists, in both animal and *in vitro* test systems, to support either contention: *short fiber is active* (e.g., King et al., 1946; Davis, 1964, 1970, 1972; Holt et al., 1964, 1965; Wagner, 1968, 1973; McIver, 1968; Gross, 1968; Suzuki and Churg, 1969; Wagner et al., 1970; Hilscher et al., 1970; Bey and Harington, 1971; Pott et al., 1972; Wagner and Berry, 1973), or *short fiber is less active or not active* (e.g., Vorwald et al., 1951; Pott et al., 1972; Stanton et al., 1972; Stanton, 1973; Reeves et al., 1974). A review of these papers suggested that material preparation and manipulation played a key role in determining beforehand whether a response would be induced. For example, Pott and colleagues produced longer latent periods for tumor response with ground fiber, as compared with responses produced with unground fiber; Hilscher and colleagues produced tumors with microtome-cut fiber (a relatively gentle size reduction method) and found no response with ball-milled samples (a vigorous method).

OBJECTIVES OF THE PRESENT STUDY

These and other observations suggest that conflicting results concerning the activity of short asbestos fiber have been brought about by property alteration through manipulation. We therefore began a study of small fibers, reduced in size by methods similar to those that produced so-called biologically "inactive" small fibers. These materials were examined by means of a number of analytical techniques to determine whether alteration of surface or structural properties had taken place. In addition, *in vitro* test systems were used to deduce any change in biological activity.

MATERIALS USED IN THE STUDY AND THEIR PREPARATION

Chrysotile asbestos occurs naturally as compressed mats of short fibers, with a large proportion of accompanying fibrils, in several major serpentine deposits in western North America. These deposits have been referred to in the mineralogical literature as the Coalinga type. Samples were obtained from the New Idria, California, deposit through the courtesy of Union Carbide Corp. This material, referred to as Calidria RG-144, was used for experimental purposes.

Impact-milling was accomplished using a Wig-L-bug amalgamator, consisting of a 2.5-cm-long, 1-cm-diameter steel cylinder, which could be attached to a vibrator operating at about 10 cyles per second. Portions of chrysotile (50 mg) were placed in the cylinder chamber with a 10 X 13 mm pellet and milled for periods ranging from 60 to 3600 s. These materials were then examined for changes in crystal structure, surface chemistry, and chemical and biological behavior as a function of the duration of ball-milling.

METHODS AND RESULTS

Transmission Electron Microscopy and Selected-Area Electron Diffraction

Portions (≤ 1 mg) of the material as received and of the milled samples were dispersed in 0.1 ml nitrocellulose (1% in amyl acetate) on a precleaned glass slide by gentle stirring. A second slide was placed over the first and the two slides were pulled apart, producing a film on each. The film was floated on water, and carbon-coated Formvar-coated grids were placed on the film. The grids were lifted out with filter paper and dried on filter paper in a petri dish. They were examined by transmission electron microscopy (TEM) (JEOL JEM-120U) at 120 kV. Photographs were obtained at direct magnifications ranging from 2800 to 20,000 directly on the TEM screen. All counting, for size distribution characterization, was done directly on photographs at a final magnification of 10,000 with the aid of a Porton graticule. Two observers participated in this process, alternating counting and size recording every 100 counts. Some 1000 objects were counted for each preparation. Interobserver measurements were made consistent by establishing counting criteria: a particle composed of at-least-two fibrils, the shorter being contiguous with and comprising at least one-half the length of the first, was called a fiber; objects counted as fibers possessed a length/width aspect ratio of at least 3:1, objects with smaller aspect ratios, composed of many fibrils, were counted as clumps; single fibrils, of any aspect ratio, including contiguous fibrils that did not meet the fiber criterion, were called fibrils.



FIGURE 1. Size distribution of fibers in milled chrysotile samples becomes progressively smaller. Electron micrographs represent fiber unmilled (A) and milled for 60 s (B), 300 s (C), and 3600 s (D).

TABLE 1. Calidria Chrysotile: Size Distribution on Comminution as Determined by Electron Microscopy

	Percentage in size class									
Treatment	≤ 0.1	0.11–0.5	0.51–1.0	1.1–2.0	2.1–3.0	3.1–4.0	4.1–5.0	5.1–10.0	> 10.1	Number counted
	Fibers (length in micrometers)									
Untreated	3.7	39.7	22.0	18.7	7.9	1.4	1.9	3.7	0.9	214
60-s mill	0.5	22.0	34.0	27.0	13.6	1.1	–	0.3	–	191
300-s mill	0.4	53.4	32.7	13.2	0.4	–	–	–	–	251
1200-s mill	8.6	79.1	12.4	0.9	–	–	–	–	–	162
3600-s mill	16.3	82.9	0.8	–	–	–	–	–	–	123
	Fibrils (length in tenths of micrometers)									
Untreated	24.8	51.8	9.9	5.8	3.3	1.9	1.3	0.8	0.6	800
60-s mill	15.7	67.5	12.5	4.0	0.4	–	–	–	–	779
300-s mill	24.7	69.0	5.3	0.9	–	–	–	–	–	962
1200-s mill	68.0	31.7	0.3	–	–	–	–	–	–	829
3600-s mill	74.8	25.1	0.1	–	–	–	–	–	–	858

Progressive grinding of chrysotile produced marked reductions in both fiber and fibril length (Fig. 1; Table 1). In the untreated chrysotile, 77% of the fibrils were less than 0.5 μm in length. In comparison, in the 3600-s milled sample, virtually the entire fibril population was smaller than 0.5 μm. Chrysotile fibers comprised 21% of the population in the untreated material and were reduced to only 13% of the 3600-s milled material. Lengths were less sharply reduced, with 95% of the fibers less than 5 μm in length in the untreated material and over 99% of the fiber reduced below 0.5 μm in length in the milled material (Table 1). Although not included in Table 1, clumps increased from 0.5% of the objects counted for the untreated material to almost 10% of the objects counted for the 3600-s milled material.

In addition to these changes, the milled asbestos possessed unusual morphological features that more readily deformed under the electron beam. Although the fibril form in milled samples resembles the form observed in untreated material, the former possesses more flattened internal capillaries and sustains greater damage per unit time under the electron beam (compare Fig. 2, A and C). Selected-area electron diffraction (SAED) patterns obtained on fibers of similar dimension in both populations display only a small loss in intensity of reflections and a decrease in streaking of the (*hk*0) reflections in the milled materials (compare Fig. 2, B and D). The loss of streaking of the (*hk*0) reflections may indicate a flattening in the *ab* plane, produced by breaking along the curved surface. These features suggested structural damage during comminution (Langer et al., 1974).

Electron microscopy demonstrated that mechanical comminution of chrysotile produces marked size reduction of both fibers and fibrils, reduces the overall fiber population to fibril form, induces the formation of clumps, and induces structural damage to the chrysotile fibril.

X-Ray Diffraction Analysis

Using a Norelco X-ray diffractometer, portions of samples of equal weight were poured into an aluminum sample holder, flattened into place with a precleaned glass slide, and subjected to X-ray analysis in the 5–60° 2θ range. Sample preparation induced preferred orientation of chrysotile fiber axes in the *ab* plane, parallel to the sample holder, which enhanced the first- and second-order reflections along the *c*-axis stacking, specifically the (002) and (004) reflections. These are normally the two most intense reflections of this mineral (Whittaker and Zussman, 1956).

Two important parameters of each peak reflection normally change on size comminution—peak intensity and width. Peak width increase, referred to as line-broadening, is related mainly to particle size decreases and subsequent relaxation of the Bragg equation for reflection reinforcement (Azaroff and Buerger, 1958). Although the chrysotile was extensively ball-milled, the chrysotile patterns showed no appreciable line-broadening

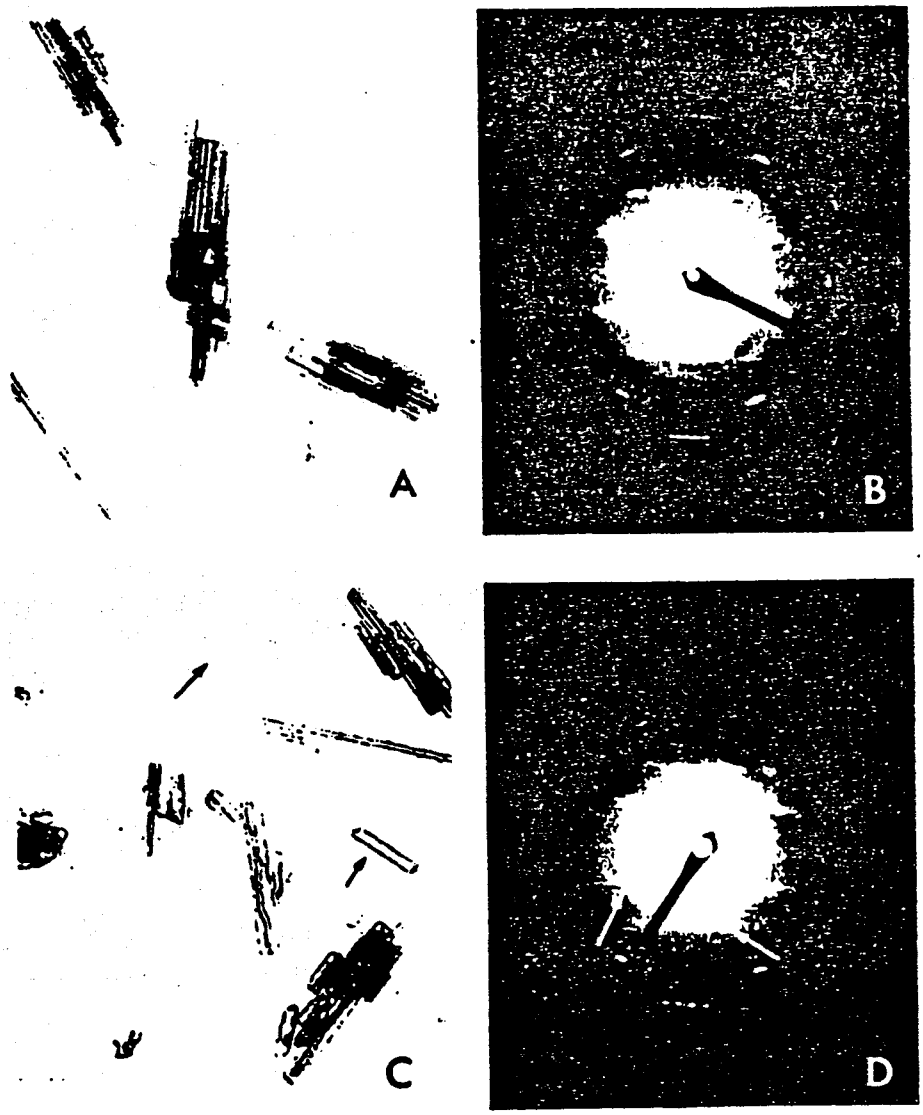


FIGURE 2. Electron micrographs of chrysotile asbestos milled for 60 s (A) and 1200 s (C) and their selected-area diffraction patterns (X 66,300). In (A) fibrils are rectilinear with intact central capillary and morphology. In (C) electron beam damage is evident, some fibrils having lost the classic morphology (arrows). (D) The selected-area diffraction pattern for (C) shows less streaking, indicating a loss of outer fibril curvature.

effects. This may be related to the inherent size distribution of the material, in that the bulk of the particles lie at or below the size limit required to produce enhanced broadening effects on comminution (Azaroff and Buerger, 1958). The factors inducing broadening, outlined in the Scherrer equation, may also be absent in the present case since the majority of the particles are already in fibril form and comminution mainly affects particle length. In this case, therefore, the orientation effects are such that the *ab* plane remains essentially unaffected.

We observed, however, a marked decrease in the total X-ray count under two major reflections, (002) and (004) (Table 2). By using a polar planimeter to measure the areas under these reflections, the total X-ray photon count may be determined as a function of the reflection area, within 1% error. Since the measurement was made from a flattened baseline with no discernible satellite peaks, radial distribution analysis for the contribution of incoherent scattering to the baseline was not deemed necessary. The relative loss of X-ray photons was greatest from the most intense reflection.

Similar loss of X-ray crystallinity for chrysotile asbestos on grinding was observed previously by Ocella and Maddalon (1963). We corroborate this and further observe that *mechanical milling of chrysotile for periods of only 5 min produces a marked alteration of its structural integrity and decrease in its crystallinity.*

Infrared Spectroscopy

Untreated and manipulated samples of chrysotile were prepared for IR spectroscopic examination by pelletization in a KBr matrix (0.25%, w/w), utilizing the standard solid preparation technique. Specimens were examined with a Perkin Elmer model 457 IR spectrophotometer in the range 200–4000 cm^{-1} ($\lambda = 2.5$–50.0 μm). Selected portions of spectra for specimens ground for 60, 600, and 3600 s are shown in Fig. 3.

Several important features may be noted in Fig. 3. The material milled

TABLE 2. Change in Total X-Ray Count (Peak Area) under Selected Reflections with Progressive Ball-Milling[a]

Treatment	Peak area (in^2) 7.35 A (002) $I_o/I_o = 100$	Peak area (in^2) 3.66 A (004) $I_o/I_o = 80$
Untreated	8.36	6.99
60-s mill	7.80	6.96
300-s mill	7.38	6.01
1200-s mill	4.92	5.72
3600-s mill	3.50	5.69

[a]Repeated for mass-equivalents (packing change). Instrumental setting: target: CuKα nickel filter; graphite monochromator; 1° 2θ/min; 4°-0.006-1° slit settings; target: operated at 45 kV/20 mA.

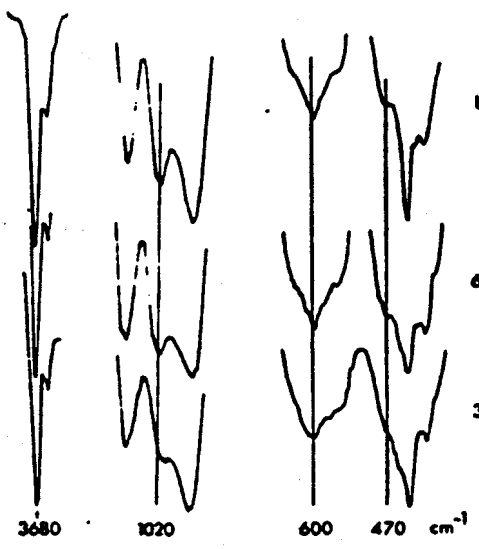


FIGURE 3. IR spectra of Calidria asbestos, untreated and after milling times of 600 and 3600 s, show the major absorption bands unchanged. Bands at 1020 and 470 cm^{-1}, tentatively assigned to interlayer Si-O-Mg, are broadened and shifted.

at 60 s produced an IR spectrum consistent with untreated chrysotile (Brindley and Zussman, 1959). Unmilled Calidria asbestos gave similar spectra, showing strong peaks at 3683 cm^{-1}, corresponding to the Mg-OH hydroxyl group, with a shoulder at 3640 cm^{-1} (probably the interlayer hydroxyl) and a triplet at 1082, 1020, and 955 cm^{-1}, possibly corresponding to the Si-O, Si-O-Mg, and Si-O(H)-Mg stretching frequencies (as suggested by IR spectra of quartz, nemalite, heated chrysotile, and kaolin, the latter the aluminum analogue of serpentine).

The assignment of these three absorption bands between 1081 and 955 cm^{-1} is tentative because the stretching and vibrational modes are difficult to resolve and uniquely assign for this mineral. Two additional triplets, corresponding to the Mg-O bonds, appear centered at 605 and 438 cm^{-1}, the latter with two shoulders at 480 and 407 cm^{-1}.

Chrysotile milled for 600 and 3600 s shows a progressive broadening and a shift in the 1020-cm^{-1} peak (Si-O-Mg) to about 1005 cm^{-1}. The shift to smaller wave number reflects a general decrease in both strength (*increasing bond length*) and a corresponding change in vibrational energy requirement. The shoulder at 480 cm^{-1} broadens and disappears on progressive milling. The OH absorption peaks (3683 and 3640 cm^{-1}) remain essentially unchanged. On the basis of the observed changes in the IR absorption modes, it can be concluded that mechanical milling alters some of the bonding modes in chrysotile, especially the surface brucite layers, but significant dehydroxylation does not occur.

Electron Spin Resonance

Electron spin resonance (ESR) spectra were obtained on solid samples or sonicated suspensions (10 mg/ml) in carbon tetrachloride, using a Varian ESR-3 instrument.

With all samples, a strong, broad resonance was observed centered at $g = 1.61$ with a width of about 850 G (Fig. 4). Hyperfine splitting ($\Delta H = 100$ G), corresponding to paramagnetic ion substitution in the crystalline lattice, was evident in the untreated and heat-desiccated (150°C) samples. Progressive milling of asbestos fiber caused a loss of hyperfine resonance in the ESR, consistent with distortion of the crystal lattice. Reduced particle size may also be partly responsible for the loss of hyperfine splitting, since the resonance characteristics are dependent on orientation effects as well. The width of the major peak remained similar in the milled samples, but the resonance appeared broadened as a result of a reduced intensity and loss of fine structure. The ESR spectrum of Calidria fiber probably reflects the superposition of two resonances, attributed to ionic substitution in the magnesia layers and defects in the

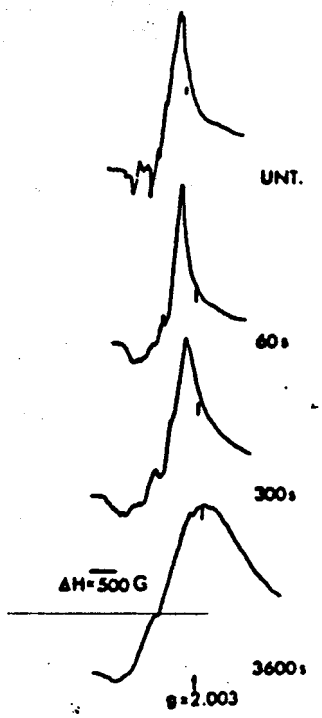


FIGURE 4. ESR spectra of successively milled Calidria chrysotile show progressive loss of hyperfine structure, attributed to crystalline changes in the brucite layer. Resonances are all centered at $g = 1.61$.

silica layer. In a chrysotile sample from another geological deposit, with different trace metal chemistries, the observed resonances (a complex sextet at $g = 2.00$ and a singlet at $g = 1.47$) were well separated.

A similar broadened appearance and loss of hyperfine splitting, with retention of the major broad resonance, was observed with Calidria chrysotile heated at temperatures below 450°C. Heating in the 600–800°C region resulted in a shift of the broad resonance to $g = 2.006$. It is generally accepted that the initial effects of heating are dehydroxylation of the brucite layer (200–400°C) followed by recoordination of the anhydrous magnesium silicate and its subsequent recrystallization to forsterite (about 600–820°C). Thus, loss of ESR hyperfine structure points to structural disruption of the magnesium-containing "brucite" layer in chrysotile.

Hemolytic Activity and Antagonism

Portions of unaltered and manipulated chrysotile were prepared and tested for erythrocyte membrane activity with the hemolytic test system outlined in Schnitzer and Pundsack (1970). This system for testing the membrane activity of asbestos minerals was developed over the last 10 yr so that the different fiber types may be compared in well-defined systems (Macnab and Harington, 1967; Schlipkoter, 1968; Secchi and Rezzonico, 1968). In most of these test systems, mature sheep erythrocytes, in plasma-free suspensions, were tested with known quantities of asbestos fibers and their hemolytic potency determined by optical measurement of released hemoglobin. In our study, mature sheep erythrocytes were also used to test the hemolytic potency of known quantities of fiber (Table 3).

With an equivalent mass of chrysotile, a marked decrease in the hemolytic potency was observed after 300 s of mechanical milling. This was demonstrated by comparing a 1-mg/ml hemolysis level with the concentration of chrysotile required to produce 50% hemolysis (Table 4).

TABLE 3. Variation of Hemolytic Activity with Fiber Manipulation

Cylinder milling, time (s)	Hemolysis at 1 mg/ml (%)	Chrysotile concentration at 50% hemolysis (mg/ml)	Percent hemolysis in the presence of antagonists	
			CMC (4 μg/ml)	PVPNO (1250 μg/ml)
(Untreated)	80 ± 5[a]	0.4	21	25
60	75 ± 6	0.4	38	19
300	52 ± 1	1.0	29	10
600	23 ± 1	2.6	19	6
1200	12 ± 1	4.4	11	5
3600	12	7.5	6	–

[a]Standard deviations determined by 10 repeat determinations.

TABLE 4. Adsorption of Diphenylpicrylhydrazyl (DPPH) to Chrysotile (Calidria)

Milling time (s)	Chemisorption (μmol DPPH/g asbestos)	Physisorption (μmol DPPH/g asbestos)
(Untreated)	4.3 ± 1.5	283 ± 2
60	6.6 ± 0.8	288 ± 2
300	6.9 ± 0.6	
600	7.9 ± 0.6	
1200	7.0 ± 0.7	
3600	3.4 ± 0.7	192 ± 6

Mechanical milling of chrysotile for 3600 s produced a material that was weakly hemolytic, requiring almost 10 times more fiber than unaltered material to produce a 50% hemolytic level.

Asbestos hemolysis may be antagonized by a number of polymers, some of which have been described previously (Schnitzer and Bunescu, 1970). Carboxymethyl cellulose (CMC) is a potent antihemolytic agent in the chrysotile hemolytic system. It has been proposed that the polyanion complex becomes bound to the chrysotile fiber through interaction with the hydrogens on the surface hydroxyl groups (Schnitzer and Bunescu, 1970). Other polymers, such as polyvinyl-pyridine-*N*-oxide (PVPNO), do not appear to interact with the same groups, so that for an antihemolytic response equal to that of CMC in the chrysotile test system, PVPNO must be used at 100 times the concentration of CMC (Table 4). In our test systems, CMC was tested at 4 μg/ml, whereas PVPNO was tested at 1250 μg/ml. With CMC at 4 μg/ml, PVPNO at 1250 μg/ml, and asbestos at 1 mg/ml, varying antagonist response was observed. The antihemolytic effectiveness of CMC decreased in the samples that were progressively milled, reflecting the reduced hemolytic potential of the milled asbestos. The hemolytic antagonism was almost eliminated in the 3600-s milled material (Table 3). The same effect was observed for the PVPNO. Both phenomena suggest that the brucite layer of chrysotile is progressively disordered on mechanical milling, altering the effects and the ability of polymers to adsorb to its surface.

Organic Free Radical Adsorption

Diphenylpicrylhydrazyl (DPPH), a stable organic free radical, is strongly adsorbed to chrysotile asbestos, a phenomenon attributable to strong interaction with the polar nitro groups and nitrogen groups (M. Wolff, unpublished data). The adsorption is twofold, an irreversible chemical adsorption resulting in reduction of DPPH to the hydrazine, and a multilayer physisorption that may involve vertical or horizontal stacking of the molecule. Chemisorption probably occurs via the hydrogen atom from the surface brucite layer, similar to the DPPH reduction reported by aromatic phenols and amines.

Chemisorption potential was measured by titration of 50-mg samples of asbestos in carbon tetrachloride with DPPH (10^{-3} *M* in CCl_4), until excess DPPH could be detected visually by its purple color in the supernatant. Results are given in Table 4. Physisorption was measured by determining the adsorption isotherm. Asbestos samples of 50 mg were mixed with portions with varying concentrations of DPPH (10^{-4}–10^{-2} *M* in CCl_4) overnight in a shaker. The DPPH remaining in the supernatant was measured spectrophotometrically (530 nm). The isotherm was determined by regression analysis of millimoles adsorbed per gram asbestos versus equilibrium concentration of DPPH. The values, given in Table 4, were calculated by extrapolating the adsorption isotherm to 10^{-2} *M*. Chemisorption was increased by ball-milling the chrysotile for 60 s, reflecting the increased surface area available for adsorption. However, milling for longer periods, up to 1 h, significantly reduced the chemisorption capacity of chrysotile. A similar reduced potential for physisorption was observed on prolonged milling.

Both of these processes can be attributed to interactions at the surface of the chrysotile fiber. Thus, brief milling produces fiber with a greater surface area, relatively unchanged in terms of chemistry. In this state, chemisorption is increased. Prolonged milling appears to degrade the surface brucite layer and disrupt the uniform proton distribution (hydrogens on the brucite). Both adsorption processes are dependent on interaction of the outer hydrogens and adsorption is therefore reduced by the structural degradation that follows prolonged mechanical milling.

DISCUSSION AND CONCLUSIONS

An asbestos fiber standard, establishing a threshold limit value (TLV) for fiber exposure to workers engaged in handling asbestos-containing dusts in the United States, was established at 2 fibers/ml on July 1, 1976. The fibers, counted by light optical methods, were to include only those longer than 5 μm. Over 3000 uses of asbestos exist in the United States, which indicates that a range of materials, processing operations, and fabrication plants are involved in supplying society with these products. The size distribution characteristics of the aerosols generated in these work areas must therefore range greatly. In addition, the exploitation of new types of asbestos deposits, primarily those in the western United States and Canada, have introduced a material that consists almost entirely of short fibers. The need to establish the biological potential of short fibers is therefore critical.

A number of studies of human lung tissues demonstrate that small particles predominate in the fiber burden of such tissues and may be implicated in human disease (Pooley et al., 1970; Langer et al., 1971,

1973; Miller et al., 1975). In addition, while some animal studies over the past 30 yr have supported the human observations, in other experimental efforts small fibers appeared to have different degrees of activity.

In studies using short fibers obtained by less vigorous methods, such as air-elutriation and water fractionation, significant responses in animals were observed. In studies where fibers were reduced in size by vigorous mechanical methods, *either no or significantly reduced responses were observed.* Comminution undoubtedly altered the crystal and chemical properties of the material. It appears that the less mechanically degraded the surface of the fiber, the greater the biological response.

Previous investigators have reported reduced crystallinity (Occella and Maddalon, 1963; Reeves et al., 1974), modified crystallinity, and reduced biological activity (Robock and Klosterkötter, 1971; Reeves et al., 1974) in milled fiber. Our data support and amplify these conclusions. The crystallinity of chrysotile was reduced in proportion to the length of milling time. The nature of the altered crystallinity appears to be confined to shifts in interlayer bonding between the brucite and silica sheets, and changes in hydroxyl configuration (but not quantity or bond strength). Supporting these conclusions are the following observations:

1. Reduced total X-ray photons, in selected reflections, without line broadening;
2. Increased susceptibility to damage by electron bombardment;
3. Changes in SAED patterns, decreased streaking of (*hk*0) reflections, suggesting relaxation of fibril curvature;
4. Retention of intensity and location of OH absorption bands; shift and broadening of absorptions assigned to interlayer Si-O and Mg-O bonds with retention of all other significant Si and Mg bond absorptions;
5. Loss of hyperfine splitting and intensity in the ESR spectrum attributed to coordination changes in the brucite layer.

Changes in surface chemistry accompany the reduction in crystallinity. The ability to reduce DPPH to the hydrazine and to physisorb DPPH is lowered with milled fiber, and these are probably both surface, stereochemically controlled phenomena. Hemolytic potency, often considered a surface-related event, is also markedly decreased in proportion to milling time. This is not related to exposure to the silica layer, in that neither hemolytic potency nor antagonism by PVPNO is increased with milling time; instead, they are reduced. The diminished surface activity of chrysotile suggests a surface structure with a distorted proton and/or magnesium ion orientation. Membrane activity in cells (both erythrocyte and macrophage) is reduced, and this interaction may be the initial biological response. After phagocytosis, a fibrotic and cytotoxic response may follow slow degradation of the chrysotile intracellularly, exposing the

silica surface, which stimulates collagen formation. Therefore a reduced response, or a longer time needed to produce a response, is expected for milled fiber compared with unmilled fiber. Indeed, this has been observed (Reeves et al., 1974; Pott et al., 1972; Klosterkötter, 1968; Hilscher et al., 1970). This theory intimates, furthermore, that there would be a faster fibrotic response to silica exposure than to chrysotile exposure, and epidemiologic evidence supports this theory; there is, for example, no "acute asbestosis" to mimic acute or accelerated silicosis (Ziskind et al., 1976).

Theoretical and experimental consideration has been given to interference of asbestos with cellular oxidation-reduction (redox) equilibrium processes, the experimental evidence concerning oxygen consumption in relation to both mineral-treated macrophages and fibrotic response in animals (Bey and Harington, 1971; Robock and Klosterkötter, 1971; Chvapil and Peng, 1975). Flowers (1975) has noted the critical role of $Fe^{2+} \gtrless Fe^{3+}$ equilibria in determining fragile cellular energy dynamics and enzymatic transformations. Participation of chrysotile asbestos in redox activity in biological systems may be predicted from chemical and physical data: the ESR spectrum and the luminescence spectrum of chrysotile; the reduction potential for TTC (Robock and Klosterkötter, 1971) and DPPH; and the oxidation potential for other organics (M. Wolff, unpublished data). Whether these properties are related to fibrosis or carcinogenesis is purely speculative, but Allison (1973) has noted that "crocidolite, the blue colour of which is due to charge transfer, has little cytotoxicity." Indeed, most minerals possess distinct ESR spectra as well (Robock and Klosterkötter, 1971).

The hypothesis that particle shape is the major etiologic mechanism in fibrotic or carcinogenic responses appears, in terms of these considerations, to be somewhat oversimplified, except insofar as morphology reflects more fundamental structural and surface physicochemical properties. Further, comparison of biological potentials of fibers of different lengths should take into account alterations of characteristics of the fibers by the preparation of varying size fractions.

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Material Safety Data

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UNION CARBIDE CORPORATION • 4625 ROYAL AVENUE • NIAGARA FALLS, NEW YORK • 14302
TELEPHONE: (716) 278-3378

4.1.5.11

EXHIBIT 3824.3

PRODUCT: Chrysotile Asbestos CHEMICAL FORMULA: $Mg_6(OH)_8Si_4O_{10}$

TRADE NAMES: "Calidria" Asbestos

PLAINTIFF'S EXHIBIT 02459

I. PHYSICAL DATA

BOILING POINT AND MELTING POINT: Not Pertinent

SPECIFIC GRAVITY ($H_2O = 1$): 2.45

VOLATILE CONTENT: Absorbed Water 1 – 4% By Weight. Structural Water Approximately 13% by Weight.

APPEARANCE: Pellets or Fine White Powder. No odor. Very Slight Solubility in Water.

II. HAZARDOUS INGREDIENTS

Not Applicable.

III. FIRE AND EXPLOSION HAZARD DATA

Material is not Combustible. No Fire or Explosion Hazard.

IV. REACTIVITY DATA

INERT MATERIAL: No Decomposition or Polymerization Conditions.

V. HEALTH HAZARD DATA

PERMISSIBLE EXPOSURE TO AIRBORNE CONCENTRATION:

The current standard of the Occupational Safety and Health Act of 1970 contains the following exposure limits:

"The 8-hour time-weighted average airborne concentration of asbestos fibers to which employees are exposed shall not exceed 5 fibers per milliliter greater than 5 microns in length, as determined by the membrane filter method at 400-450X magnification (4 millimeter objective) phase contrast illumination. No employee shall be exposed at any time to airborne concentrations of asbestos fibers in excess of 10 fibers per milliliter, longer than 5 microns." (Federal Register – Vol. 37, June 7, 1972, page 11320).

EFFECTS OF OVER EXPOSURE: Prolonged over exposure may result in lung damage.

EMERGENCY AND FIRST AID PROCEDURES: Not applicable. Material has no acute toxicity.

VI. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED: Avoid inhalation of dust. Remove spilled material by vacuum cleaner or by water wash.

WASTE DISPOSAL METHOD:

If reasonably foreseeable handling will not produce airborne concentrations in excess of exposure limits, no special procedures are required. When limits are likely to be exceeded, waste and scrap shall be collected and disposed of in impermeable sealed bags or other closed, impermeable containers, suitably labelled.

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