NEW ADDITIVES INDUCE THIXOTROPY, PROVIDE SAG AND VISCOSITY CONTROL

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About twelve years ago a Union Carbide exploration geologist was tramping through central California in search of nickel or other metallic mineral deposits which would be of value to the Corporation. Although neither of us realized it in 1957, what he found is what I'm here to talk about this evening:

CALIDRIA ASBESTOS

The word "asbestos" is a commercial term applied to several fibrous silicate minerals which are fire-proof and capable of being processed into flexible fibers. Although there are six different varieties of asbestos, chrysotile is by far the most common and accounts for some 90% of world production. Canada produces 1½ million tons per year, while in the United States small quantities are mined in Vermont, Arizona and California. California accounts for over 50% of U.S. production.

There are certain characteristics which are unique to chrysotile asbestos, and which make it the most-used variety:

1. A lower index of refraction, 1.51 to 1.55
2. Softest and most flexible fibers
3. Positive or cationic surface charge
4. High tensile strength, up to 800,000 psi

Figure 1 compares the physical properties of the six different types of asbestos, and you will note the major disadvantage of chrysotile is poor resistance to acid. However, in spite of this, it is estimated that chrysotile asbestos is found in over 3000 applications.

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The Source of CALIDRIA Asbestos is a unique deposit located in the southern part of the Diablo Mountain range, in Fresno and San Benito Counties (see Figure 2). It is in what is known as the New Idria mining district, which has long been famous as the oldest producing mercury mine in the United States. All exploration activities were centered in the nearby town of Coalinga, and the deposits became known as Coalinga Asbestos.

The Coalinga deposit is unique for several reasons, not the least being that it is thought to be the largest single mineral deposit in the world. Rich asbestos ore has been found over an area of 40-50 square miles, and to depths of over 500 feet. Conservative estimates indicate that over one hundred million tons of Chrysotile asbestos are available. Of course Union Carbide does not control all the claims and is not the only company mining the deposit. But, based on exhaustive drilling programs, we feel that we have the richest deposits and ample ore supply for up to one hundred years of operation. Although mine owners try to keep such information confidential, Canada's ore reserves have been estimated at less than 50 million tons.

Chrysotile asbestos occurs only in serpentine, a fine-grained rock composed almost entirely of hydrous magnesium silicate minerals similar to chrysotile in composition. Figure 3 depicts its crystal structure. The Canadian and most other deposits of serpentine contain chrysotile in cross-fiber veins that are rarely more than half an inch thick. A typical ore contains only 6-10% fiber, of random lengths and tightly bonded together in a parallel configuration. (see Figure 4).

The Coalinga deposit bears little resemblance to other serpentine bodies found throughout the world since most of the mass has been highly sheared and pulverized. It consists of soft, friable sheets and clumps of asbestos fibers, and the only other known ore body of this type is the Stragari deposit in Yugoslavia. In contrast to the cross-fiber arrangement of conventional ores, the Coalinga deposit occurs as a swirling mesh of disoriented fibers (see Figure 5). Each fiber or fiber bundle is only in point contact with its neighbor. The "fiber assay" of the ore we process ranges from 50-60% and is all classed as short fiber, similar to a Canadian Grade 7.

As mentioned before typical Canadian deposits yield varying fiber lengths, ranging from several inches down to several microns. These are designated by Canadian standards from Grade 3 (spinning fibers) to Grade 7 (shorts and floats). In addition to removing large quantities of rock from asbestos fibers, the fibers must also be classified by length. Conventional Canadian processing methods include blasting, crushing, grinding, and air classifying. Figure 6 shows the result of processing coalinga ore by the very best dry methods. Fiber bundles are still very much in evidence and the full potential of the fiber cannot be utilized.

We mine the asbestos ore by conventional open pit methods. After scraping off 10 to 20 feet of overburden, ripper-equipped bulldozers and self-propelled scrapers are used to remove the ore from the deposit. The ore is loaded into bottom-dump trailers through a 3/4-inch screen and hauled to the mill site. Because of the high production rates obtainable with a minimum amount of equipment, the mine is operated only during the summer season. Inclement weather and poor road conditions preclude efficient operations during other parts of the year. Now let me summarize the unusual characteristics of the Coalinga deposit:

1. All chrysotile
2. All short-fiber
3. Random-oriented fibers
4. Over 50% fiber content
5. About 20% moisture content

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To take advantage of the unique features of the Coalinga deposit, Union Carbide developed a hydraulic beneficiation process to provide the product shown in Figure 7. Conventional mineral processing techniques such as wet screening and grinding, are utilized; but the process is proprietary and I cannot describe it in detail. I can say that it consists primarily of three systems: rock-fiber separation, refining, and special treatment. This provides us with three basic product categories: fiber, colloidal and modified. Lets take a close look at the fiber before we proceed to a discussion of particular grades and their various applications. It is this individual fiber, its purity and liberation, which makes CALIDRIA Asbestos different from any other asbestos product available today.

You will remember from Figure 3, depicting the crystal structure of chrysotile asbestos, that there is a slight curvature in the configuration. This represents the tubular form of the fibers, which consist of about ten concentric layers of brucite (magnesium hydroxide) and silica. The tubes have an external diameter of 260Å and an internal diameter of 110Å. Electron micrographs, recently made in Japan of the ends of the fibers, have proven the tubular theory. The length of the fibers varies greatly, probably from 100 to 1000 times the diameter; but we feel that the average L/D ratio is about 200. This means that the average fiber length is about 5 microns; and, from this, we have estimated that there are 10^{14} fibrils in one gram of CALIDRIA Asbestos. (For mathematic buffs this means that if all the fibers in one gram were placed end to end they would stretch out 300,000 miles).

But let's look at some more practical and measurable numbers and physical characteristics. From strictly geometrical considerations, an assemblage of closely packed hollow tubes with the diameters mentioned previously

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would have a surface area of 105 square meters per gram ($35m^2/g$ internal and $70m^2/g$ external). Based on BET-nitrogen tests, our asbestos products have surface areas of 60 to $80m^2/g$. This compares to 10 to $30m^2/g$ for average Canadian asbestos, and verifies the electron microscope observations that there is little or no foreign material between the fibers. Also, since we use a wet process, the tube interiors are probably cleaned out to some extent.

Some interesting values are shown in Figure 8 and should facilitate a comparison between asbestos and materials with which you are more familiar.

To summarize, CALIDRIA chrysotile asbestos fibers have the following important characteristics:

1. High surface area, $60\text{-}80m^2/g$
2. High tensile strength, up to 800,000 psi
3. Cationic surface charge
4. Colloidal form, average L/D of 200
5. Extremely high purity, 90-99% fiber
6. Essentially inert
7. High temperature stability to about 700°C.
8. Low refractive index, 1.51-1.55

As I mentioned previously Canadian asbestos is classified by fiber length into Grades 3 through 7, described as follows:

Grade 3 - Spinning fibre
4 - Shingle fibre
5 - Paper fibre
6 - Waste
7 - Shorts

Grade 7 is divided into numerous sub-grades, such as: 7D, 7M, 7R, 7T, etc.; which have slightly different characteristics. Figure 9 compares the

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"average" Canadian Grade 7 with CALIDRIA products.

Figure 10 shows all the CALIDRIA products and their major market applications. The discussion which follows, to the best of my ability, will be about products and applications of direct interest to you.

I don't know if the tape joint, or drywall industry is considered to be in the coatings field; if not, it is certainly a related area. Figure 11 shows a typical ready-mix tape joint compound utilizing CALIDRIA S-G 210. The important factor to note is that the S-G 210 content is only one half the usual amount of asbestos used in such a formulation. Mineral content and water demand are maintained constant by increasing the inexpensive limestone addition. Textured coatings utilize two other products: S-G 130, a coarser grind than S-G 210, and T-135, a titanated asbestos product.

To digress just a moment, T-135 is colloidal, or High Purity Asbestos co-flocculated with anatase TiO_2. It was the first of our modified products. Figure 12 is an electron micrograph which shows how the TiO_2 particles are dispersed along the fibers. They are bound together by their opposite electrical charge and cannot be separated by mechanical energy. T-135, in the paper industry, usually replaces TiO_2 on a pound-for-pound basis with no loss in brightness or opacity. This is due to the efficient dispersion of the TiO_2 by the asbestos fibers. T-135 is just being introduced to the texture coating formulators and is showing very good promise as a valuable additive. Good body and high brightness can be achieved with a single product.

The potential for an asbestos/rutile product is obvious and we are working toward that end. Even though CALIDRIA fiber is very small, the particle size is presently too large for widespread application in finish coatings, especially interior.

An application where the particle size has been adequately small to really offer some advantages is in asphalt compounds. CALIDRIA Resin Grade 110 was developed for this application, especially in automobile undercoatings, and has proved to be quite valuable. Figure 13 shows the improved thickening efficiency of R-G 110 in a coal tar residue (CP-524). Besides offering good bodying at low concentrations, R-G 110 is essentially non-abrasive and meets the demanding performance of airless spray applications.

Viscosity and thixotropy are two very important words used when talking about liquid resin systems. Viscosity, of course, is a measure of a material's resistance to flow; or, as Webster so aptly puts it: "the state of being viscous". (You can check this when you get home, but he defines VISCOUS as "having viscosity".) Webster, at least in his Collegiate Edition, avoids thixotropy completely; but it is a property which is required in a coating, so we can't ignore it. A thixotropic resin is one which is "thin" when energy is applied, such as pumping or spraying; but "thick" under static conditions. You might think of catsup as thixotropic: thick in the bottle, but when you apply energy to the bottom--look out! A better example might be DuPont's Lucite paint, or approved equal, which spreads easily with just the energy from a brush stroke; although, in the can, it looks like paste. Resin-Grade 144 is a particularly effective thixotrope and viscosity control agent for epoxy resin systems. Figure 14 depicts some of its typical physical characteristics. It disperses readily in liquid resins and hardeners with a Cowles Dissolver or similar high-shear mixer, and over-mixing does not destroy its effect. Epoxy systems containing R-G 144 have excellent aging characteristics; and, up to 2 or 3 phr, are amazingly clear.

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Resin stability is the main reason that R-G 144 has been included as the thixotrope in the California Division of Highways specification for adhesives used in applying lane markers. Formulations for both Standard-Set and Rapid-Set adhesives are shown in Figure 15. At storage temperatures which sometimes reach 115°F., adhesive components containing pyrogenic silica were subject to drastic changes in thixotropy and viscosity. The state found that not only did R-G 144 provide a stable resin, but it also did not detract from adhesion or strength properties. Processing advantages, including reduced cost, are also realized.

Unlike some other thixotropes, R-G 144 is effective with amine hardeners; and no amine salts are required for viscosity build or thixotropic stability. The thickening effect of different thixotropes is shown in Figures 16 & 17.

Figures 18 & 19 depict the thixotropic effect of R-G 144 and two other thixotropes in epoxy and hardener respectively. With epoxy/hardener systems, each loaded with 4% R-G 144, 70 mil thicknesses can be held at room temperature; and up to 40 mil thicknesses can be held, sag-free, at 80°C. Figure 20 shows the results of some of these tests.

The value of R-G 144 as a thixotrope is not limited to epoxy resin systems, as it performs equally well in many other organic systems. It is being used as a thickener for greases, bituminous mastics and sealers, butyl rubber and polysulfide sealants, heat curable vinyl plastisols, casein and phenolic adhesives, etc. In addition to viscosity control and thixotropy, R-G 144 also provides some measure of reinforcement.

The first single-crystal whiskers used by man were asbestos fibers. As mentioned earlier, the tensile strength of asbestos fibrils has been

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measured at more than 800,000 psi, as strong as the strongest filaments. But so far, strengths achieved in composites do not go beyond those achieved with glass-mat reinforcements. We have found good whisker reinforcement with R-G 144 in rigid vinyls (with excellent see-through up to 30 phr loading), nylon molding compounds, polysulfones and others.

The whisker theory says that above some critical volume loading, discontinuous short fibers reinforce a given matrix as well as a continuous one of the same material. This is true because the many short fibers are in such close proximity that the central load bearing portions can transfer an applied load from one to the other without the fiber ends becoming involved. The basic requirement for most resin systems is that the 4D ratio be at least 90. The R-G fiber, at 200:1, is well above the minimum; and Figure 21 depicts the superior reinforcement of VYNS (a PVC-PVA copolymer) with R-G 144 compared to two Canadian asbestos products. These data represent the first work done in this area and show the distinct advantages of a high purity, fully-liberated fiber product which contains 99% asbestos rather than the 60% normally contained in competitive asbestos products.

Only modest improvements are effected in several of the low cost, high volume resins such as styrenes and polyethylenes. However, very impressive results have been achieved in polymers derived from polar monomers, such as phenoxy, polysulfone and nylon. These data are tabulated in Figure 22. Dramatic increases in tensile, flexural, and impact strength are effected with additions of 15-30% R-G 144. In Nylon-6, R-G 144 imparts improvements very similar to chopped glass, at considerably less cost. Similar improvements have also been found in Nylon 6/10 and 6/6.

Although R-G 144, at high loadings, is effective in thickening polyester

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resin systems, it was apparent that this product could not compete with existing thixotropes in such applications. Through the efforts of Dr. Steve Chwastiak of our Niagara Falls R & D staff, another "new" asbestos product was developed.

R-G 244 is a chemically modified fiber developed to provide maximum thickening efficiency and thixotropy in polyester spray-up and hand lay-up laminating resins. Figure 23 compares the thickening efficiency of R-G 244 and pyrogenic silica in a typical polyester resin.

It is also a very effective thickener in vinyl resin sealants and for organosols and plastisols used in a wide variety of adhesives, coatings, mastics and sealants. Figure 24 depicts a suggested heat-curable vinyl sealant formulation in which R-G 244 imparts a high degree of sag control and promotes adhesion. In most systems R-G 244 does not contribute color or opacity. Optimum efficiency, greatest stability, and lowest cost are obtained through the use of sonic dispersers and high energy mixers. However, especially at low viscosity levels, R-G 244 can be incorporated with low shear, propeller-type stirrers. Since R-G 244 imparts little, if any, color, it is being rapidly accepted as a thixotrope for polyester gel coats.

The thixotropic effect which R-G 244 imparts to a polyester resin is depicted in Figure 25. Here you will note that a high shear, where a resin would be sprayed, the viscosity is lower than with pyrogenic silica; and at low shear, where the resin would come to rest on a surface, extremely high viscosity is developed. This prevents sagging and facilitates the maintenance of a smooth uniform coating.

You no doubt have noted during my discussion that in almost every application,

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sag or viscosity control has been an important factor. This physical characteristic is required in almost all liquid systems, aqueous, or resinous; and including coatings, adhesives, sealants, laminates, and molding compounds. And the secret to the success of CALIDRIA Asbestos is related directly to its ultimate purity and fiber liberation. I hope that through this paper I have conveyed the idea that CALIDRIA Asbestos fiber is different and that its range of applications is limited only by your imagination.

List of Figures

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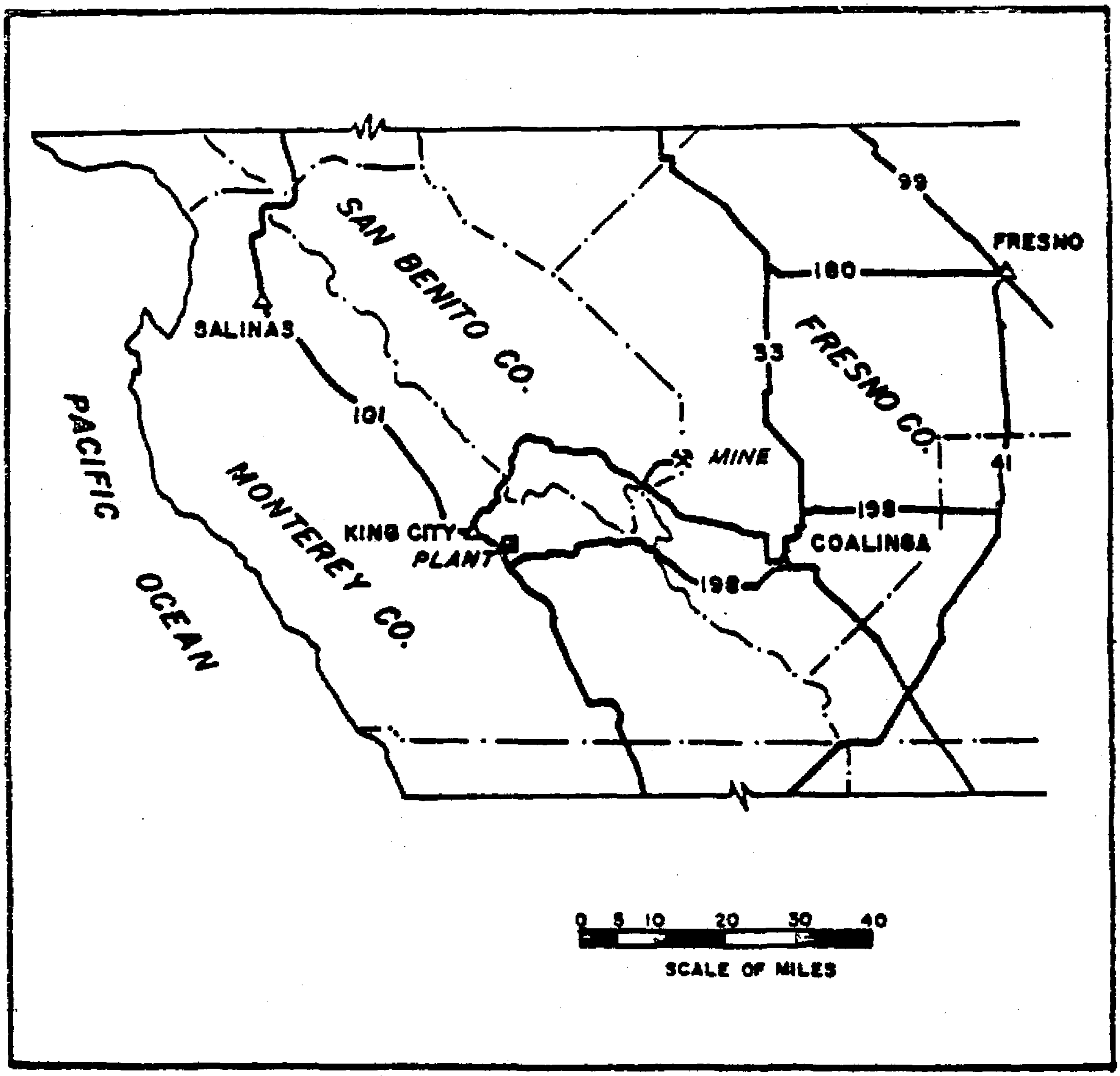
PHYSICAL PROPERTIES OF ASBESTOS MINERALS

PROPERTY	CHRYSOTILE	ANTHOPHYLLITE	CROCIDOLITE	ACTINOLITE	TREMOLITE	AMOSITE
Composition	$Mg_3Si_2O_5(OH)_4$	$Mg_7Si_8O_{22}(OH)_2$	$Na_2Fe_3Fe_2Si_8O_{22}(OH)_2$	$Ca_2Fe_5Si_8O_{22}(OH)_2$	$Mg_5Ca_2Si_8O_{22}(OH)_2$	$(Fe,Mg)_7Si_8O_{22}(OH)_2$
Crystal Habit	Fine, thin, easily separable fibers	Prismatic crystals and fibers	Long brittle fibers	Prismatic crystals and fibers	Prismatic crystals and fibers	Prismatic crystals and fibers
Color	White, gray, greenish	Gray-white	Blue	Green	White, gray-white, greenish	Ash gray or brown
Luster	Silky	Vitreous to pearly	Silky to dull	Silky	Silky	Vitreous to pearly
Occurrence	Altered ultrabasics and intruded limestone	Crystalline schists and gneisses	Fe-rich, argillaceous schists	Metamorphosed limestones and crystalline schists	Metamorphosed limestones and Mg-rich rocks	Crystalline schists
Veining	Cross-fiber, Slip-fiber, Massive fiber	Slip-fiber Massive fiber	Cross-fiber	Slip-fiber Massive fiber	Slip-fiber Massive fiber	Cross-fiber
Hardness	2.5-4	5.5-6	4	6	5.5	5.5-6
Specific Gravity	2.4-2.6	2.8-3.1	3.2-3.3	3.0-3.2	2.9-3.2	3.1-3.3
Refractive Index (mean)	1.51-1.55	1.61	1.7	1.63	1.61	1.64
Texture	Soft to harsh also silky	Harsh	Soft to harsh	Harsh	Harsh	Harsh
Tensile Strength (psi)	80,000-100,000	4000	100,000-300,000	1000	1000-8000	16,000-90,000
Electric Charge	Positive	Negative	Negative	Negative	Negative	Negative
Resistance to Acids and Alkalis	Poor-Acid Good-Alkalis	Very good	Good	Fair	Good	Good
Flexibility	Very good	Poor	Good	Poor	Poor	Good
Impurities Usually Encountered	Magnetite, chromite, calcite	Magnetite	Magnetite	Calcite	Calcite	Magnetite

Fig. 1



Location of Union Carbide's CALIDRIA Asbestos operation

Fig. 2

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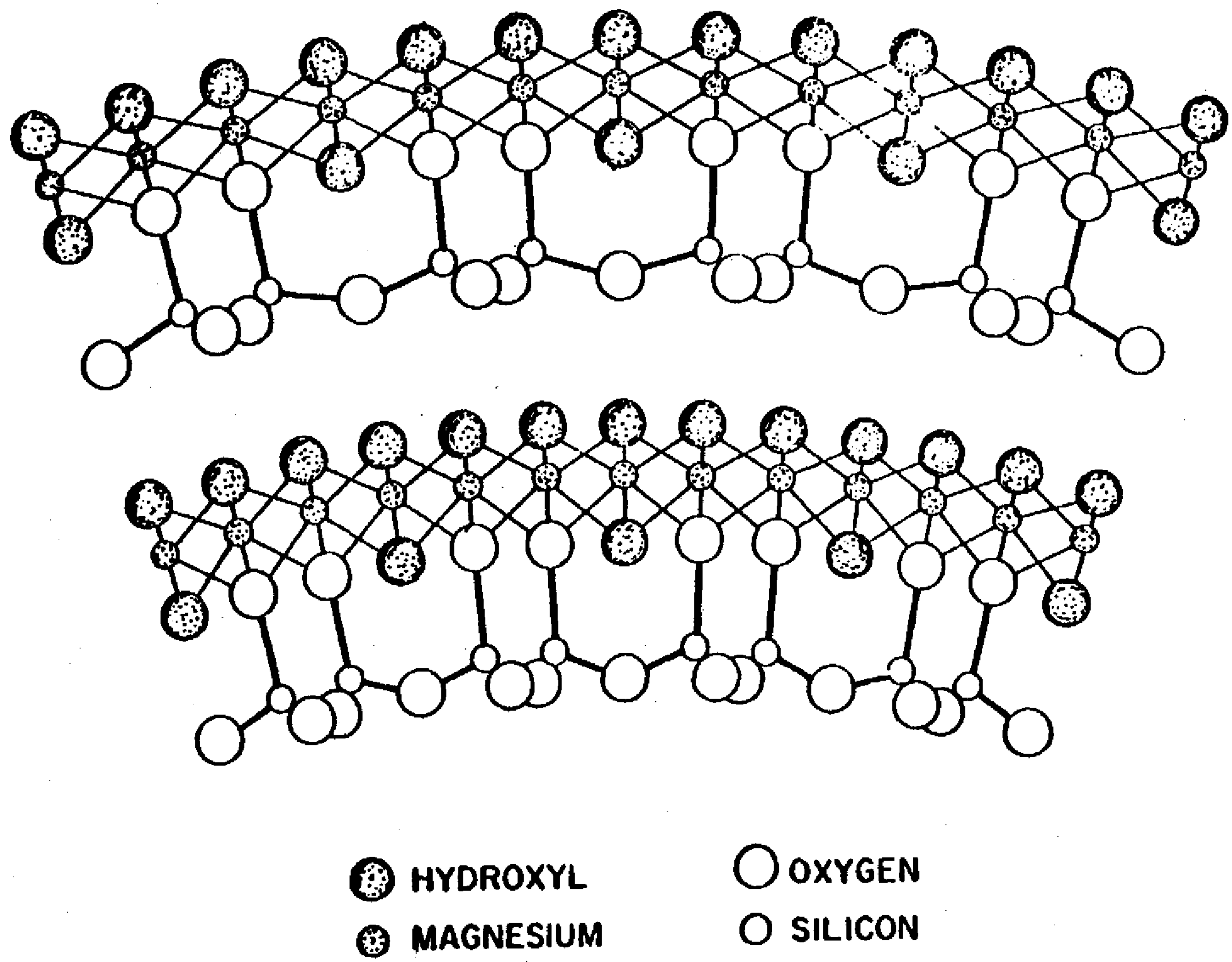

FIGURE 3. Crystal structure of chrysotile asbestos.

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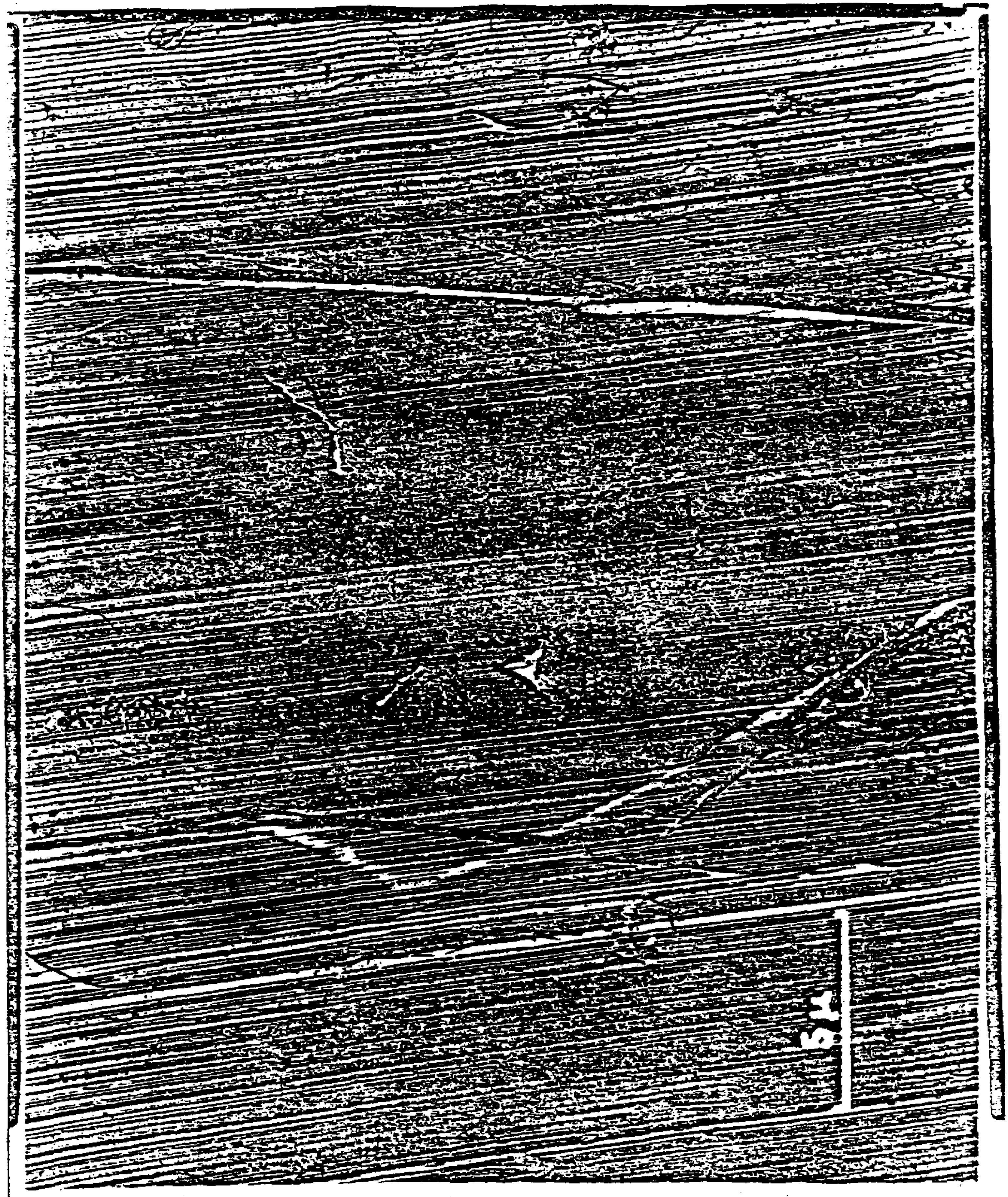

Fig. 4 - Electron Micrograph of typical Canadian asbestos fiber structure

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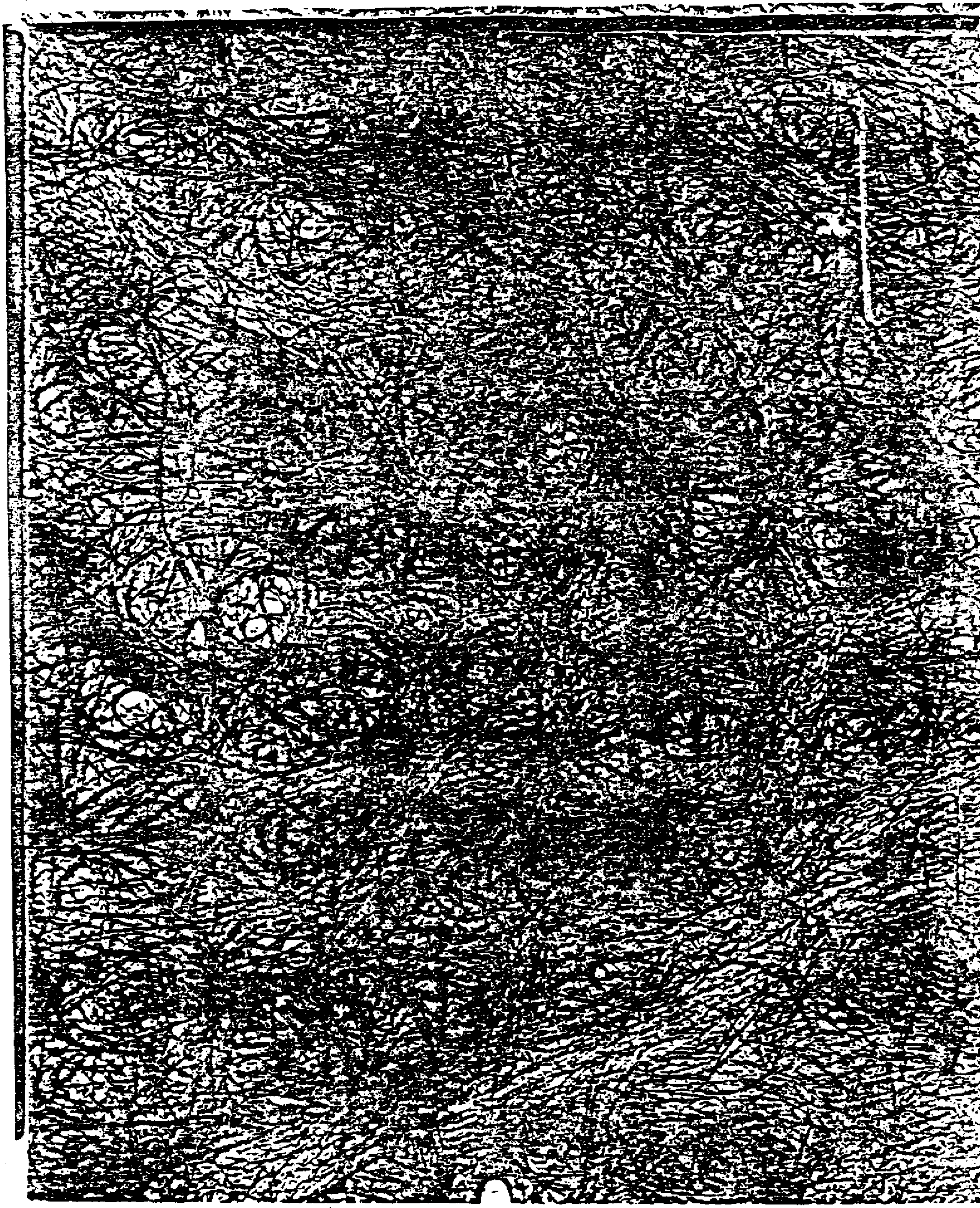

Fig. 5 - Electron Micrograph of typical Calidria asbestos fibers

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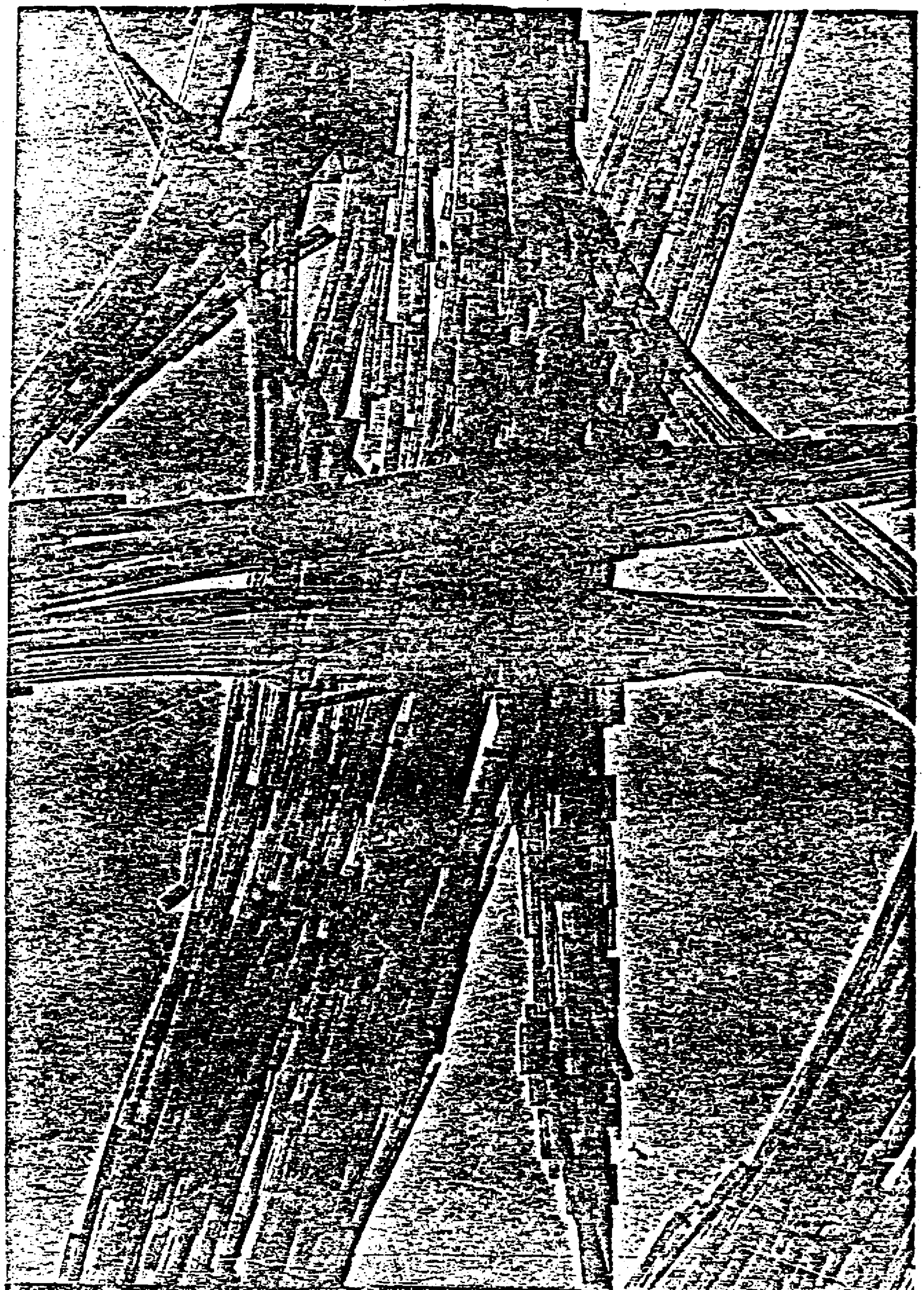

Fig. 6 - Electron Micrograph of dry processed asbestos fibers A07732

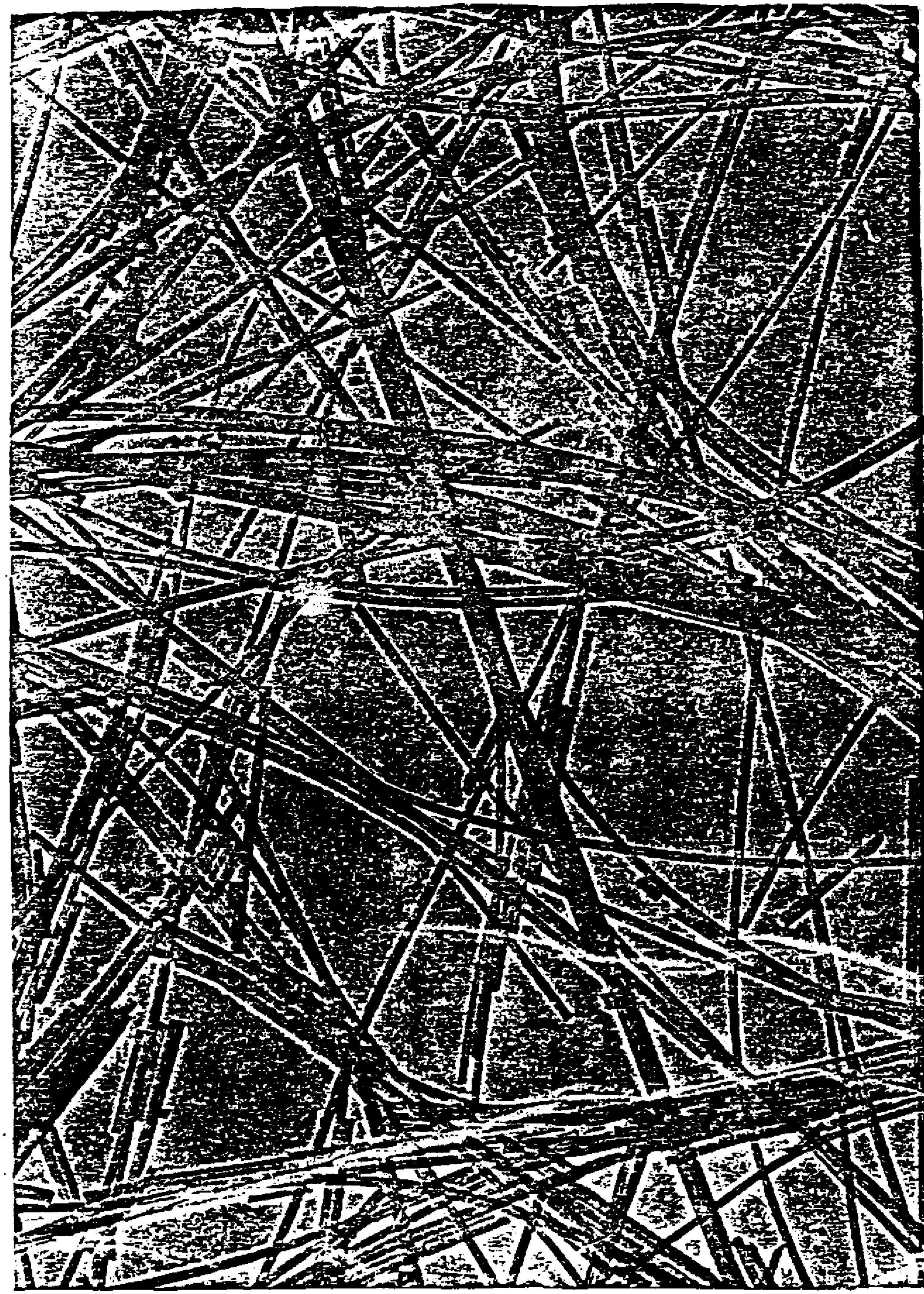

Fig. 7 - Electron Micrograph of wet processed Calidria asbestos fibrils

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COMPARATIVE PHYSICAL PROPERTIES OF WELL-KNOWN FIBERS

Fiber	Diameter, inches	Surface Area m^2/gm	Tensile Strength, psi
Human Hair	0.0016	-	-
Wool	0.0100	1.0	-
Nylon	0.0003	0.3	-
Glass	0.0003	-	100-200,000
Cotton	0.0004	0.7	73-89,000
Piano Wire	-	-	300,000
CALIDRIA ASBESTOS	0.000001	60-80	up to 800,000

Fig. 8

PHYSICAL PROPERTIES OF CHRYSOTILE ASBESTOS

PROPERTY	AVERAGE CANADIAN	UCC PRODUCTS: STD. GRADE	UCC PRODUCTS: HIGH PURITY
SURFACE AREA $M^2/G.$	10-30	50-60	60-80
OIL (DOP) ADSORPTION G./10 G.	4-6	8-10	10-14
WATER RETENTION ML. H_2O/20 G.ASB.	12-20	23-32	33-40
REFLECTANCE %	54-70	62-72	74-77
MAGNETITE %	3-6	<2.0	<0.60

Fig. 9

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CALIDRIA PRODUCT DESIGNATION	APPLICATION
S-G 100	Vinyl asbestos and asphalt floor tile
S-G 144	" " " " " "
S-G 130	Texture coatings, acoustic compounds
S-G 210	Tape Joint compounds
HPP	Pulp and Paper Industry
HPO	P & P, waste treatment, pollution control
T-135-P	P & P
T-135-O	P & P, textured coatings
R-G 110	Asphalt compounds, polyester pre-mix
R-G 144	Thixotropic thickener, resin systems
R-G 244	" " , polyester resins

CALIDRIA Asbestos Market Applications

Fig. 10

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TJC READY-MIX

STARTING POINT FORMULATION, 1-GALLON MIXER, 4000 GRAMS DRY WEIGHT

Ingredients and Order of Addition	% by wt. dry basis	grams to weight	dry grams	grams water
1. Water (equivalent to 36.0% by wt.) (c)	--	--	--	1002.0
Note: Start the mixer on slow stirring				
2. CELLOSIZE TJC Grade Union Carbide	0.50 (a)	20.0	20.0	--
Note: Add the particles slowly. Make sure no lumps are added. Mix until the particles are wet.				
3. Bacteriastat, "Dowicide" A (Dow Chemical)	0.20 (a)	8.0	8.0	--
Note: Continue stirring until the thickner is in solution. Usually takes 4-5 minutes.				
4. Pigment Dispersant: "Daxad" 30 (Dewey and Almy), about (25% total solids)	0.60	96.0	24.0	72.0
5. UCAR Latex 131, Union Carbide (59.0-61.0% total solids)	6.60	440.0 (b)	264.0	176.0
6. Filming Aid: Ethylene Glycol Union Carbide	1.00	40.0	40.0	--
Note: Mix until the above mixture is homogeneous (well dispersed)				
Add the fillers below individually or as a mixture				
7. Asbestos, Calidria SG-210 Grade, Union Carbide	4.50	180.0	180.0	--
8. Mica (P-80-F), (Western Mica)	21.00	840.0	840.0	--
9. Clay, ASP-400, (Minerals and Chemicals Phillip)	4.00	160.0	160.0	--
10. Antifoam: NOPCO PD No. 1, (Nopoco Chemical)	0.10	4.0	4.0	--
11. Calcium Carbonate, No. 1 White, (Thompson-Weinman)	61.50	2460.0	2460.0	--

The above mixture is mixed for 120 minutes in a 1-gallon Baker-Perkins Sigma Blade Type mixer at 79 r.p.m.

NOTES:

(a) These can be added as a 2.0 percent by weight pre-mix concentrate. The concentrate is prepared using the addition of bacteriastat as indicated. When this is done, a corresponding correction must be made in the initial water charge.

(b) Based on an average of 60.0% total solids.

(c) Based on the fillers recommended here. The water demand will differ with the type of dry fillers.

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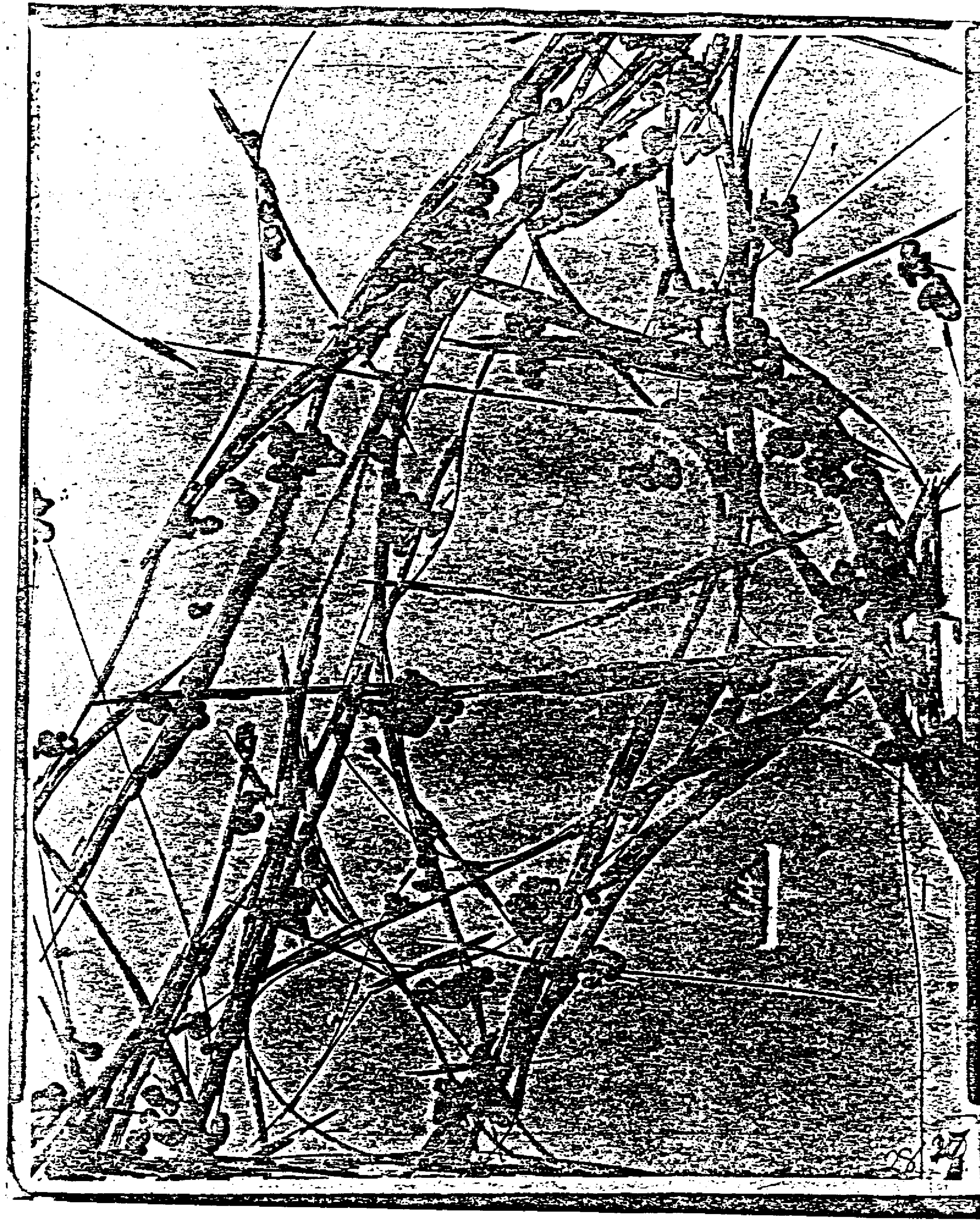

Fig. 12 - Electron Micrograph of Titanated Asbestos, CALIDRIA Type T-135

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COMPARATIVE THICKENING PERFORMANCE OF VARIOUS MATERIALS IN COAL TAR RESIDUE

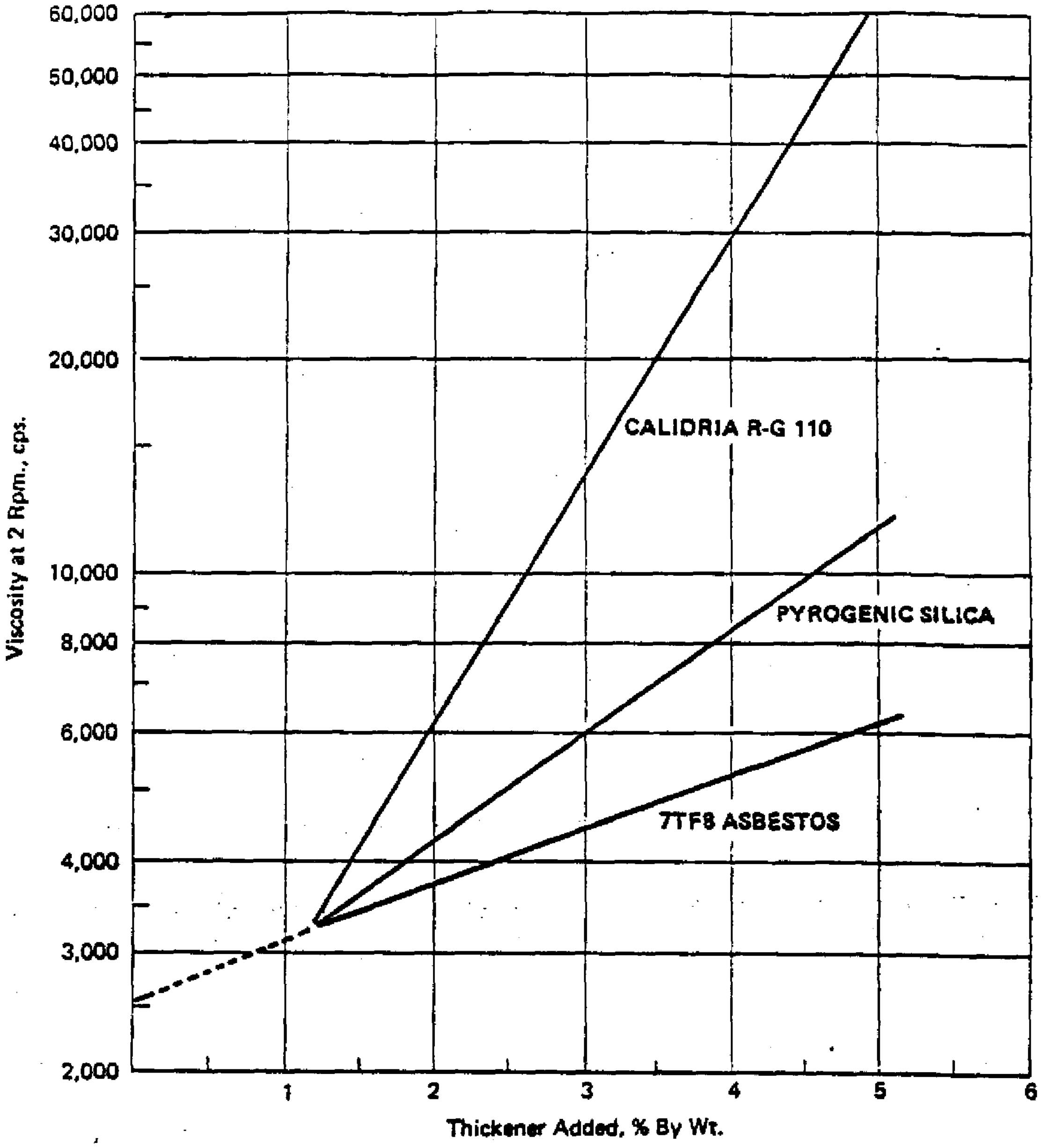

Fig. 13

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CALIDRIA R-G 144

Typical Physical Characteristics

Specific Gravity	2.45
Moisture Content, % by Wt.	2.0 max.
Surface Area, Sq. meters per gram	60 approx.
Reflectance, G.E. Brightness	72-76
Nature of Surface Charge	Electropositive (Cationic)
pH in Water (2% slurry)	9.0
Bulking Value, gal./100 lb.	4.8
Oil Absorption (DOP) lb./100 lb.	120
Refractive Index, n_d 25°C.	1.54-1.56
Aspect Ratio (Average L/D)	200:1
Tensile Strength, psi*	824,000 max. (281,000-436,000)
Tensile Modulus, psi*	23.2×10^6
Dry Bulk Density, lb./cu. ft. (fully aerated)	4

*1968 Modern Plastics Encyclopedia, p. 594

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Fig. 14

EPOXY ADHESIVES FOR PAVEMENT MARKERS

	Parts by Wt.
RAPID SET TYPE:	
Package A:	
Epoxy Resin	100.00
RESIN-GRADE ASBESTOS	3.00
Titanium Dioxide	1.62
Package B:	
Polymercaptan Hardener	60.00
2,4,6-Tri(dimethylaminomethyl)phenol	6.00
Alkyl Subs. Polynuclear Aromatic Oil	15.00
2-Ethyl Hexanoic Acid	0.20
Carbon Black	0.05
RESIN-GRADE ASBESTOS	2.00
Glass Spheres	36.36
STANDARD SET TYPE:	
Package A:	
Epoxy Resin	100.00
Titanium Dioxide	7.31
RESIN-GRADE ASBESTOS	5.00
Talc	37.64
Package B:	
N-Aminoethyl Piperazine	23.16
Nonylphenol	52.00
Carbon Black	0.22
Talc	77.37
RESIN-GRADE ASBESTOS	1.00

Fig. 15

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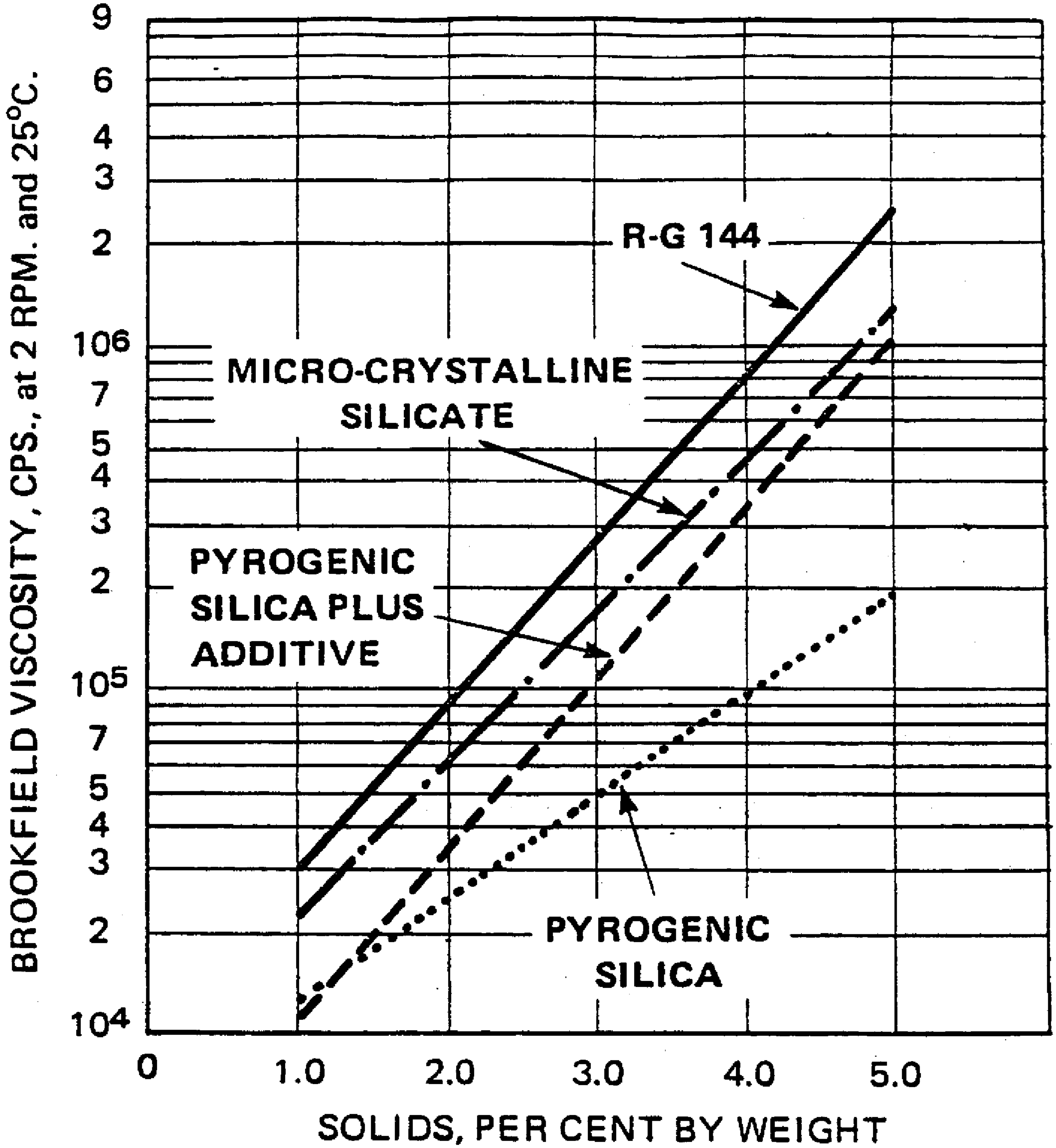

EFFECT ON VISCOSITY OF VARIOUS THICKENERS IN
BAKELITE EPOXY RESIN ERL-2774

Fig. 16

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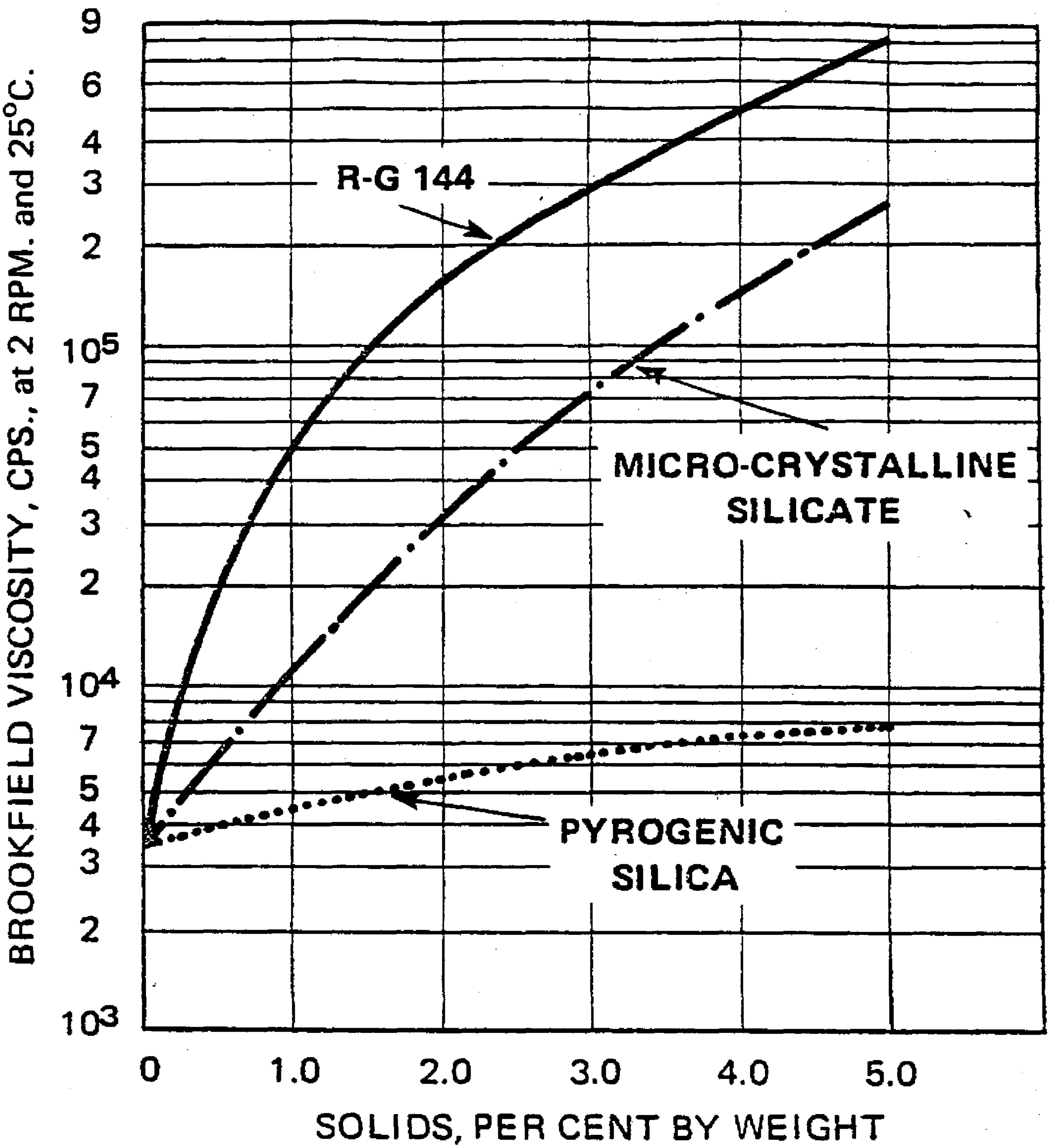

EFFECT ON VISCOSITY OF VARIOUS THICKENERS IN
BAKELITE RESIN HARDENER ZZL-0814

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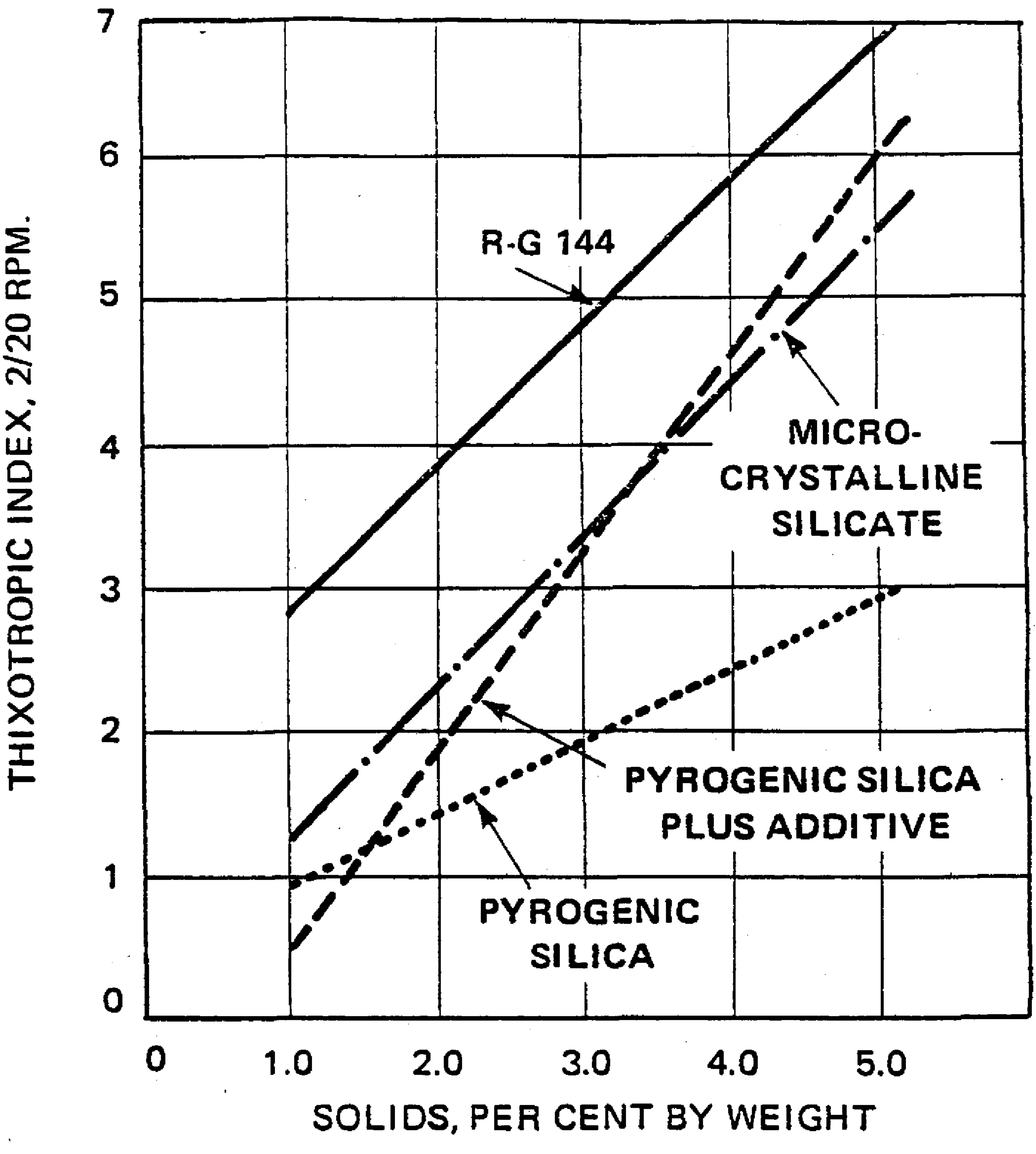
Fig. 17



EFFECT ON THIXOTROPY OF VARIOUS THICKENERS IN
BAKELITE EPOXY RESIN ERL-2774

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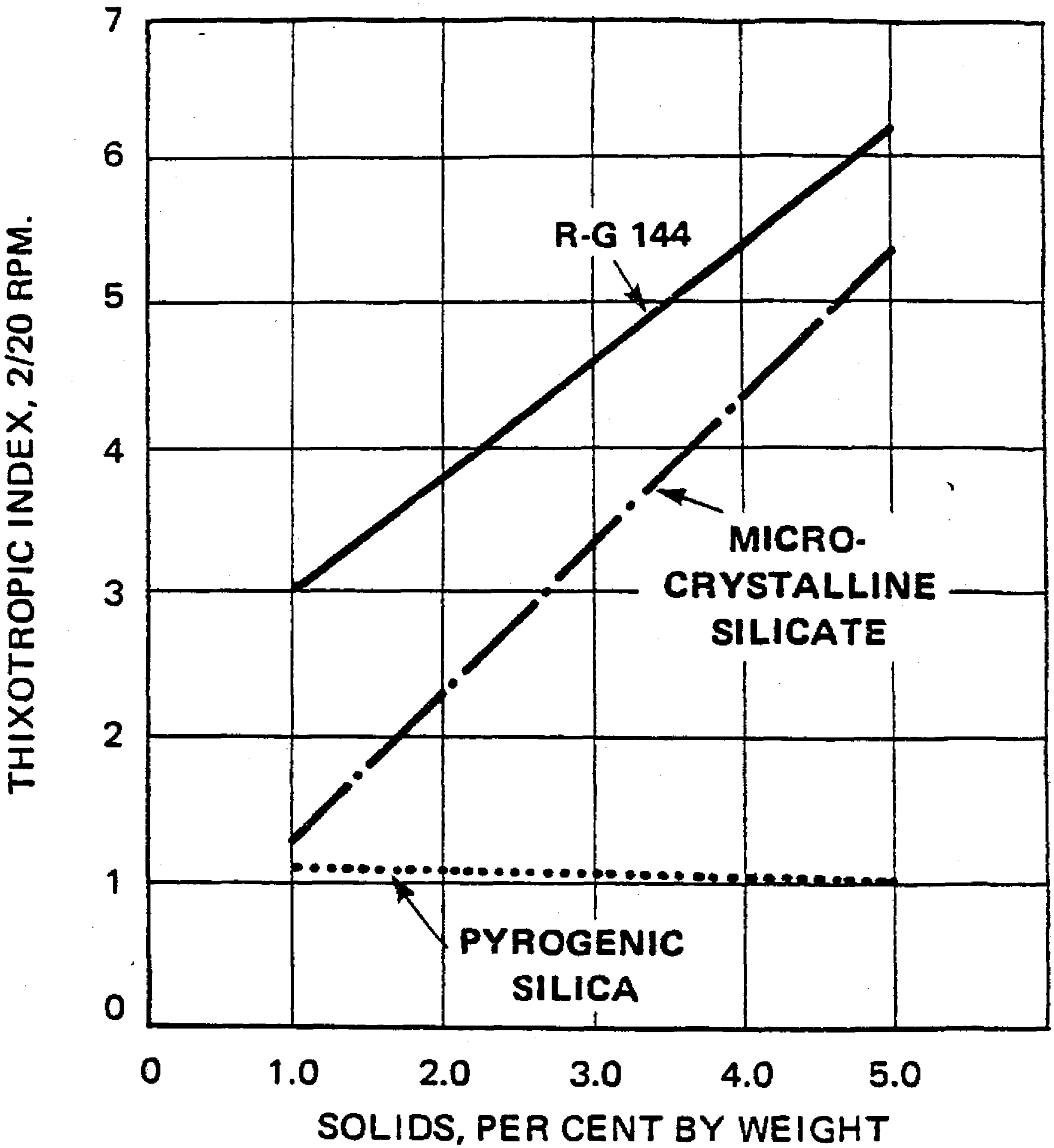
Fig. 18



EFFECT ON THIXOTROPY OF VARIOUS THICKENERS IN
BAKELITE RESIN HARDENER ZZL-0814

A07745

Fig. 19

Table 1 THICKENING OF BISPHENOL-BASED RESINS WITH *CALIDRIA* RESIN-GRADE 144 ASBESTOS

Ingredient	Parts by Weight											
BAKELITE ERL-2774	100			100			100			100		
CALIDRIA Resin-Grade 144 Asbestos	1			2			3			4		
Brookfield RVF Viscosity, cps. X 10^{-4}	RPM.		Thixotropic Index (T. I.) (a)	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)
	2	20		2	20		2	20		2	20	
24 hours	34	22	1.5	137	39	3.5	250	53	4.7	464	87	5.3
7 days	32	20	1.6	132	36	3.6	244	54	4.5	430	76	5.7
30 days	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	480	94	5.1
Vertical Drawdown, mil (c)												
Room Temperature	(b)			(b)			(b)			125		
45 days	(b)			(b)			(b)			125		

Ingredient	Parts by Weight											
BAKELITE ERL-2795	100			100			100			100		
CALIDRIA Resin-Grade 144 Asbestos	1			2			3			4		
Brookfield RVF Viscosity, cps. X 10^{-3}	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)
	2	20		2	20		2	20		2	20	
24 hours	18	3.8	4.7	38	6.3	6.0	70	11	6.4	91	13	6.9
7 days	16	3.7	4.3	35	6.8	5.1	68	12	5.5	122	22	5.5
30 days	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	125	25	5.0
Vertical Drawdown, mil (c)												
Room Temperature	(b)			(b)			(b)			80		
45 days	(b)			(b)			(b)			70		

(a) Thixotropic index (T. I.) $= \frac{\text{viscosity at 2 rpm.}}{\text{viscosity at 20 rpm.}}$

(b) Not run.

(c) Vertical Drawdown: A 2-inch wide drawdown was made on a horizontal sandblasted steel panel. The panel was immediately raised to a vertical position and any sag noted. If no sag occurred in 10 minutes, the procedure was repeated and the thickness increased until sagging occurred.

Table 2 THICKENING OF AMINE HARDENERS WITH *CALIDRIA* RESIN-GRADE 144 ASBESTOS

Formulation	Parts by Wt. BAKELITE ZZL-0814 ....100 CALIDRIA Resin-Grade 144 Asbestos 4			Parts by Wt. BAKELITE ZZL-0820 .....100 CALIDRIA Resin-Grade 144 Asbestos 4			Parts by Wt. BAKELITE ZZL-0854 .....100 CALIDRIA Resin-Grade 144 Asbestos 4		
Brookfield RVF Viscosity, cps. X 10^{-4}	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)	RPM.		Thixotropic Index (T. I.)
	2	20		2	20		2	20	
24 hours	187	36	5.3	67	32	2.1	102	23	4.5
7 days	172	34	5.1	66	32	2.1	104	23	4.6
30 days	177	34	5.2	67	35	1.9	104	24	4.4
Vertical Drawdown	Mil			Mil			Mil		
Room Temperature (R. T.)	70			40			40		
50°C.	20			—			—		
80°C.	—			40			40		
30 days at R. T.	70			40			40		
30 days at 80°C.	—			40			40		

A07746

Fig. 20

REINFORCED VYNS-COMPRESSION MOLDED

	None	R-G 144	7RF9	7R05
Tensile Strength, psi.	7600	9000	7700	7800
Tensile Modulus, 10^3 psi.	396	531	470	490
Elongation, %	2	3	16	6
Izod, ft-lb/in.	0.6	0.5	0.5	0.5
HDT, °C.	63.0	69.9	64.6	63.3
Color	Lt. Gray	Lt. Tan	Dk. Gray	Dk. Gray
Clarity	Clear	Clear	Opaque	Opaque

Formulation:

VYNS	100.00
Temex 5	1.20
Advastab CH-90	0.50
Advastab ABC-18	0.75
Stearic Acid	1.00
Asbestos	10.00

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Fig. 21

MECHANICAL PROPERTIES OF INJECTION MOLDED SAMPLES

	Phenoxy		P-1700 Polysulfone		Nylon-6	
	0% R-G 144	20% R-G 144	0% R-G 144	15% R-G 144	0% R-G 144	30% R-G 144
Tensile Strength, psi.	9250	18000	10000	14000	9000	20000
Tensile Modulus, 10^3 psi.	470	1070	370	850	-	-
Flexural Strength, psi.	-	-	-	-	11000	30000
Flexural Modulus, 10^3 psi.	-	-	-	-	260	1500
Elongation, % at yield	4.7	3.5	5.7	3.9	4.0	4.1
Izod, ft-lbs./in.	2.3	0.6	1.2	1.2	1.3	0.9
HDT, ^oC.	86.5	88.8	170	180	58	196

Fig. 22

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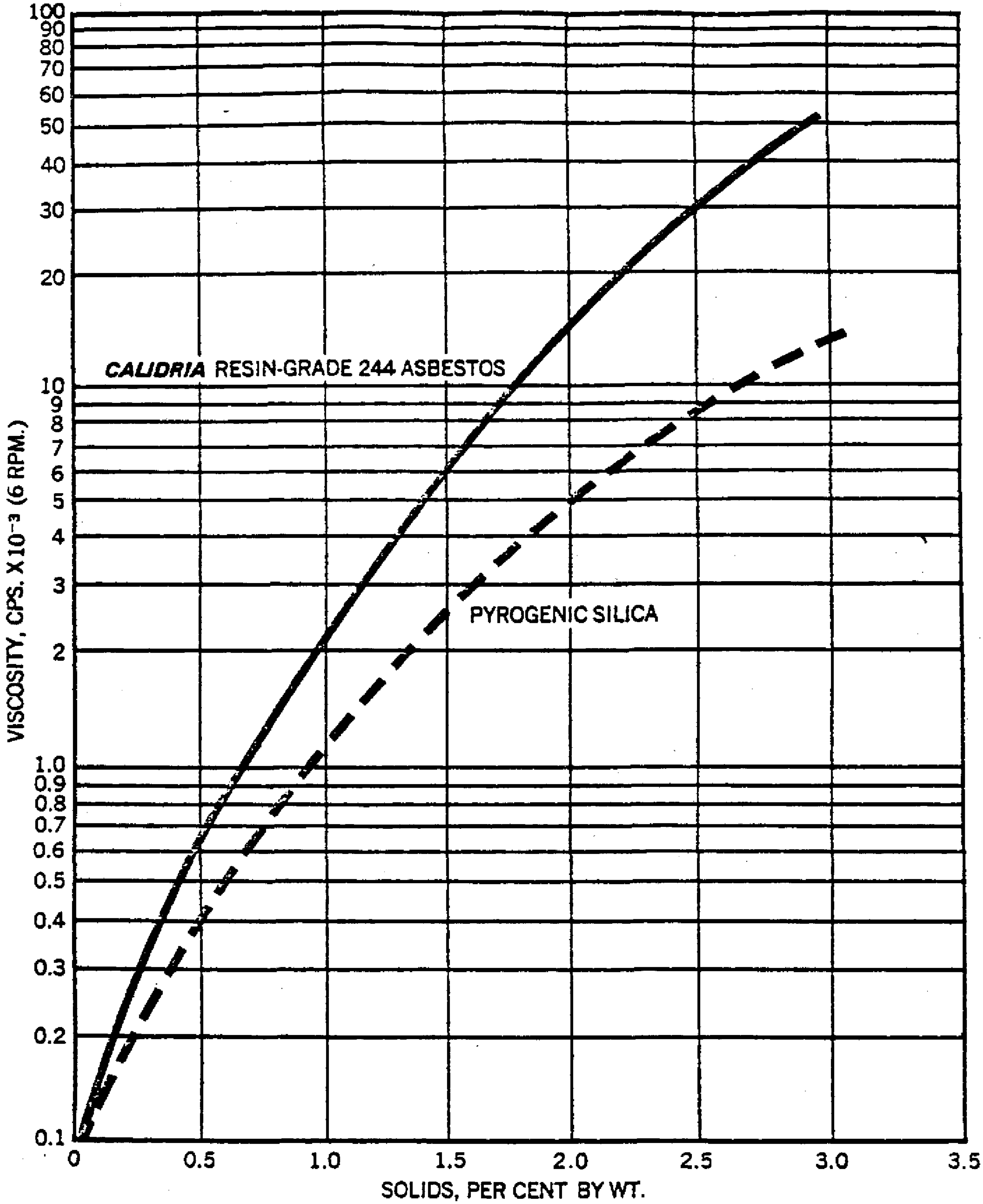

Comparison of Thickening Efficiency of Resin-Grade 244 Asbestos with that of Colloidal Silica in Polyester Resin

A07749

Fig. 23

TYPICAL HEAT-CURABLE VINYL SEALANT FORMULATION

Ingredient	Per Cent by Weight
BAKELITE Vinyl Dispersion Resin QYLF-2	24.54
BAKELITE Vinyl Resin Solution VMCC	3.92
"Elvacite" 2044(a)	0.98
"Hycar" 1411(b)	0.37
"Camel White"(c)	29.20
FLEXOL Plasticizer 10-10	29.20
FLEXOL Plasticizer TCP	2.70
"Monomer X-970"(d)	4.91
"Mark" LL(e)	0.49
Resin-Grade 244 Asbestos	3.68
"Dicup" R(f)	0.01
	100.00

.Dissolve BAKELITE Vinyl Resin Solution VMCC in FLEXOL Plasticizer 10-10 at about 100°C. Dissolve "Elvacite" 2044 in FLEXOL Plasticizer TCP at 100°C. Mix the two solutions and all the other ingredients together in a pony, "Hobart" or similar mixer.

(a) Acrylic resin; Du Pont, Wilmington, Delaware
(b) Powdered rubber; B. F. Goodrich, Akron, Ohio
(c) Calcium carbonate; H. T. Campbell and Son's Corporation, Baltimore, Maryland
(d) Polymerizable monomer; Rohm and Haas, Philadelphia, Pennsylvania
(e) Stabilizer; Argus Chemical Corporation, Brooklyn, New York
(f) Catalyst; Hercules, Wilmington, Delaware

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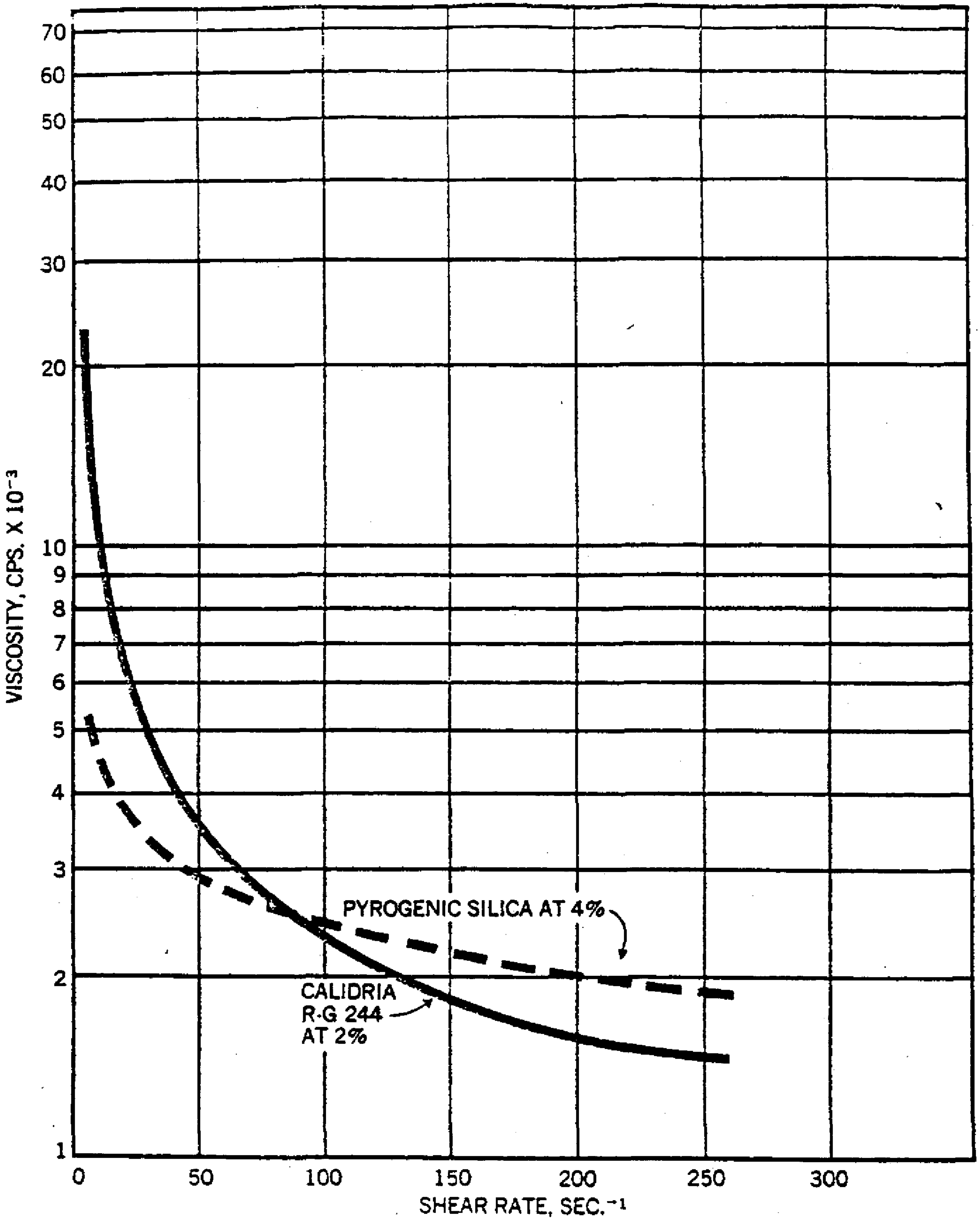
Fig. 24



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Comparative Thixotropic Characteristics CALIDRIA R-G 244 Vs Pyrogenic Silica

Fig. 25

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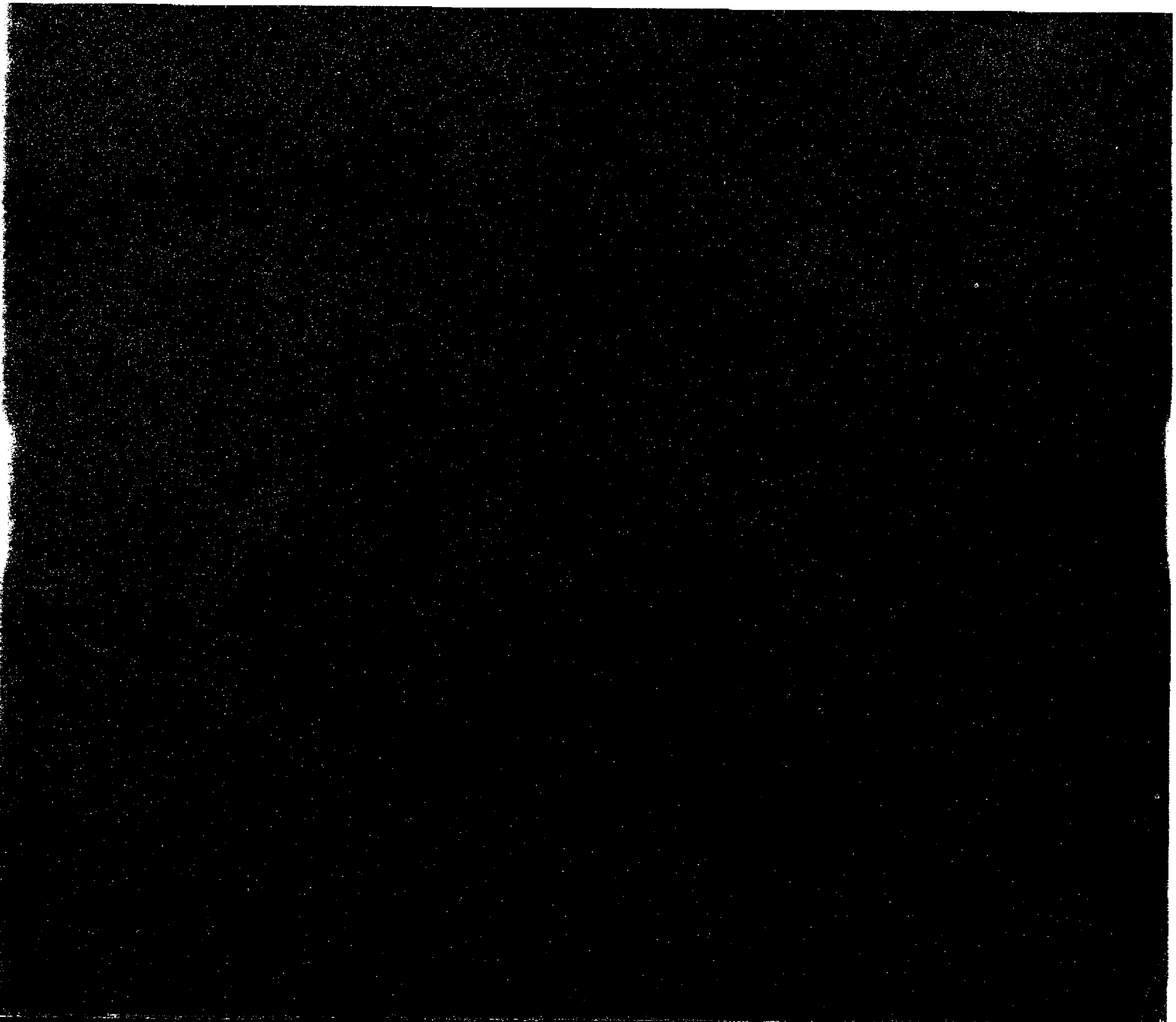
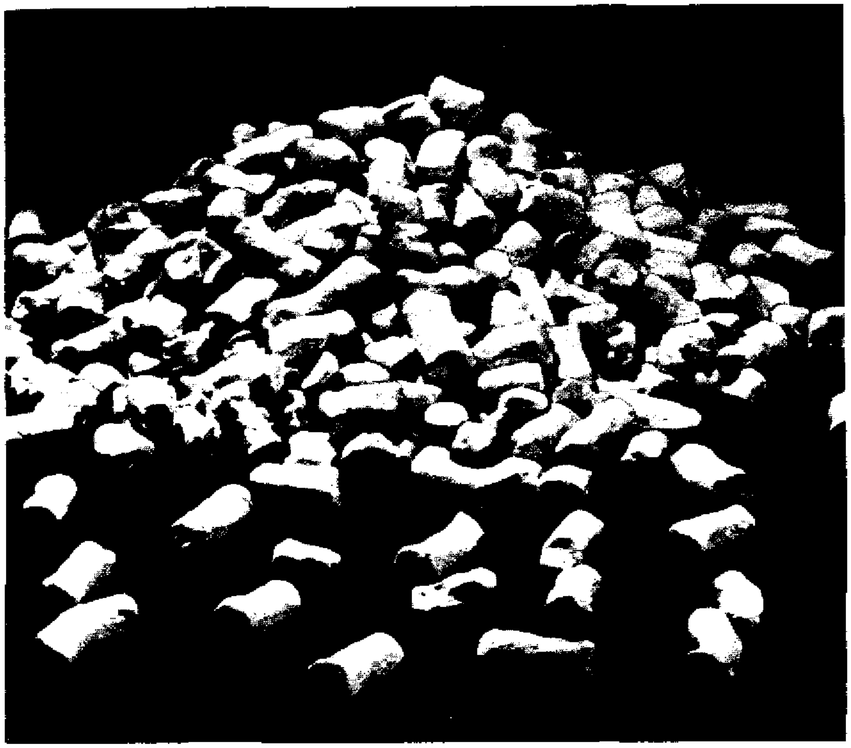
FEBRUARY 14, 1966





New type of asbestos shows advantages in papermaking

Blair L. Ingalls,
Tech. Service Rep., Mining and Metals Division,
Union Carbide Corp.
and
Charles P. Klass,
Associate Editor, Paper Trade Journal

Unique product, when used as ingredient in furnish, has increased filler retention and save-all recovery, improved opacity, enhanced softness and helped to disperse pitch.

In 1958, Union Carbide began work on an unusual deposit of chrysotile asbestos 160 miles south of San Francisco, Cal. Unlike conventional deposits that extend through the host rock, this deposit was not associated with hard, consolidated rock masses. Wet processing techniques were then developed to produce a high-purity asbestos product—grit-free and of such high brightness that it could be used in paper. In fact, radiometric determinations have shown that this asbestos is considerably less abrasive than ordinary fillers or bleached sulphite pulp.

When added to the pulper or beater, this high-purity asbestos behaves in an unusual manner. The pellets of asbestos (pellets are used for compactness in shipping) open up and disperse into short fibers that mix thoroughly with the furnish components. Being positively charged, the fibers then attract negatively charged furnish components, including cellulose and fines, titanium dioxide, clay, and dyestuffs. Asbestos thus improves the retention of these components on the wire, substantially reducing the loss of solids to the white water.

The presence of asbestos in the papermaking system also allows improved recoveries of solids in the saveall. Asbestos attracts fines in the same manner as on the machine, thereby reducing the loss of solids in the mill effluent.

Mills adding asbestos for retention generally use about 2½ per cent, replacing a similar amount of clay. The improved retention provided by the asbestos also allows reductions in pigment additions such as titanium dioxide and clay. Since the mining and metals division of Union Carbide sells this asbestos in the price range of many cellulose pulps, savings in pig-

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FIGURE 1—Electron micrographs (x24,000) of commercial 50 lb. offset containing 1.68 per cent TiO_2 and 22.5 per cent clay. Sheet at left does not contain asbestos and has densely packed agglomerates of TiO_2 (black) and clay (gray, angular) with large surrounding voids. Sheet at right contains 1.5 per cent asbestos and has a more uniform distribution of TiO_2 and clay. Thus, latter structure provides better light-scattering efficiency.

ment costs are significant. To these savings can be added the reduction in solids losses at the save-all.

Effective TiO_2 extender

An additional benefit obtained from having asbestos in the furnish is its ability to improve opacity by optimizing the light-scattering efficiency of titanium dioxide. Thus, less titanium dioxide is needed in the sheet to obtain a given opacity, lowering costs.

This effect is illustrated by the electron micrographs of commercial sheets shown in Figure 1. Ideally, the particles of titanium dioxide should be scattered uniformly throughout the sheet so that the optimum surface area and size for light scattering can be retained. Without asbestos, however, the particles tend to agglomerate, reducing the light-scattering efficiency. By having an opposite charge, asbestos fibers attract titanium dioxide and help keep the particles distributed more uniformly than previously.

Other benefits

Some mills are using asbestos to prevent pitch buildup. In this way, asbestos helps keep cleaner felts and fourdrinier wires, reducing machine breaks and down time, and reduces rejections for paper blemishes. From 0.6 to 2 per cent asbestos, depending on mill conditions, has been found to prevent pitch agglomeration and keep it dispersed in a finely divided form throughout the pulp. Mills using asbestos for pitch control also have ob-

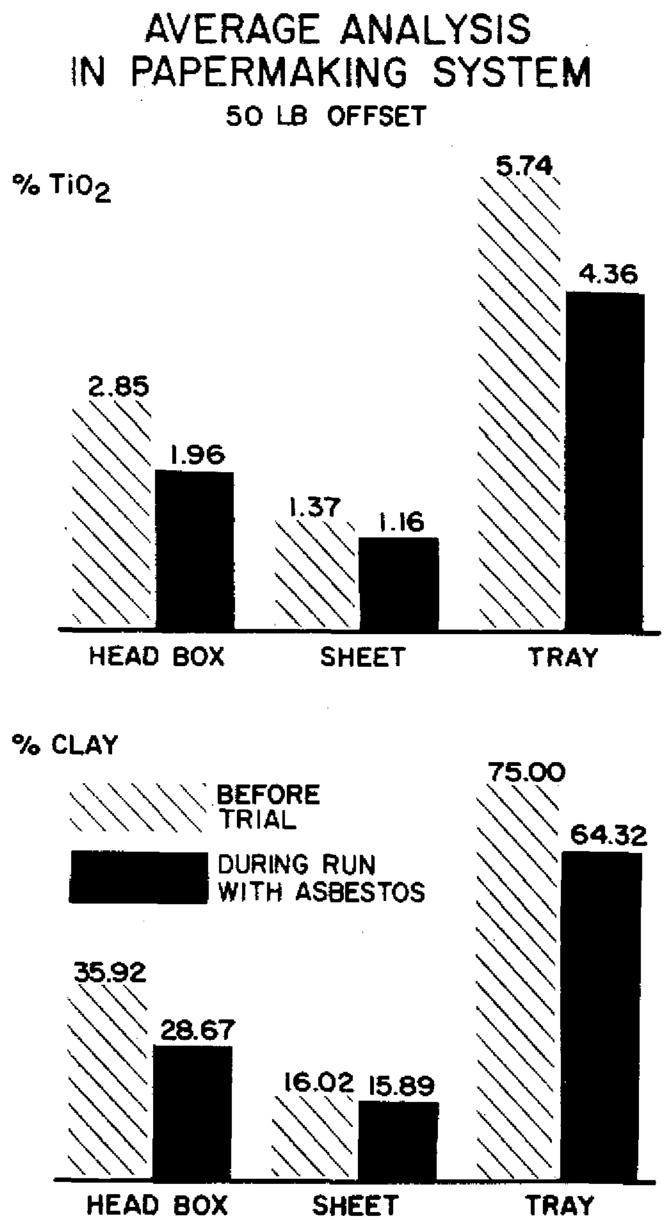

FIGURE 2—Average analyses in papermaking system producing 50 lb. offset. During the 7 hours that 1.7 per cent asbestos was added to the system, TiO_2 retention increased from 48 to 62 per cent while clay retention increased from 45 to 57 per cent across the wire.

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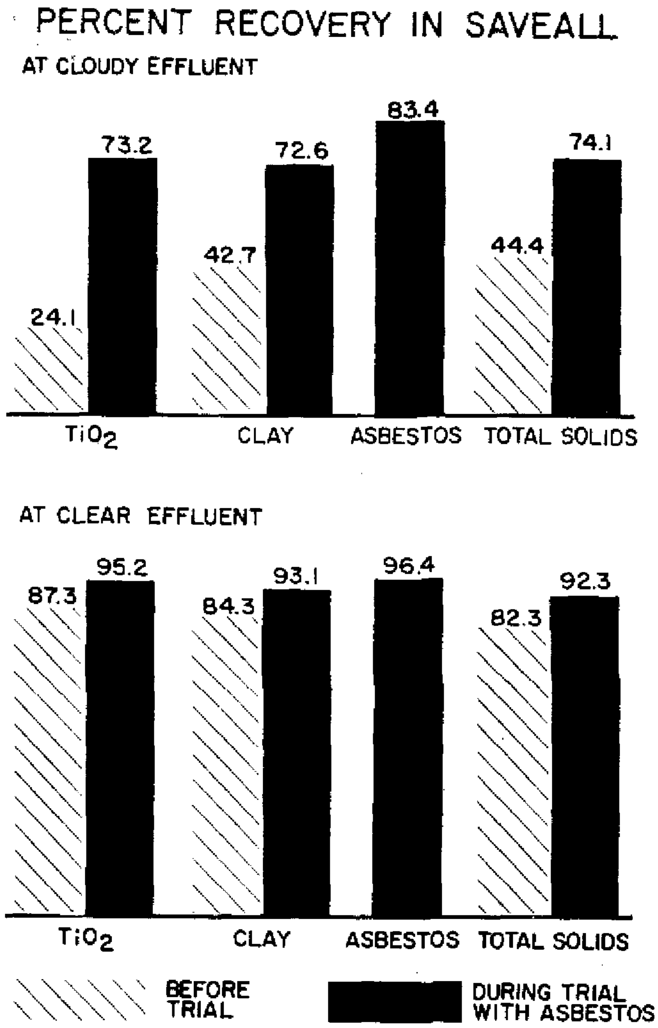

FIGURE 3—The presence of asbestos in this drum-filter saveall increased solids recoveries from 44.4 to 74.1 per cent at the cloudy effluent and from 82.3 to 92.3 per cent at the clear effluent.

tained improved retention of fillers.

In addition, mills making tissues and towels have added asbestos to improve softness. A two to four per cent asbestos content in the sheet gives improved hand feel, and its effect on sheet softness is readily measurable on Handle-o-meter and other softness measuring devices. Where economically attractive, asbestos allows mills to replace hardwood with stronger softwood without sacrificing softness.

To date, over 100 mills have evaluated asbestos and many are using it on a regular basis. Some of the results of this mill experience are given below.

Retention improved 28%

In one production run on 50-pound offset paper, asbestos was used to improve the retention of the furnish components. The trial run lasted for seven hours, during which 1.7 per cent asbestos was added to the pulper, replacing 3.4 per cent clay.

Figure 2 shows the titanium dioxide and clay analyses at various points in the papermaking system before and during asbestos usage. Retention calculations from these figures indicate that titanium dioxide and clay retention across the wire improved about 28 per cent during the asbestos trial. Average titanium dioxide retention increased from 48 to 62 per cent. Clay retention improved from 45 to 57 per cent. The average retention for asbestos during the trial was 69 per cent on the wire and 86 per cent for the overall system.

This improved retention substantially reduced the buildup of solids in the head box and in the tray water. At the head box, titanium dioxide and clay levels were reduced by about one-third and one-fifth respectively. In the tray water, solids were reduced by 36 per cent during the trial with asbestos. Tray-water reductions for titanium dioxide and clay were 49 and 43 per cent respectively.

The presence of asbestos in the papermaking system also substantially improved the recovery of solids in the save-all. The solids content, per cent ash, and per cent titanium dioxide of the influent and effluent are shown below:

	No Asbestos	With Asbestos
Save-all Influent		
Solids, lb./1000 gal.	19.1	15.0
% Ash	45.6	38.7
% TiO_2	2.42	1.41
Save-all Effluent		
Solids, lb./1000 gal.	4.16	2.24
% Ash	75.2	76.1
% TiO_2	4.45	3.57

Based on these figures, save-all recoveries improved from 78 to 85 per cent with the use of asbestos. Solids losses at the effluent were reduced 46 per cent. Of even greater economic significance, losses of titanium dioxide in the effluent were reduced by 58 per cent.

Retention save-all recoveries gain

Similar results were obtained by a mill making 50-pound offset printing paper. In a four-hour trial, 2.4 per cent asbestos was added to the pulper. Clay was reduced in two steps from 27.4 to 18.0 per cent while titanium dioxide was reduced from 8.40 to 7.12 per cent. Despite these reductions, the titanium dioxide content of the reel averaged the same as before (at 5.2 per cent), indicating an increase in titanium dioxide retention from 63 to 73 per cent. The clay content of the reel decreased slightly; however, over-

TABLE I—Production Run on 30-pound Towel

	Per Cent Asbestos in Paper 0	2	3	4
Basis Weight (lb./24 in. x 36 in.—480)	30.0	30.1	29.8	30.4
Softness (Crush Test)	2200	1700	1680	1680
% Stretch	6.5	7.4	7.2	7.1
Wet Tensile Aged				
Machine Direction	2.7	—	2.8	2.7
Cross Direction	1.7	—	1.5	1.6
Dry Tensile (1-in. strip)				
Machine Direction	9.6	—	9.3	8.6
Cross Direction	5.7	—	5.5	5.5
Wet Tear				
Machine Direction	30	—	36	42
Cross Direction	34	—	42	52

all clay retention increased from 49 to 56 per cent, Opacity averaged 94 per cent while brightness averaged 85 per cent, the same as before the trial.

A detailed analysis at the drum-filter save-all showed that asbestos also substantially improved recoveries at both the cloudy and clear effluents. As shown in Figure 3, asbestos improved recoveries at the cloudy effluent from 44.4 to 74.1 per cent. At the same time, recoveries at the clear effluent were improved from 82.3 to 92.3 per cent. In terms of losses, asbestos reduced solids in the cloudy effluent from 0.85 to 0.38 lb./1000 gal. At the clear effluent, asbestos reduced solids from 0.27 to only 0.11 lb./1000 gal.

Opacity improved

Another mill tried asbestos in hopes of improving titanium dioxide retention and meeting opacity specifications at lower titanium dioxide levels. The grade of paper used in the trial was substance 10 opaque register bond. During this eight-hour production run, 1.2 per cent asbestos was added to the pulper, replacing three per cent clay. This addition was less than the 2.5 per cent asbestos addition that the mill had planned on making. Nevertheless, impressive results were obtained.

The titanium dioxide and clay analyses before and during the trial are shown in Figure 4. Single-pass retention calculations showed that titanium dioxide retention increased by 15 per cent during the use of asbestos. The average asbestos retention across the wire was 54 per cent. At the same time, tray-water and save-all effluent solids decreased markedly. Solids in the tray water declined from 35.7 to 15.5 lbs./1000 gal. while the solids in the save-all effluent dropped from 0.84 to 0.17 lbs./1000 gal.

Of major significance to this mill was its ability to meet its minimum opacity specification of 74 per cent at

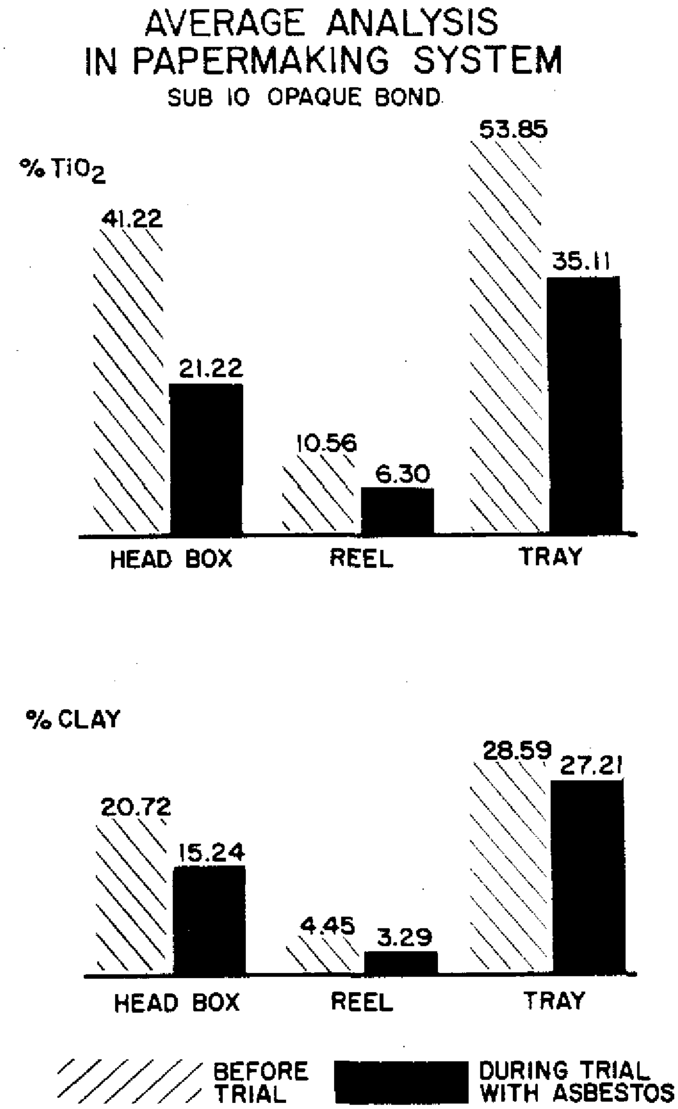

FIGURE 4—Average analyses in papermaking system producing sub. 10 opaque register bond. During this 8 - hour production run, a 1.2 per cent asbestos addition increased TiO_2 retention by 15 per cent.

lower titanium dioxide levels. The titanium dioxide content of the sheet was reduced from 10.56 per cent before the trial to 6.30 per cent with asbestos. Despite this severe drop, opacity specifications were met with 1.13 per cent asbestos in the sheet, as shown in Figure 5. Although data on opacity before the trial are limited, the curves indicate that the asbestos-bearing sheet needed 20 per cent less titanium dioxide to obtain the same opacity as the sheet without asbestos. Thus, asbestos improved the light-scattering efficiency of the titanium dioxide.

Similar results were obtained in a six-hour trial by a mill making thirty-pound pouch paper (82 G.E. brightness). A two per cent asbestos addition was made to the beater, replacing a similar amount of clay. The titanium dioxide addition was cut by 16.7 per cent in hopes of obtaining equivalent opacity values at reduced titanium dioxide levels. Retention of titanium dioxide increased from 60 to 84 per cent with the asbestos addition. Average opacity during the run with asbestos was 62.6 per cent, a slight improvement over the 61.9 per cent average before the trial. Average brightness was 85.1 per cent, up slightly from 84.6 per cent before the use of asbestos.

TABLE II—Production Run on 13.5-pound Toilet Tissue

FURNISH					PROPERTIES				
					Softness (Handle-o-Meter)			Tensile (lb./5" x 5½")	
TIME	*Pine and Broke*		*Hardwood*	*Asbestos*	Machine Direction	Cross Direction	% Stretch	Machine Direction	Cross Direction
1:25	20% Pine		80%	0	4.0	13.0	37.5	2.7	1.8
1:45	80% Pine		20%	3%	—	—	—	—	—
2:50	60% Pine	15% Broke	15%	3%	6.3	14.5	32.5	5.0	1.5
3:30	60% Pine	20% Broke	20%	3%	6.8	9.0	19.3	4.7	1.6
4:45	40% Pine	20% Broke	40%	3%	6.5	11.5	22.5	4.0	1.5
5:55	40% Pine	20% Broke	40%	3%	6.0	10.0	24.4	3.3	1.5

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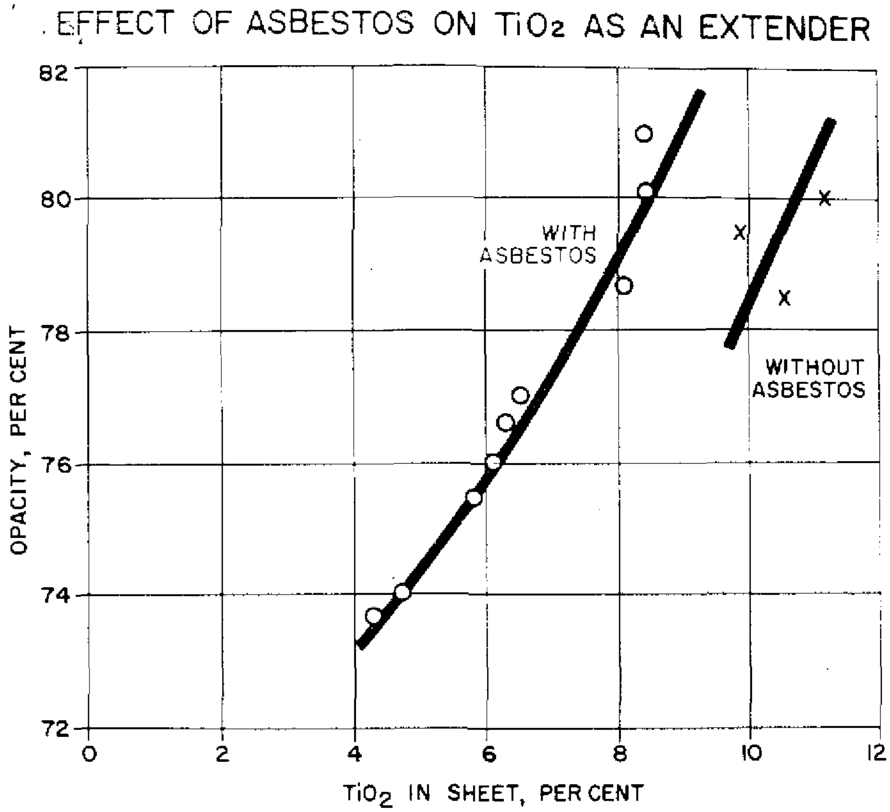

FIGURE 5—Sub. 10 opaque register bond containing 1.13 per cent asbestos met opacity specifications at lower TiO_2 levels than paper containing no asbestos. Thus, asbestos improved the light-scattering efficiency of TiO_2.

Softness improved 20%

In this trial run at another mill, enough asbestos was added to the pulper to obtain two, three and four per cent asbestos in 30-pound toweling. The object of the trial was to determine if asbestos would improve softness of the stock. The results are shown in Table I. Using the crush test as the measure of softness, the mill found that softness improved from 2200 without asbestos to 1680 with four per cent asbestos. (Lower values indicate improved softness.) Thus, an improvement of over 20 per cent was achieved.

At the same time, per cent stretch increased from 6.5 to 7.1, and wet tear strength was improved 40 per cent in the machine direction and over 50 per cent in the cross direction. There was no significant change in either the wet tensile aged or dry tensile strength with the addition of asbestos.

Another mill took advantage of the improved softness provided by asbestos by increasing its use of pine in the furnish. This mill normally used an 80 per cent hardwood, 20 per cent pine furnish, because it needed at least 80 per cent of the short-fibered hardwood to meet softness specifications of its 13.5 pound toilet tissue.

As shown in Table II, a three per cent asbestos addition was used during the four-hour production run while the mill made various adjustments in its furnish. For the first three hours, pine and broke were increased to 80 per cent of the furnish. Then, for the last hour, a 60 per cent pine-broke furnish was used.

The properties of the tissue are also shown in Table II. With the 80 per cent pine-broke furnish, softness declined somewhat according to Handle-o-meter readings. (Higher values indicate reduced softness.) When the pine and broke in the furnish were reduced to 60 per cent, softness values began to return to pre-trial conditions in the machine direction and were better than before the trial in the cross direction.

Per cent stretch and tensile values went through similar cycles. Based on this trial and subsequent tests, mill management concluded that the increased softness provided by asbestos would allow them more flexibility in their choice of furnish components and still produce equal or better quality tissue.

These typical examples from mill experience show that asbestos can be an effective retention agent, extender, and softening material. Proper use can lead to extensive savings and improvements in the papermaking process.

This paper contains asbestos too...

The paper on which this reprint was printed contains Union Carbide's high-purity asbestos "T." The rigid opacity and brightness specifications for this high-quality paper were maintained when asbestos "T" was substituted for part of the TiO_2 in the furnish. This substitution allowed substantial savings in furnish costs.

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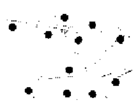
Have you used these PELLETS as a wet-end additive?

These pellets of Union Carbide high-purity asbestos burst into short, non-abrasive fibers when added to a pulper or beater. The fibers disperse uniformly throughout the pulp and give these improvements and cost savings:

over 100 Mills have ...



IMPROVED PITCH CONTROL

Union Carbide asbestos effectively prevents pitch buildup. In this way, it helps keep cleaner felts and fourdrinier wires, reduces machine breaks and down time, and reduces rejections for paper blemishes. Several mills with severe pitch problems have found that 1% asbestos keeps pitch harmlessly dispersed throughout the sheet.

EFFECTIVE TiO_2 EXTENDER

Asbestos improves opacity by optimizing the light-scattering efficiency of TiO_2. Thus, higher opacity can be obtained at lower TiO_2 levels, reducing TiO_2 costs. A typical mill reduced TiO_2 content of its sheet from 10.6 to 6.3% without any loss of opacity.

IMPROVED RETENTION OF FURNISH

Positively charged asbestos strongly attracts negatively charged pigments and fillers. A typical mill improved TiO_2 retention from 65.5 to 88% with 2% asbestos and saved $3.60 per ton. Another improved single-pass retention of all fillers by 21% with 3% asbestos. Also, the large surface area of asbestos readily absorbs dyes, improving retention and reducing two-sidedness.

INCREASED SOFTNESS

Tissues and towels containing Union Carbide asbestos have improved softness. One mill increased softness of towels by 20% with 3% asbestos. It also improved wet tear and per cent stretch. Another mill used asbestos to replace hardwood with stronger softwood without sacrificing quality. The change also netted significant savings in furnish costs.

BETTER SAVEALL EFFICIENCY

With asbestos in the saveall, mills have improved their recoveries of solids. Improvements have been made in flotation, filtration, and sedimentation types of savealls. One mill increased saveall recoveries from 74 to 93%, saving $27,000 per year. By discharging a clearer effluent, it also reduced river pollution.

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UNION CARBIDE **ASBESTOS**

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