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September 5, 1978

Mr. John Marsh
Director, Environmental Affairs
Raybestos Manhattan Corp.
100 Oakview Drive
Trumbull, CT 06611

Dear Mr. Marsh:

The circumstances surrounding the work by Krishna Seshan of the University of California on asbestos fibers released from brake linings is unfortunately very typical of the irresponsible attitude towards environmental hazards and asbestos fiber in particular. The pattern includes initial release of the information in a sensational manner to the press with a promise that the complete work will be published at a later date in a respected journal. This is followed by editorials in and/or letters to the editors of other journals covering this same material which was released to the press. When the work is finally published, it is generally found to bear no resemblance to the promises made in the original releases. The allegations which were originally made are unfounded and in fact, the final paper may leave a totally different impression than was created in the initial releases.

The final publication by Mr. Seshan which appeared in the July 1978 issue of Environmental Research is a relatively straight-forward discussion on the use of dark field electron microscopy to study "deformed chrysotile". As he pointed out, however, the samples selected for brake lining dusts did not represent the material which would be present in the air and heavily traveled areas. It is typical of the dust to which workers in a brake lining shop would be exposed

The most significant point about Seshan's article is that there is no reference whatsoever to the health effects of brake lining dust and particularly the health effects that have been ascribed to deformed chrysotile fibers in the advance publicity. Many of the newspaper articles reported that experts at the Mt. Sinai School of Medicine had determined that deformed chrysotile was more biologically active than normal fibers. This is totally incorrect. In a paper by A. M. Langer, et al in the Journal of Toxicology and Environmental Health, 4, 173-188 (1978), it is stated that:

> "It appears that the less mechanically degraded the surface of the fiber, the greater the biological response."

The source of original opinion which was expressed by Mr. Seshan in the press is completely unknown at the present time.

In the editorial which appeared in the April issue of the American Industrial Hygiene Association Journal, it is claimed that Mr. Seshan's technique now resolved the controversy which purportedly exists concerning the fate of asbestos fibers during the normal wear of brake linings. Some contend that the fibers are destroyed, whereas others contend that a high percentage of the fibers remain intact. In all studies that I am aware of on brake lining dusts, the so-called deformed fibers observed by Mr. Seshan would have been included in the total determination of asbestos fibers remaining after brake lining wear. The techniques, therefore, do not resolve such a controversy if, in fact, it does exist.

In addition to Mr. Seshan's irresponsible handling of the information prior to publication, there are many points in his paper which indicate that he is not particularly well qualified in the field of electron diffraction.

Very truly yours,

J. P. Leineweber

J. P. Leineweber, Ph.D.
Technical Director
Health, Safety & Environment Dept.

JPL:jh

cc P. Kotin, M.D.
E. M. Fenner
D. Poutiatine

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ENVIRONMENTAL RESEARCH 16, 383 – 392 (1978)

# On the Utility of Dark-Field Electron Microscopy in the Determination of the Degree of Deformation In Chrysotile Asbestos: An Environmental Research Application

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Received June 21, 1977

The degree of microcrystalline deformation in fibers of chrysotile asbestos may be distinguished using high resolution dark-field electron microscopy. This is demonstrated by comparing undeformed chrysotile with Union Internationale Contre le Cancer (UICC) standard reference samples. The UICC samples are shown to be partially deformed as a result of milling in the mixing process. Samples of used and unused brake shoe lining dust were examined using this technique; it is shown that chrysotile asbestos in various stages of deformation—relatively undeformed to heavily deformed—survives in automobile brake drum dust. Such dark-field images can serve to identify the source of asbestos found in environmental pollution samples.

## INTRODUCTION

There is a controversy in the literature whether or not fibers of chrysotile asbestos survive in automobile brake drum dust: two studies (Rohl *et al.*, 1976; Alste *et al.*, 1976) report that the fibers do survive and earlier work (Lynch, 1968; Hickish and Knight, 1970) reports that they do not. The latter claim that the chrysotile is converted to forsterite under the high temperatures attained in the braking process.

As high resolution dark-field electron microscope images are sensitive to the degree of deformation, they can be used to distinguish between deformed and undeformed fibers and thus to resolve these two differing sets of results. It is shown using this technique that chrysotile asbestos fibers in various states of deformation—relatively undamaged to heavily deformed and recrystallized—exist in automobile brake drum dust.

## SAMPLE SELECTION AND PREPARATION

Four samples were selected: (A) undeformed chrysotile ore samples from serpentine outcrops of Calaveras County (California); (B) slightly deformed UICC reference standards of Canadian chrysotile milled during preparation to reduce fiber size (Timbrell *et al.*, 1969); (C) unused brake lining dust, collected during burnishing prior to installation of new brake shoes; and (D) brake drum dust collected from the front and rear brake drums of a State vehicle obtained during brake shoe service (Seshan and Smith, 1977).

Samples were transferred directly to Formvar-coated electron microscope grids and coated with carbon on both sides.



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## EXPERIMENTAL

As the high resolution dark field method is described in great detail elsewhere (Hirsch *et al.*, 1969), only a very brief description is included here. An electron beam striking a polycrystalline specimen with grains of different orientation (e.g., A and B in Fig. 1) is diffracted into cones, causing the typical polycrystalline ring pattern. The high-resolution dark-field method consists of tilting the incident beam so that the part of the diffracted ring passes through the optic axis of the microscope (Fig. 1b). The tilting is accomplished with the electronic beam tilt device. Then an aperture collects intensity only from those crystallites diffracting into this part of the ring, e.g., B (Fig. 1c).

Various factors involved in the interpretation of the diffraction patterns of chrysotile asbestos fiber bundles are shown in Fig. 2. The actual lattice of chrysotile is a defected, scrolled crystal with fiber axis along *a* (Yada, 1967). The reciprocal lattice of this crystal should be some form of a spiral, equispaced along the $a^*$ axis. Zvyagin (1967) and Whittaker (1966) have studied diffraction effects from concentric cylinders. How deformation and shear will affect the diffraction patterns has not, to the author's knowledge, been studied and is under study here.

The simpler case of an undeformed defect-free chrysotile fiber, where the fiber is idealized as a series of concentric cylinders, as first proposed by Whittaker (1969), is shown in Fig. 2i. The reciprocal lattice then consists of a series of concentric rings; shown in Fig. 2ii (only the two rings in the 2kl layer are drawn). The electron diffraction pattern represents the intersection of the reflecting or Ewald sphere (ES, Fig. 2ii) with these rings (Hirsch *et al.*, 1969). This ought to result in a series of spots as shown in the -2kl layer line. Streaked patterns are, however, obtained from single fibers of chrysotile (Yada, 1967; Seshan and Smith, 1977).

The explanation for the streaking probably lies in refraction effects and the fiber shape (Yada, 1969); it could also result from the various faults produced during the

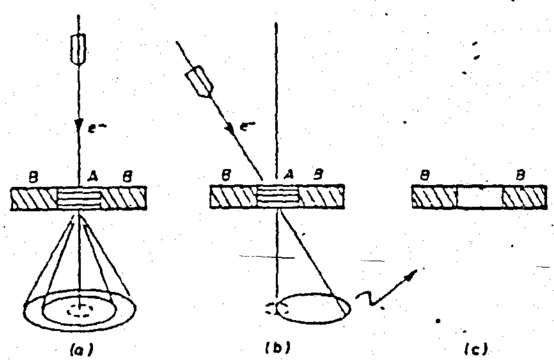


FIG. 1. Illustration of the high resolution dark-field method: (a) The bright-field image from a selected area of a polycrystal, illustrated with two grains, A and B. (b) The situation after gun tilt: only a portion of the diffracted intensity is collected by placing the objective aperture as shown. (c) The resulting high-resolution dark-field image with only favorably oriented grains, e.g., B showing diffracted intensity or "lighting up."

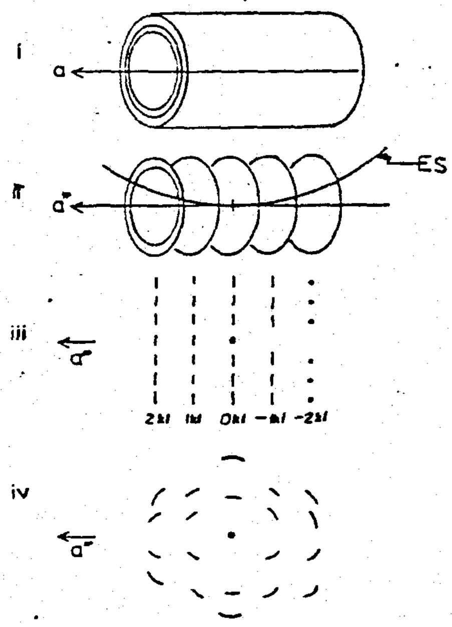


FIG. 2. Illustration of the real and reciprocal lattice of a defect-free chrysotile fiber (i) and (ii) idealized as a series of concentric cylinders. The actual structure is a defected spiral sheet (Yada, 1967). The reciprocal lattice of the ideal fiber is then a series of equispaced concentric rings along the $a^*$ axis, as in the 2kl layer; when these rings intersect, the Ewald sphere (ES) spots ought to be produced as shown on the -2kl layer line. However, streaks are observed (Yada, 1967), arising probably from the spiral shape of the fiber defects and strains formed during the scrolling process. When a fiber bundle (fibers of different orientations) is imaged, the layer lines are smeared out, yielding a typical "arcuate" pattern as in Fig. 3b.

grówth of the crystal. The influence of these faults on the diffraction patterns and their influence on deformation needs further study.

When bundles of fibers are involved, the streaks are replaced by arcs (Figs. 2iv and 3b), showing a strong tendency toward a texture and yielding the typical "arcuate" patterns observed by several researchers (e.g., Rohl *et al.*, 1976). The dark-field image obtained by imaging any part of the arc, as shown in Figs. 1 and 3b, should yield uniform intensity, *if* the crystal is homogeneous. This is the case to be expected *only* in the case of the undeformed fibers—and is consistent with the experimental observations in Figs. 3a and 3b.

## RESULTS

Bright- and dark-field images of naturally occurring chrysotile (A) are shown in Fig. 3. The dark field is obtained by imaging a portion of the diffracted intensity, as explained above. The result is a uniform contrast, as would be expected from an undeformed crystal.

The striking feature of the dark-field images is the great intensity along the hollow canals and this needs further investigation. The intensity difference cannot be explained on the basis of differences in absorption alone; it appears that some

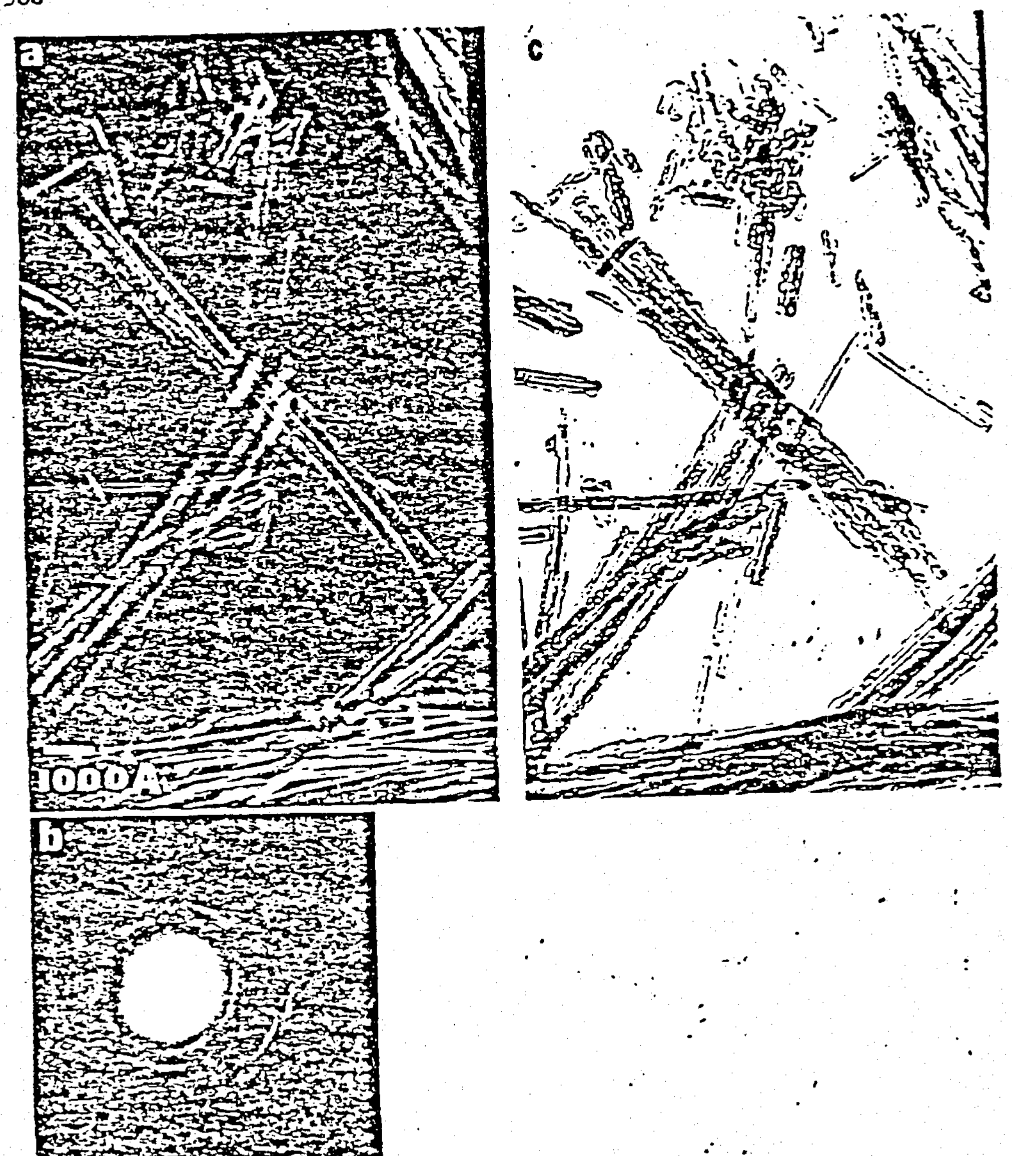


FIG. 3. Sample (A): natural chrysotile. (a) and (b) Dark-field and diffraction pattern. Notice the unusually bright and undamaged internal canals; the crystal is homogeneous and undeformed. A faint outline of the objective aperture is seen in the diffraction pattern of Fig. 3b. (c) Illustrates the blistering as a result of exposure to the beam.

diffraction processes are operative: Notice that the canals are sometimes bright and sometimes dark. In the crystalline part, however, the intensity is uniform and it is clear that these fibers are free of gross deformation.

Chrysotile fibers, like most sheet silicates, are beam-sensitive to 100-keV electrons (Langer *et al.*, 1974; Seshan, 1975). Precaution must therefore be exercised while obtaining the high resolution dark-field images, because upon focusing the

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condenser, the fibers tend to become blistered. In the dark-field image shown in Fig. 3a, precaution was taken to *prevent* any beam damage; the condenser was not focused, and the beam was tilted in the dark field mode. The condenser was then

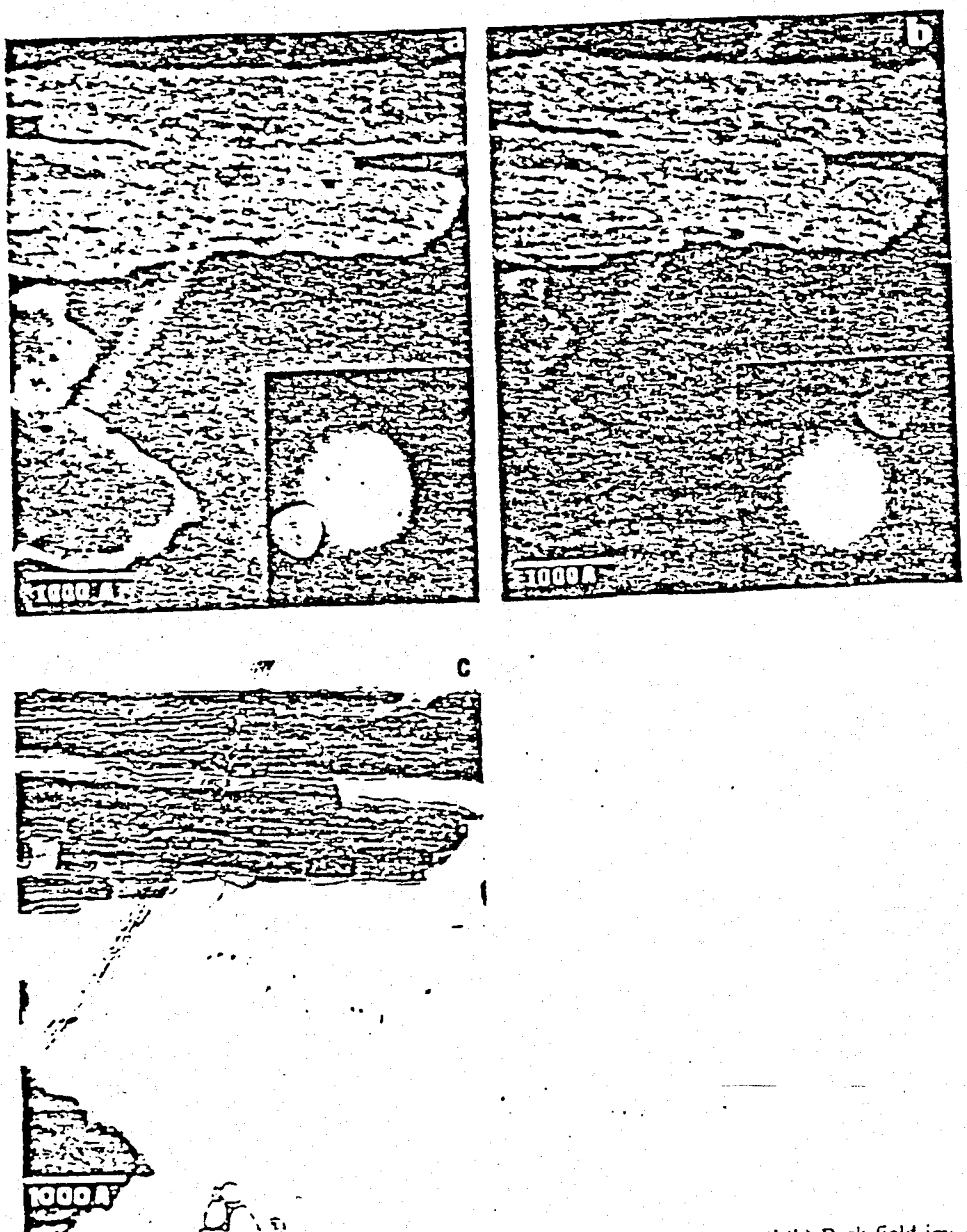


FIG. 4. Sample (B): UICC Standard Reference Canadian chrysotile. (a) and (b) Dark-field images that illustrate that the ball milling during the mixing step converts the chrysotile into a fine-grained polycrystal. The aperture is moved from one part of the ring to another, resulting in an entirely different set of grains lighting up. (c) The bright-field image from which little information can be obtained.

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focused to obtain the diffraction pattern shown in Fig. 3b. The resulting beam damage is shown in Fig. 3c. The use of beam sensitivity to distinguish chrysotile from other non-beam-sensitive materials, e.g., the amphiboles, has been discussed by Langer *et al.* (1974).

Dark- and bright-field images of deformed UICC standards (B) are shown in Figs. 4a–4c). The effects of deformation are clearly seen in the dark-field images (4a and 4b) and in the electron diffraction patterns but not in the bright-field

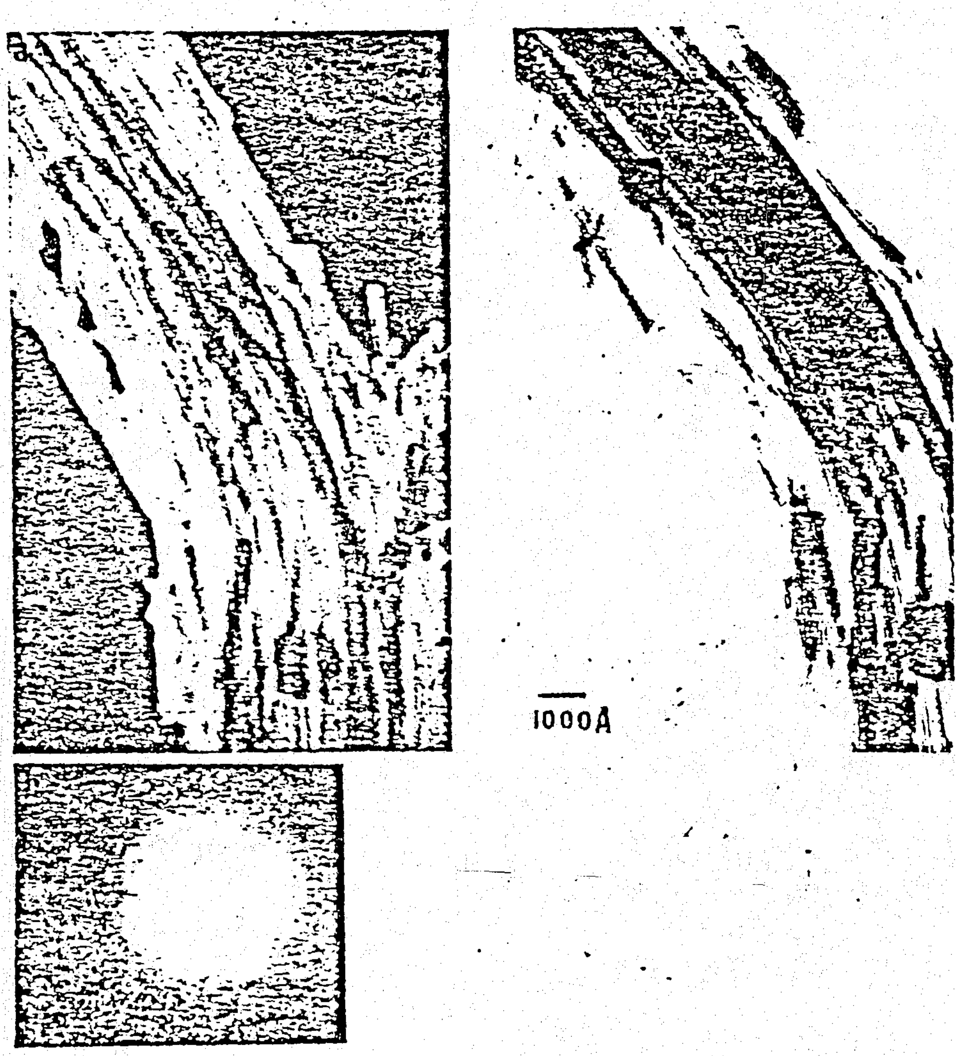


FIG. 5. Sample (C): Burnishing dust from an automobile brake drum prior to installation. (a) Dark field, (b) diffraction pattern, and (c) bright field. Notice the well-preserved canal which shows up (the dark-field image) in (a), indicated by the arrow and arrowhead. This and the well-preserved diffraction pattern (b) shows that the fibers are not as deformed as the UICC samples—a conclusion that cannot be inferred from the bright-field image (c).

images (4c). The clear internal canals of the undeformed sample (A) are destroyed; there appear small submicron (100 Å) areas which light up as if they were grains or microdomains of different orientations; consistent with this observation, the strongly textured diffraction patterns of the undeformed fibers (Fig. 3) are changed to those of a polycrystal. At the present the crystallographic and microstructural nature of the deformation is not clear and warrants further study. The effect of translating the aperture to a different part of the diffracted ring is shown in Figs. 4a and 4b. The result is that "grains" in a different orientation "light up" or show diffracted intensity signifying that this is truly a diffraction effect.

To isolate the effects of deformation during the braking process, unused brake shoe burnishing dust (C) was examined (Figs. 5a and 5b). The bright-field image (B) is not informative, whereas the dark-field image clearly shows some intact internal canals (see arrow and arrowhead Fig. 5a) resembling the undeformed

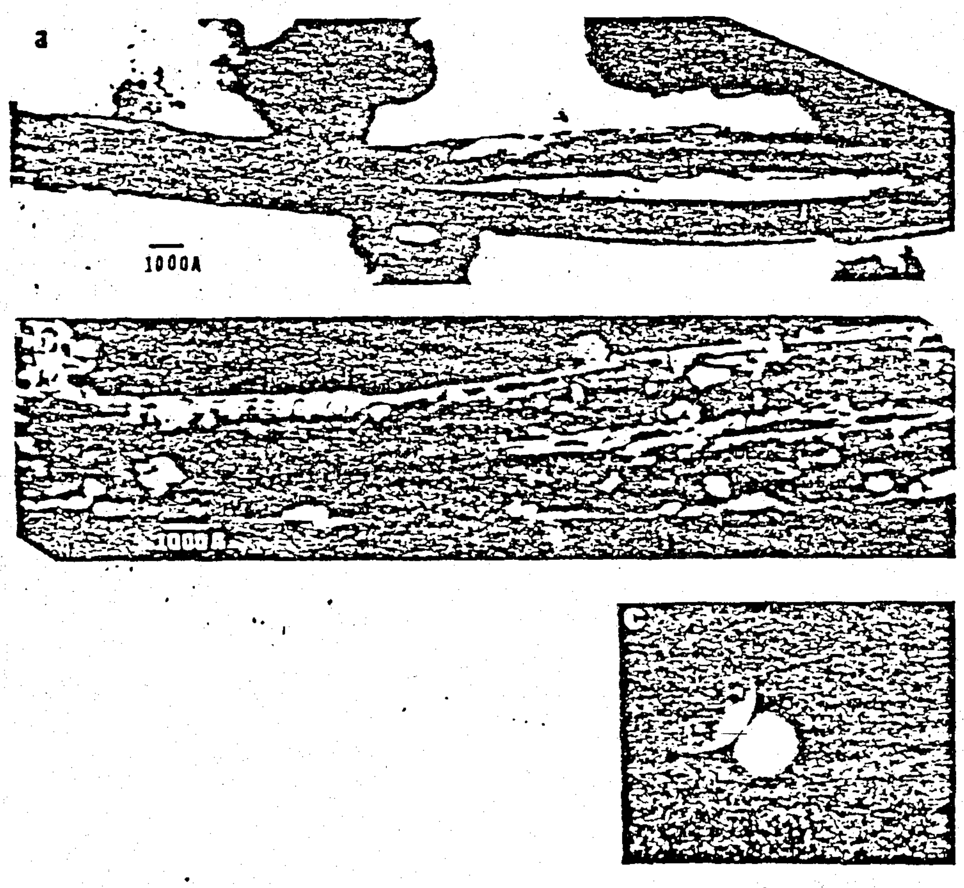


FIG. 6. Sample (D): Brake drum dust after use in a state vehicle. (a) Bright field and (b) dark field. Although the bright field is not distinctive, the high-resolution dark field and the selected area diffraction patterns are remarkably different. The crystal is quite inhomogeneous with very large grain sizes; this can happen for a variety of reasons (see text).

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chrysotile (Fig. 3). There are also small deformation domains which clearly resemble the UICC standard (B) samples. These fibers are therefore deformed less than the UICC standard samples (Fig. 4), as some intact internal canals can still be seen. It is impossible to derive this conclusion from the bright-field range.

Samples of heavily deformed chrysotile fiber found in brake drum dust are shown in Fig. 6 in the bright and dark field. Whereas the effects of deformation are not evident in the bright-field image, the difference in the dark-field image is quite striking. The crystal is inhomogeneous. This is reflected in the electron diffraction pattern, now showing a number of spots (Fig. 6c). The mottled contrast of black and bright areas could arise from one of several causes: severe surface deformation leading to uneven crystal thickness, conversion (or "grain growth" under heat and deformation) to a large grain polycrystal, or transformation of local areas into a new crystalline phase (e.g., forsterite). Further investigation into carefully deformed chrysotile is required to decide which it is. It is, however, quite clear that these identifying effects are associated only with the samples found in the used brake drum dust.

Undeformed and unaltered chrysotile is also found in the brake drum dust collected after use (sample D, Fig. 7). This was confirmed by electron diffraction patterns which were indexed after the camera constant was calibrated using a co-deposited gold standard, with the following results:

| | | | | |
|---|---|---|---|---|
| Used brake dust | diameter (Å) | 2.62 | 2.34 | 1.49 |
| Yada (1967) | diameter (Å) | 2.60 | 2.30 | 1.46 |
| | hkl | 130 | 220 | 005 |

There is also clear dark-field evidence that not all the fibers are deformed. Figure 7 shows the dark- and bright-field images of fibers found in the brake drum dust; the dark-field image resembles that of the UICC chrysotile asbestos (B, shown in Fig. 4) and those in the unused brake lining (C, shown Fig. 5), the "grain sizes" being the same as in the UICC samples. Based upon this observation, it is concluded that a variety of products ranging from almost undeformed to completely transformed chrysotile products exist in brake drum dust.

## DISCUSSION AND CONCLUSIONS

It is demonstrated that high-resolution dark-field electron microscopy can distinguish the degree of deformation in chrysotile asbestos fibers. In particular, it has been shown that UICC standard chrysotile has undergone microdeformation as a result of ball milling in the preparation step. The dark-field method may then be used by environmental researchers to trace the origins of asbestos fibers.

The dark-field images suggest that there are significant changes in the microstructure of chrysotile upon deformation, the cystallographic and microstructural details of which are complex and are worthy of further study.

There are several references to the beam sensitivity of chrysotile (Yada, 1967; Langer *et al.*, 1974). The utility of using this effect to distinguish chrysotile from other non-beam-sensitive materials could be of value to environmental pollution research.

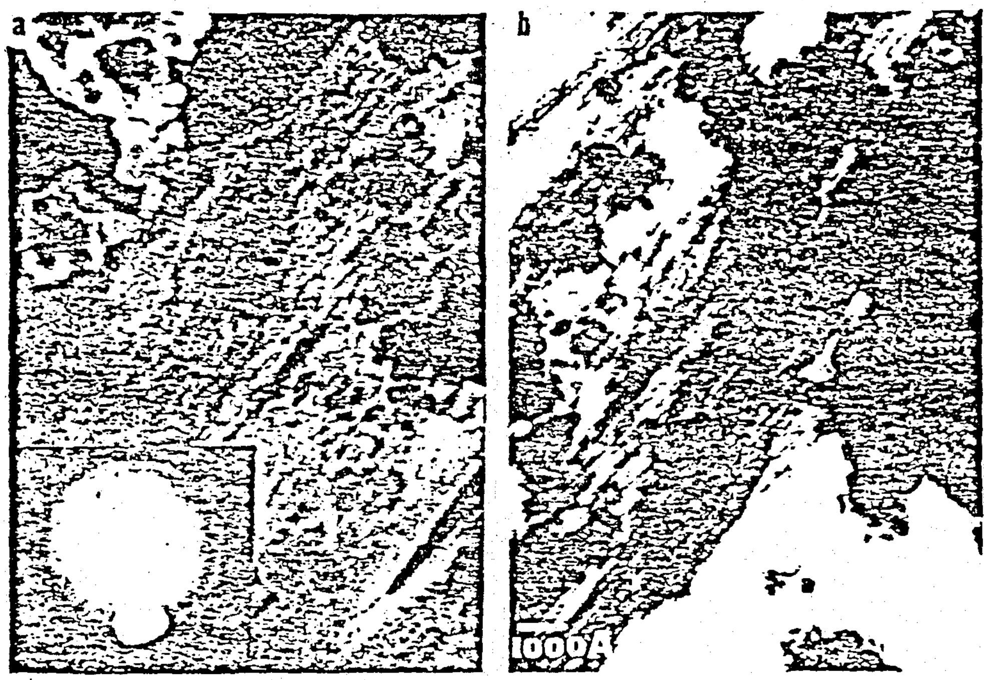


FIG. 7. Sample (D): Automobile brake drum dust after use. (a) Dark field and (b) bright field. This shows that relatively undeformed fibers survive in the brake drum dust. The grain sizes in the dark-field images (a) are comparable to those in the burnishing dust (Fig. 5a) or the UICC samples (Fig. 4a), indicating little deformation during use.

This preliminary study also shows the need to study details of the growth of the chrysotile asbestos and the nature of the defects involved, if all the diffraction and deformation effects are to be understood.

## ACKNOWLEDGMENTS

I thank G. R. Smith of the Air Industrial Hygiene Laboratory (AIHL) Berkeley for bringing this problem to my attention and preparing the samples. I acknowledge useful discussions with him and Dr. Walter John and thank Professor J. Washburn for encouragement. This work was supported financially by the U.S. Energy Research and Development Administration.

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# Automobile brake linings may be a health hazard . . .

Automobile brakes — normally associated with averting danger — may, in fact, be producing dangerous substances and releasing them into the atmosphere, according to a researcher at the University of California's Lawrence Berkeley Laboratory (LBL).

The concern is being expressed by Krishna Seshan, a materials science engineer at LBL's Materials and Molecular Research Division, who has shown that automobile brake drum linings produce substances that may be hazardous to our health.

The substances that Seshan has been studying are thin, single fibers of asbestos — so thin, in fact, that even the most powerful microscopes illuminated with visible light cannot detect their presence. Looking through an electron microscope — an instrument with as much as 10,000 times the resolution of conventional light microscopes — Seshan found that the minute particles of dust created by automobile brake drums contain filaments of deformed "chrysotile" asbestos, a type of asbestos that many researchers consider a health hazard.

These fibers, according to public health officials, may not be particularly dangerous to the average citizen since people driving cars breathe, at most, only small amounts of brake drum dust. The real hazard of chrysotile asbestos, say these experts, is to workers such as brake repairmen who use compressed air to blow asbestos fibers from brakes daily and may breathe as much as a million particles of asbestos in each cubic meter of air.

Many medical experts, most notably Dr. Irving Selikoff of Mt. Sinai Hospital in New York City, contend that chrysotile asbestos is hazardous to lung tissue because such forms are minute and rough enough to prevent the mucous covering of the lung from dislodging it. Once in the lungs, asbestos never dissolves. And this substance is often found in the lungs of factory workers, construction workers, auto mechanics, office workers and even in the lungs of spouses and children of asbestos workers.

Asbestos is a mineral, says Seshan. And approximately 900 million tons of this chrysotile mineral are mined in the United States annually. Much of it is milled or woven into a blanket-like material, then used to insulate or fireproof equipment such as steam pipes, roof linings and ship hulls.

To date, Seshan estimates, about 90 percent of the asbestos used in the United States is milled under heat and pressure. And, because of these processing methods, most of the asbestos we breathe is deformed in some way or another. Still, many medical researchers in the U.S. have ignored the health problems connected with these asbestos deformations, says Seshan.

For that reason, Seshan, an expert in electron microscopy, was asked by the California Department of Health's Air and Industrial Hygiene Laboratory to help develop a method of identifying asbestos fibers found commonly in air samples. This investigation, claims Seshan, was the way in which he was introduced to the health hazards of chrysotile asbestos and how he eventually turned to the problem of automobile brake drums.

According to Seshan, most automobile brakes operate by grinding pads against a lining of heat-resistant asbestos, an action that introduces what he terms "process defects" in the asbestos fibers heated and ground against hot brake drums. Such fibers had long been suspected by many scientists to be a constituent of brake drum dust. But other researchers contended that the high friction developed in braking simply disintegrates the asbestos and leaves no asbestos fibers at all.

Neither theory could be verified, because a microscopic technique capable of illuminating chrysotile asbestos with their defects had not yet been applied. Seshan however, solved this controversy by employing a special microscopy technique.

Using what electron microscopists term a "dark field image" — a method of observing small particles by looking at the diffracted or "scattered" electrons — Seshan managed to illuminate the tiny fibers. By doing this, he not only confirmed that chrysotile asbestos is present in automobile brake drum dust, but also discovered that some of the fibers show further significant damage.

In a preliminary report on the project soon to be published in the scientific journal, ENVIRONMENTAL RESEARCH, Seshan concludes "that chrysotile asbestos fibers in various states of deformation — relatively undamaged to heavily deformed and recrystallized — exist in automobile brake drum dust."

What this means, he says, is that some of the asbestos in brake drum dust may be more of a

*more on A-26 . . .*



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health hazard than the ordinary chrysotile form, because much of it is further deformed. And deformation in asbestos fibers, say increasing numbers of scientists, may play a significant role in causing lung disease or cancer.

"There are many factors that contribute to environmental pollution," says Seshan. "But what we have shown is that brake drum dust certainly introduces deformed asbestos into th atmosphere."

Samples for the research were prepared by G.R Smith of the California State Health Department's Air and Industrial Hygiene Laboratory. Lawrence Berkeley Laboratory is operated by the University of California under contract with the U.S Department of Energy.

## now it's Andersen Samplers

Andersen 2000 Inc., manufacturer of the widely-known Andersen samplers and control equipment line known as HEAF and CHEAF, has sold the sampler division in its entirety, including patents, tooling, manufacturing rights and existing contracts to Thomas P. Roth, who was President of Andersen 2000 Inc. for the past eight years. Mr. Roth announced that the sampler division will be changing its name from Andersen 2000 Instruments to Andersen Samplers Inc. and that plans are underway to expand the product line as rapidly as possible. Mr. Roth further stated that the sales rate this year indicates that the company will experience its best year since inception. The new company is located at 4215-C Wendell Drive, Atlanta, Georgia 30336. Phones: (404) 691-1910 and (800) 241-6898.