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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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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

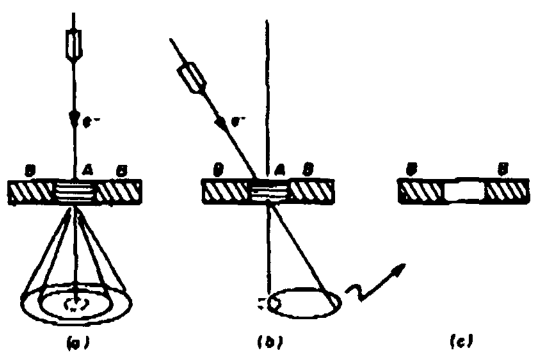

FIG. 1. Illustration of the high resolution dark-field method: (a) The bright-field image from a selected area of a polycrystal, illustrated with two grains, A and B. (b) The situation after gun tilt; only a portion of the diffracted intensity is collected by placing the objective aperture as shown.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

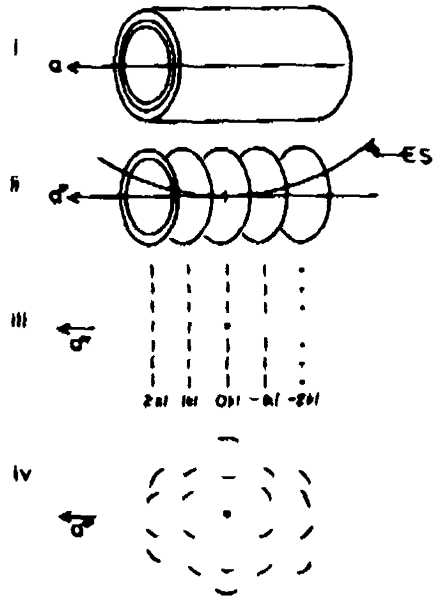

FIG. 2. Illustration of the real and reciprocal lattice of a defect-free chrysotile fiber (i) and (ii) idealized as a series of concentric cylinders. The actual structure is a defected spiral sheet (Yada, 1967). The reciprocal lattice of the ideal fiber is then a series of equispaced concentric rings 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.

growth 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

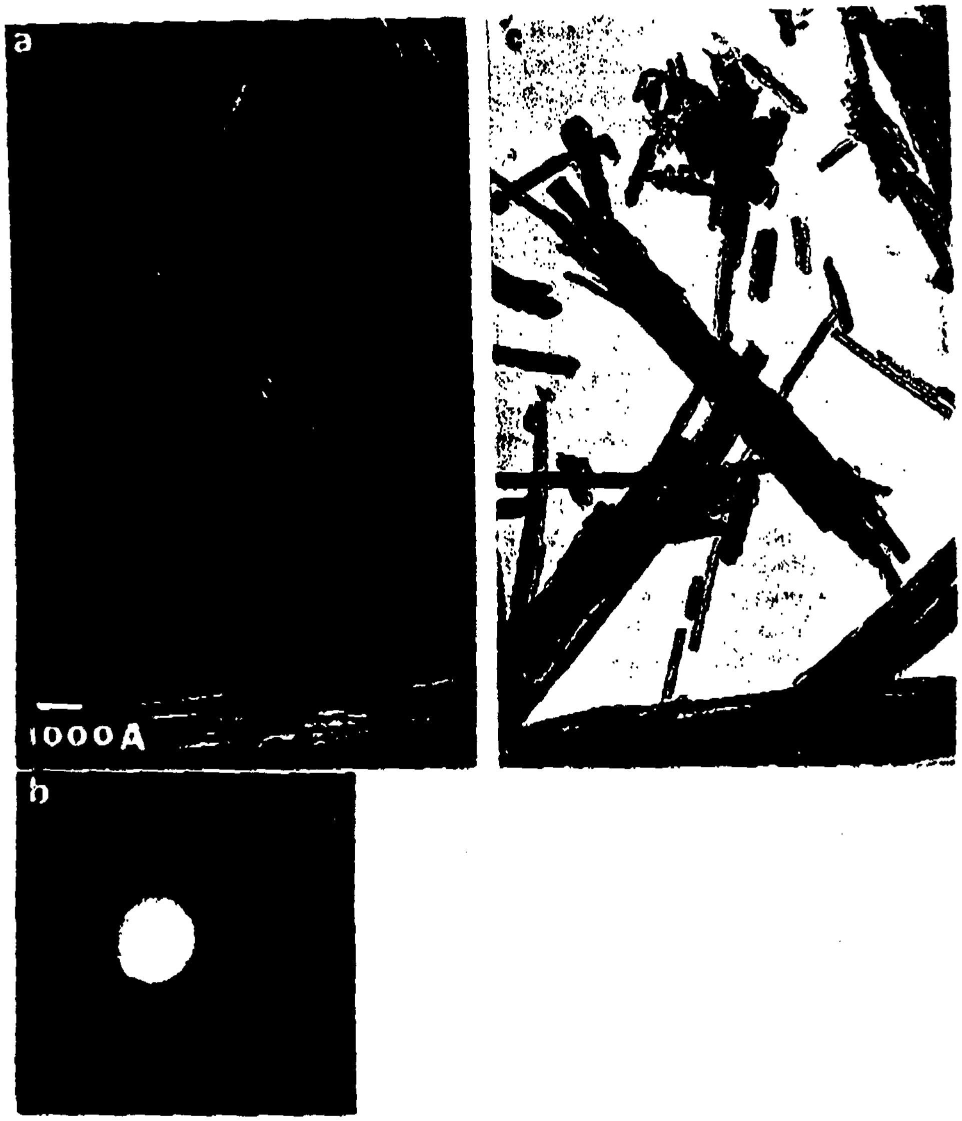

FIG. 3. Sample (A): natural chrysotile. (a) and (b) Dark-field and diffraction pattern. Notice the unusually bright and undamaged internal canals; the crystal is homogeneous and undeformed. A faint outline of the objective aperture is seen in the diffraction pattern of Fig. 3b. (c) Illustrates the blistering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

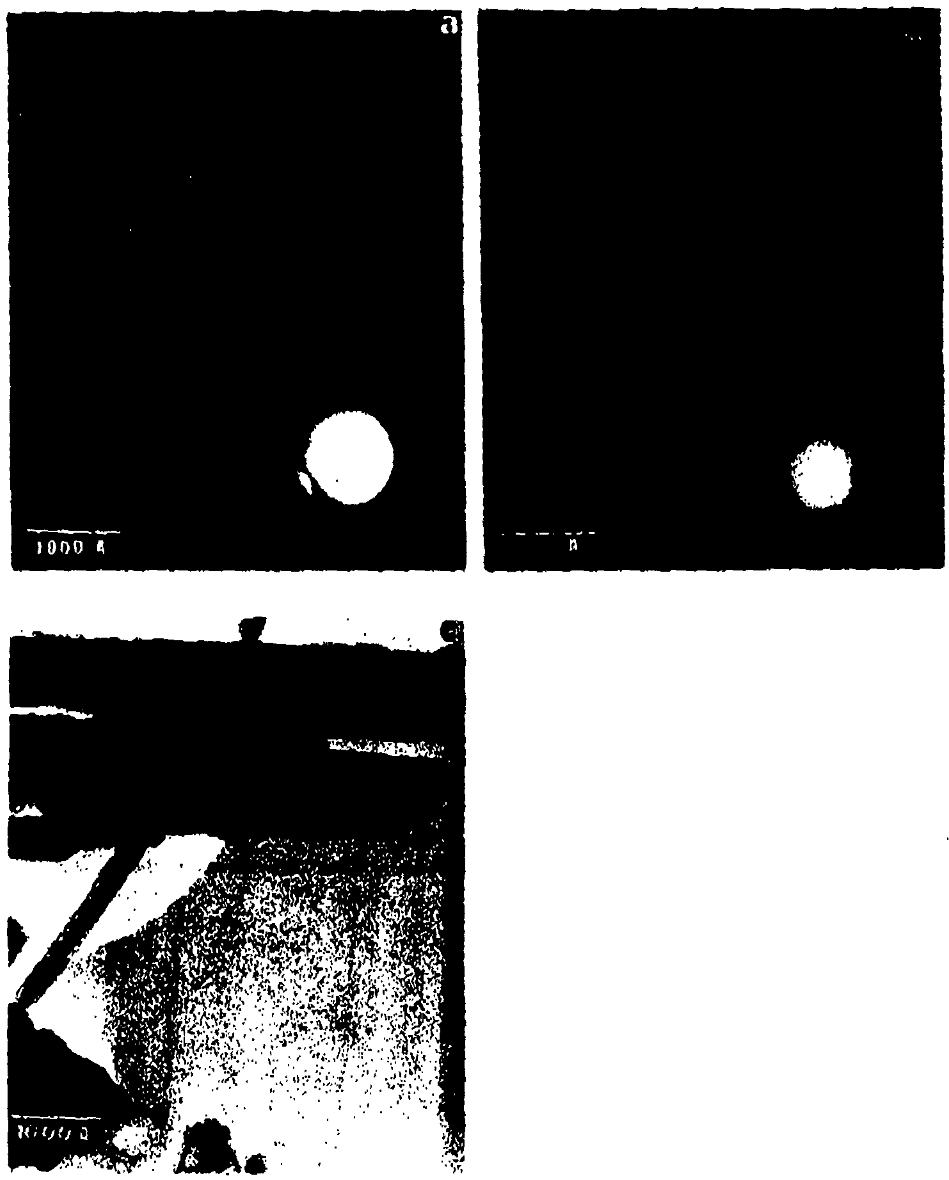

FIG. 4. Sample (B): UICC Standard Reference Canadian chrysotile. (a) and (b) Dark-field images that illustrate that the ball milling during the mixing step converts the chrysotile into a fine-grained polycrystal. The aperture is moved from one part of the ring to another, resulting in an entirely different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

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

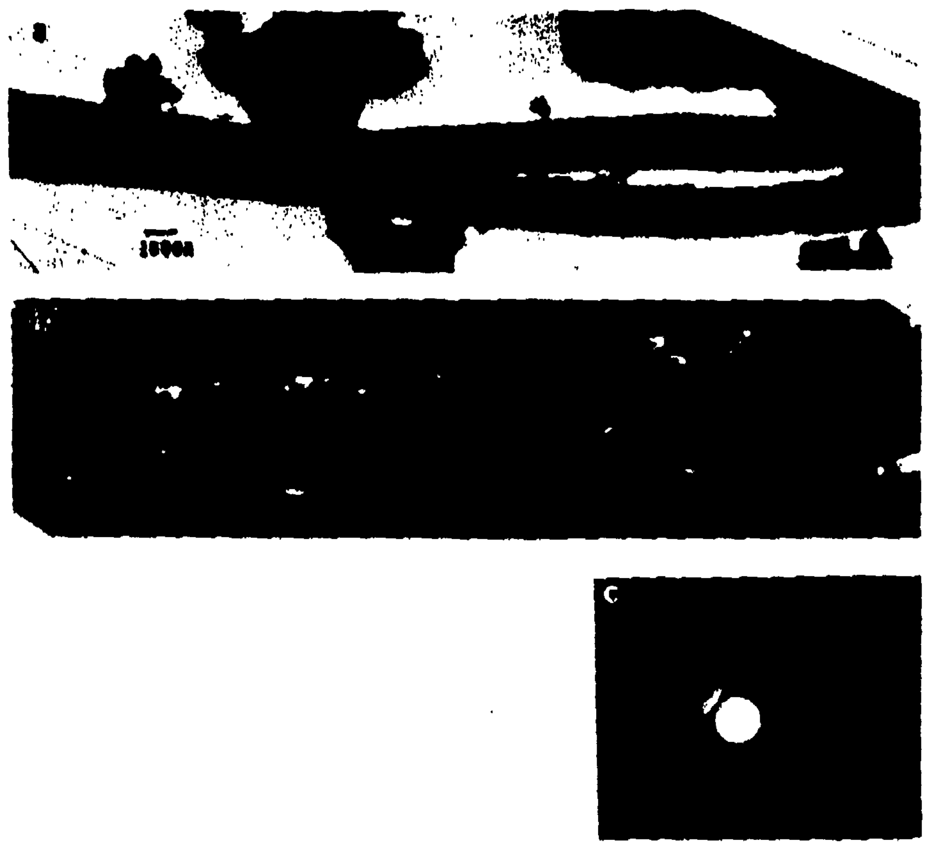

FIG. 6. Sample (D): Brake drum dust after use in a state vehicle. (a) Bright field and (b) dark field. Although the bright field is not distinctive, the high-resolution dark field and the selected area diffraction patterns are remarkably different. The crystal is quite inhomogeneous with very large grain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

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.

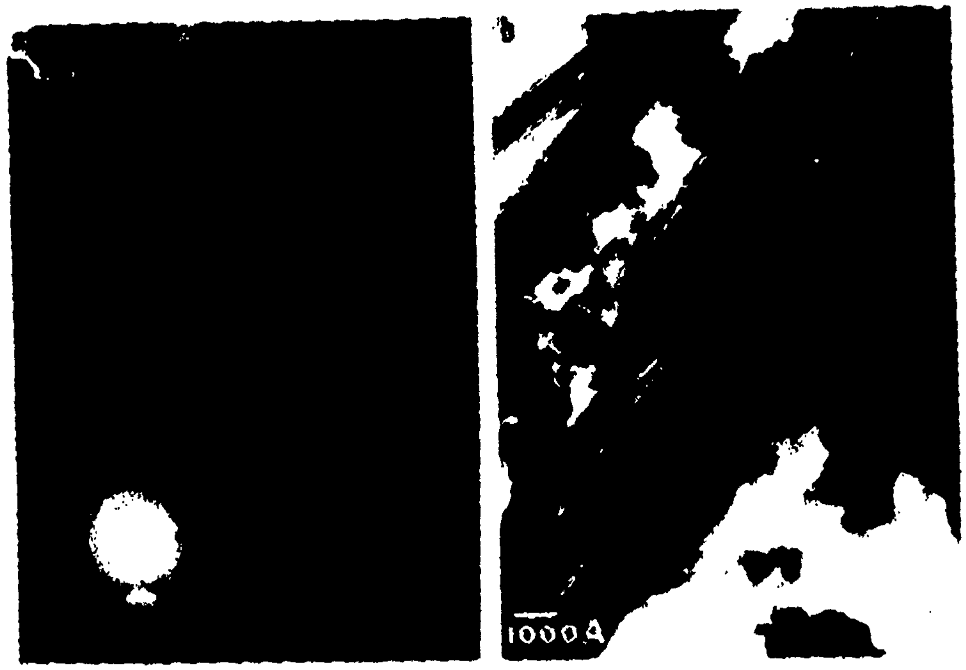

FIG. 7. Sample (D): Automobile brake drum dust after use. (a) Dark field and (b) bright field. This shows that relatively undeformed fibers survive in the brake drum dust. The grain sizes in the dark-field images (a) are comparable to those in the burnishing dust (Fig. 5a) or the UICC samples (Fig. 4a),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

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TOXIC MATERIALS NEWS IN BRIEF

Cancer control and prevention has been largely ignored by National Institutes of Health, UCLA Public Health Dean Lester Breslow told a national cancer conference recently, and suggested the government's cancer prevention program be taken out of National Cancer Institute. "Time after time in the past 25 years the National Institutes of Health has relegated cancer control and disease control generally to the back washes of the institutes, failed to seek adequate funding or take leadership, or literally squeezed it out of the budget," Breslow said. "Cancer control needs its own strong advocates."

President Carter, meanwhile, has decreed that April is "Cancer Control Month" -- a designation intended to educate people to "take advantage of available resources to prevent needless suffering and death... Cause and prevention research remains one of our highest priorities," Carter said, "because prevention offers the best hope for ultimate control of cancer."

National Cancer Institute has announced publication of bioassay reports on dye pigment diarylanilide yellow and pesticides methoxychlor, malathion and trifluralin. Only trifluralin was found to be carcinogenic -- in the livers of female mice. All four reports will be available next week from Office of Cancer Communications, NCI, Bethesda, Md. 20014.

Asbestos brake [redacted] fibers which are deformed enough to be especially hazardous, La[redacted] has announced. Seshon said [redacted] the hazard presented, and when these fibers are released in the air, they expose repairmen to heightened threats of lung disease and cancer.

Consumer Product Safety Commission would need additional funding of $5-million to implement pending legislation ordering safety rules for cellulose insulation, CPSC Chairman John Byington told a Senate Appropriations Subcommittee last week. Byington also noted that if the agency is required to deal with various chronic hazards identified in an emerging National Cancer Institute study, an additional $5-million and 50 staff positions will be required. Byington asked that Congress appropriate $3.4-million more for CPSC than the $44.8-million President Carter had recommended in his budget.

Occupational Safety and Health Administration has named 11 members to a new standards advisory committee on skin hazards. Committee was formed to identify the occupational exposures in industry which pose a hazard to the skin and to develop a set of guidelines for OSHA to use in drafting a proposed standards on skin hazards.

Department of Agriculture's nitrosamine panel has recommended the department issue a warning that "the risk of cancer is increased when fried bacon or the rendered fat from it are consumed." The panel called nitrosamines "a potent carcinogen" and said they are consistently found in bacon treated in the home.

New Jersey's Department of Environmental Protection has released preliminary results of a statewide groundwater testing program which is examining 500 wells for selected organic compounds, pesticides and metals. DEP Commissioner Rocco Ricci said early results show that water quality, in most cases, is far better than the Federal drinking water standards, although 20 violations were found out of 250 wells. Almost all of the wells contained traces of some of the chemicals being sampled, with the majority of wells contaminated by organic compounds located in heavily populated industrial areas and those contaminated by pesticides more prevalent in agricultural spots. State will similarly test air and surface water, DEP said.

Justice Department has filed a $20-million suit against Outboard Marine Corp., Waukegan, Mich., charging the firm with discharging 2-million pounds of polychlorinated biphenyls into Waukegan Harbor and Lake Michigan. The government asked the court to order the firm to clean up the accumulated PCBs.

Illinois Attorney General's office has filed suit against Amoco Oil Co., and Amoco Pipeline Co. in an attempt to recover more than $838,000 in penalties and damages from the companies for two spills of xylene last December. The first spill occurred near Danville when a pipeline transporting the petroleum by-product broke, allowing 700,000 gallons of the substance to leak into the Wabash River. The second spill happened near Humrick with only a few hundred gallons escaping, but vapors were so strong in the area of the spill that local residents had to be evacuated. 46.4

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GRANTS & CONTRACTS

Environmental Protection Agency has awarded University of California, Riverside, $112,000 to study chemical and mode of action of insecticides; Texas A&M Research Foundation, College Station, $85,000 to study baculovirus pesticides and identify markers for genetic studies; University of Miami, Coral Gables, Fla., $81,100 to study storage and excretion of halogenated and nonhalogenated organophosphorous pesticides in animals and man; Florida State University, Tallahassee, $36,838 to study high sensitivity FT NMR studies of environmental toxic materials;

California Department of Food and Agriculture, Sacramento, $500,000 for California's pesticide enforcement program; Nevada Department of Agriculture, Reno, $46,000 for Nevada pesticides enforcement program; Arizona Structural Pest Control Board, Tempe, $37,500 for Arizona pesticides enforcement program plan; Oregon State University, Corvallis, $95,947 to study bioavailability of cadmium from a variety of food-crops potentially grown on land used for sewage sludge disposal; California Department of Food and Agriculture, Sacramento, $133,580 for certification and implementation of pesticide applicator programs in state of California;

University of Michigan, Ann Arbor, $33,532 for development of *in vitro* test system for evaluation of teratogens; Cryptanalytic Computer Sciences, Inc., Cherry Hill, N.J., $47,975 to refine, verify and implement the substructural analyses method (SAM) for early-warning toxicity prediction; Interstate Electronics Corp., Anaheim, Calif., $444,960 for environmental impact statements on ocean dumping sites; Development Planning and Research Associates, Inc., Manhattan, Kan., $33,903 for development of the economic aspects of guidance for applicants for section 301(c) variances of the Federal Water Pollution Control Act; and North Carolina State University, Raleigh, $72,163 to study cytological effects of human exposure to potentially mutagenic environmental pollutants.

National Institute of Arthritis, Metabolism, and Digestive Diseases has awarded Mason Research Institute, Worcester, Mass., $59,176 for toxicological evaluation of iron chelators.

National Cancer Institute has awarded International Agency for Research on Cancer, Lyon, France, $1,074,151 for evaluation of carcinogenesis risk of chemicals to man; E.G. & G. Mason Research Institute, Rockville, Md., $629,450 for continuation of carcinogenesis bioassay data support system to the bioassay program; and Brandeis University, Waltham, Mass., $126,421 for production and detection of antibodies to chemical carcinogens and other small molecules of interest in cancer research.

U.S. Army Medical Research and Development Command has awarded Mount Sinai School of Medicine of the City University of New York, New York, N.Y., $110,000 for continuation of research on purification of influenza virus polypeptide antigens and studies of their immunogenicity and toxicity; and Midwest Research Institute, Kansas City, Mo., $260,000 for continuation of research on animal toxicity studies of new drugs.

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FOR THE RECORD

[redacted]

Hazardous spill rules and designations. Environmental Protection Agency. March 13 FR 10474.

Meeting April 3-4 in Washington, D.C., of Science Advisory Board's Environmental Health Subcommittee to discuss report on pentachlorophenol contaminants. EPA. March 15 FR 10730.

Proposed exemption from tolerance requirement for pesticide chemical sodium chlorate. EPA. March 16 FR 10943.

Request for information on occupational exposure to ethylene dibromide. Occupational Safety and Health Administration. March 17 FR 11248.

Phase-out rules for nonessential aerosol fluorocarbons. EPA. March 17 FR 11301.

Permanent standard for occupational exposure to dibromochloropropane. OSHA. March 17 FR 11514.

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