

July 15, 1976

To: Asbestos Study Committee

Subject: Mount Sinai (Dr. A. N. Rohl) Paper: "Asbestos Exposure during Brake Lining Maintenance and Repair"

On February 6, 1976, I advised the Asbestos Study Committee that I had received a paper entitled "Asbestos exposure during brake lining maintenance and repair" from Dr. A. N. Rohl of Mount Sinai. You may refer to my February 6, 1976 covering letter.

I have now received from Dr. Rohl copies of page proofs of that article as it will appear, Dr. Rohl believes, in the August 1976 issue of Environmental Research.

This is essentially the same paper presented by Dr. Rohl at the May 1974 meeting of the American Conference of Governmental Industrial Hygienists (ACGIH). It has been up-dated and expanded to include papers in 1974-75 for reference.

In reviewing this, I do not believe his figures include fiber counts of asbestos longer than 5 microns on an 8 hour time weighted average (TWA) basis. The emphasis continues to be turning to asbestos fibers shorter than 5 microns and their measurement by other than optical microscopy.

EWD/erc  
Enc:

E. W. Drislane  
Executive Director

P-FMSI- 0039

PLAINTIFF'S  
EXHIBIT  
WV-06046



## Asbestos Exposure during Brake Lining Maintenance and Repair<sup>1</sup>

ARTHUR N. ROHL, ARTHUR M. LANGER, MARY S. WOLFE, AND  
IRVING WEISMAN

*Environmental Sciences Laboratory, Mount Sinai School of Medicine of the City  
University of New York, New York, New York 10029*

Received December 10, 1975

Data obtained on asbestos exposure of garage mechanics during brake lining maintenance and repair work show that fiber concentrations frequently in excess of regulated limits are common. The presence of chrysotile, ranging from 2 to 15%, in brake drum dusts, was demonstrated by X-ray diffraction, transmission electron microscopy, selected area electron diffraction, and electron microprobe analyses. Unaltered chrysotile was found, both in fiber and fibril form, in air and brake drum dust samples. The chrysotile asbestos content of personal air samples, taken during automobile brake repair work, was measured both by optical and electron microscopic techniques. While a positive correlation exists between the types of measurements, the present technique of optically counting asbestos fibers may considerably underestimate the levels of total asbestos exposure.

### INTRODUCTION

During the past decade, significant disease risk has been found associated with the inhalation of asbestos fibers in a number of occupational and environmental circumstances other than in asbestos mining, milling and manufacturing, where serious hazard was already known (Wagner *et al.*, 1960; Newhouse and Thompson, 1965; Selikoff *et al.*, 1964, 1965; Harries, 1968).

Such exposures were found in the construction industry and in shipbuilding, as well as in other industrial settings where asbestos products were used. More recently, asbestos exposure has been suggested to occur during automotive brake lining repair and installation work, and measurable concentrations of asbestos fiber were observed in the work environment of workmen involved in these operations (Hickish and Knight, 1970; Hatch, 1970; Boillat and Lob, 1973). With limited data available, however, uncertainty remained regarding the type and extent of asbestos exposure during this work. Some investigators have questioned whether free asbestos fibers survive the high temperatures produced during braking action (Lynch, 1968; Hickish and Knight, 1970; Hatch, 1970) contending that asbestos decomposes as a result of the high point contact temperatures produced at the interface of the brake drum or disc and brake lining.

We have sought to obtain information concerning asbestos exposure of workmen engaged in brake lining maintenance and brake shoe installation, by analysis of residual dusts recovered from brake linings and by direct measurement of the

<sup>1</sup>This research was supported by Center Grant ES 00026 of the National Institute of Environmental Health Sciences of the U.S. Department of Health, Education and Welfare. Assistance was also provided in part by the Health Research Council of the City of New York HRC U 3329 and by the Ford Motor Company.

free asbestos fiber content of workroom air in areas where these operations take place. In the United States, an estimated work force of at least 900,000 auto mechanics and garage workers is potentially exposed to asbestos in the servicing of both brake and clutch linings. Furthermore, much brake dust enters the general environment during automobile use (Jacko and DuCharme, 1973), to add more to the burden of asbestos air pollution (Selikoff, Nicholson, and Langer, 1972).

#### *Asbestos in Friction Materials*

In the United States, an estimated 118 million pounds of asbestos is used annually for the production of brake friction materials (Jacko and DuCharme, 1973). After processing (cutting, grinding, punching), the asbestos in the material sold is approximately 103 million pounds per year. In addition, asbestos contained in automotive clutch friction materials amounts to 4.5 million pounds annually.

#### *Major Constituents of Brake Linings*

A number of materials is commonly used in the manufacture of the three major automotive brake lining components (binder, fiber reinforcer, and property modifier). These are listed in Table 1.

**Binder.** The binders used in the automotive industry today are primarily phenolic-type resins, which are noted for high binding efficiency and ability to withstand pyrolytic breakdown. Other materials have been used, in varying proportions and in addition to resins, for binder improvement (Table 1).

TABLE 1  
COMMON COMPONENTS OF AUTOMOTIVE BRAKE LININGS\*

| Binder and organic friction modifiers | Fiber reinforcer                 | Property modifier                            |
|---------------------------------------|----------------------------------|----------------------------------------------|
| Phenolic-type resin                   | Chrysotile asbestos <sup>b</sup> | Lead compounds                               |
| Rubber                                | (grades 4-7)                     | Zinc compounds                               |
| Tire scrap                            | Unaltered                        | Antimony oxide                               |
| Pitch                                 | Calcined                         | Iron oxide                                   |
| Cork                                  | Mixed fiber                      | Copper metal                                 |
| Gilsonite                             |                                  | Brass chips                                  |
| Cashew nutshell resin and particles   |                                  | Clay minerals                                |
| Drying oils                           |                                  | Barite (BaSO <sub>4</sub> )                  |
|                                       |                                  | Wollastonite (CaSiO <sub>3</sub> )           |
|                                       |                                  | Quartz (SiO <sub>2</sub> )                   |
|                                       |                                  | Cryolite (Na <sub>3</sub> AlF <sub>6</sub> ) |
|                                       |                                  | Rutilstone (SiO <sub>2</sub> )               |
|                                       |                                  | Coke (C)                                     |
|                                       |                                  | Coal (C)                                     |
|                                       |                                  | Gilsonite (C)                                |
|                                       |                                  | Graphite (C)                                 |
|                                       |                                  | Carbon black (C)                             |
|                                       |                                  | Molybdenum sulfide (MoS <sub>2</sub> )       |
|                                       |                                  | Fluorapatite (CaF <sub>2</sub> )             |

\* See Carroll, 1962; Anderson, 1969; Anderson, 1973; Jacko and DuCharme, 1973; Berk, et al., 1975.

<sup>b</sup> Chrysotile fiber constitutes about 50% by weight of most automotive brakes currently manufactured in the United States.

COPYRIGHT

**Fiber.** For fiber reinforcement of the friction product, chrysotile asbestos is used almost exclusively. The mineral typically comprises from 40 to 50% of the brake product. Fiber grades 4 through 7 are used, and occasionally, several sizes are admixed or even calcined to improve performance characteristics.

**Modifiers.** Perhaps the widest range of materials used in friction products are the property modifiers. Nineteen representative compounds are listed in Table I. Modifiers are used for a number of purposes: they are included to increase brake shoe "density," making the brake surface able to withstand high pressures (e.g., barite); they are included as "lubricants" to reduce the coefficient of friction along the brake surface, and thereby prevent "grabbing" (e.g., lead compounds); they act as "friction agents" increasing the coefficient of friction and enhancing the braking action of the shoe (e.g., brass chips); they act as internal "abrasives," which help to "recondition" the braking surface and remove deposited decomposition products (e.g., rottenstone, quartz); they act as "heat sinks," reducing binder pyrolysis and fiber decomposition thereby extending the useful life of the lining (e.g., brass chips, metals, etc.).

It is important to note that one major purpose of the reconditioning agents is to retard the formation of forsterite (a mineral not originally present in the brake material, but created by dehydroxylation and recrystallization of chrysotile asbestos at high temperatures) which may accumulate on the surface of the brake lining. The hardness of the forsterite (Mohs, 6.5-7.0) is such that it tends to score and gouge brake drums and discs (hardness 3-3.5), degrading them prematurely. Therefore, recrystallization of chrysotile to forsterite is an unwanted effect, hindered insofar as possible by the modifiers present in the matrix.

#### *Materials of Biological Interest*

Asbestos, quartz, and heavy metals are constituents of automotive brake linings, each warranting special consideration from the viewpoint of biological activity. The focus of this report is limited to the problem of chrysotile asbestos exposure.

#### *Mechanisms of Degradation of Brake Linings during Use*

Brake wear is dependent upon many factors, such as the temperature generated at the surface of the brake shoe during braking operations. At any one time, only a small percentage of the rubbing area is in contact with the wheel, with "hot spots" generated, ranging up to 800 to 1000°C (Carroll, 1962; Anderson, 1969). It is not uncommon during moderate braking action, to attain temperatures as high as 500°C (Carroll, 1962). Some investigators have suggested that, in addition to binder pyrolysis, chrysotile completely dehydroxylates under these conditions and "reduces to powder" where it is swept off the brake facing (Carroll, 1962). However, this hypothesis is oversimplified, in that other important processes, besides thermal wear, contribute to shoe breakdown, and brake shoe degradation. (Burwell, 1957). For example, the effects of abrasive wear and microshear have been investigated. When monitored by X-ray diffraction, chrysotile in brake materials displays structural strain and substructure fragmentation, caused by shear during braking processes (Mirzamani *et al.*, 1973). This shear strain produces material fatigue which, with binder pyrolysis, can cause brake lining disintegration at

temperatures far below those required for chrysotile dehydroxylation. Therefore, brake lining disintegration may liberate partially altered, or unaltered, chrysotile fibers.

#### *Thermal Decomposition of Chrysotile*

Differential thermal analysis indicates that chrysotile undergoes dehydroxylation at 630 to 680°C and recrystallizes (anhydrous magnesium silicate to forsterite) ( $\text{Mg}_2\text{SiO}_4$ ) at about 810 to 820°C (e.g., Martinez, 1966; Daykin, 1971; Berry, 1971; Monkman, 1971; Harris, 1971). These temperature ranges are subject to great variation as a function of the chemistry of the fiber, particle size, instrumental variations, sample packing, etc. Also, forsterite has been noted to form, during prolonged static heating, at considerably lower temperatures (Bates and Comer, 1957; Martinez, 1966; Brindley and Hayami, 1965; Naumann and Drescher, 1956). In general, temperatures in excess of 570°C are required for dehydroxylation and incipient forsterite formation in chrysotile. Extensive study of both the thermal behavior of chrysotile and brake lining composition and design indicates that chrysotile fiber may survive in the decomposed lining dust.

### METHODS

#### *Analysis of Brake Drum Dust (Decomposed Lining)*

Ten samples of automobile brake drum dusts were collected and examined by optical microscopy, X-ray diffraction, transmission electron microscopy and scanning electron microscopy with microchemical capability, for the purpose of determining the presence or absence of chrysotile.<sup>2</sup>

Optical microscopy, employing polarized light, was generally not useful for detecting asbestos in brake drum dust. A number of factors are considered responsible for this phenomenon including the low relief and birefringence of chrysotile and the nature of the matrix, consisting largely of road dust, resin binder, and pyrolyzed residue, which, in optical microscopic preparations, readily obscures the smaller asbestos fibers.

X-ray diffractometry, in the continuous and step-scan mode, was performed on all dusts. Chrysotile reflections ( $hkl = 002; 020; 004$ ) were observed in all ten samples. Quantitative determination of chrysotile content was made by comparison of unknowns with calibrations of chrysotile dilution standards. The weight occurrence ranged from about 2-15%, with an average ranging from 3-6%. Lead compounds, quartz, calcite, mica, clays, barite, graphite, and alpha-iron particles were identified as well. In several samples, weak, diffuse reflections suggested the presence of forsterite, but positive identification could not be made using this technique.

#### *Identification of Chrysotile by Electron Microscopy*

Transmission electron microscopy, selected area electron diffraction, and elec-

<sup>2</sup>We acknowledge the cooperation of the United Automobile Workers, Local Union No. 259 and the Automobile Dealers Industrial Relations Association in helping us obtain these samples in auto maintenance shops in the New York area. Each sample was taken from "a typical job" under way at the time.

Iron microprobe analysis of the brake dusts were carried out on each of the ten samples after preparation by a technique which disperses the dust particles in a nitrocellulose film without altering particle size distribution. Free chrysotile fiber bundles and fibrils were observed in all ten samples (Fig. 1). Selected area electron diffraction analysis of representative fibers demonstrated the preservation of the chrysotile structure (Figs. 2A, B). Some patterns displayed arcuate reflections suggestive of interfibril rotation and intrafibril displacement (Figs. 2A, B). Occasionally, fibers were observed without characteristic chrysotile morphology, with mottled surfaces and obliterated fibrils, indicating partial or complete recrystallization. Electron diffraction patterns obtained from these particles displayed

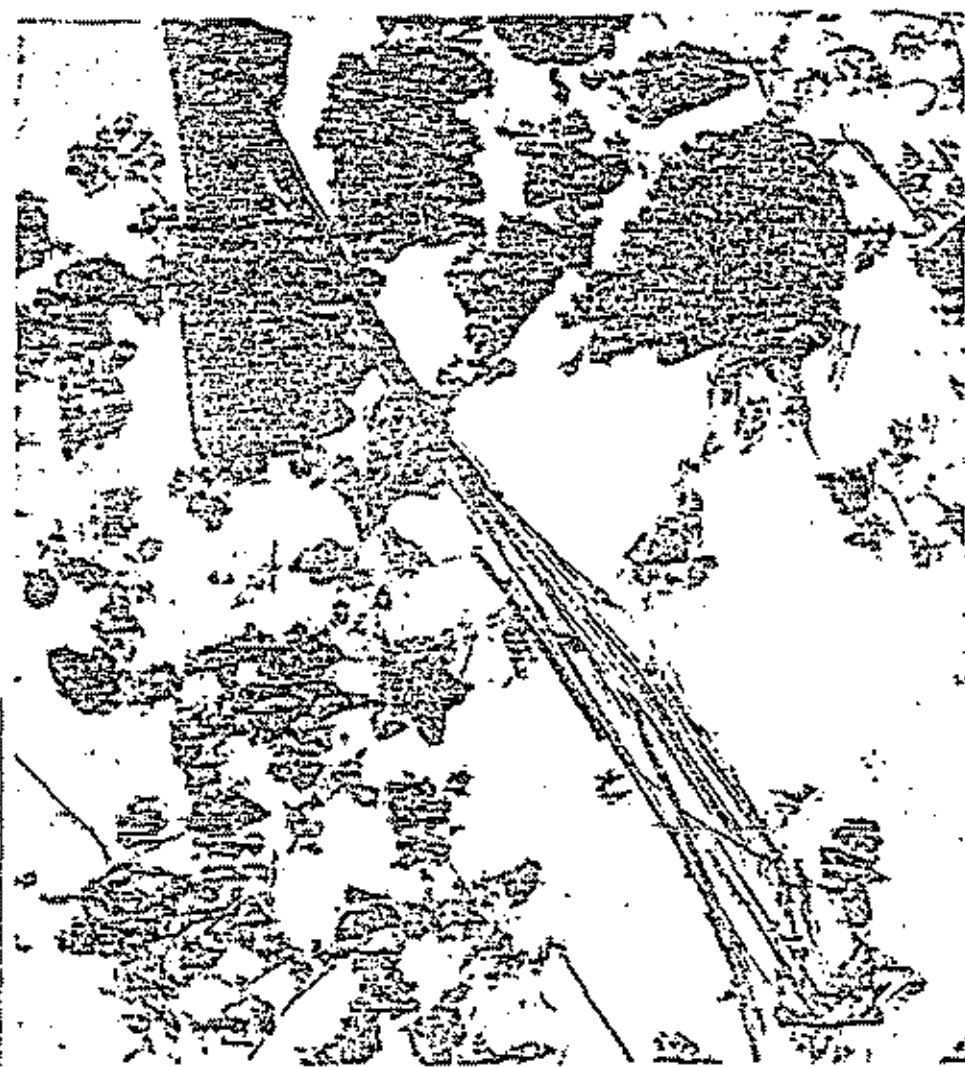


FIG. 1. Electron photomicrograph of large chrysotile bundle in brake drum dust (33,000 $\times$  magnification). Other particles include phenol resin binder and road dust debris.

COPYRIGHT

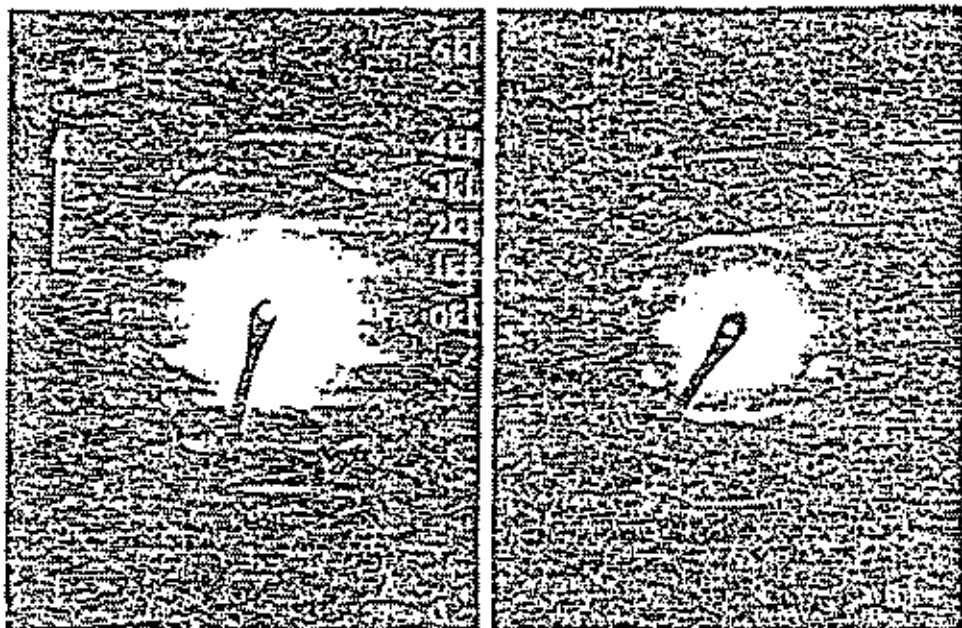


FIG. 2. Selected area electron diffraction patterns obtained on fibers of chrysotile obtained during air sampling at brake repair shops. In A, the reciprocal  $a^*$  axis is marked  $a^*$  as are the layer lines in the (0K1) series. Indexing of upper right quadrant yielded 16 reflections corresponding to single crystal X-ray diffraction analysis of Whitaker and Zussman, 1956. Pattern in (B) displays "smearing" of reflections in a "clockwise" manner suggesting interplanar rotation.

polycrystalline characteristics of multiple random reflections or Debye-Scherrer rings rather than the distinctive single fiber chrysotile pattern (Fig. 2B). Microchemical analysis with a probe technique on the unaltered fibers showed them to possess the usual Mg:Si ratio of chrysotile. In addition to free chrysotile fiber bundles and fibrils, chrysotile was also frequently observed projecting from the margins of binder fragments (Fig. 3).

Free asbestos fibers present in the decomposed lining dusts were sized at 42,000 $\times$  magnification. The results, seen in Table 2, show that most fibers are too small to be seen by optical microscopy; almost all of them are shorter than 0.4  $\mu\text{m}$  in length; virtually all are of respirable size ( $\sim 5 \mu\text{m}$ ). Hutch (1970) in reporting on optical fiber counts obtained from brake cleaning operations with compressed air jet, found that 94% of the fibers fell in the 2-5  $\mu\text{m}$  length category, while only 6% were longer than 5  $\mu\text{m}$ . Jacko and DuCharme (1973) made size distribution measurements of asbestos fibers in brake dusts generated during dynamometer tests, using both optical and electron microscopy. They found, at magnifications of 22,000 $\times$  that 30% of the fibers were from 0.25 to 0.50  $\mu\text{m}$  in length and that 60% were longer than 0.5  $\mu\text{m}$ . Some discrepancies between our data and those of Jacko and DuCharme may be attributed to their use of the lower magnification (22,000 $\times$  vs 42,000 $\times$ ), at which fibers shorter than 0.20  $\mu\text{m}$  may not be easily seen or identified on the electron microscopic screen. Thus, both the optical fiber count data in other studies and the electron microscopic fiber size distribution data

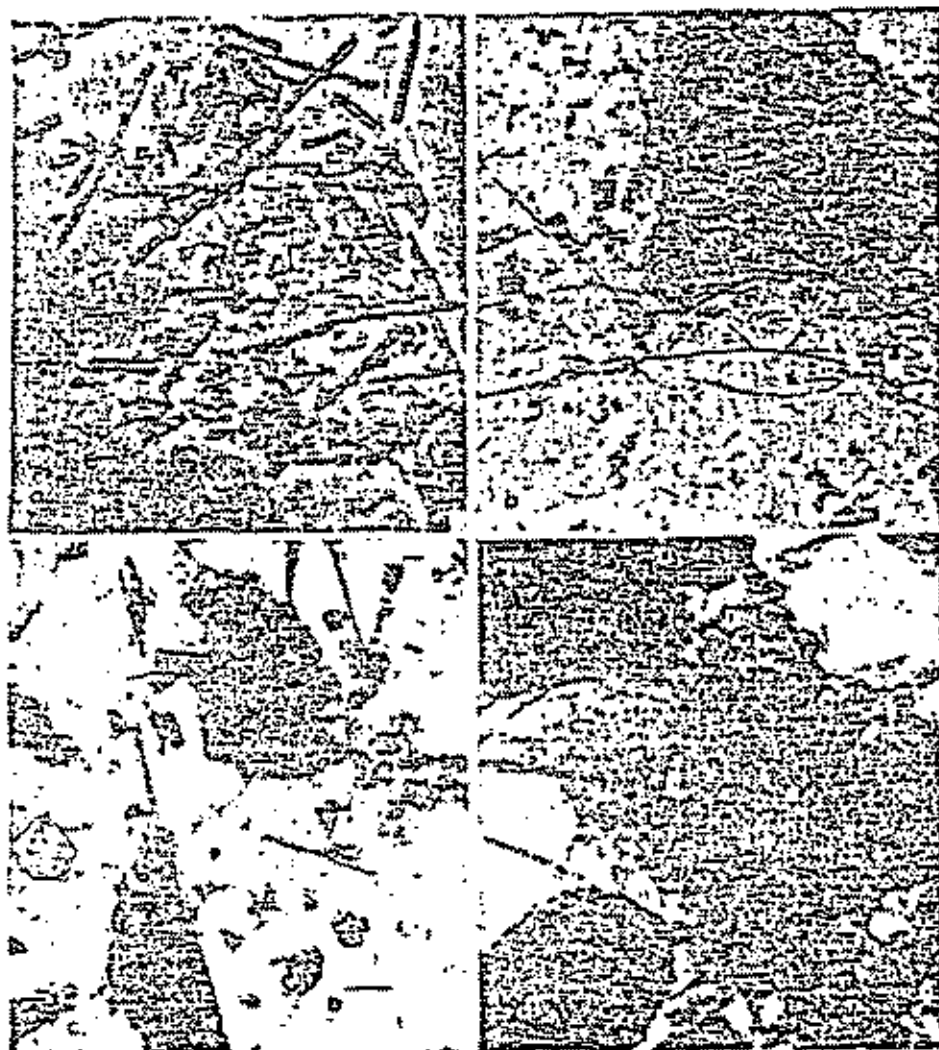


FIG. 3. Electron photomicrographs of brake drum dusts. Chrysotile is present in both free fiber and fibril form. Opaque granular material is road dust or phenolic binder. a.  $\times 10,800$ ; b.  $\times 9,300$ ; c.  $\times 30,000$ ; d.  $\times 30,000$ .

indicate that the chrysotile fiber population generated by brake wear is a strongly skewed one, with almost all fibers concentrated in the smaller than  $5 \mu\text{m}$  region. No attempt was made to size the asbestos-binder particulates.

#### *Personal Air Sampling during Brake Repair Work*

Personal air sampling for asbestos exposure during brake lining maintenance and repair was carried out at franchised auto dealer garages, taxi fleet repair shops, and a municipal truck repair shop, all located in New York City.<sup>2</sup> Personal

<sup>2</sup> Assistance in providing opportunity for sampling was given by the Department of Air Resources, New York City.

TABLE 2  
LENGTH DISTRIBUTION OF CHRYSOIDEI FISHES IN BEAK DUNE DEEP

| Sample | 750-1500Å<br>N (%) | 1500-2250Å<br>N (%) | 2250-3000Å<br>N (%) | 3000-3750Å<br>N (%) | Total<br>(%) |
|--------|--------------------|---------------------|---------------------|---------------------|--------------|
| 1      | 40                 | 34                  | 11                  | 11                  | 96           |
| 2      | 32                 | 23                  | 32                  | —                   | 87           |
| 3      | 20                 | 25                  | 25                  | —                   | 70           |
| 4      | 26                 | 37                  | 26                  | 7                   | 96           |
| 5      | 57                 | 17                  | 4                   | —                   | 78           |
| 6      | 23                 | 9                   | 12                  | 12                  | 56           |
| 7      | 50                 | 26                  | 21                  | 2                   | 99           |
| 8      | 29                 | 30                  | 21                  | 17                  | 97           |
| 9      | 6                  | 47                  | 18                  | 10                  | 75           |
| 10     | 11                 | 6                   | 31                  | 31                  | 79           |

\* Fibers counted and sized at  $\times 42,000$ ; all fibers have diameters from 250 to 500 Å.

air samples were taken during and after brake repair work and at varying distances from the work sites in other areas of the garages and shops. The latter samples were intended to provide information concerning levels of asbestos exposure which garage employees other than those doing brake work might experience.

### Asbestos Exposure during Automobile Brake Repair Work

Air samples were first taken in the breathing zone of mechanics doing brake repair work. These peak exposure measurements were taken over periods of 3-5 minutes during which the workers were blowing dust from brake drums. The air samples, taken on membrane filters, were processed, and fiber counts made in accordance with the procedures which have been adopted by the Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labor (Bayer, Brown, and Zumwalde, 1973). Essentially, the analysis consists of counting fibers 5 to 100  $\mu\text{m}$ , in a fixed area of a Porton graticule, using phase contrast microscopy at a magnification of 400 $\times$ . This microscopic method enhances image contrast and allows large asbestos fibers to be readily seen and counted.

- When a vehicle is brought into a repair shop for brake lining inspection or replacement, the wheel is removed and loose dust is removed from the drums and back plates, generally by means of a compressed air jet. A recent survey of brake repair establishments in Baltimore and Washington revealed that this is the standard method in those cities (Castleman *et al.*, 1975). A similar situation exists in New York City. The cloud of dust that is produced is visible for several minutes afterwards (Fig. 4). Table 3 shows that fiber concentrations are high in the operator's area under these conditions (an average concentration of 16 fibers/ml), and that there are significant concentrations at least 20 ft away. Background or area sampling during the same operation shows that, at least 14 minutes after jet air blowing and up to 75 ft away, asbestos concentrations are still measurable even by optical microscopy. The data in Table 3 indicate that an asbestos concentration gradient, dependent on distance and time, is associated with this operation. It is evident that any person 65-75 ft away can be exposed. Current (interim) regulations of OSHA prohibit concentrations of 5 fibers/ml or more, longer than 5  $\mu$ m, as



FIG. 4. Removal of dust from brake drum and back plate by pneumatic air blowing at automobile garage.

a time-weighted average for workers, and concentrations above 2 fibers/ml will be illegal after 1976. Regulations set a peak concentration (maximum excursion) of 10 fibers/ml of air. Newly proposed standards are designed to set a limit of 0.5 fibers/ml (500,000 fibers/m<sup>3</sup>), with a maximum excursion of 5 fibers/ml.

It was generally found that there was minimal, if any, effort to control dust in most garages. Workmen do not use respiratory protection. There was little awareness of the potential hazard of brake dust.

In a single instance, brake drum cleaning was not done with a compressed air jet, but with a dry hand brush. Fiber concentrations were somewhat less (2.5 fibers/ml) at the operator level, but background levels 12 ft away were the same as with air jet cleaning.

#### *Asbestos Exposure during Truck Brake Repair and Installation Work*

Personal air sampling was also conducted at the New York Department of Sanitation truck repair shop, where various kinds of brake application and repair work are performed. Used truck brake linings are salvaged by grinding the surface to remove grease and dirt, and new linings are ground to expedite break-in. The edges of new linings are beveled on a grinding wheel or arc machine to avoid noise problems. (Fig. 5). Holes are drilled or punched into the brake lining, which

1. COVER 311

TABLE 3  
ASTHESIOS CONCENTRATIONS DURING AUTOMOBILE BRAKE SERVICE\*

| Operation                                                                                | Distance (ft)                | Number of samples | Fiber concentration (fibers/ml) |          |
|------------------------------------------------------------------------------------------|------------------------------|-------------------|---------------------------------|----------|
|                                                                                          |                              |                   | Mean                            | Range    |
| Blowing dust out of brake drums with compressed air jet                                  | 3-5                          | 4                 | 16.0                            | 6.4-39.8 |
|                                                                                          | 5-10                         | 3                 | 3.3                             | 2.0-4.2  |
|                                                                                          | 10-20                        | 2                 | 2.6                             | 0.4-4.8  |
| Background samples taken at varying distances and lapsed times, after brake drum blowing | Distance from operation (ft) | Time lapse (min)  | Concentration (fibers/ml)       |          |
|                                                                                          | 10                           | 0                 | 0.3                             |          |
|                                                                                          | 20                           | 0                 | 0.8                             |          |
|                                                                                          | 12                           | 5                 | 0.2                             |          |
|                                                                                          | 30                           | 5                 | 0.1                             |          |
|                                                                                          | 65                           | 7                 | 0.1                             |          |
|                                                                                          | Distance (ft)                | Number of samples | Fiber concentration (fibers/ml) |          |
|                                                                                          |                              |                   | Mean                            | Range    |
| Cleaning brake drums with dry brush                                                      | 1-3                          | 2                 | 2.3                             | 1.3-3.6  |
| Background samples taken 3 minutes after cleaning brake drums with dry brush             | 12                           | 3                 | 0.1                             | 0-0.2    |

\* Fibers 5-100  $\mu$ m in length, counted by optical microscopy.

\* The new proposed Asbestos Standard of the U. S. Department of Labor records asbestos exposure in fibers/ml, noting that a workman might respire approximately 8 m<sup>3</sup> of air per working day, retaining an unstated proportion of inhaled fibers. The above table omits reference to air content of fibers < 5  $\mu$ m in length.

is then riveted onto a steel plate. Some of these operations are similar to those done during the manufacture of brake shoes. Table 4 summarizes the results of personal air sampling in the course of this work. During light grinding of truck brake shoes (Fig. 6), an average peak concentration of about 4 fibers/ml was found in the breathing zone of the operator. The data show that measurable fiber concentrations are found 25 ft or more away. At a distance of 25 ft, for example, a concentration of 1 fiber/ml (1,000,000 fibers/m<sup>3</sup>) was found. Much larger numbers of shorter fibers would simultaneously be inhaled. During the beveling of truck brake shoes on a grinding machine, very high concentrations of fibers were found in the vicinity of the operator. The average of five air samples was about 37 fibers/ml. Area samples, taken up to 30 ft away from this operation, demonstrated the presence of airborne fibers. It was of interest to note that, at the time of this sampling, from eight to 15 other garage mechanics were working within this

CONCLUSION



FIG. 3. Reveling of truck brake linings at municipal garage. Arrow indicates accumulation of asbestos dust.

perimeter and were exposed to asbestos. Fiber levels for other kinds of operations at the truck garage are given in Table 4.

Boillat and Lob (1973) have reported fiber concentrations measured during drilling holes for rivets and grinding. They found values ranging from 0.3 to 29.2 fibers/ml; four of the nine values exceeded 5 fibers/ml.

#### *A Comparison of Fiber Levels Visible by Light Microscopy and Electron Microscopy*

In the ten brake drum dust samples examined, it was found that asbestos fibers shorter than  $0.4 \mu\text{m}$  predominated (Table 2). The OSHA Asbestos Standard does not require that short fibers ( $< 5 \mu\text{m}$  in length) be counted or controlled. This oversight may have considerable biological significance in that small chrysotile fibers readily produce asbestos disease (Holt, Mills, and Young, 1964, 1965; Davis, 1965; Pott, Huuh, and Friedrichs, 1972; Wagner, Berry and Timbrell, 1973).

TEXT



FIG. 6. Renewing of municipal track brake linings by light grinding to remove grease and dirt.

Hilscher *et al.*, 1970). Attention has recently been again called to the potential importance of this question (Bouhuys, 1975).

There is little published information on the numbers of, and sizes of, submicroscopic asbestos fibers in occupational exposures. The present study afforded an opportunity to collect data on the relationship between submicroscopically- and optically-visible fibers for this specific industrial exposure. Eight air samples were selected for both light and electron microscopic examination. Six of these were taken during brake drum dust removal operations with optical fiber counts recorded from 0.1 to 3.6 fibers/ml. The other two samples were taken during light grinding of automobile brake shoes.

#### *Preparation and Analysis of Air Samples*

One square centimeter sections of the eight membrane filters were mounted, dust side down, on microscopic slides and ashed in low temperature activated

CONYER III

TABLE 4  
ASBESTOS CONCENTRATION DURING TRUCK BRAKE SERVICE\*

| Operation                                   | Distance<br>(ft) | Number of<br>samples | Fiber concentration<br>(fibers/ml) |           |
|---------------------------------------------|------------------|----------------------|------------------------------------|-----------|
|                                             |                  |                      | Mean                               | Range     |
| Renewing used linings by grinding           | 3-5              | 10                   | 3.8                                | 1.7-7.0   |
| Background to grinding used linings         | 10               | 2                    | 1.5                                | 1.2-1.7   |
|                                             | 25               | 2                    | 0.8                                | 0.6-1.0   |
|                                             | 60               | 1                    | 0.2                                | —         |
| Beveling new linings                        | 3-5              | 3                    | 37.3                               | 23.7-72.0 |
| Background to beveling new linings          | 8                | 1                    | 0.6                                | —         |
|                                             | 12               | 2                    | 0.4                                | 0.3-0.5   |
|                                             | 30               | 1                    | 0.3                                | —         |
| Punching rivets into brake linings          | 3-5              | 2                    | 1.5                                | 1.9-2.0   |
| Chipping rust off used brake linings        | 3-5              | 1                    | 2.4                                | —         |
| Sweeping floor around grinder               | 3-5              | 1                    | 3.6                                | —         |
| Background to sweeping floor around grinder | 15               | 1                    | 3.1                                | —         |

\* Fibers 5-100  $\mu$ m in length, counted by optical microscopy.

oxygen to remove organic materials. The ashed residue was dispersed in a drop of nitrocellulose solution. The dispersal was accomplished by a "rubout" technique using the edge of a watch glass (Nicholson, Rohl and Ferrand, 1971). By this method large asbestos fiber bundles are broken into their constituent smaller fibrils and large agglomerates of inorganic materials, which normally obscure the presence of asbestos fibers, are broken into particles small enough to allow virtually all asbestos to be seen. By placing a second slide over the ground residue and nitrocellulose solution and then gliding the two slides apart, a thin film is produced. The dried film is cut into segments which are then floated off in water. The film is mounted onto Formvar-coated electron microscopic grids. Typically, four grids are prepared from each sample and one square on each grid is scanned in the electron microscope at 42,000 $\times$  magnification to determine the quantity of chrysotile present. By estimating the length and diameter of each fiber, and assuming a cylindrical fiber geometry, the mass of chrysotile per grid square is determined. Representative electron photomicrographs of chrysotile fibers and fibrils are shown in Figs. 7 and 8.

## RESULTS

A comparison of the optical microscopic fiber counts and the electron microscopic total asbestos mass calculations obtained from the eight samples is shown in Table 5. Figure 9, showing the same data, is plotted on logarithmic paper, and visual inspection indicates that a positive correlation exists between the optical and electron microscopic results, although the data are limited and the amount of

CUTTING



FIG. 7. Electron photomicrograph of air sample taken during brake drum blowing (see sample No. 4, Table 5). Large numbers (70-100) of chrysotile, some of which are marked by granular particulates, presumably road dust (65,000 total magnification).

scattering precludes a regression analysis. For example, from these data it may be possible to predict that, during the grinding of new brake linings (Sample No. 6, Table 5), a worker could be exposed to about 0.5 mg of asbestos daily in circumstances in which the time-weighted TLV of 5 fibers/ml would not have been exceeded. Similarly, Fig. 9 shows that, since a microgram of asbestos represents on the order of 1 million fibers per cubic meter of air (of greatly varying diameters and lengths), extremely high concentrations of submicroscopic fibers are present up to 65 ft away from brake repair work (e.g., Sample No. 5, Table 5), even though fiber levels in such a case are barely detected, if at all, by the standard optical counting technique. These limited data indicate that the standard (OSHA) optical fiber counting method may be only a fractional indicator of total asbestos exposure, at least in the case of automobile repair work. They also indicate that the total exposure is much higher than the OSHA technique records, in terms of

CONTINUED



FIG. 8. Electronmicrograph of air sample of cluster of chrysotile fibrils in background sample (see sample No. 3, Table 5 (53,000 $\times$  magnification).

asbestos fiber number, mass, and surface area. Additional studies relevant to this and other kinds of asbestos exposure are needed to confirm and extend these findings. It is important to note that particles of asbestos-containing pulverized brake lining were not included in this mass determination. Their importance, in terms of biologic potential, is presently unknown.

#### SUMMARY AND CONCLUSIONS

(1) Chrysotile asbestos fiber is a major component of brake lining materials. Degradation of the lining is brought about by a combination of factors, which

CONFIDENTIAL

TABLE 2  
COMPARISON OF OPTICAL AND ELECTRON MICROSCOPIC FIBER COUNTS

| Operation                                                                               | Optical<br>microscopy<br>(fibers/ml) | Electron<br>microscopy<br>( $\mu\text{g}/\text{m}^3$ ) |
|-----------------------------------------------------------------------------------------|--------------------------------------|--------------------------------------------------------|
| 1. Blowing dust off drum with air jet (10 ft away)                                      | 2.0                                  | 1.27                                                   |
| 2. Background to blowing out brake drum (10 ft away)                                    | 0.3                                  | 0.2                                                    |
| 3. Blowing dust off drum with air jet (20 ft away)                                      | 0.4                                  | 1.1                                                    |
| 4. Background to blowing out brake drum (20 ft away)                                    | 0.8                                  | 0.1                                                    |
| 5. Background to blowing out brake drum (65 ft away—7<br>minutes after blowing stopped) | .1                                   | 0.2                                                    |
| 6. Cleaning brake drum with hand brush                                                  | 3.6                                  | 6.5                                                    |
| 7. Light grinding of new linings before installation                                    | 4.7                                  | 53.0                                                   |
| 8. Light grinding new linings before installation                                       | 2.7                                  | 66.0                                                   |

include thermal stress, material fatigue, and shearing. Modifying agents are included in brake linings which lower the contact temperature between the lining and wheel interface; this, in turn, prevents binder pyrolysis and chrysotile fiber dehydroxylation. The amount of chrysotile fiber which survives the braking operation is related to a number of additional factors, including some which are external to the properties and quality of the lining itself. As a consequence, degradation may occur at temperatures significantly lower than that required for the dehydroxylation of chrysotile, with the persistence of fibers.

(2) Ten samples of dust were taken from automobile brake drums in New York City, and analyzed. Optical microscopy was of limited usefulness. X-ray diffraction analysis, using both continuous and step-scan modes demonstrated the presence of chrysotile in all dust samples. The proportion of chrysotile ranged from about 2–15%, and averaged about 3–6%. This included both free fibers and chrysotile which survived in pulverized binder as particulates. Forsterite, the

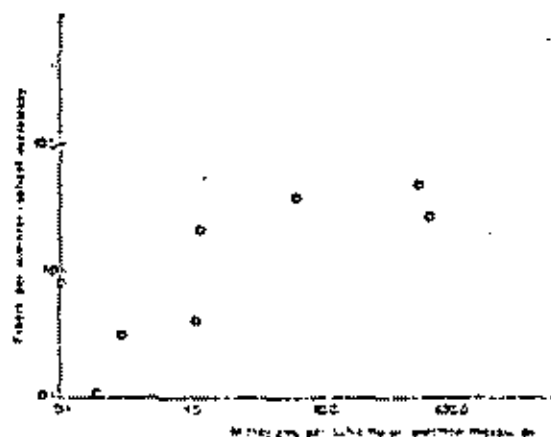


FIG. 9. Comparison of optical and electron microscopic fiber counts.

thermal transformation product of chrysotile could not be unequivocally identified by continuous scan X-ray diffraction.

- (3) The presence of chrysotile asbestos in the ten dust samples was further verified by transmission electron microscopy, selected area electron diffraction and electron microprobe analyses. Chrysotile was found, both in fiber and fibril form, with unaltered structure and chemical composition. Its frequency of occurrence was consistent with, but lower than the quantitative determination made by X-ray diffraction analysis. However, it should be noted that X-ray diffraction analysis is based on both free fibers and fibers present in clumps; the latter would obscure the presence of discrete fibers on electron microscopic study. In addition to unaltered fiber, partially altered and completely recrystallized fibers were also seen.

(4) Size distribution analysis at 42,000 $\times$  magnification in the ten samples indicate that about four-fifths of all chrysotile, in fiber form, is shorter than 0.4  $\mu$ m in length. These fibers are too small to be seen by optical microscopic techniques.

(5) Personal air sampling was conducted during brake repair work in automobile garages in New York City. Standard optical microscopic procedures for fiber counting were used. In samples taken in the vicinity of repairmen blowing dust from automobile brake drums with compressed air, an average concentration of 16 fibers/ml was measured. Background and time-lapse samples indicate that measurable concentrations exist at least 75 ft from the work site and for at least 14 minutes after jet air blowing.

(6) Personal air samples were taken at a municipal truck repair facility where various brake fabrication and application operations are performed. Grinding of truck brake shoes resulted in an average concentration of about 4 fibers/ml (4,000,000/m<sup>3</sup>). During beveling, an average fiber count of 37 fibers/ml was measured. Exposure levels during drilling, punching rivets, and cleanup were also measured. Background measurements show that fiber concentration gradients are produced during truck brake repair and application work. During light grinding of truck brake shoes, measurable fiber concentrations were found 25 ft or more away, as well as up to 30 ft from brake beveling operations. The background measurements, during both automobile and truck brake work, indicate that many employees in garages other than brake lining workers are potentially exposed to asbestos, including other mechanics and shop management.

(7) Eight air samples taken during automobile brake repair work were analyzed by other optical and electron microscopy. A positive correlation was found to exist between optical fiber counts ( $> 5 \mu$ m) and the total chrysotile mass calculations based on sizing all fibers at 42,000 $\times$  magnification. These data indicate that standard (OSHA) optical fiber counts may be a useful index of total free asbestos exposure during brake repair work. They also demonstrate that the total free asbestos exposure, in terms of fiber number, mass, and surface area is much greater than the optical counting techniques indicate.

(8) Attention is called to the fact that in addition to asbestos, other biologically active substances, including free silica and lead compounds, have been identified in brake lining dusts. Their concentrations in brake work environments are not known, and warrant investigation.

CONFIDENTIAL

(9) Potentially hazardous asbestos exposure exists during automotive brake servicing. It has been reported that approximately 900,000 persons are employed in such work in the United States. It is recommended that stringent industrial hygiene measures to control exposure be implemented as rapidly as possible.

#### ACKNOWLEDGMENT

We thank Drs. A. E. Anderson, R. L. Gealer, and L. Eichen of The Ford Motor Company for their valuable comments in reviewing the manuscript.

#### REFERENCES

- Anderson, A. E. (1969). Wear in brake materials. In *Proc. Amer. Soc. Metals Wear Conference*.
- Anderson, A. E., Gealer, R. L., McCune, R. C., and Sprys, J. W. (1973). Asbestos emissions from brake dynamometer tests. Soc. Auto Engin. Meeting, Detroit, Michigan, 14-15 May, 1973. Paper No. 730549.
- Bark, L. S., Moran, D., and Percival, S. J. (1975). Chemical changes in asbestos-based friction materials during performance—a review. *Wear* 34, 131-139.
- Bates, T. F., and Comer, J. J. (1957). In *Proc. 6th Nat'l Conf. Clays and Clay Mineralogy*, Int. Monog. Ser. 6, 237-248.
- Bayer, S. G., Brown, T. A., and Zumwahr, R. D. (1975). Document TR-84, U.S. Department of Health, Education and Welfare, Public Health Service, National Institute for Occupational Safety and Health, Cincinnati, Ohio.
- Berry, E. E. (1971). Thermal analysis of various chrysotiles using evolved water analysis techniques. In *Proc. 2nd Intl. Conf. Physical-Chemical Asbestos Minerals*, Louvain Univ., 6-9 September, 1971, paper 2-7 15 pp.
- Boilat, M.A., and Lob, M. (1973). Risk of asbestosis in workers employed in replacing automobile brake linings. *Schweizerische Medizinische Wochenschrift* 103, (39), 1354-1359.
- Bouhuys, A. (1973). Fibers and fibrosis. *Ann. Intern. Med.* 83(6), 895-899.
- Brindley, G. W., and Hayami, R. (1965). Mechanism of formation of forsterite and enstatite from serpentine. *Min. Mag.* 35, 189-195.
- Burwell, J. T. (1957). Survey of possible mechanisms. *Wear*, 1, 119-141.
- Carroll, W. G. (1962). The manufacture of brake linings. *Brit. Plastics* August, 414-417.
- Castleman, B., Camarota, L. A., Frisch, A. J., Mazzocchi, S., and Crawley, R. G. (1973). The hazards of asbestos for brake mechanics. *Public Health Rep.* 90 (No. 3) 254-256.
- Daykin, C. W. (1971). A study of the infrared spectra of chrysotile and related minerals. In *Proc. 2nd Intl. Conf. Physical-Chemical Asbestos Minerals*, Louvain Univ., 6-9 September, 1971, paper No. 2-6, 7 pp.
- Davis, J. M. J. (1965). Electron-microscope studies of asbestosis in man and animals. *Ann. N. Y. Acad. Sci.* 132, 98-111.
- Harries, P. G. (1968). Asbestos hazards in naval shipyards. *Ann. Occup. Hyg.* 11, 135-145.
- Harris, A. M. (1971). The effects of grinding on the structural and thermal properties of chrysotile asbestos fibers. In *Proc. 2nd Intl. Conf. Physical-Chemical Asbestos Minerals*, Louvain Univ., 6-9 September, 1971. Paper No. 3-2A, 6 pp.
- Hatch, D. (1970). Possible alternatives to asbestos as a friction material. *Ann. Occup. Hyg.* 13, 25-29.
- Hickish, D. E., and Knight, K. L. (1970). Exposure to asbestos during brake maintenance. *Ann. Occup. Hyg.* 13, 17-21.
- Hiltscher, W., Sethi, S., Friedrichs, K. H., and Pott, F. (1970). Zusammenhänge Zwischen Asbestose und Faserlänge. *Naturwissenschaften* 57, 356.
- Holt, P. F., Mills, J., and Young, D. K. (1964). The early effects of chrysotile asbestos dust on the rat lung. *J. Path. Bact.* 87, 15-23.
- Holt, P. F., Mills, J., and Young, D. K. (1965). Experimental asbestosis with four types of fibers: Importance of small fibers. *Ann. N. Y. Acad. Sci.* 32, 87-97.
- Jucko, M. G., and DuCharme, R. T. (1973). Brake emission: Emission measurements from brake and clutch linings from selected mobile sources. EPA Report. 68-04-0020.

CONTINUED

- Langer, A. M., and Peasley, F. D. (1973). Identification of single asbestos fibers in human tissues. In *Biological Effects of Asbestos* (H. Bogovski, et al. Eds.), pp. 19-23. I.A.R.C., Lyon, France.
- Langer, A. M., Mackler, A. D., and Peasley, F. D. (1973). Electron microscopical investigation of asbestos fibers. *Envir. Health Persp.* 9, 63-80.
- Lynch, J. R. (1968). Brake lining decomposition products. *J. Air Pollution Control Assoc.* 18, 824-826.
- McConnell, J. D. C. (1967). Electron microscopy and electron diffraction. In: "Physical Methods in Determinative Mineralogy" (J. Zussman, Ed.), pp. 335-370. Academic Press, New York.
- Martinez, E. (1966). Chrysotile asbestos: Relationship of the surface and thermal properties to the crystal structure. *Canada Mining and Metall. Bull.* 69, 414-420.
- Monkman, L. J. (1971). Some chemical and mineralogical aspects of the acid decomposition of chrysotile. In *Proc. 2nd Intl. Conf. Physical-Chemical Asbestos Minerals*, Louvain Univ. 6-9 September, 1971, paper No. 3.2, 9 pp.
- Naumann, A. W., and Dresher, W. H. (1966). The influence of sample texture on chrysotile dehydration. *Amer. Mineral.* 51, 1200-1211.
- Newhouse, M. L. (1965). Epidemiology of mesothelial tumors in the London area. *Ann. N. Y. Acad. Sci.* 132, 579-602.
- Nicholson, W. J., Rohl, A. N., and Ferrand, E. F. (1971). Air pollution in New York City. In "Proceedings of the Second International Clean Air Congress" (H. M. Englund and W. T. Berry, Eds.), pp. 136-139. Academic Press, New York.
- Pott, F., Huth, F., and Friedrichs, K. H. (1972). Tumors of rats after i.p. injection of powdered chrysotile and benz(a)pyrene. *Zbl. Bak. 1. Abt. Orig.* 155, 461.
- Selikoff, I. J., Churg, J., and Hammond, E. C. (1964). Asbestos exposure and neoplasia. *JAMA* 188, 22-38.
- Selikoff, I. J., Hammond, E. C., and Churg, J. (1968). Asbestos exposure, smoking and neoplasia. *JAMA* 204(12), 106-112.
- Selikoff, I. J., Nicholson, W. J., and Langer, A. M. (1972). Asbestos air pollution. *Arch. Envir. Health*, 25, 1-13.
- Wagner, J. C., Berry, G., and Timbrell, V. (1973). Mesotheliomas in rats after inoculation with asbestos and other materials. *Brit. J. Cancer* 28, 173.
- Whitaker, E. J. W., and Zussman, J. 1956. The characterization of serpentine minerals by x-ray diffraction. *Min. Mag.* 31, 107.