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ASBESTOS EMISSIONS FROM BRAKE

DYNAMOMETER TESTS

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ABSTRACT

Dynamometer tests of a production disc brake provided new information on asbestos fiber emissions during breakin, normal use, and high temperature use conditions. Both ambient air and brake cooling air were sampled isokinetically, using 0.45 μm filters. Examination of test and background filters required a clarification process to maximize fiber detectability, the use of transmission electron microscopy (at 40,000 X) for detection, and electron diffraction for positive identification of asbestos fibers. Most of the lining asbestos was found to be converted to a non-fibrous material by the high flash temperatures of the braking surface. Less than 0.02% of the lining wear was released as asbestos fibers. The concentration of asbestos fibers in the urban atmosphere, due to brake usage, was conservatively estimated at less than 0.07×10^{-9} grams per cubic meter. Based on this upper bound, the use of brakes was judged to be not significant as a source of atmospheric asbestos.

INTRODUCTION

Asbestos has been a major constituent of automotive friction materials for more than 50 years. It is used to impart strength, flexibility, and heat resistance to a brake lining and to enhance friction and wear properties. Most present brake linings use resin or rubber binders and chrysotile asbestos, together with organic and inorganic friction modifiers and fillers. The asbestos content varies with formulation, from a low of 25% to about 65% by weight. Minimum asbestos levels are found in some high performance European disc brake linings which are highly filled with metals and inorganic constituents. Brake linings in the U. S. average about 50% asbestos content.

Of a total U. S. annual asbestos consumption of 800,000 tons^(730 Mkg), about 28,000 tons^(25 Mkg) of chrysotile asbestos are purchased annually for friction materials of all types (1). Of this, it has been calculated that brake lining wear consumes about 12,000 tons^(11 Mkg) of asbestos per year. Roughly an equal amount remains on brake shoes at the time of replacement or is manufacturing wastage.

Recent tests have shown that densely populated urban atmospheres often contain significantly higher asbestos concentrations than surrounding areas (2). Background asbestos levels in the atmosphere result from the natural weathering of asbestos-bearing rock and soil, as well as from mining, farming, and excavating. The generally higher urban concentrations suggest commercial and industrial sources. Brake lining and clutch facing wear was suggested by Thomson (3) as a possible source for higher asbestos levels in the urban atmosphere.

Lynch (4), in a study undertaken by the Public Health Service, reported the findings of several brake dynamometer and friction machine tests in which wear debris was trapped on a filter and subsequently examined by means of a transmission electron microscope (TEM). He concluded

that "free fibers from brake lining wear seem to be an inconsequential health factor in urban air pollution." Lynch detected no free fiber from an automobile clutch and a bus drum brake, but some free fibers were found in one test of an experimental disc brake.

With mounting concern over air quality in general, and asbestos pollution in particular, this study was initiated in 1970 to provide additional data on the asbestos emissions from disc brakes.

OBSERVATIONS OF LINING WEAR

The near absence of free asbestos fiber from lining wear has been reported by Luxon (5) using X-ray diffraction and by Lynch (4) using the TEM (transmission electron microscope). Several authors have suggested that interfacial temperatures during braking could be high enough to decompose the chrysotile asbestos into non-fibrous thermal degradation products. Analytical relationships exist which permit calculation of interfacial temperatures (6). However, several of the significant parameters are difficult to determine accurately for heterogeneous materials such as brake linings. The asbestos crudes (larger fiber bundles) were calculated to reach their rapid decomposition temperature during normal braking at speeds above 56 MPH (25 m/s) as an upper bound value and above 18 MPH (8 m/s) as a lower bound value. An experimental approach was undertaken to provide closer bounds.

Added insight into the thermal decomposition of asbestos fibers in brake lining wear was attempted by direct visualization of the frictional process. A small laboratory friction test machine was constructed using a thermal shock resistant (Vycor) glass rubbing surface (replacing the conventional cast iron) in which the friction interface was directly viewed with a low power (7-50X) binocular microscope (7). Scaled rubbing velocities were used to compensate for the thermophysical property differences between the glass and cast iron.

Moderate scaled velocities, roughly equivalent to 12 MPH (5 m/s), provided a view of intermittently incandescent asbestos crudes. During the initial burnishing operation resinous material surrounding these asbestos crudes was observed to pyrolyze, producing microbeads of condensation products around the crude. These organic products of resin degradation and the apparently powdered asbestos decomposition products were seen to smear into platelets, often of such size as to be discernible to the unaided eye.

At higher rubbing velocities (over 30 MPH, or 13 m/s) the platelets formed a surface char layer under the action of more severe thermal and mechanical action. The larger asbestos crudes then could be seen to glow with apparent depth and for greater time durations, often several seconds.

The actual brake lining contact area was only a few percent of the total available surface, with contact spots moving in a random manner with time. From these friction visualization studies it appeared that local flash temperatures and severe mechanical action could be major factors in the breakdown of asbestos fibers for most brake usage. Examination of the lining surfaces revealed the presence of non-fibrous magnesium silicate in both crystalline (Forsterite) and amorphous phases. Magnesium silicate is a thermal degradation product of chrysotile asbestos. Forsterite transformations have been reported to occur at 600°C over a period of hours. Differential thermal analysis (DTA) studies in our laboratory indicated this transformation occurs within seconds at 820°C.

Special brake lining formulations were then prepared and tested on the glass visualization apparatus and a Friction Assessment and Screening Test (FAST) machine.(8). Chemical reactions were found to take place at the friction interface which would require a flash temperature rise of 740°C to initiate when an equivalent of 35 MPH (16 m/s) rubbing speed was used on the FAST machine. At this same speed melting of inorganic lining additives and metal particles confirmed brake flash temperatures up to 980°C.

Based on these findings, it would not appear surprising for few asbestos fibers to be emitted from brakes in normal usage. However some mechanical removal of fiber appeared possible during the first several brake applications with new linings. Also, high brake temperatures possibly could weaken the organic binders and cause increased fiber emissions.

TEST PROCEDURES

Complete sample collection and examination procedures, along with sample data calculations are included as Appendixes I, II, and III. Briefly, the tests were performed as follows: a new Pinto disc brake assembly was installed on a single station brake dynamometer in a room which was cleaned of extraneous asbestos sources. Air from within the room was blown through a diffuser screen to provide a velocity distribution over the brake which approximated that of vehicle usage. The air stream in front of and behind the brake was sampled isokinetically, using matched $0.45 \mu\text{m}$ filters, holders, and air pumps. Note the system schematic in Figure 1 and the actual test setup in Figure 2. The brake exhaust air was discharged out of the building.

The first pair of filters were used during the first 82 burnish stops, to represent "breakin" conditions. After further burnishing, a second pair of filters collected samples during 560 "normal use" brake applications. A third set of filters then were utilized in a "high temperature use" test of 41 brake stops.

All brake applications were made from a 40 MPH (18 m/s) equivalent speed. Breakin and normal use tests employed brake torques corresponding to one-quarter "g" (4.9 m/s^2) deceleration. This torque level was doubled for the high temperature tests.

During the normal use procedure, the test filter was located for 20 brake applications at each of 28 grid locations in the exhaust duct throat, to insure a representative sampling of the air flow over the brake. This test grid

and filter may be seen in Figure 3. A central collection site in the test grid was used for the "breakin test" and the final "high temperature" test.

Samples of the three pairs of filters (breakin, normal use, and high temperature use) were subjected to a clarification process involving low temperature ashing to oxidize all organic material and mechanical action to separate the particles. This assures maximum detectability of asbestos fiber (2).

RESULTS AND DISCUSSION

Transmission electron microscopy at 40,000 magnification was used in the search for fibers. At this magnification the ultimate fibrils appear to be above one millimeter (0.040 inch) in diameter. Quantity, length, and apparent diameter measurements provided data for calculation of asbestos fiber mass per unit of filter area. Coupled with dimension, mass, and flow determinations from the dynamometer tests, this data was used to calculate the emitted asbestos fiber concentration in the collected wear dust, in the cooling air stream, and from the brake lining worn. The size distribution of collected fibers was not determined by this method, since the clarification process involved sufficient mechanical action to reduce most fiber bundles to the ultimate fibril size.

Additional samples of the "normal use" test filters were examined on the TEM without recourse to the clarification process, in an effort to determine the asbestos fiber size distribution. Roughly 10% of the asbestos fiber was visible on the background sample, based on the results from corresponding samples after clarification. The largest observed fiber bundle was 0.20 μm in diameter and over 1.1 μm long. A similar direct TEM search of the "normal use" test filter revealed about 2% of the asbestos fibers observed after clarification. This reduced percentage of visible fiber was attributed to the greater concentration of obscuring matter in the test filter. However, the largest observed asbestos fiber in the test filter (0.13 μm in diameter and over 1.2 μm long) was about the same size as was found on the background sample.

The similar, low fiber content of both background and test filters precluded a fiber size distribution estimate. However, it appeared that the quantity of the larger asbestos fibers on the test filter was no greater than that of the background filter.

This supports the observation from the lining wear visualization tests that normal brake wear degrades most of the asbestos fibers. A brake lining grade of asbestos appears on the TEM as in Figure 4. The fiber bundles are composed of strong, but weakly adhering fibrils of about $0.03\ \mu\text{m}$ (roughly 1 microinch) diameter. Mechanical action causes the larger fibers to "open" into smaller fibers or even fibrils, as illustrated in Figure 5. Contrast these "raw material" fibers with one of the larger fibers (Figure 6) and one of the more typical fibrils (Figure 7) from the "normal use" test filter.

The similar, low fiber content of both background and test filters required clarification to permit an asbestos fiber count, thus providing more accurate fiber mass determination, but obscuring the actual fiber size distribution. Therefore, the calculations of fiber concentration (Table 1) were expressed as asbestos mass per unit mass of lining wear dust and asbestos mass per unit mass of lining worn. Asbestos fiber concentration in the ambient air (background) and in the brake exhaust air (test) was calculated in units of nanograms (10^{-9} grams) per cubic meter of air. However, the actual asbestos emissions from brake usage would be diluted substantially through mixing. The asbestos concentration in urban air due to brake usage was estimated, based upon existing automotive exhaust lead dilution data. These calculations appear in Appendix III.

All the test results in Table 1 have been reported as ten times the calculated test values, to allow for possible losses in collection, processing, and counting. These values, therefore, should provide upper bounds for asbestos emissions from brake usage. For example, the local (Detroit, Michigan) atmospheric asbestos concentration ranges from 0.5 to 13.4 nanograms per cubic meter. The

observed background asbestos value was 1.9 ng/m^3 , for the normal use test, but is reported in Table 1 as 19 ng/m^3 . The low asbestos emissions from the test disc brake under "normal use" conditions is underscored by the addition of but 13 ng/m^3 (1.3 ng/m^3 observed) in the undiluted exhaust air stream.

TABLE 1

ASBESTOS EMISSIONS FROM "NORMAL USE" BRAKING

Dynamometer Data for a Production Disc Brake*

. Background Asbestos in Ambient Air	$<19 \times 10^{-9} \text{ g/m}^3$
. Asbestos Fiber from Brake in Exhaust Air	$<13 \times 10^{-9} \text{ g/m}^3$
. Total Asbestos Fiber in Exhaust Air	$<32 \times 10^{-9} \text{ g/m}^3$
. Estimated Brake Asbestos Fiber in Urban Air	$<0.07 \times 10^{-9} \text{ g/m}^3$
. Asbestos Fiber from Brake in Airborne Wear Dust	$<0.05\%$
. Asbestos Fiber Released from Lining Wear	$<0.02\%$

* Reported values are 10 times the observed test values to provide upper bounds

The lining wear rate during the first 82 breakin stops was found to be about five times above the "normal use" rate. Asbestos fiber release during breakin was also higher, an average sevenfold increase. However, since the breakin wear is less than 1% of the total lining wear, the increase of emitted asbestos fiber resulting from this temporary sevenfold increase would be about 3%, when averaged over the life of the linings.

High temperature brake usage also increased lining wear rates, in this case, by a factor of eleven. Asbestos fiber emissions increased by less than a factor of three. Frequent vehicle operation under such high temperature

Conditions would lower lining life to levels far below present averages. However, even if all brake wear provided the same fiber emission rate as found in the high temperature use test, the percentage fiber release to the atmosphere would still be under 0.06% of the lining wear.

The remaining brake wear was a mixture of non-fibrous organic and inorganic matter. Forty-seven percent of the estimated 62 to 77% collectable wear debris were accounted for by the test filter on the normal use test.

The remaining 15 to 30% presumably were retained on the lining edges, the caliper, spindle, rotor, wheel, and tire. Accurate measurement of this material was not possible, due to the added retention of dust from the ambient air.

More precise values of brake lining asbestos emissions or the determination of their particle size distributions appear possible, for these low fiber concentrations, only by testing brakes in an asbestos free atmosphere. This approach was used in an EPA sponsored study (9), where pre-filtered air was flowed through sealed brakes at a flow rate greatly reduced from normal.

CONCLUSIONS

1. Automotive brake usage provides a very small emission of asbestos fiber (less than 0.02% of the lining worn).
2. Automotive brake usage provides a very small asbestos fiber input to urban atmospheres (estimated to be below 0.07 ng/m³).
3. Intense local heating and severe local mechanical action causes the decomposition of most asbestos fiber in brake linings during typical usage.

SAMPLE FILTER PREPARATION

Microporous membrane filters with $0.45 \mu\text{m}$ pores were selected to assure high retention of asbestos fibrils and most of the wear dust powders. A matched pair of Gelman sampling pumps and 35 mm diameter holders were used. Thin metal cones of 12° included angle were fabricated and sealed to the filter entrance. These cones increased the tip entrance velocity to that of the exhaust air duct so isokinetic sampling could be achieved. The cone tips were carefully matched in size. Flowmeters and differential pressure indicators were installed in the system to monitor the filter airflow during each test and to set the tip entrance velocity before each test.

Tests were performed on the unused filters to determine their weight change with variation of humidity. Filter weights were measured on a microbalance to the nearest 10 micrograms. Filters were placed in the center of the designated exhaust duct grid and at a fixed position upstream of the brake, but below the diffuser screen. This latter (background) filter was located where the upstream air velocity equalled the average over the test grid. In this way the sampling was isokinetic with essentially equal volume flows through both filters.

TEST PROCEDURE

All brake stops were conducted from the same speed equivalent (40 MPH, or 18 m/s) to maintain fixed air flow conditions. Burnish and "normal use" brake applications were at 0.25 "g" (2.45 m/s^2) deceleration and with a two minute time interval. This provided a peak rotor temperature of 180°C (350°F). The number of brake applications were selected to provide about one gram of lining wear per test.

Breakin wear was monitored for the first 82 stops. No sampling was performed for about 200 more brake applications, while the linings and rotor developed essentially steady-state conditions.

The "normal use" test was then performed on this burnished brake assembly. Twenty brake applications were made under the same conditions, with the test filter located sequentially at each of the twenty-eight grid locations. The filter cone entrance velocity was adjusted to match the grid velocity at each relocation. Four grids were used to monitor exhaust velocity. Slight adjustments were sometimes required to compensate for drift which appeared to be external wind initiated.

A third test was performed to provide an estimate of the fiber emissions from a hot brake assembly. As in the breakin test, the test filter was positioned in a central location for this procedure. Thirty-one stops were made at 0.5 "g" (4.9 m/s^2) and minimal time interval until the rotor attained 410°C (770°F). This temperature was then maintained by adjusting the application time interval. Ten additional stops were made as the brake was allowed to cool.

All filter weight determinations were performed at equilibrium conditions and then corrected for humidity. After use, the filters were individually stored in covered glass containers. Lining weights were taken after removal of wear debris but before they had cooled completely, to minimize weight changes from water absorption. Between tests the linings were stored in a dry jar.

The relevant test data are included in the following table. A slight pad drag caused the outboard lining to wear above expectations on the "normal use" test. Since this added work was not included in the lining wear rate calculations, the specific wear is above the usual range for this lining. No adverse effect on the test results would be expected to have resulted from this drag. Similar pad drag effects may occur on cars, when smooth road conditions prevent "pad knockback."

Test	Breakin	Normal Use	Hi Temperature Use
Brake Speed, RPM	535 (40 MPH)	535 (40 MPH)	535 (40 MPH)
Brake Decel, "g"	0.25 (2.45 m/s ²)	0.25 (2.45 m/s ²)	0.50 (4.9 m/s ²)
Wheel Load, kg	257 (567 lb)	257 (567 lb)	257 (567 lb)
Brake Applications	82 "	560	41
Total Energy, kW-h	0.938 (1.25 hp-hr)	6.405 (8.54 hp-hr)	0.469 (0.625 hp-hr)
Max. Apply Temp, °C	115 (240°F)	115 (240°F)	410 (770°F)
Total Lining Wear, g	1.10	1.60	1.07
Lining Wear Rate, g/kW-h	1.17 (0.051 $\frac{\text{in}^3}{\text{hp-hr}}$)	0.25 (0.011 $\frac{\text{in}^3}{\text{hp-hr}}$)	2.28 (0.100 $\frac{\text{in}^3}{\text{hp-hr}}$)

APPENDIX II

SAMPLE EXAMINATION

PREPARATION AND EXAMINATION OF ASBESTOS CARRYING SAMPLES FROM TEST FILTERS*

1. All slides, dishes, scalpels, and other utensils used in the following preparations were cleaned in acetone, followed by rinse in 200 proof ethanol.
2. An area of measured dimension was selected at random from the test filter, cut and placed particle side down on a clean glass slide.
3. Several drops of acetone were placed on the filter segment to partially dissolve and secure it to the plate.
4. The samples were ashed for a period of two hours by using a low temperature ashers at a chamber pressure of 0.5 torr (70 Pa) oxygen and power of 200 watts.
5. Several drops of a 1% solution of nitro-cellulose in amyl acetate were placed on the residue, and a clean watch glass was used to grind the mixture for a period of five minutes.
6. A second clean glass slide was then placed over the mixture of nitro-cellulose and residue, and a "smear" obtained by pressing the two slides together and then sliding them apart.
7. The films thus formed, were permitted to dry and then removed by scoring the edge of the slide with a scalpel and "floating" the film free from the slide in a distilled water bath. It was found that the film was most easily removed from the slide introduced in Step 6.

*Sample preparation techniques outlined below are similar to those reported by Selikoff, et al. in Reference 2.

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8. Approximately 10 electron microscope grids (3 mm, finder grids) were placed at random on the floating film, and the film was lifted by putting a clean slide on top of the film and drawing the slide down through the water so as to trap the grids between the slide and the film (which should now cling to the slide).
 9. A carbon layer of approximately $0.06\ \mu\text{m}$ was deposited on the film to prevent charging during examination in the transmission electron microscope (TEM).

Direct examination specimens were prepared by depositing a carbon layer on the dust side of the test filter and dissolving the filter in acetone. Electron microscope grids were used, both to support the sample and to provide grid location reference marks.

TEM EXAMINATION AND COUNTING PROCEDURES

Approximately ten electron microscope grids were prepared for each of the five filter samples analyzed. Four grids were arbitrarily selected from each sample and two grid squares on each grid were scanned for asbestos. The individual grid squares are approximately $90\ \mu\text{m}$ on each side and were examined at a TEM magnification of about 40,000. For each grid area scanned, photographs were taken, where possible of the first, last, and one randomly chosen fibril for the purpose of determining an average fibril diameter accurately. Measurements were then made visually; that is each fibril, fiber, or asbestos bundle was compared to known calibration marks on the electron microscope screen to estimate the lengths. The length could be estimated to within 20%, as determined by the photographic measurements. The marks on the screen are 0.5 cm apart corresponding to $0.125\ \mu\text{m}$ when a magnification of 40,000 is used. This approach was taken because it was impractical to photograph all the fibrils and, furthermore, length measurements were not as critical as diameter measurements in determining fiber volume. Where both measurement methods were used, the values providing the greatest indicated brake asbestos levels were chosen. The results are shown in the following table:

ASBESTOS CONCENTRATION ON FILTERS

<u>Sample</u>	<u>Sample Identification</u>	<u>Concentration (ng/cm² of filter)</u>
A	Test-normal stop-new brakes	15.32
B	Background for A	1.06
C	Test-normal stop-burnished brakes	7.98
D	Background for C	4.64
E	Test-high temperature stop-burnished brakes	5.37
F	Background for E - not used, insufficient sample	
-	Blank - unused filter	0.33

From photographic measurements of 120 chrysotile fibrils, the asbestos fibril average diameter was determined to be $0.0337 \mu\text{m}$ with distributions similar to that observed by other workers (10). From 45 fibrils of triple jet-milled chrysotile the average diameter was determined to be $0.0316 \mu\text{m}$ with a standard deviation of $0.0063 \mu\text{m}$.

ASBESTOS IDENTIFICATION

Asbestos can be identified in the transmission electron microscope in one of two ways. The first and absolute method is by electron diffraction. Such a diffraction pattern is presented as Figure 8. Measurement of diameters and correlation of these measurements with a known standard gives the interplanar spacings of the material. Comparison of these spacings with the ASTM file identifies the material as clino-chrysotile (asbestos).

The second method of identification is by appearance. Figure 9a represents an image of asbestos obtained in the TEM. Fine lamellae are observed within the fibril which are parallel to the long axis. This appearance is characteristic of chrysotile asbestos fibrils. Because of the nature of the electron beam, radiation and heat damage can occur in the material markedly

