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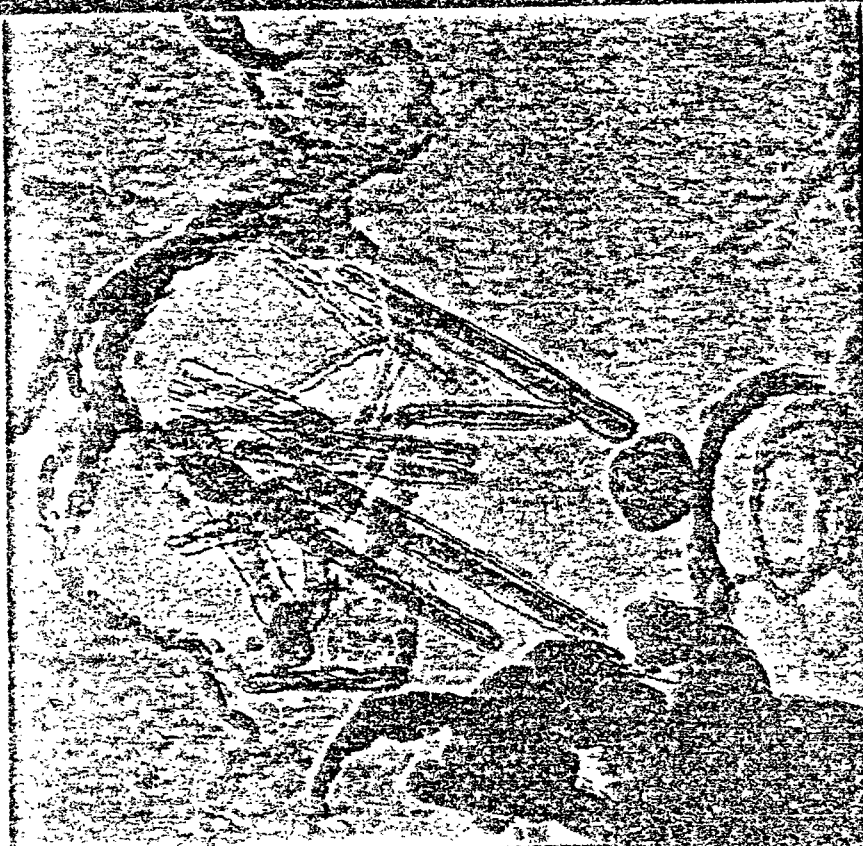
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irregular or nodular interstitial opacities of limited extent and intensity on their films. Silica or asbestos exposure had occurred in 22% of the work force examined. Such exposures had occurred in various job categories in the titanium facility as well as in prior occupations. Eight of the 26 workers with abnormal X-rays had had silica or asbestos exposure. No clear pattern of restrictive disease in relation to X-ray findings could be seen.

Summary and Conclusions

Clinically significant or symptomatic pulmonary disease was infrequent in a survey of 207 currently employed production workers in a plant producing titanium dioxide from ilmenite ore. Evidence of airways obstruction was found in 47% of all workers (including 38% of workers who had never smoked regularly). This abnormality was not frequently accompanied by disabling shortness of breath. Despite the fact that approximately 90% of the group of workers examined had worked for 20 years or more, radiological changes consistent with pneumoconiosis were relatively few, and unrelated to the respiratory abnormalities observed.

We conclude (with the caveats inherent in a prevalence study in which only half of the eligible long-term workers were examined) that occupational exposure associated with titanium production by the sulphate process may commonly cause undesirable irritation of the upper and lower respiratory tract and functional abnormalities of the lung, but does not result in an important incidence of serious occupational lung disease. Individual workers may, however, suffer unwanted abnormalities. These findings, of course, do not speak to the presence or absence of increased risk of malignant pulmonary disease. This is being separately studied.

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REFERENCE

Miller A, Chuang M & Selikoff I J
(1976) *American Review of Respiratory Diseases* 113, Suppl., p 89 (abstract)

Asbestos Content of Dust Encountered in Brake Maintenance and Repair

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Asbestos in Brake Linings

The composition of automotive brake linings includes chrysotile asbestos fibre which comprises about 50% of the friction material. The exposure of garage workers to asbestos during brake lining maintenance and repair has recently been investigated (Rohl *et al.* 1976). This important issue was studied because a large labour force is potentially exposed (over one million people in the United States alone). Consequently it was thought essential to determine if chrysotile fibre survives braking, and to measure the amounts liberated as an aerosol during maintenance and repair operations.

Investigators in the past have expressed doubt as to whether chrysotile fibres can survive the high temperatures generated during braking (Lynch 1968, Hickish & Knight 1970, Hatch 1970). Chrysotile is alleged to be subjected to temperatures in excess of 800°C, which would cause its thermal transformation to forsterite or to an amorphous magnesium silicate phase. While 'hot spots' up to 1000°C may be attained (Carroll 1962), the heat distribution is nonuniform, and other processes, in addition to thermal wear, contribute to degradation of brake linings. For example, abrasion and macroshear may also cause physical breakdown (Burwell 1957, Mizutani *et al.* 1973). Accordingly, brake lining disintegration by these mechanisms may liberate partially altered or even unaltered chrysotile fibres.

Analysis of Brake Drum Dust

Initially, ten samples of automobile brake drum dusts from brake repair shops in New York City were collected and examined by optical microscopy, X-ray diffraction, transmission electron microscopy and energy dispersive X-ray spectroscopy, to determine the presence of chrysotile.

Optical microscopy: The detection of chrysotile in brake drum dust by optical microscopy is hindered by the nature of the debris matrix, consisting largely of opaque pyrolyzed phenolic-type resin binders and road dust. Chrysotile, particularly small fibres, has low optical relief and low birefringence, which further hinder its identification. Only in rare instances have large fibres, with optical

Table 1

Chrysotile asbestos content of brake drum dusts

	No. of samples	X-ray diffraction (step-scan)		Transmission electron microscopy No. positive
		No. positive	Weight percent Mean Range	
Great Britain	8	6●	1.8	8
West Germany	8	5●	2.4	8
France	1	1	2.5	1
United States of America	10	10	4.5	10
Finland	5	3	1.8	5
Western Australia	7	4	1.4	7
	39	29	$\bar{x}=2.4$ ± 1.1	39

● 1 sample possibly positive

properties consistent with chrysotile, been observed with this technique.

X-ray diffraction: The ten brake dust samples were analysed by X-ray diffractometry, in both continuous and step-scan mode. The diagnostic reflection selected for chrysotile ($3.66 \text{ \AA}$; $hkl=(004)$) was step-scanned in the fixed-count mode. By comparison with external standards, the amount of chrysotile present can be determined. Chrysotile reflections were observed in all samples, with weight percentages estimated to range from 2 to 15 (average 4.5). Lead compounds, quartz, carbonate minerals, clays, halite (NaCl), graphite, micas and alpha-iron were also identified in various samples.

Twenty-nine additional brake drum dust samples were collected by colleagues in four European countries and Australia. The samples were obtained from areas representing variable circumstances, such as driving conditions, friction material composition, type of automobile and climate. The results of X-ray diffraction analyses are presented in Table 1. Of the 39 total samples analysed (including 10 United States samples) chrysotile was found in 29, or about three-fourths. The mean chrysotile content varied from 1.4% in the seven Australian samples to 4.5% in the New York City samples.

The thermal breakdown product of chrysotile, i.e., forsterite, which might be expected to form as a result of recrystallization, was not unambiguously detected in any sample.

Transmission electron microscopy (TEM): In order to verify the results of X-ray diffraction analysis, the brake dust samples were prepared for electron microscopic analysis by means of a technique which disperses the dust particles in a nitrocellulose film without altering particle sizes. Both free chrysotile fibre bundles and fibrils were observed in all 39 samples. Most of the chrysotile retained its characteristic morphology without significant alteration, and selected area electron diffraction patterns obtained on representative fibres dem-

onstrated the preservation of crystal structure as well (Fig 1).

Fibre size distribution: In ten brake dusts sampled in New York City, free asbestos fibres were sized by TEM at magnification 42 000. The results showed that about 80% of chrysotile is in free fibril form and is shorter than $0.4 \mu\text{m}$ in length. Over 57% have lengths of about $0.2 \mu\text{m}$. At magnification 40 000, such a fibre would be about 1 cm long. If lower magnification were used to scan for asbestos, significant numbers of fibres might not be detected.

It is obvious that most fibres are too small to be seen by optical microscopy. The Asbestos Standard adopted by the Occupational Safety and Health Administration (OSHA) of the US Department of Labour is limited to optical microscopy and neglects to count or control fibres less than $5 \mu\text{m}$ long. On the other hand, accumulating evidence suggests that such small asbestos fibres may produce disease (Holt *et al.* 1964, Davis 1965, Pott *et al.* 1972, Wagner *et al.* 1973, Hilscher *et al.* 1970, Bouhuys 1975).

Air sampling: Eight personal air samples taken during brake repair work were selected for electron microscopic analysis. This was done in order to positively identify chrysotile in the samples and to determine whether a systematic relationship existed between optically and submicroscopically visible fibres for this type of exposure. The membrane filters were ashed in plasma oxygen to eliminate organic materials and the residue was prepared for electron microscopy by a 'rubout' technique (Nicholson *et al.* 1971), which comminutes large chrysotile fibre bundles into individual fibres and fibrils. Large inorganic particles are likewise reduced in size, permitting all chrysotile to be seen and measured. Chrysotile was identified in the eight samples, in both fibre and fibril form (Fig 2). By measuring a large number of fibres at magnification 42 000 and converting the volumetric data into mass, a concentration per volume of air is determined. Comparison of optical microscopic

fibre counts and the electron microscopic asbestos mass calculations indicates that a positive correlation exists between the two sets of data. These results show that the standard (OSHA) optical fibre counts may be only indicative of the total asbestos exposure.

Asbestos Exposure of Workmen

After the identification of chrysotile in the brake drum dusts, asbestos fibre exposure during maintenance and repair was determined by personal air sampling carried out at automobile repair shops,

taxi fleet repair shops and a municipal truck repair shop in New York City. Air sampling and analytical methods for the determination of fibre concentrations were in accordance with the OSHA techniques (Bayer *et al.* 1975). Present regulations of OSHA prohibit asbestos concentrations of 5 fibres per millilitre (f/ml) or greater, longer than 5 μm as a time-weighted average, and concentrations above 2 f/ml will be illegal after July 1976. Peak concentrations or maximum excursions of 10 f/ml are permitted by the regulations.

In brake lining inspection and repair, the wheel

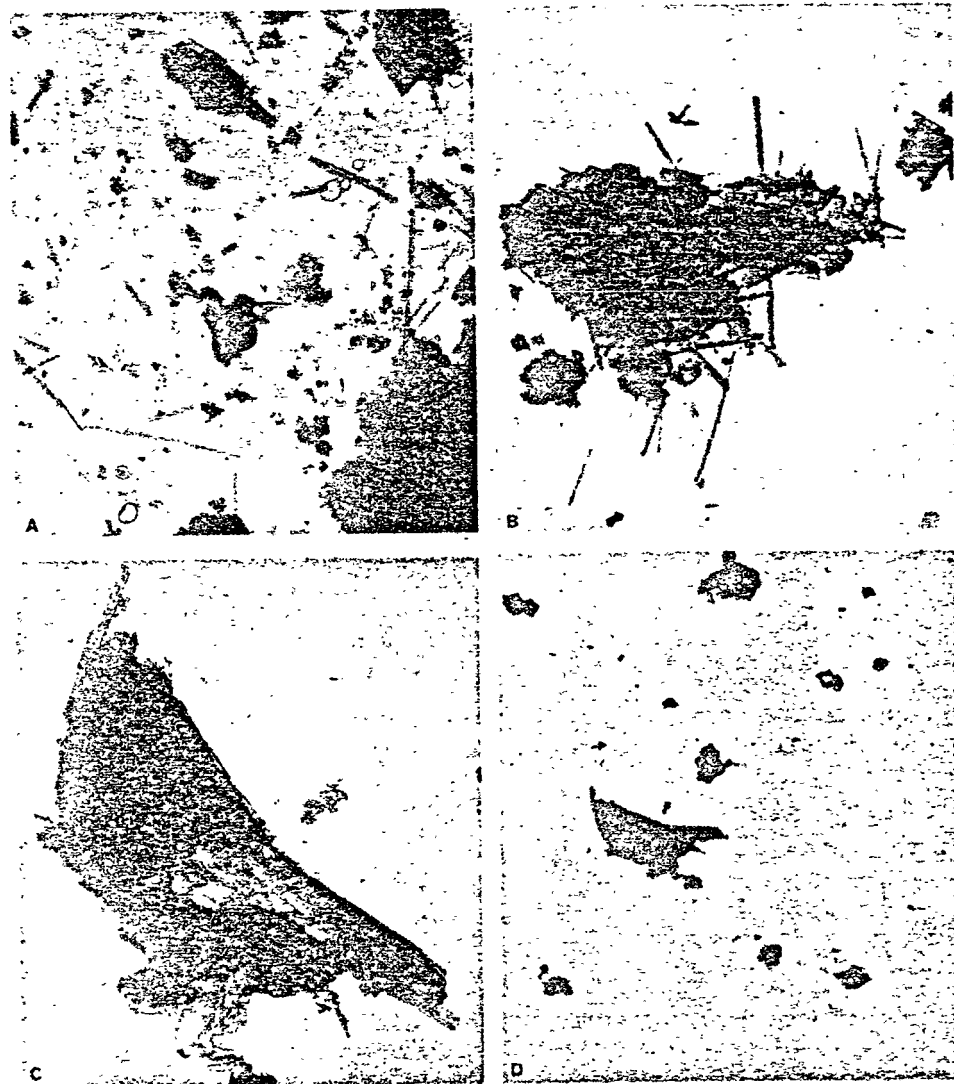


Fig 1 Electron photomicrographs of brake drum dusts, taken at various magnifications. A, the numerous chrysotile fibrils have average lengths of 0.4 μm or less ($\times 30\,000$). B, large numbers of chrysotile fibres imbedded in, and protruding from, opaque particle, probably pyrolyzed phenolic resin binder ($\times 30\,000$). C, large chrysotile fibre bundle ($\times 45\,000$). D, large particle in left centre of photograph is the same as in C, but cannot be identified at low magnification ($\times 5400$)

is removed from the axle and loose dust is commonly removed from the drum and back plates by means of a jet of compressed air. A survey of 220 garages in Baltimore and Washington, DC has shown that this is the method of choice in 80% of the shops (Castleman *et al.* 1975). A similar situation exists in New York City. The data in Table 2 show that fibre concentrations are high in the breathing zone of the operator during compressed air blowing. An asbestos concentration gradient, diminishing with time and distance away from the operation, appears to occur. Persons up to 22 m from such activity are exposed to measurable concentrations of asbestos.

Personal air sampling was also conducted at New York City Department of Sanitation where truck brakes are repaired. Used linings are salvaged by machine grinding to remove dirt and grease from the surface. New linings are bevelled by grinding to reduce noise and improve break-in. Accordingly, these studies relate to levels of asbestos exposure which may be experienced by workers engaged in brake lining manufacturing. Table 2 shows that fibre concentrations experienced during grinding ranged from 1.7 to 7.0 f/ml of air in the breathing zone of the operator. The background or area samples for this operation ranged from 1.2 to 0.2 f/ml, with a general decrease

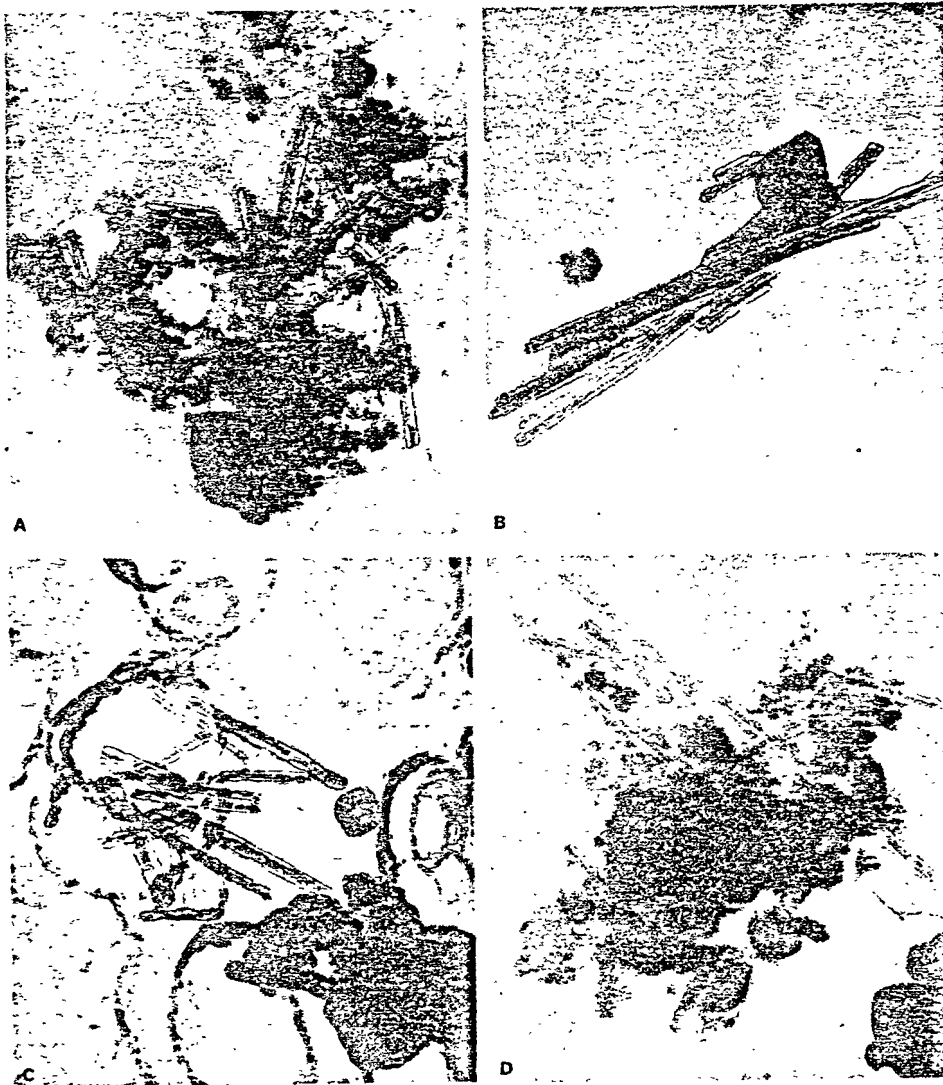


Fig 2 Electron photomicrographs of personal air samples taken during brake repair work. Clumps of chrysotile are associated with opaque particles of road dust and resin binders. A, B, $\times 60\,000$. C, D, $\times 72\,000$

Table 2

Personal air samples, automobile and truck brake repair

	No. of samples	Peak fibre concentration (fibres per ml)	
		Mean	Range
<i>Automobile brake repair</i>			
Blowing dust from brake drums:			
Distance 1-1.5 m	4	15.0	6.6-29.4
Distance 1.5-3 m	3	3.3	2.0-4.2
Distance 3-6 m	2	1.6	0.3-4.8
Background (5 min after air jet blowing, distance 3.6-16 m)	2	0.2	0.1-0.2
Background (7-14 min after air jet blowing, distance 19.6-22.6 m)	2	0.1	0.1
	13		
<i>Truck brake repair</i>			
Renewing used linings by grinding (distance 1-1.5 m)	10	4.8	1.7-7.0
Background to grinding used linings:			
Distance 3.3 m	2	1.5	1.2-1.7
Distance 8.3 m	2	0.8	0.6-1.0
Distance 20.0 m	1		0.2
Bevelling new linings	4	37.3	23.7-72.0
Background to bevelling new linings:			
Distance 2.4 m	1		0.6
Distance 3.6 m	2	0.4	0.3-0.5
Distance 9.1 m	1		0.3
	23		

away from the operator. From six to ten other mechanics work within an area up to 20 m from this operation are exposed to asbestos as well. Since a person breathes about one cubic metre of air an hour, multiplication of the fibre concentrations by one million gives the number of fibres inhaled during this period. Fibre concentrations measured during bevelling of truck linings were as high as 72 f/ml and averaged about 37 f/ml. Background counts were measured up to 9.1 m away from this operation (0.3 f/ml). Fibre concentrations measured during drilling holes for rivets and grinding ranged from 0.3 to 29.2 f/ml, as reported by Boillat & Lob (1973). Four of the nine values exceeded 5 f/ml.

Conclusions

The existence of significant exposure during brake servicing operations necessitates the following measures:

- (1) Implementation of industrial hygiene procedures to control exposure.
- (2) Clinical studies of garage mechanics to determine evidence of asbestos-related disease.
- (3) Epidemiological studies of the mortality experience of exposed workers.

In addition, the entire variety of dusts and other materials present in brake repair work should be characterized in order to determine its disease potential, especially silica and lead compounds.

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Neurotoxic Properties of Certain Aliphatic Hexacarbons

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During the summer of 1973 an outbreak of peripheral neuropathy developed among a large group of employees of a fabric manufacturing plant in Ohio, USA (Billmaier *et al.* 1974). The disease was characterized by distal weakness and sensory loss symmetrically in both the hands and the feet (Allen *et al.* 1975). The most severely affected individuals worked in the printing department where colouring inks, dissolved in volatile solvents, were applied to the surfaces of plastic coated fabrics. For several years the printing process required the use of a 9:1 solvent mixture containing methylethylketone (MEK) and methylisobutylketone (MIBK). Methyl-*n*-butylketone (MBK) was gradually introduced in the summer of 1972 to replace the MIBK. Methyl-*n*-butylketone was in its maximal use by December 1972 and the first case of peripheral neuropathy occurred shortly thereafter. The recent introduction of MBK into the printing department of the plant, coupled with other isolated outbreaks of neuropathy in individuals chronically exposed to MBK, suggested that this compound had neurotoxic properties. MBK produced peripheral neuropathy in

several species of experimental animal (Duckett *et al.* 1974, Mendell *et al.* 1974, Spencer, Schaumburg, Raleigh & Terhaar 1975). These studies demonstrated that prolonged intoxication by inhalation or subcutaneous injection caused the insidious development of symmetrical weakness first in the hindlimbs and later in the forelimbs. The first signs of peripheral neuropathy developed after 4 to 12 weeks of continuous inhalation of 200-600 parts/10⁶ of MBK, and after 12 to 16 weeks of intermittent inhalation of 1300 parts/10⁶ of MBK. The onset of MBK neuropathy was associated with a reduction in the sciatic nerve conduction velocity (Mendell *et al.* 1974), an indication of nerve damage also found in rats and monkeys inhaling 1000 or 100 parts/10⁶ MBK intermittently for periods of 3 and 8 months respectively (Johnson 1975), the figure of 100 parts/10⁶ being the recommended Threshold Limit Value in the United States. Recent studies have suggested that concurrent exposure to MEK and MBK will produce neuropathy more rapidly than in animals exposed to MBK alone (Saida *et al.* 1976). Methyl-ethylketone alone or MBK alone produce no neurotoxic effects (Spencer & Schaumburg 1976).

The purpose of the present paper is to emphasize the importance of chronic testing of potentially neurotoxic compounds in experimental animals, to describe the range of hexacarbon compounds which have been identified as neurotoxic agents and, finally, to characterize and illustrate the pathological basis for the onset of the nervous system disease. A total of seven hexacarbon compounds have been tested in this study (Table 1).

Table 1
Hexacarbon compounds tested

- | | |
|-----------------------------------|--|
| (1) <i>n</i> -hexane | CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ |
| (2) methyl- <i>n</i> -butylketone | CH ₃ COCH ₂ CH ₂ CH ₂ CH ₃ |
| (3) 2,5-hexanedione | CH ₃ COCH ₂ CH ₂ COCH ₃ |
| (4) 2,5-hexanediol | CH ₃ CHOH(CH ₂) ₂ CHOHCH ₃ |
| (5) 2,4-hexanedione | CH ₃ COCH ₂ COCH ₂ CH ₃ |
| (6) 2,3-hexanedione | CH ₃ COCOCH ₂ CH ₂ CH ₃ |
| (7) 1,6-hexanediol | HOCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH |

The first compound, *n*-hexane, an important solvent and a minor component of petrol, was indicted in several reports as a possible neurotoxic agent (Herskowitz *et al.* 1971, Korobkin *et al.* 1975). Rats were exposed continuously to atmospheric levels of 400 to 600 parts/10⁶ of *n*-hexane for up to five months, 500 parts/10⁶ being the US Threshold Limit Value for *n*-hexane (*see also* Schaumburg & Spencer 1976). The second compound, methyl-*n*-butylketone, the solvent implicated in the outbreak of neuropathy, was administered to cats by subcutaneous injection of 150 mg/kg twice daily for periods up to six months (*see also* Spencer & Schaumburg 1976). The third compound, 2,5-