

INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT
ON ORGANOPHOSPHORUS EXPOSURES

at

Michigan Casting Center
Ford Motor Company
Flat Rock, Michigan

SURVEY CONDUCTED BY:

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Industrial Hygiene Section
Industrywide Studies Branch
Division of Surveillance, Hazard Evaluations and Field Studies
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Cincinnati, Ohio

PURPOSE OF SURVEY:

This survey was initiated for the purpose of identifying a population of workers that could be used in a study to determine whether any neurological effects are associated with occupational exposure to organophosphorus compounds.

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**STANDARD INDUSTRIAL
CLASSIFICATION OF PLANT:**

3714

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ABSTRACT

A walk-through survey was conducted at the Michigan Casting Center, Ford Motor Company to determine the suitability of the workforce for studying delayed neurotoxic effects in workers from exposure to organophosphate (OP) esters. Airborne samples were collected in the Molding Department to determine OP ester exposures from the use of hydraulic fluids. Samples were collected on Millipore Type AA filters for approximately 2 hours at a hydraulic fluid pump station and the hydraulic fluid storage facility. Two types of OP esters were found in the airborne samples using gas chromatographic analysis.

Only one of the OP esters, triphenyl phosphate, could be identified from the airborne samples. The unidentified OP ester was estimated to be quantitatively similar to the triphenyl phosphate concentration, therefore, an estimation of total OP ester exposure for each sample was performed. The highest triphenyl phosphate concentration was 0.014 mg/m^3 (OSHA standard is 3.0 mg/m^3), while the highest total OP ester concentration was estimated at 0.028 mg/m^3 .

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is mandated under Section 20(a)(7) of the Occupational Safety and Health Act of 1970 to conduct and publish industrywide studies of the effect of chronic or low level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in aging adults.¹ This study was initiated due to recently conducted epidemiologic studies which have suggested that delayed neurotoxic effects may exist in workers exposed to organophosphorus (OP) esters which are used in commercial and industrial applications, other than as pesticides. Even though many of the OP pesticides are known neurotoxins, little is known about the health effects of exposure to other OP compounds (particularly the aryl phosphates) and their commercially important end products. Because of the expanding production and use of non-pesticide OP esters (i.e. in plastics, hydraulic fluids, lubricants, air filter media, flame retardants, etc.) and the health implications reported from exposure to OP pesticides, NIOSH elected to study the subclinical neurologic effects in workers with chronic occupational exposures to non-pesticide OP esters. Based on the above criteria, the Michigan Casting Center of the Casting Division of Ford Motor Company was selected as a potential study cohort.

HISTORY OF NON-PESTICIDE ORGANOPHOSPHORUS ESTERS

Uses

The first OP compounds, tetraethyl pyrophosphate and triphenyl phosphate, were synthesized in the 1850's; however, there was no commercial usage of OP compounds until the turn of the century when triphenyl phosphate was utilized as a plasticizer.² In the 1930's the insecticidal and fungicidal properties of OP compounds were discovered with tetraethyl pyrophosphate being the first commercial OP insecticide in 1944.³

Other research and development of OP esters was primarily concentrated in the areas of plastics and lubricants, and by the 1950's OP compounds were commonly used in these areas with the combined production of the primary OP esters of tricresyl phosphate and triphenyl phosphate being increased to 21 million pounds. By 1973 their combined production had increased to approximately 50 million pounds, with the production of more recently developed esters like isodecyldiphenyl phosphate and isopropyldiphenyl phosphate also continuing to increase.⁴

Excluding pesticide formulations, the primary uses of OP esters continue to be in the manufacture of plastics, hydraulic fluids, and lubricants, and to a lesser extent as flame retardants, in air filter media, lacquer coatings, wood preservatives, and methylating agents. The major markets for OP esters are in the plasticized products industries such as transportation, building and construction, electrical/electronics, furnishings, packaging, and housewares/appliances. Of these, the principal market is in the manufacture of automobile and other motor vehicle interiors in which numerous polyvinyl chloride products are utilized.^{4,5}

The fastest growing usage for OP esters is in the manufacture of fire-resistant hydraulic fluids and lubricants additives. The two principal types of OP hydraulic fluids being manufactured are phosphate ester oil blends and "pure" synthetics. The phosphate ester oil blends contain between 30% and 50% OP esters in addition to petroleum oil and a coupling agent; the pure synthetic OP hydraulic fluids contain only a mixture of OP esters.⁴ For example, a typical synthetic OP fluid could contain tricresyl phosphate, trixylenyl phosphate, and other triaryl phosphates. OP ester-lubricant additives are usually of three general types; extreme pressure agents, anti-wear agents, and stick-slip moderators.⁴ The first two types are used in systems with some type of gears and account for over 80% of all OP lubricant additives. Among the other uses for these agents are: cutting oils, machine oils, transmission fluids, and cooling lubricants.

Health Effects

The neurotoxicity of OP compounds can be traced to the 1920's with most of the reported neuropathies occurring in tuberculosis patients treated with phosphocreosote. However, the neurotoxicity of phosphocreosote was not recognized until 1930 when a massive epidemic of poisoning involving more than 16,000 people was studied. This so-called "Ginger Paralysis" involved a fluid extract of ginger containing a high ethanol content (accounting for its popularity during Prohibition) and a mixture of cresyl phosphates, which was used to extract the ginger.^{6,7}

Early studies reported that only the "ortho" isomer among symmetrical cresyl phosphates produced toxic effects. It therefore became standard practice for mixed esters to be produced from coal-tar stock containing less than a specified amount of ortho-cresol. Despite this precaution, other outbreaks of triorthocresyl phosphate poisoning have occurred involving acute exposures due to ingestion of contaminated food products or water.

The characteristic effect of triorthocresyl phosphate exposure, and that of many other OP's, is delayed neurotoxicity. Clinical effects are not seen until 8 to 14 days after exposure to the OP substance. The time between exposure and onset of symptoms varies with the route and degree of exposure. Many OP compounds are recognized cholinesterase inhibitors which can lead to disturbed function of cholinergic synapses involving the neuromuscular junctions in skeletal, cardiac, and smooth muscle.⁹

Behavioral effects of both acute and chronic exposure to OP's have also been reported. However, behavioral abnormalities following acute OP intoxication have received substantially more attention and are better documented. Giddiness, anxiety, depression, restlessness, irritability, memory disturbance, and difficulty concentrating are among the possible behavioral effects due to acute OP poisoning.^{10,11} Studies of chronic OP exposure to workers suggest similar psychological and behavioral effects with reported memory and concentration functions sufficiently impaired to interfere with work and reading ability.^{12,13,14}

DESCRIPTION OF FACILITY

The Michigan Casting Center, in Flat Rock, Michigan, of the Ford Motor Company's Casting Division, has been located at this site since 1971. Manufacturing at the plant has been primarily the casting of iron automotive engine blocks and components. Typical operations at the plant consist of coremaking, patternmaking, melting, pouring, and casting (molding). The area of interest during the survey was in the Molding Department, especially around the hydraulic pump station (near the #1 mold line), and in the storage room which contained new and reclaimed hydraulic fluid. Air sampling was performed in this department because of the use of hydraulic fluids which contained a blend of organophosphate esters.

DESCRIPTION OF WORKFORCE

At the time of the survey, the Michigan Casting Center employed approximately 2400 hourly workers; of these, about 500 worked in the Molding Department. Workers not included in this department, but who often worked in areas where hydraulic fluids were used, included the job types of oiler, pump man, cleanup man, and machine repairman. The workforce is comprised mostly of men (90%), and is divided among three 8-hour work-shifts a day with most of the employment on the first and second shifts.

DESCRIPTION OF PROCESS

The Molding Department is located between the departments of Melting, Finishing, and Core Making Departments (see Figure 1). Within the Molding Department are five mold lines capable of casting automotive engine blocks, heads, and accessory parts of iron. At the time of the survey only the #1, #2 and #5 mold lines were operational.

Molten iron is transferred from the adjacent Melting Department overhead in 50-ton ladles from the melt furnaces to an appropriate holding furnace and then taken by tram car to the mold line. The furnace maintains the metal in a molten state (2750°F) until poured into a mold at each mold line. Once cast, the pieces are air-cooled and are conveyed to the Finishing Department where rough edges are trimmed with all scrap and defective pieces recycled back into the melt process.

Areas with the greatest potential for organophosphate esters were the pump stations (located next to each mold line in the Molding Department and west end of the Melting Department) where hydraulic fluid is recirculated to the melt furnaces and molding machines. Likewise, a potential for exposure existed around the perimeter of the tanks (located at the north end of Molding Department) where new and reclaimed hydraulic fluids were stored.

Once the hydraulic fluids have lost their desired operational properties they are transferred to a holding tank outdoors (north end of building) and before being picked up by an outside contractor (Aztec Oil, Flint, Michigan) two to three times/year for reprocessing. Approximately 40% to

50% of the hydraulic fluid is reclaimed by the contractor during reprocessing; the reclaimed fluid is returned to the plant and supplemented with virgin hydraulic fluid. At the time of the survey both Fyrtek 295 (Stauffer Chemicals Company) and Pydraul 312C (Monsanto Industrial Chemicals Company) fire resistant hydraulic fluids were used. Both types of fluids are considered to be OP ester blends.

DESCRIPTION OF EXPOSURES

All workers in the Molding Department have a potential for exposure to OP esters with the most probable areas of exposures being around the molding machines and near the housing of the hydraulic system pumps. However, the hydraulic system at the molding machines was completely enclosed with little or no hydraulic fluid leakage. Therefore, no air sampling for OP esters was performed in these areas since it was felt that exposures would be minimal.

Within both the Molding and Melting Departments hydraulic fluid pumps are housed in enclosed rooms (8 feet by 15 feet). Three pumps are used at each location for recirculating the hydraulic fluid and maintaining the pressure in the hydraulic system. At each pump a drip pan is used to collect hydraulic fluid which leaks from the pump system.

At the north end of the building where new and reclaimed hydraulic fluid is stored, some leakage of fluid was noted around the storage tanks. The fluid from these tanks is pumped within an enclosed system to the pump stations in the Melting and Molding Departments.

Because of the relatively high molecular weights for most of the common OP esters (usually between 325 and 410) and their low vapor pressure, the prospect for high airborne exposures at room temperature (70 - 80°F) is remote. Therefore, it was assumed that OP exposures were more likely to occur near the hydraulic pump station due to the elevated temperatures (~120°F) of the hydraulic fluid in the pumps.

Besides the potential for airborne OP ester exposure, the possibility of dermal exposure and subsequent skin absorption also exists. However, no evaluation was made at the time of the survey as to the extent of dermal exposure.

DESCRIPTION OF MEDICAL, INDUSTRIAL HYGIENE AND SAFETY

The plant has the services of two full-time medical physicians who are responsible for pre-employment and periodic physical examinations of employees. Pre-employment examinations include chest x-ray, audiometry, visual acuity, lung function, and blood and urine tests. The medical department also has a number of licensed nurses who are at the plant 24 hours/day to provide emergency treatment. Likewise, there is at least one employee in each department per shift with formal first aid training.

The Safety Department at the plant is responsible for insuring safe work practices and conditions, and providing and maintaining safety equipment. Workers in the Molding Department are provided safety glasses and shoes; those workers handling hot metal castings are provided with thermal gloves. No respiratory protection is required in this department, but is available upon request. Facilities for changing clothes and taking showers are provided. Periodic safety meetings and inspections are held with management and hourly employees to discuss problem areas and make recommendations.

The Ford Motor Industrial Hygiene and Toxicology Department, a central staff function, performs periodic industrial hygiene inspections of the plant. No airborne sampling for OP esters had been done prior to this survey.

DESCRIPTION OF RECORD SYSTEM

A hard copy employment record, in addition to a computerized file, is maintained on every employee. Demographic information includes address, date of birth, social security number, date of employment, marital status, number of dependents, education, and previous employment history. Once employed, a clock number is assigned and recorded in the personnel file for each worker; in addition, the job title, pay rate, department number, and job code are likewise entered into the file. All subsequent changes in job title or transfer to other departments are likewise recorded. It appears that the type of personnel information collected and the maintenance of the records are adequate for conducting a medical study of delayed neurotoxicity in workers.

DESCRIPTION OF SURVEY METHODS

Stationary airborne samples for OP esters were collected in areas where exposures were thought to be most prevalent, the pump station next to the number 1 mold line in the Molding Department and the room used for storing new and reclaimed hydraulic fluid. Locations of airborne samples are illustrated in Figure 1. Samples were collected using Millipore Type AA, 0.8 μm pore size filters and a battery-operated Staplex BS pump at a calibrated flow rate of 12.0 liters per minute over approximately 1 to 2 hours.

Airborne samples were analyzed using NIOSH Method No. P&CAM Number S209 with some minor modifications.¹⁵ The analysis was performed by gas chromatography (GC) using a flame photometric detector (FPD) in the phosphorus mode. The column was operated at a temperature of 230°C isothermal. Each filter sample was desorbed with 10 ml of ethanol; the desorbed samples were allowed to stand for 1 hour at room temperature and a 5 μl aliquot of each was injected into the GC for analysis.

A bulk liquid sample was collected of the hydraulic fluid which was being recirculated through the casting machines in the Molding Department. This sample was a mixture of both the virgin and reclaimed hydraulic fluids. The bulk sample was analyzed in the same manner as the OP esters airborne samples.

RESULTS AND DISCUSSION

The results of the two airborne samples for OP esters are presented in Table 1. Both airborne samples showed a similar chromatograph pattern with two major OP ester peaks observed. One of the peaks was identified as triphenyl phosphate; this peak was quantitated and a concentration determined. The second peak could not be identified as it did not compare to the retention times for any of the available standards; however, assuming the response of the FPD for the second peak is similar to triphenyl phosphate and considering the size of the peak, it was estimated that the amount was equivalent to that found for triphenyl phosphate. Therefore, the same concentration value was assigned to the unknown peak for the purpose of determining the total OP ester concentration for each sample.

As noted in Table 1, the airborne concentrations for total OP esters (0.024 and 0.028 mg/m³) and in particular for triphenyl phosphate (0.012 and 0.014 mg/m³), were relatively low when compared to the OSHA 8-hour TWA standard of 3.0 mg/m³ for triphenyl phosphate. Based on the environmental conditions and continuity of the operations which existed during sample collection it would be reasonable to assume that the magnitude of concentrations observed is probably typical of normal conditions.

The hydraulic fluid sample was analyzed by diluting with pure ethanol (2000:1) and injecting 1 μ l into a gas chromatograph. The fluid showed a complicated chromatogram containing five phosphate peaks. Only the peak of triphenyl phosphate could be identified from the pattern.

CONCLUSIONS AND RECOMMENDATIONS

As indicated from the airborne sample results, exposure concentrations to total OP esters appear to be relatively low with triphenyl phosphate being identified as one of the major ester components. Triphenyl phosphate has been shown to have low acute toxicity for rats, mice, and guinea pigs, however, it will produce delayed generalized illness and paralysis in cats and monkeys.^{16,17} When administered orally or injected in alcohol solution into rats, mice, guinea pigs, and cats it was found to be slowly absorbed; likewise, it was shown to be poorly absorbed through the skin and did not produce skin irritation.¹⁶ In a medical study of workers engaged in the manufacture and use of triphenyl phosphate, with average airborne exposures of 3.5 mg/m³,¹⁶ only a reduction in red blood cell cholinesterase activity was observed. To date, animal studies and medical observations are inconclusive as to the demyelinating neurotoxic effect of triphenyl phosphate to man.

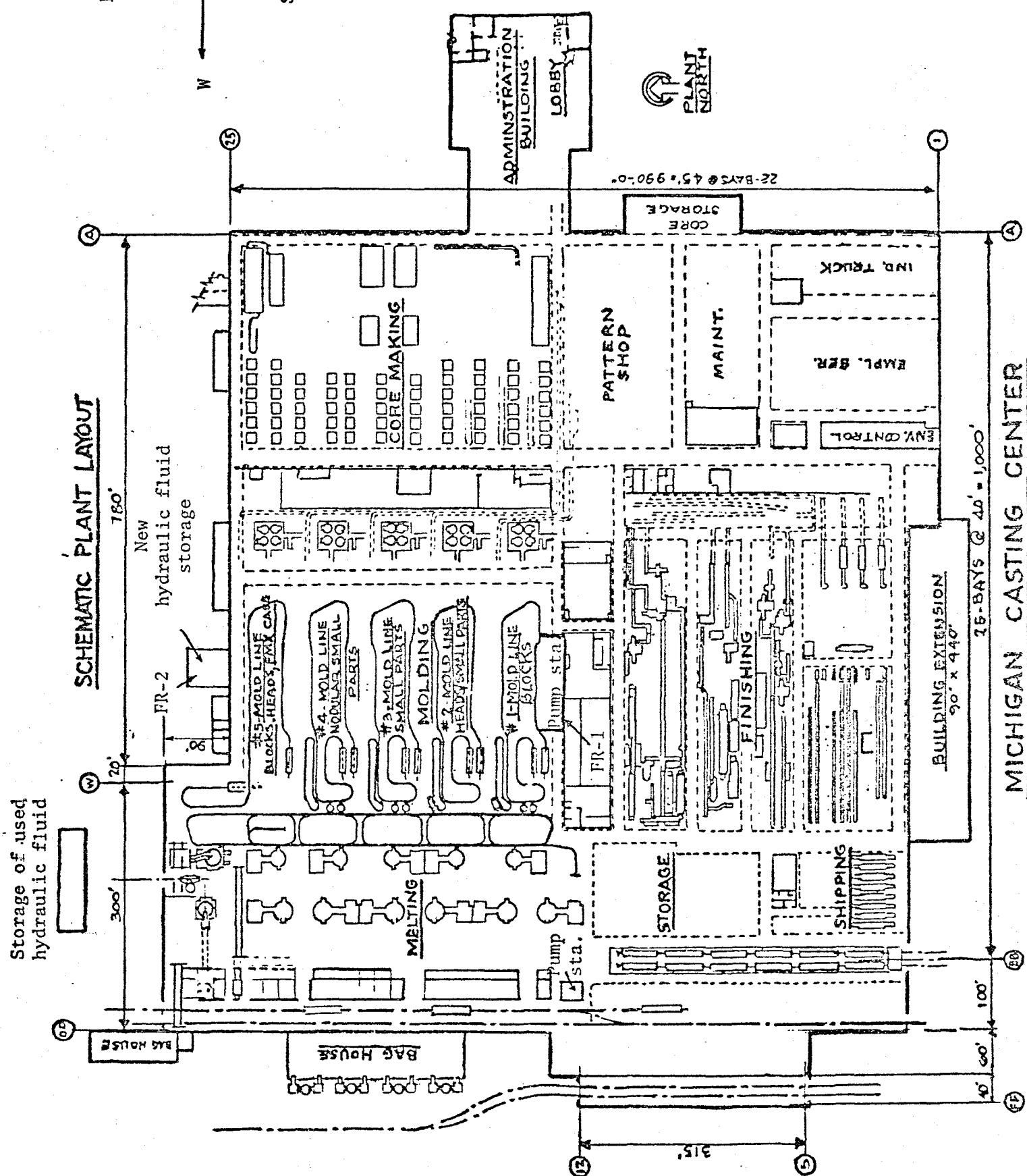
Although airborne exposures to the unidentified OP esters were found at low concentrations, the potential for causing delayed neurotoxic effects is unknown. Likewise, even though triphenyl phosphate has been shown to be poorly absorbed through the skin, the absorption rate of the other OP's found in the study is not known. Therefore, skin absorption may be a greater potential route of entry than inhalation for employees working with these hydraulic fluids. When handling of these fluids is required, it would be advisable to prevent skin contact by wearing suitable protective apparel and gloves.

Because of the small number of workers who are potentially exposed to OP esters, and due to the lack of identification and uncertainties of skin absorption for some OP esters, the Ford Flat Rock, Michigan Casting Center was determined not to be suitable as an appropriate population for studying delayed neurotoxic effects.

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MICHIGAN CASTING CENTER

TABLE 1
AIRBORNE SAMPLE RESULTS FOR ORGANOPHOSPHATE ESTERS
MICHIGAN CASTING PLANT, FLAT ROCK, MICHIGAN
MARCH 14, 1980

Sample Number	Sample Location	Flow Rate (lpm)	Volume (liters)	Triphenyl Phosphate (mg/m ³)	Total Phosphate Ester Concentration (mg/m ³)
FR-1	At hydraulic system pump station. Molding Department	12	1260	0.014	0.028
FR-2	At storage facility where new and reclaimed hydraulic fluid is housed	12	972	0.012	0.024

NOTE: 8-hr. OSHA TWA standard for triphenyl phosphate - 3.0 mg/m³
Lower limit of detection for triphenyl phosphate - 1 μ g/sample