INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT ON ORGANOPHOSPHORUS EXPOSURES

at

Rochester Products Division
General Motors Corporation
1000 Lexington Avenue
Rochester, New York

SURVEY CONDUCTED BY:
Ralph D. Zumwalde
Charlotte Cottrill

DATE OF SURVEY:
October 12, 1979

REPORT WRITTEN BY:
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Industrial Hygiene Section
Industry-wide Studies Branch
Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
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.

EMPLOYER REPRESENTATIVES:

Thomas Husted, Plant Manager
Steve Savnier, Personnel Director
Stu Phelps, Plant Engineering
Thomas Gilligan, Toxic Substances Control Chemist
William Kilgore, Corporate Industrial Hygienist
Wayne Burdett, Safety and Security

EMPLOYEE REPRESENTATIVE: Joseph Musson, UAW Union

STANDARD INDUSTRIAL CLASSIFICATION OF PLANT: 3592

Mention of a company's name, brand, or trademark does not constitute endorsement by the National Institute for Occupational Safety and Health.

ABSTRACT

A walk-through survey was conducted at the Rochester Products Division of General Motors 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 Die Cast Department to determine OP ester exposures from the use of hydraulic fluids. Samples were collected on Millipore Type AA filters for approximately 4 hours at various stationary locations within the department. A total of 13 OP esters were found in the airborne samples using gas chromatographic analysis.

Only 2 of the 13 OP esters, triphenyl phosphate and diphenyl 2-isopropyl phenyl phosphate, could be identified; ten of the remaining esters were found in trace amounts, the other could not be identified. The highest triphenyl phosphate concentration was 0.057 mg/m^3 (OSHA Standard is 3.0 mg/m^3) while the highest diphenyl 2-isopropyl phenyl phosphate was 0.013 mg/m^3. The highest total OP ester concentration was estimated at 0.15 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 industry-wide 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 based on 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.[2,3] 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. plastics, hydraulic fluids, lubricants, air filter media, flame retardents, etc.) and the health implications reported from exposure to OP pesticides, NIOSH has elected to study the subclinical neurologic effects in workers with chronic occupational exposures to non-pesticide OP esters. Based on the above criteria, Rochester Products Division of General Motors was selected as a potential study cohort.

HISTORY OF NON-PESTICIDE ORGANOPHOSPHORUS ESTERS

Uses

The first OP compounds, tetra ethyl 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.[4] In the 1930's the insecticidal and fungicidal properties of OP compounds were discovered with tetra ethyl pyrophosphate being the first commercial OP insecticide in 1944.[5]

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 isodecyl diphenyl phosphate and isopropyl diphenyl phosphate also continuing to increase.[6]

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 in air filter media, lacquer coatings, wood preservatives, methylating agents, and as flame retardants. The major markets for OP esters are in the plasticized products industries such as transportation, building and construction, electrical/electronics, furnishings, packaging, and housewares/applicances. Of these, the principal market is in the manufacture of automobile and other motor vehicle interiors in which numerous polyvinyl chloride products are utilized.[6,7]

The fastest growing usage for OP esters is in the manufacture of fire-resistant hydraulic fluids and lubricants. 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 a mixture of OP esters.[6] 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.[6] 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.[8,9]

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.[10] The time between exposure and onset of symtoms 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.[11]

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, irritiability, memory disturbance, and difficulty concentrating are among the possible behavioral effects due to acute OP poisoning.[12,13] 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.[14,15,16]

DESCRIPTION OF FACILITY

Rochester Products is a Division of General Motors Corporation which has been located at this site (Rochester, New York) since 1937. Initial manufacturing at the plant consisted of electrical components for automotive use; during World War II this was expanded to include specialized electrical components for aircraft. In the late 1940's production was expanded to include the manufacturing of automotive carburetors and locks; the making of locks was discontinued in 1977. The area of interest during the survey was the Die Cast Department which is housed in a separate area of the plant. All aluminum and zinc die casting of carburetors takes place in this area. Air sampling was performed in this department because of the use and recycling of hydraulic fluids which contained a blend of OP esters.

DESCRIPTION OF WORKFORCE

At the time of the survey Rochester Products employed approximately 5000 hourly workers, of these, 219 worked in the Die Cast Department. Workers in the Die Cast Department consisted of 163 operators, 31 die cast set operators, 16 die cast alloy operators, 6 metal pot tenders, and 3 fork lift operators; not included in this department but who often worked in the area were 13 maintenance workers and an inspector. The workforce which is comprised mostly of men (∿95%) is divided among three 8-hour workshifts a day with most of the employment on the 1st and 2nd shifts.

DESCRIPTION OF PROCESS

The Die Cast Department has been located in this area of the plant since 1965 and consists of approximately 120 die cast machines (60% zinc and 40% aluminum) with five zinc and four aluminum furnaces (Figure 1). Also located in this department is the hydraulic fluid recovery and reclamation system.

The department is sub-divided into zinc and aluminum areas where the respective metal carburetors are casted. Between the rows of casting machines the molten metal is transfered overhead in pots from the melt furnaces to an appropriate holding oven which maintains the metal in a molten state until poured into a casting machine. Once cast the pieces are either air-cooled or quenched with water as they come out of the die cast machines, rough edges are trimmed, and all scrap and defective pieces are recycled into the process.

The greatest potential for exposures to organophosphate esters is found at the die cast machines where leaks of hydraulic fluid and water are captured in a trough around the perimeter of each machine and near the hydraulic reclamation system. The water and spent hydraulic fluid from the die cast machines are recovered in the basement of the plant (a metal grate floor allows fluid to run into the basement) where they are pumped into a 500 gallon heated ($60^{o}F$) settling tank. The fluid is retained in the tank where most of the water is separated and transferred to the industrial water treatment system. Once the tank becomes filled with hydraulic fluid it is pumped through a 25 micrometer pore filter and into a second holding tank. Subsequently, the hydraulic fluid is recirculated through a 5 gallon per minute vaporizing system for 32 hours. This sytem reduces the water content in the fluid to 0.2% which is about twice the amount typically contained in virgin hydraulic fluid. After the water is removed, the fluid is pumped to a third heated tank and filtered through Fuller's Earth to reduce the acidity.

Hydraulic fluid which cannot be reclaimed inhouse is collected in another holding tank and processed by outside contractors (3 to 4 times/year). Approximately 40% to 50% of the hydraulic fluid is recovered with the balance supplemented with virgin hydraulic fluid. At the time of the survey both Houghto-Safe 1120 (F. Houghton Company) and Fyrquel 220 (Stauffer Chemical Company) fire resistant hydraulic fluids were used. Only Fyrquel 220 was being used up until 1977. Both types of fluids are considered synthetic blends containing various OP esters (e.g. tri-aryl, triosopropyl phenyl phosphates).

DESCRIPTION OF EXPOSURES

All workers in the Die Cast Department have a potential for exposure to OP esters with the most probable areas of exposure found around the die cast machines and the reclamation system. Because of the molecular weights for most of the common OP esters (usually between 325 and 410) and their low vapor pressures the potential for high airborne exposures at room temperature is remote. However, the likelihood of OP exposures near the die cast machines is enhanced due to the elevated temperatures ($\sim 100^{\circ}F$) of the hydraulic fluid.

Besides the potential for airborne OP ester exposure, the possibility of dermal exposure and subsequent skin absorption exists. No evaluation was made at the time of the survey as to the extent of dermal exposure. Other exposures which may have been present in the work environment included airborne zinc, aluminum, ethylene glycol, polyethers, and isopropyldiethanolamine soap.

Ventilation in the Die Cast Department consisted of local exhaust at the melt furnaces with a wet scrubber used for fume collection, and general dilution ventilation at a rate of 220,000 cfm for the entire department. General dilution ventilation was achieved by drawing air up through the grated portion of the floor and exhausted out the roof by 8 fans.

DESCRIPTION OF MEDICAL, INDUSTRIAL HYGIENE AND SAFETY

The plant has the services of a full-time medical physician who is 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 and physician assistants 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. According to the plant's medical physician no medical abnormalities among workers in the Die Cast Department have been attributed to an occupational exposure.

The Safety and Security Department exists at the plant to insure safe work practices and conditions, and to provide and maintain safety equipment. Workers in the Die Cast Department are provided work clothes, safety glasses, and shoes; those workers handling hot metal castings are provided with thermal gloves. No respiratory protection is required in this department. 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.

Industrial hygiene responsibilities are handled through the Laboratory Services Section, Materials and Chemical Engineering Department which is responsible for monitoring and analyzing metal fumes and organic vapors in the Die Cast Department. The General Motors Industrial Hygiene Department performs periodic inspections of the plant and is available for additional assistance upon request. No airborne sampling for OP esters had been performed prior to this survey because of the low probability of the occurrence of excessive exposure levels. Since an Occupational Safety and Health Administration (OSHA) standard exists for zinc oxide fume (5 mg/m^3) periodic airborne sampling has been performed in the Die Cast Department by plant personnel; zinc exposures have been below the OSHA standard.

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 the Die Cast Department in areas where exposures were thought to be possible. Locations of all airborne samples are illustrated in Figure 1. Samples were collected using MSA Model G sampling pumps with Millipore Type AA, 0.8 micrometer pore size filters at a calibrated flow rate of 2.0 liters per minute over approximately a 4-hour period. In a similar manner, additional simultaneous sampling was performed by Rochester Products personnel to compare sample results.

Airborne samples were analyzed using NIOSH Method No. P&CAM Number S209 with some minor modifications.[17] The analysis was performed by gas chromatography (GC) using a flame photometric detector in the phosphorous mode. The column was operated at a temperature of 230°C isothermal. Each filter sample was desorbed with 10 milliliters of ethanol; the desorbed samples were allowed to stand one hour at room temperature and a 5 microliter (ul) aliquot of each was injected into the GC for analysis.

Since ethylene glycol is used in small amounts as a mold release agent on the die cast machines one of the stationary OP airborne samples (N-083) was also analyzed for ethylene glycol. This sample was analyzed using gas chromatography with a flame ionization detector and a Porapak Q column. No samples were collected for airborne zinc or aluminum since exposure data from the company indicated low concentrations, and because exposure to these metals was felt not to be a confounding exposure should a neurotoxic study be conducted.

A bulk liquid sample was collected from the spent hydraulic fluid coming out of the die cast machines and from the mixture of virgin hydraulic fluids. These two bulk samples were analyzed in the same manner as the airborne OP samples.

RESULTS

The results of the 6 airborne samples for OP esters are presented in Table 1. All 6 samples showed a similar chromatographic pattern with 3 major OP ester peaks. The chromatograms also had a similar pattern of about 10 minor OP peaks of varying sizes. None of the minor peaks exceeded 10% of any major peak size on the chromatograms. Two of the major peaks were identified as triphenyl phosphate and diphenyl 2-isopropyl phenyl phosphate; these peaks were quantitated and concentrations determined. The third major peak could not be identified as it did not compare to any of the available standards; however, assuming the response of the flame photometric detector for the third 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 for the purpose of determining the total OP ester concentration for each sample. None of the 10 minor OP peaks could be identified but were assumed to be esters and, as a group, were equivalent to about 15% of the 3 major peaks for any given sample. Therefore, approximate concentrations were calculated for these 10 minor peaks and are reported in Table 1. No ethylene glycol was found in sample N-083.

Triphenyl phosphate was the only OP ester identified for which an OSHA standard exists (the 8-hour time-weighted average is 3 mg/m^3); however, the highest concentration found for triphenyl phosphate was 0.057 mg/m^3 for a sample collected near a zinc die cast machine. Likewise, the highest diphenyl 2-isopropyl phenyl phosphate concentration was 0.013 mg/m^3 found for this same sample with an estimated total OP ester concentration of 0.15 mg/m^3.

Each of the 2 liquid hydraulic fluid samples was analyzed by diluting (2100:1) with pure ethanol and injecting 1 ul into a gas chromatograph. Both fluids showed complicated chromatograms containing about 10 peaks with both samples having a similar chromatographic pattern. Only the peak of triphenyl phosphate could be identified from each pattern.

DISCUSSION

As indicated from the airborne sample results, exposure concentrations to total OP esters appears 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.[3,16] 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/m^3, only a reduction in red blood cell cholinesterase activity was observed.[3] To date, animal studies and medical observations are inconclusive as to the demyelinating neurotoxic effect of triphenyl phosphate to man.

Although airborne exposures to diphenyl 2-isopropyl phenyl phosphate were found at even lower concentrations, the potential for causing delayed neurotoxic effects is unknown; likewise, the same is true for the 11 unidentified OP esters found in the air samples. Although 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 this workforce.

Because of the lack of identification for all OP ester exposures and due to the uncertainties of OP ester skin absorption the Rochester Products facility was determined not to be suitable as an appropriate study population at this time.

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Table 1

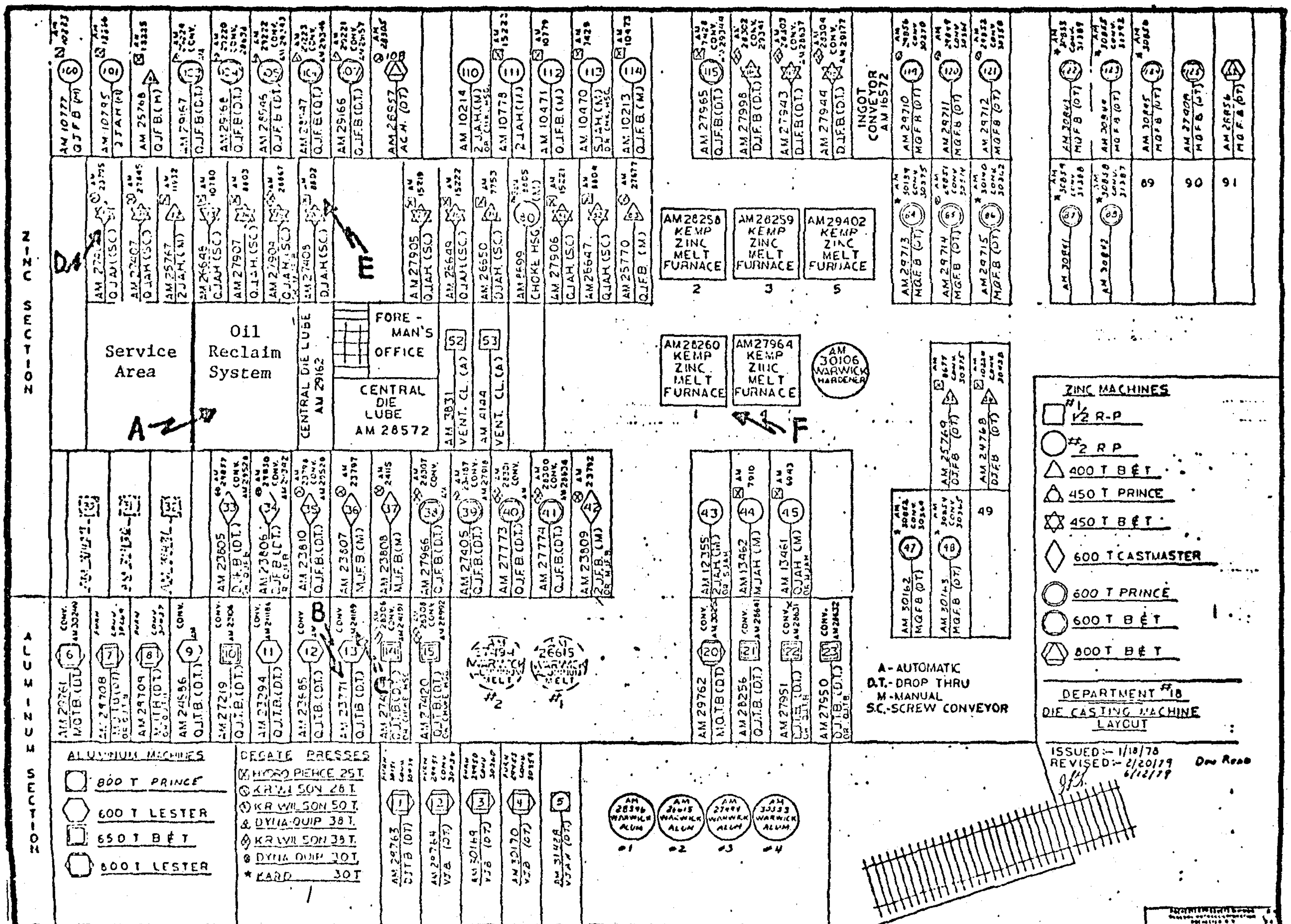
Airborne Sample Results For Organophosphate Esters
Die Cast Department
Rochester Products Division, Rochester, New York
(10/12/79)

Sample Number	Location	Flow Rate (Lpm)	Volume (liters)	mg/m^3				
				Triphenyl Phosphate	Diphenyl 2-isopropyl Phenyl Phosphate	3rd Major Peak (∿ equal to Triphenyl Phosphate)	Other* Phosphate Esters 10 Minor Peaks	Total Phosphate Ester Concentration
N-026	Next to hydraulic fluid reclamation system - between filters & storage tank	2.0	482	0.054	0.011	0.054	0.021	0.140
N-077	Back of #13 aluminum die cast machine	2.0	474	0.015	0.003	0.015	0.006	0.039
N-078	Casting take off station at the #13 aluminum die cast machine	2.0	476	0.017	0.003	0.017	0.006	0.043
N-079	Casting take off station at the #70 zinc die cast machine	2.0	492	0.041	0.009	0.041	0.016	0.107
N-080	Back of #76 zinc die cast machine	2.0	488	0.057	0.013	0.057	0.023	0.150
N-083	Near zinc melt furnaces	2.0	480	0.008	0.001	0.008	0.003	0.020

Note:
OSHA Standard - Triphenyl Phosphate (8-hour TWA) 3 mg/m^3
* Minor Peaks of Phosphate Esters estimated at 15% of the 3 combined Major Peaks
Lower Limit of Detection: triphenyl phosphate - 1 µg/sample
diphenyl 2-isopropylphenyl phosphate - 0.4 µg/sample

Figure 1

Die Cast Department - OP Sample Location
Rochester Product, Rochester, New York



Airborne Samples:

A-N026	D-N079
B-N077	E-N080
C-N078	F-N083

PUBLIC HEALTH SERVICE
CENTER FOR DISEASE CONTROL

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November 25, 1980

Mr. Thomas Husted
Plant Manager
Rochester Products
Division of General
Motors Corporation
1000 Lexington Avenue
Rochester, New York 14606

Dear Mr. Husted:

Please find enclosed three copies of the final report of the survey conducted at your facility on October 12, 1979. I appreciate your review comments concerning proprietary information and for errors observed in process terminology. Based on your critique some changes have made in the final report. As a standard procedure, copies of this report are being forwarded to OSHA Headquarters, the NIOSH Regional Office, and the UAW Local and International Union.

Thank you again for your cooperation in this study. If you have any questions, please call me at (513) 684-3255.

Sincerely yours,

Ralph D. Zumwalde
Industrial Hygienist
Industrial Hygiene Section
Industry-wide Studies Branch
Division of Surveillance, Hazard
Evaluations and Field Studies

3 Enclosures
cc:
Thomas O'Donnell
C. Cottrill, EPA
Joseph Musson, UAW Local
UAW International