INDUSTRIAL HYGIENE WALK-THROUGH SURVEY REPORT
ON ORGANOPHOSPHORUS EXPOSURES

AT

Chevron Chemical
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DATE OF SURVEY:
March 29, 1979

DATE OF REPORT:
July 27, 1979

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Cincinnati, Ohio

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 (PL 91-596) 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.

This study has been initiated based on recently conducted epidemiologic studies which have suggested that delayed neurotoxic effects may exist in workers exposed to organophosphorous (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 many 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. The Chevron Chemical Company was selected as a potential study cohort.

HISTORY OF NON-PESTICIDE ORGANOPHOSPHOROUS 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.[1] In the 1930's, the insecticidal and fungicidal activities of OP compounds were discovered with tetra ethyl pyrophosphate being the first commercial OP insecticide in 1944.[2]

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.[3]

Excluding pesticide formulation, the primary uses of OP esters continues 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 a flame retardent. The major markets for phosphate 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.[3,4]

The fastest growing usage for OP esters is in the manufacture of fire-resistant hydraulic fluids and lubricants with the two principal types of OP hydraulic fluids being manufactured as 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 fluids contain a mixture of only OP esters.[3] For example, a typical synthetic OP fluid could contain tricresyl phosphate, trixylenyl phosphate, and other trialkyl phosphates.

OP ester lubricant additives are usually of three general types: extreme pressure agents, anti-wear agents, and stick-slip moderators.[3] The first two types of agents are used in systems with some type of gears and together 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 which contained a high ethanol content (accounting for its popularity during Prohibition) and a mixture of cresyl phosphates which was used to extract the ginger.[5,6]

Early studies reported that only the "ortho" isomer among symetrical 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 (TOCP) poisoning occurred involving acute exposures due to ingestion of contaminated food products or water.

The characteristic effect of TOCP exposure, and that of many other organophosphates, is delayed neurotoxicity. Clinical effects are not seen until eight to fourteen days after entry of the organophosphorous substance.[7] The time between exposure and onset of symptoms varies with the route and degree of exposure. Many organophosphorous compounds are recognized cholinesterase inhibitors which can lead to disturbed function of cholinergic synapses involving the neuromuscular junctions in sketetal, cardiac, and smooth muscle.[8]

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, initiability, memory disturbance, and difficulty concentrating are among the possible behavioral effects due to acute OP poisoning.[9,10] 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.[11,12,13]

DESCRIPTION OF FACILITY

Chevron Chemical is owned by Standard Oil of California in the Petrochemicals Division. The plant site was selected in the early 1940's because of its proximity to water transportation making it ideally suited for producing diesel oil lubricants. At present the company is primarily involved in manufacturing blending components into lubricating oil additives. Typically, additives are added to produce high temperature, zinc, calcium, and ashless lubricating oils. Among the many other additives, approximately 28,000 gallons of tricresyl phosphate are used yearly as a blending component in six products.

DESCRIPTION OF WORKFORCE

Chevron Chemical currently has approximately 320 employees; of these employees, 230 work in production (i.e. operators, utility persons, mechanics, trainees, supervisors, etc.) with the remainder in administration (i.e. office personnel, technicians, chemists, etc.). The production workforce is comprised mostly of men (95%) which comprise 4 work crews. The four work crews work one of the three 8-hour shifts a day on a rotating basis.

All new employees in the production areas start as a trainee and learn to work in all areas of the plant. Upon completion of this apprenticeship they are assigned into a specific work division. However, almost all employees switch job assignments depending upon the workload.

DESCRIPTION OF PROCESS

Tricresyl phosphate (TCP) is purchased from the FMC Corporation under the trade name of Kronitex TCP which has been the only organophosphate here used since 1959. Liquid TCP is received by tank truck and rail car and pumped to a storage tank. From the storage tank the TCP is pumped through a circular manifold where varying percentages of TCP can be pumped to any one of three blending tanks. Other additives and oil are added and blended to make one of six different products. These blended oil products are then pumped into rail cars, tank trucks, and to a lesser extent (10%) into barrels, and shipped. The manufacturing of these special organophosphorous blends is sporadic and, on the average, usually accomplished within a few days during a month. Almost all formulating and blending operations at this facility are performed within enclosed systems with few process points where workers come into direct contact with the chemicals.

A typical oil blend would contain the following mixture:

- Calcium oil base detergent
- Zinc dithiophosphate
- Sulfurized ester
- Foam inhibitor
- Acrylic polymer & refined natural oil
- Other hydrocarbon base oils

For the special blends a small percentage of TCP is added.

DESCRIPTION OF EXPOSURES

Approximately 8-10 employees per shift have a potential for exposure to TCP. The most probable area of exposure would be near the barrel filling operation which usually requires 3-4 employees. The only other areas where exposures might occur would be at the inlet and outlet points on the tank rail cars, at the circular manifold, and when a small sample of the oil additive is removed from the blending tanks for testing.

DESCRIPTION OF MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

The plant retains Dr. Serio for medical services requiring a doctor. For minor injuries and emergency medical care, each shift has trained first aid personnel available. All new employees receive a pre-employment physical in addition to a complete physical examination which is required at specified age increments. Medical examinations include chest x-ray, hearing, visual, lung function, blood, urine, prostrate, and EKG tests. Dr. Serio maintains all medical records along with any toxicological or industrial hygiene data on materials used by the company. No medical abnormalities among workers have been attributed to an occupational exposure.

Industrial hygiene and safety responsibilities are handled by Mr. Cowles, however, yearly industrial hygiene evaluations are made by corporate industrial hygienists who work out of the Chevron Environmental Health Center, Richmond, California. Airborne samples for TCP have not been collected at this plant. Personal protective equipment, such as: clothing, safety glasses, hard hats, and respirators is supplied by the company. Safety shoes are furnished to the employees at cost.

DESCRIPTION OF RECORD SYSTEM

Chevron Chemical retains employee cards and personnel folders on each active employee. The employee cards contain name, address, date of birth, social security number, payroll number, initial date of employment, division name-dates and job title, and accident record. The personnel folders contain an absentee record, employee warning notices, department transfer slips, leave application, and other employee information.

Although specific information and dates are kept on employee job titles and divisions most employees move around the plant performing various work duties depending on the workload. Hence, most job types are potentially exposed to all materials used in the company.

DISCUSSION OF RESULTS

Since TCP is used only in specialty oil and fluid lubricants, its potential for exposure to workers is sporadic. The blending and packaging processes for TCP operate when a special request is received. These processes may take from 1 to 3 days and on the average occur once a month. During the one day survey no TCP was being used, therefore, only stationary samples were collected in areas where spills may have occurred on previous occasions.

Paired airborne samples were collected near the loading and unloading station for tank rail cars, at the circular manifold, and at the barrel filling operation. One sample from each paired group was shared with the company for TCP analysis. Samples were collected on Millipore Type AA membrane filters at a flow rate of 2.0 liters per minute for a 4 hour time period. Filters were analyzed according to the NIOSH S-209 and S-210 methods with some modifications (i.e. desorbed with ethyl alcohol, temperature range of 150-230°C isothermal, column - OV101 changed to SP2100).[14] NIOSH sample analysis indicated exposures to be below the lower detection limit of the analytical method (0.2 mg/sample) with concentrations less than 0.8 mg/m^3. Since the NIOSH results indicated no exposures to TCP the Chevron Chemical Company decided not to pursue the analysis of their samples.

Even though samples were collected during no TCP activity, the small usage of TCP at infrequent intervals would probably pose only a minimal exposure to a small number of workers. Under these circumstances the Chevron Chemical Company would not meet the criteria as an appropriate study population.

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