Industrial Hygiene Survey Report of Worker Exposures to Organotins at Red Panther Chemical Company Clarksdale, MS 38614

Survey Dates
June 26 and 27, 1984

Survey Conducted By

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16. Abstract (Limit: 200 words)

Breathing zone samples were analyzed for tricyclohexyltin-hydroxide (13121705) (TCHH) at Red Panther Chemical Company (SIC-2879, SIC-5191), Clarksdale, Mississippi in June, 1984. The survey was part of a NIOSH study for occupational exposure to organotins, as a component of an assessment to determine the feasibility of conducting a reproductive effects study. The samples were taken during production of a miticide containing TCHH. Company personnel records were reviewed. Work practices were observed. Organotin concentrations, reported as tin, ranged from 0.07 to 3.4 milligrams per cubic meter (mg/m3), corresponding to 0.2 to 11mg/m3 TCHH. The OSHA standard for organotin compounds, as tin, is 0.1mg/m3. Twenty four potentially exposed male workers were identified. All employees in the formulation area were required to wear respiratory protection, although some workers wearing dust masks used only the upper strap to hold them in place. The authors conclude that most workers were exposed to organotin concentrations that exceeded the OSHA limit. TCHH concentrations should be reduced by improving local exhaust ventilation. The facility could contribute 24 potentially exposed workers to the NIOSH reproductive effects study.

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CONTENTS

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Mention of company names or products in this report does not constitute endorsement by the National Institute for Occupational Safety and Health.

Abstract

An industrial hygiene survey was conducted at the Red Panther Chemical Company, Clarksdale, Mississippi, to measure worker exposure to tricyclohexyltin hydroxide (TCHH), an organotin compound, at selected operations during the formulation of Plictran(R) 50 W Miticide. This survey was conducted as part of a NIOSH-sponsored investigation of the extent of worker exposure to organotin compounds. NIOSH authorized the investigation as part of an assessment of the feasibility of conducting a study of reproductive effects.

Worker exposures to airborne organotin in the formulation areas were determined by collecting air samples on glass fiber filters and analyzing them by solvent extraction and determination of the tin contents of the extracts by flame atomic absorption spectrophotometry (AAS). Other sampling (cellulose ester membrane filters) and analytical methods (acid digestion followed by flameless AAS) also were used and the results were compared. Results obtained using acid digestion and flame AAS for cellulose ester membrane filter samples were lower than the results obtained using solvent extraction and flame AAS for glass fiber filter samples. An attempt was made to analyze the glass fiber filter extracts by flameless (graphite furnace) AAS; however, for reasons discussed in the report (extended storage periods), the flame AAS results were felt to be the more reliable.

Eight-hour, time-weighted average organotin concentrations for production workers ranged from 0.07 to 3.4 milligrams per cubic meter of air (mg/m^3), as Sn. Corresponding TCHH levels ranged from 0.2 to 11 mg/m^3. A forklift driver and a foreman were exposed to less than 0.006, and 0.007 mg/m^3 of organotin, as Sn, respectively. Corresponding TCHH levels were less than 0.02, and 0.02 mg/m^3, respectively. All employees were required to wear respiratory protection, although some individuals used only the upper strap to hold the respirator in place. Therefore, the organotin concentrations reported reflect potential exposure levels, and do not necessarily represent actual exposures.

At the time of this survey, there were 24 potentially exposed males and no females available for possible inclusion in a reproductive effects study. Since Plictran(R) is formulated in campaigns of a few weeks' duration according to anticipated demand for the product, organotin exposure could vary considerably from month to month and from season to season during the year. A decision regarding the feasibility of conducting a reproductive effects study will be made following evaluation of the information contained in the report by NIOSH epidemiologists.

Plictran(R) 50 W Miticide is a trademark of The Dow Chemical Company.

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1.0 INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH), Division of Surveillance, Hazard Evaluations, and Field Studies (DSHEFS), Industry-Wide Studies Branch (IWSB), is currently sponsoring an investigation of the extent of occupational exposure to organotins. The investigation was initiated after several reports of animal studies suggested possible adverse reproductive effects associated with several organotin compounds.[1,2,3,4,5] NIOSH authorized the investigation as part of an assessment of the feasibility of conducting a study of reproductive effects among workers exposed to organotins.

Occupational exposures to organotins may occur in the production of organotins, and during the manufacture, formulation, and use of organotin containing products. Organotins are principally used as stabilizers for polyvinyl chlorides (PVCs), as catalysts in the plastic and rubber industries, and as biocides.

Clayton Environmental Consultants, Inc., under contract to NIOSH, is conducting this study. The scope of this study, in brief, includes:

Task I. Review of toxicologic literature and identification of producers of organotins, formulators of organotin-containing products, and users of organotin-containing products.

Task II. Walkthrough (information gathering) surveys of facilities producing, formulating and/or using organotin/organotin-containing compounds.

Task III. In-depth industrial hygiene surveys to document worker exposures.

During the walkthrough surveys (and in-depth industrial hygiene surveys where applicable), information was also obtained which would aid in an assessment of the feasibility of conducting a study of potential reproductive effects related to organotin(s) present.

The survey at the Red Panther Chemical Company, Clarksdale, Mississippi was conducted to evaluate organotin exposures during the formulation of an organotin-containing agricultural product--a biocide. Both the Task II walkthrough and the Task III in-depth industrial hygiene survey were combined in this survey which was conducted June 26 and 27, 1984.

2.0 AUTHORITY

Studies of this nature are authorized under the Occupational Safety and Health Act of 1970, Public Law 91-596 (December 20, 1970). Specifically, NIOSH and NIOSH-authorized representatives have been authorized to conduct field research studies in industry, to evaluate findings, and to report on these findings. Section 20(a)7

states that NIOSH shall conduct and publish industry-wide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in the aging adult population. Section 20(b) further states that NIOSH is authorized to conduct investigations and question employers and employees as provided in Section 8 of this Act in order to carry out the functions and responsibilities under this Section. Section 20(c) further states the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for purposes of conducting studies relating to responsibilities under the Act.

3.0 CHEMICAL INFORMATION

The Red Panther Chemical Company formulates Plictran(R) 50 Wettable Powder (containing 50% tricyclohexyltin hydroxide) Miticide. The chemical formula for tricyclohexyltin hydroxide is $(C_6H_{11})_3SnOH$. It has a molecular weight of 385.02 and exists as white crystals. The vapor pressure is negligible at 25 °C; thus, exposure would most likely be to the particulate form. Other names for this organotin include: Cyhexatin, Dowco 213(R), and TCHH. The chemical structure of TCHH is shown in Figure 1 below.(6)

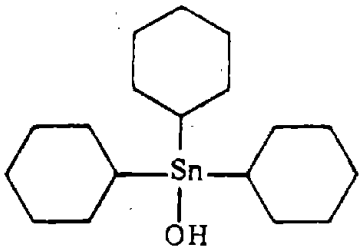

Figure 1. Chemical Structure of TCHH

4.0 DESCRIPTION OF FACILITY

The Red Panther Chemical Company has three owners--MFC Services (Madison, Mississippi), Tennessee Farmers' Co-op (La Vergne, Tennessee), and Alabama Farmers' Co-op (Decatur, Alabama).

The facility has a total of 11 buildings on its 6.8 acre site. Crop pesticides are formulated in three "dust plants" and two "liquid plants": one dust plant is housed in one building, the other two dust plants are in a second building, and the two liquid plants are located in two separate buildings. The facility has been in operation since approximately 1949.

Dust Plant No. 1, where Plictran(R) 50 Wettable Powder (50% tricyclohexyltin hydroxide) is formulated, has been in operation since 1950.

5.0 DESCRIPTION OF WORKFORCE AND RECORDKEEPING SYSTEM

A total of 89 people are employed at the Red Panther Chemical Company plant. They work over three shifts—0800 to 1600 hours, 1600 to 2400 hours, and 2400 to 0800 hours, as shown in Table I.

TABLE I
Workforce by Shifts and Type of Activity

Description	No. of Employees			
	Shift 1	Shift 2	Shift 3	Total
Plictran Formulation Workers Only	8	8	8	24
Foreman (also in other areas)	1	1	1	3
Millman/Formulator	1	1	1	3
Filler Operator	1	1	1	3
Final Weigh Operator	1	1	1	3
Bag Seamer	1	1	1	3
Packer/Boxer	2	2	2	6
Forklift Driver (also in other areas)	1	1	1	3
Total Production Workers, including Plictran Formulation Workers	40	23	17	80
Administrative Workers	9	--	--	9

Eighty-six of the 89 employees are men; the three women are employed in the administrative department. The age of the workforce ranges from 18 to 65. Most of the production workers have elementary or secondary educations.

Personnel records for each worker are maintained. They include job application forms, change of status (with respect to responsibility or pay), and work history. Records could go back as far as 1949 and records for terminated employees are also maintained. A standard form--the personnel/payroll transaction form--is used for each employee's personnel file.

6.0 DESCRIPTION OF OPERATIONS

One worker (the millman/formulator) weighs out bags and containers of the dry ingredients on floor scales. TCHH is supplied in bags with a drawstring closure at the bottom to facilitate dispensing whole or partial-bag quantities directly into the feed tray or into a fiber drum. The dry materials flow from the feed tray into the foot of a bucket elevator that conveys them to the first blender (a ribbon

mixer). Local exhaust is provided at the back of the feed tray to control dust as dry ingredients are added and as residual material is broom-swept from the tray into the elevator.

After all dry ingredients have been added to the first blender, wet ingredients are sprayed into the first blender. When the first blender finishes its cycle, the material drops into the holding hopper that feeds the first hammermill. Material exiting the first hammermill is pneumatically transferred to the second ribbon blender. On completion of the second blender's cycle, the batch drops into the holding hopper that feeds the second hammermill, from which it is pneumatically transferred to the third ribbon blender. After the third blending, the material drops into another holding hopper from which it is fed into a sifter that removes large particles. The finished product is received at a "packing" hopper and is transferred by auger conveyor to the automatic packaging line.

In the packaging operation, one worker (filler operator) places bags on the bulk filling dispenser, which meters most of the powder into each bag. The bag then moves along the conveyor, where a trickle of powder is automatically added to bring the bag and contents to the specified weight. The conveyor then transports the bag to a check-weigh scale; over- or underweight bags are diverted to another station where a worker (final weigh operator) makes final adjustments by hand and places them back on the shaker-conveyor to the seamer/sealer. One worker (bag seamer) tends the sealer/seamer from which the bags are conveyed to a turntable. Two workers (packer/boxers) at the turntable place the bags in cardboard boxes, which then are sealed and stacked on pallets.

The packaging line is provided with a local exhaust system (flanged slot hoods at the bulk fill and trickle fill points and canopies above the conveyor section between the bulk fill and trickle fill points and above the shaker-conveyor).

Two other workers (a shift foreman and a forklift truck driver) are present in the dust plant for brief periods at irregular intervals.

The greatest potential for exposure to TCHH appeared to be in weighing, staging, and adding of dry ingredients; in bulk and trickle filling; and in hand adjusting weights of bags rejected by the check-weigh scales.

7.0 SUMMARY OF HEALTH EFFECTS AND TOXICOLOGY

Organotins exhibit a broad spectrum of toxicities, depending on the number and length of alkyl or aryl groups. Of the various classes, i.e., $RSnX_3$, R_2SnX_2, R_3SnX, and R_4Sn (where R = alkyl or aryl groups; X = anions, such as Cl^- or OH^-), R_3SnX compounds are known to be the most toxic. Within a particular class, the lower alkyl groups are the most toxic, with the C_1 through C_3 groups significantly more toxic than the higher alkyl groups.[7,8]

Many organotin compounds are skin irritants and may be absorbed through the skin.[9]

One measure of chemical toxicity is the LD_{50}. Animal toxicity data, expressed as LD_{50}s (the dose expected to be lethal in 50% of the animals in a group of the same species when administered by the stated route), are usually obtained using rats or mice. Materials with LD_{50} values of 500 to 5,000 mg/Kg (single oral dose, rats) are classified as "slightly toxic" materials. Materials with LD_{50} values of 50 to 500 mg/Kg are classified as "moderately toxic" materials, whereas chemicals with LD_{50} values of 1 to 50 mg/Kg are rated as "highly toxic" chemicals.[10]

According to the 1983 Supplement to the 1981-82 Registry of Toxic Effects of Chemical Substances (RTECS), the oral LD_{50}s of TCHH for rabbit, guinea pig, and chicken are 458, 780, and 654 mg/Kg, respectively, and an oral LD_{50} of 180 mg/Kg for rats has been reported.[11] The RTECS is a compendium of data extracted from the scientific literature. It is the RTECS editorial policy to give preference, in reporting data, to studies in which the lowest total dose was administered over the shortest period of time to produce the toxic effect stated. On the basis of reported LD_{50}s, therefore, TCHH can be described as moderately toxic.

During a brief review of the toxicologic literature in connection with organotins, several reports were uncovered which suggested possible adverse reproductive effects associated with several organotin compounds. The following discussion provides brief synopses of these studies.

(a) The pregnancy rates among mature female rats exposed to 2 mg/m^3 of tributyltin bromide x 2 hours per day by inhalation for 1 to 4 months and mated with unexposed males were reduced in a dose-related manner by up to 100%; partial recovery of pregnancy rates was observed following cessation of exposure. Male rats similarly exposed and mated with unexposed females did not exhibit reduced ability to impregnate. No histological changes were observed in male testes; atrophy of the uterus was observed in females.[1]

(b) Female rats were given 20 or 40 mg/kg/day by gavage of dioteyltin bis(isoctylmercaptoacetate) (DOTM) or dibenzyltin bis(isoctylmercaptoacetate) (DBTM) - two stabilizers and plasticizers - for three months followed by mating either with or without cessation of exposure during gestation. The exposed rats showed significant differences from the controls with respect to fetal absorptions, death of fetuses, fetal and placental weights, but only when exposure continued during gestation.[2]

(c) Male and female rats and guinea pigs administered the fungicides triphenyltin acetate (TPTA) and triphenyltin hydroxide (TPTH) at doses ranging from 5 to 50 ppm (TPTA) and 2.5 to 50 ppm (TPTH)

in the diet for 90 days showed, inter alia, decreases in the weights of the uterus and testes, but only at the higher doses (20 to 50 ppm).[3]

(d) Mature male rats given 20 mg/kg TPTA or triphenyltin chloride (TPTC) via the diet for 19 days suffered, after TPTA, overall weight loss of approximately 10% and a decrease of 25 to 50% in the size of the testes. Histologically, the testes showed degenerative changes and abnormalities; all animals were considered to be sterile. TPTC treatment produced similar but less severe effects and 60 to 70% sterility. However, observed effects may be secondary to overall weight loss and/or possible interference with blood flow or the blood clotting mechanism.[4]

(e) The ovaries of female rats administered TPTA and TPTC via the diet (20 mg/kg/day) and killed at intervals from 4 to 24 days from the start of administration of the compounds were significantly smaller than controls by five days, and, histologically, showed a decrease in the number of mature follicles and corpora lutea.[5]

Results of reproductive and teratological studies pertaining to tricyclohexyltin hydroxide (TCHH) have been reported. No effects on fertility, gestation, viability, or lactation were observed in rats fed 4 to 6 mg/Kg per day for three generations. Female rabbits received oral doses of 3 mg/Kg per day on the 8th through the 16th days of gestation. There was no evidence of ill effects as judged by criteria of fertility, gestation, viability, and lactation, or by examination of fetuses for teratogenic effects.[6]

It should be emphasized that, with the exception of one of these studies, all studies were based upon oral administration of the organotin in question. Further, it should be stated these these were animal studies. Therefore, such studies may not be necessarily indicative of the hazard potential associated with inhalation of these compounds, nor may they be necessarily indicative of human reproductive responses to these compounds.

8.0 OCCUPATIONAL EXPOSURE CRITERIA

Standards for occupational exposures (via inhalation) to organotin compounds have been established or recommended by the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH), and NIOSH as follows:

OSHA[12]: 0.1 mg/m^3 (as Sn); an 8-hour, time-weighted average (TWA) permissible exposure limit (PEL) for organotins

ACGIH[13]: (1) 5 mg/m^3 (as TCHH); an 8-hour, TWA threshold limit value (TLV) for TCHH (tricyclohexyltin hydroxide; cyhexatin).

(2) 0.1 mg/m^3 (as Sn); an 8-hour, TWA threshold limit value (TLV) for organotins

(3) 0.2 mg/m^3 (as Sn); a short-term exposure limit (STEL) TLV for up to 15 minutes for organotins

NIOSH[14]: (1) 0.1 mg/m^3 (as Sn); a 10-hour work shift in a 40-hour workweek TWA criterion

(2) 0.05 mg/m^3 (as Sn); an action level as a TWA

ACGIH has adopted the TLVs for organotins with a "skin" notation, a warning of the potential for percutaneous absorption. The TLVs for inhalation exposures are based on the presumption that there is no concurrent exposure via the skin and oral ingestion routes. It should be noted that all of the aforementioned exposure limits and recommendations have been established for organotin compounds as a group (total organotin, measured as tin). Only one limit has been established for any specific compound: ACGIH has adopted a separate 8-hour, TWA TLV of 5 mg/m^3 for TCHH, without a skin notation.[13]

The ACGIH TLV of 5 mg/m^3 for TCHH corresponds to about 1.5 mg/m^3 of elemental tin. This level is substantially higher than the 0.1 mg/m^3 TLV for organotin compounds in general. ACGIH states that the 0.1 mg/m^3 TLV appears (sic) to be based on the more toxic members of the group. ACGIH recommends that the TLV for TCHH (5 mg/m^3 TWA and 10 mg/m^3 STEL) be retained for the present.[6]

9.0 DESCRIPTION OF INDUSTRIAL HYGIENE, MEDICAL, SAFETY, AND OTHER ENVIRONMENTAL PROGRAMS

9.1 INDUSTRIAL HYGIENE PROGRAM

There is no formal industrial hygiene program established at the Red Panther Chemical Company. Industrial hygiene services, such as exposure monitoring, training in hazards, advice on protective equipment, and industrial hygiene concerns in production, are provided by companies with whom production is contracted. These companies send industrial hygienists or other representatives to evaluate and monitor operations and exposures. In addition, annual safety and health inspections are conducted by Red Panther's workers' compensation insurance carrier. There is no routine air monitoring. Reports on these studies by outside industrial hygienists, often including exposure data and (if needed) recommendations for corrective action, are sent to Red Panther.

9.2 MEDICAL PROGRAM

The medical program at Red Panther is run by a local medical clinic on an "on call" basis. The plant has an agreement for emergency care with a local hospital. The plant provides the hospital with material safety data sheets (MSDS) and other necessary information on products and materials being handled.

No pre-employment physical examinations are provided for new employees, but health history questionnaires are filled out by all new employees. No specific tests or examinations directed to organotin exposure are given to employees handling TCHH.

Foremen and assistant foremen on each shift take Red Cross first aid courses and cardiopulmonary resuscitation (CPR) training annually.

9.3 SAFETY PROGRAM

The safety program in this plant is run by the Safety Committee, which consists of 10 to 11 members, including all foremen and supervisors. The committee meets bimonthly, and the foremen fill out inspection forms and critique their own operations.

Personal protective equipment, including respirators (replaceable cartridge respirator, mandatory for the millmen/formulators; and a choice of disposable dust masks or replaceable cartridge respirators for other workers), clothing, safety glasses, gloves, bump caps, and steel-toed shoes (millmen/formulators only), is provided and required for use in Plictran$^{(R)}$ formulation.

Eyewash, shower, clothing change, and lunchroom facilities are provided. There are written safety rules, and safety-related notices are posted conspicuously in production areas.

9.4 OTHER ENVIRONMENTAL PROGRAMS

There are written procedures for handling discharges, and a written spills prevention and countermeasures plan.

10.0 DESCRIPTION OF ENGINEERING CONTROLS

At the feed tray, an exhaust hood with a dust collector is provided to control dust generated as dry raw materials are added.

In the Plictran$^{(R)}$ packaging operation, local exhaust provisions are:

(a) Flanged slot hoods at bulk and trickle filling spouts,
(b) Canopy hood above conveyor between filling spouts and check-weigh conveyor, and
(c) Long canopy hood above shaker conveyor.

Flexible ducts connect the local exhaust hoods for the packaging operation to a dust collector.

11.0 EVALUATION SCOPE

Worker exposures to total organotin (measured as Sn), TCHH, and total dust were evaluated; personal samples were collected on workers of various job titles in the Plictran(R) production area during three shifts on June 26 and 27, 1984. The first and second shifts on June 26, and the first shift on June 27, 1984 were investigated. One area sample was also taken near a process equipment leak, approximately equidistant between the formulation and bulk filling areas (about 20 feet from each location), to evaluate its contribution to ambient concentrations.

Short-term area samples were also taken during activities which generated significant amounts of visible airborne particulate.

12.0 SAMPLING AND ANALYTICAL METHODS

12.1 SAMPLING METHODS: ORGANOTINS AND TOTAL PARTICULATE

Two different filter media were used in the collection of organotin samples.

In personal and area sampling for organotin compounds as specified in NIOSH Method P&CAM 368, samples are normally obtained using glass fiber filters followed by XAD-2 sorbent tubes in series to collect both solid and vapor states of organotins.[15] However, since TCHH is a solid with a very low vapor pressure, samples were obtained with filters only. All of the filters were preweighed before sampling to permit determination of total particulate.

NIOSH Method S183 for sampling (and analysis) of Tin, Inorganic Compounds Except Oxides, specifies that samples be collected with cellulose ester membrane filters.[16]

Full-shift and short-term samples were taken using glass fiber filters to determine concentrations of total organotin (and TCHH) and total particulate. Two short-term samples were also taken using cellulose ester membrane filters to determine concentrations of total particulate and total organotin (and TCHH). These two samples were taken simultaneously with two of the glass fiber filter samples to permit a comparison of the two sampling and analytical methods, as a preliminary indication of whether or not the widely-used sampling and analytical technique for inorganic tin could be applied to sampling and analysis for TCHH.

12.2 ANALYTICAL METHODS

12.2.1 Organotin

The organotin (TCHH) collected on the glass fiber filters was extracted from the filters using 5 mL of 0.1% acetic acid by volume in acetonitrile (as specified in P&CAM 368) and the extracts were analyzed for elemental tin content by both flame and flameless atomic absorption spectrophotometry (AAS).

Four of the samples were further analyzed by subjecting the sample aliquots to the additional separation procedure for specific organotins (also according to P&CAM 368). This procedure employs use of high pressure liquid chromatography (HPLC) followed by analysis (for elemental tin content) by graphite furnace AAS. However, as indicated previously, since only one organotin, TCHH, is used at this facility, this separation step was, in reality, unnecessary. This additional separation procedure was undertaken to ascertain any differences in analytical results that might arise due to the separation procedure.

During preliminary work with the flameless (graphite furnace) AAS, difficulties were encountered in obtaining stable instrument response to standards prepared from TCHH in 0.1% acetic acid/acetontrile. For this reason, the filter extracts were analyzed immediately by flame AAS (nitrous oxide-acetylene flame); in this analysis, the instrument response was stable. Later, when the graphite furnace problems had been resolved, the same filter extracts (and, for four samples, HPLC-separated fractions) were analyzed by flameless AAS. Because of the considerable delay between the flame AAS and furnace AAS analyses (42-56 days) and the unknown stability of sample extracts and HPLC fractions stored for extended periods, the flame AAS results were considered to be the more reliable indicators of airborne organotin concentrations.

Analytical recovery and variability data were obtained for the flame AAS analysis. Analytical recovery was determined by spiking glass fiber filters with known amounts of TCHH (corresponding to the range of values found in analysis of the samples), extracting the filters with 0.1% acetic acid in acetonitrile, and analyzing the extracts by flame AAS. The data thus obtained are summarized below.

TCHH Added (micrograms as Sn)		Mean Analytical Recovery (%)	Coefficient of Variation (C.V.)
10.0	(N=6)	195	0.17
50.0	(N=6)	85	0.13
100.	(N=6)	91	0.15
500	(N=6)	89	0.049
1000	(N=5)	81	0.10
2000	(N=5)	77	0.035

Although certain of the recovery values fall outside the range NIOSH considers acceptable for a "validated" method, the reproducibility of results, as evidenced by the coefficients of variation, indicate that the flame AAS analysis (with correction for recovery) provides satisfactory estimates of organotin concentrations at all but the lowest levels encountered in this study.

The cellulose ester membrane filter samples were digested with concentrated nitric and sulfuric acids and analyzed by flame AAS to determine their elemental tin contents. NIOSH recommends this method for measurement of inorganic compounds of tin except oxides.[16]

Sampling and analytical methods attempted in connection with this survey for organotins are summarized in Table II.

TABLE II

Sampling and Analytical Methods for Organotins

Sampling Media	Analytical Methods
Glass fiber filter[15]	Extraction; flame atomic absorption spectrophotometry (AAS)
Glass fiber filter[15]	Extraction; graphite furnace AAS
Glass fiber filter[15]	Extraction; HPLC separation; graphite furnace AAS[15]
Cellulose ester membrane filter[16]	Acid digestion; flame AAS[16]

The results of analysis by flame AAS, corrected for analytical recovery, were used to calculate the concentrations of airborne organotin (as Sn and as TCHH) reported in Tables III and IV. Because the results of analysis by flameless AAS were considered questionable (due to the extended period of storage before final analysis), those data are not included in this report.

12.2.2 Total Particulate

Total particulate was analyzed gravimetrically after drying the sample-containing filters over a desiccant to constant weight. The limit of detection was 0.1 mg per filter, which is equivalent to an airborne concentration of 0.2 mg/m^3, assuming a 500-L air sample.

13.0 RESULTS AND DISCUSSION

13.1 GENERAL

Results of sampling and analysis are presented in Appendix A, Tables III and IV. Because of atypical formulation schedules and certain "unusual" exposure-related conditions, only certain samples appeared to be representative of a full shift of "normal" operations; these samples are indicated by an asterisk in Table III.

13.2 EXPOSURE INFERENCE FROM PERSONAL SAMPLE DATA

All employees in the Plictran(R) formulation area were required to wear respiratory protection, although some workers wearing dust masks used only the upper strap to hold them in place. Therefore, actual employee exposure to TCHH may have been less than that suggested by the reported data.

13.3 COMPARISON OF DATA BY ANALYTICAL METHODS

Table IV presents results of analysis of tandem samples using two different types of filters--glass fiber filters and cellulose ester membrane filters. Glass fiber filters were extracted with acetic acid in acetonitrile and the extracts analyzed using flame AAS; cellulose ester membrane filters were digested in nitric and sulfuric acids and the resulting solution analyzed using flame AAS. Results using cellulose ester membrane filters were lower than results using glass fiber filters. This is due most likely to the loss of organotin during the digestion of the cellulose ester membrane filters, which resulted in a lower elemental tin content being measured by the AAS. The conclusion, based on comparison of the results of analysis for the two sets of samples, is that the sampling and analytical method for inorganic tin compounds (NIOSH Method S183) is not suitable for the determination of airborne TCHH.

13.4 WORKER EXPOSURE TO ORGANOTIN

All of the workers in the Plictran(R) formulation and packaging operations were required to wear respiratory protection (although some workers used only the upper strap on disposable dust masks); therefore the air sampling results from this study may be more indicative of "potential" than "actual" inhalation exposure.

Table V summarizes 8-hour, time-weighted average (TWA) personal sampling data by job types and/or work processes. As indicated in the table, sampling results for millmen/formulators indicated the highest organotin concentrations—0.39 to 3.4 mg/m^3(expressed as elemental Sn). Corresponding levels, expressed as TCHH, were 1.3 to 11 mg/m^3. Breathing zone concentrations for bag seamer/sealers (as Sn) ranged from 0.17 to 0.61 mg/m^3. Corresponding levels (as TCHH) were 0.54 to 2.0 mg/m^3. Sampling results for workers at other operations, such as the filling-packaging machine, final weighing, and packing/boxing, indicated similar ranges of organotin concentrations [0.07 to 0.32 mg/m^3 (as Sn)]. The corresponding levels (as TCHH) were 0.2 to 1.0 mg/m^3. The

forklift driver and the foreman were exposed to the lowest levels (less than 0.006, and 0.007 mg/m^3, respectively). As TCHH, these levels were less than 0.02, and 0.02 mg/m^3, respectively.

It should be noted that for all but four workers (a forklift driver, a foreman, a filler operator, and a final weigh operator), sampling results indicated 8-hour, TWA concentrations that are equal or exceed the OSHA PEL and the NIOSH-recommended limit of 0.1 mg/m^3 (as Sn). However, only one sample (a millman/formulator) indicated a concentration (11 mg/m^3) that exceeded the ACGIH TLV of 5.0 mg/m^3 (as TCHH).

As presented in Table IV, short-term area sampling near the millman's breathing zone results indicated an average organotin concentration (as Sn) of 71 mg/m^3 (230 mg/m^3 as TCHH) over a sampling period of 11 minutes when the millman/formulator was filling a barrel, adjusting its weight, and staging raw materials. This sample appears to represent a maximum, worst-case exposure, as problems were encountered securing the drawstring closure of a bag of TCHH. It is highly probable that a significant contribution to the 11 mg/m^3 8-hour, TWA indication for millman/formulator occurred during this short time period. Depending on how frequently such problems are encountered, the 11 mg/m^3 indication may or may not be typical of everyday exposure potential.

An area sample was taken approximately 7 feet (horizontal distance) from the #2 Mill (5 feet above floor level). The sample, obtained near a leak above the star valve, indicated a 7-hour, TWA concentration of 0.08 mg/m^3 (as Sn) (see Table III). This result is indicative of the contribution of a leak to ambient concentrations. In this case, the leak and other contributions resulted in a local concentration that is more than 50% of the OSHA PEL.

13.5 WORKER EXPOSURE TO TOTAL PARTICULATE

Results of analyses for total particulate indicated 8-hour, TWA concentrations of 11 and 2.2 mg/m^3 for millmen/formulators monitored on two shifts. In the case of the 11 mg/m^3 concentration, it should again be pointed out that this concentration may not be representative of typical levels due to the previously discussed problem in securing the drawstring closure of a bag of TCHH. Eight-hour, TWA total particulate concentrations for other job groups ranged from 0.7 mg/m^3 (a filler and a final weigh operator) to 6.5 mg/m^3 (a bag seamer/sealer).

13.6 WORKER POPULATION AVAILABLE FOR A REPRODUCTIVE EFFECTS STUDY

Based upon workplace exposure data collected and employment data provided by the company, there are presently 24 potentially exposed males and no females available for inclusion in a possible reproductive effects study. All employees evaluated were required to wear respiratory protection, although respirators were not always worn properly. Therefore, actual exposures to TCHH may be lower

than the sampling results indicate. The organotin-containing miticide is formulated in campaigns of a few weeks' duration from time to time throughout the year, in anticipation of demand for the product; therefore, potential exposures could differ considerably from month to month and from season to season.

14.0 CONCLUSIONS

14.1 WORKER EXPOSURE TO ORGANOTINS

(a) Workers in most jobs (except the foreman and the forklift driver) were potentially exposed to 8-hour, TWA organotin concentrations exceeding the OSHA PEL and NIOSH-recommended exposure limit of 0.1 mg/m^3 (expressed as elemental tin). The concentrations measured during this study may represent, to some extent, "unusual" situations more than "normal" operations, due to factors such as atypical formulation and packaging schedules, and unanticipated short-term exposure to high concentrations. With the exception of the millman/formulator's sample, the results of sampling on the June 26 afternoon shift probably provide the best reflection of concentrations during a "normal" work shift.

(b) The millmen/formulators were potentially exposed to the highest 8-hour, TWA concentrations of organotin—0.39 to 3.4 mg/m^3 (expressed as Sn). Corresponding levels, expressed as TCHH, were 1.3 to 11 mg/m^3. Potential exposures of bag seamer/sealers ranged from 0.17 to 0.61 mg/m^3 (expressed as Sn). Corresponding TCHH levels were 0.54 to 2.0 mg/m^3. Workers at other operations, such as filling, final weighing, and packing/boxing, were potentially exposed to similar ranges of organotin concentrations—0.07 to 0.32 mg/m^3 (expressed as Sn). Corresponding TCHH levels were 0.2 to 1.0 mg/m^3. The forklift driver and the foreman were exposed to the lowest levels--less than 0.006, and 0.007 mg/m^3, respectively, corresponding to TCHH levels of less than 0.02, and 0.02 mg/m^3, respectively.

(c) Short-term sampling results indicated that an organotin concentration of 71 mg/m^3 (expressed as Sn)--230 mg/m^3 as TCHH--occurred over a sampling period of 11 minutes when a millman/formulator was filling a barrel, adjusting its weight, and staging raw materials. This sample appeared to represent a maximum, worst-case exposure, as problems were encountered securing the drawstring closure of a bag of TCHH.

(d) The TWA concentration (as TCHH) in the same millman/formulator's breathing zone for that date (11 mg/m^3) exceeded the ACGIH TLV of 5.0 mg/m^3 (as TCHH). It is highly probable that a significant portion of this potential exposure occurred during the 11-minute period described above.

(e) An area concentration of 0.08 mg/m^3 (expressed as Sn) was measured near a leak above the star valve feeding the #2 Mill. Subjective observation (visible dust emission from the leak) indicated that this source contributed significantly to the ambient concentration in that area of the workroom.

15.0 RECOMMENDATION

Organotin (TCHH) concentrations should be reduced to levels below the OSHA PEL and NIOSH-recommended standard of 0.1 mg/m^3. Reduction in airborne concentrations may be attained by improving the effectiveness of the local exhaust ventilation systems in place at the time of the evaluation and prompt action in the repair of leaks in process equipment such as the star valve feeding the #2 Mill.

16.0 FEASIBILITY OF CONDUCTING A REPRODUCTIVE EFFECTS STUDY

A decision regarding the feasibility of conducting a reproductive effects study will be made following evaluation of the information contained in this report by NIOSH epidemiologists.

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APPENDIX

SAMPLING AND ANALYTICAL RESULTS

TABLE III

Airborne Total Dust and Organotin Concentrations

Sample Description	Sample Number	Sampling Date (1984)	Sampling Time	Air Volume (Liters)	Sampling Period Only			8-Hour Time-Weighted Average		
					Total Dust (mg/m^3)	Organotin as Sn (mg/m^3)	Organotin as TCHH (mg/m^3)	Total Dust (mg/m^3)	Organotin as Sn (mg/m^3)	Organotin as TCHH (mg/m^3)
Personal samples:										
Filler operator 1	AE-26	6/26	1046-1157 1245-1539	354	2.8	0.37	1.2	1.4	0.19	0.62
Filler operator 2	AE-23*	6/26	1603-2330	675	1.9	0.34	1.1	1.8	0.32	1.0
Filler operator 1 (No bagging after lunch, ran out of material)	AE-24	6/27	0831-1153 1237-1534	559	0.9	0.1	0.3	0.7	0.08	0.3
Personal samples:										
Bag seamer/sealer 1	AE-32	6/26	1059-1159 1248-1541	352	2.3	0.34	1.1	1.1	0.17	0.54
Bag seamer/sealer 2	AE-09*	6/26	1605-2332	694	6.9	0.65	2.1	6.5	0.61	2.0
Personal samples:										
Final weigh operator 1	AE-31	6/26	1043-1158 1249-1540	360	2.2	0.29	0.93	1.1	0.15	0.47
Final weigh operator 2	AE-34*	6/26	1606-2331	656	2.1	0.32	1.0	1.9	0.30	1.0
Final weigh operator 1 (Helped clean up small spill) (No bagging after lunch, ran out of material)	AE-07	6/27	0833-1154 1236-1534	555	0.9	0.09	0.3	0.7	0.07	0.2
Personal samples:										
Packer/boxer 1	AE-22	6/26	1048-1156 1244-1542	369	1.9	0.2	0.8	1.0	0.1	0.4
Packer/boxer 2	AE-33*	6/26	1608-2329	670	1.5	0.16	0.50	1.4	0.14	0.46
Personal samples:										
Millman/formulator 1	AE-37	6/26	1615-2332	651	12.	3.8	12.	11.	3.4	11.
Millman/formulator 2 (Cleaned up small TCHH spill)	AE-25	6/27	0837-1154 1240-1534	526	2.9	0.50	1.6	2.2	0.39	1.3
Personal sample:										
Forklift driver	AE-13*	6/27	0845-1201 1238-1533	559	2.0	< 0.009	< 0.03	1.5	< 0.006	<0.02
Personal sample:										
Foreman	AE-17*	6/27	0849-1207 1245-1423 1441-1534	527	3.4	0.01	0.03	2.5	0.007	0.02
Area sample:										
7 feet from #2 Mill, elev. 5 ft; leak above star valve that feeds mill	AE-39	6/26	0839-1543	625	1.4	0.08	0.2	1.2	0.07	0.2

*Sample is probably representative of day-to-day exposure since work activities were not affected by atypical formulation schedules/exposure-related occurrences.

L.O.D.:

(1) Organotin by solvent extraction and flame AAS: 0.005 mg (as Sn) per sample, based on 195% recovery at the detection limit; equivalent to an airborne concentration of 0.01 mg/m^3 (as Sn) (assuming a 500-L air sample).
(2) Total particulate: 0.1 mg per sample, equivalent to an airborne concentraton of 0.2 mg/m^3 (assuming a 500-L air sample).

TABLE IV

Comparison of Results of Short-Term Sampling Using Two Sampling and Analytical Methods

Sample Description	Sample Number	Sampling Date (1984)	Sampling Time	Air Volume (Liters)	Total Dust (mg/m^3)	Organotin as Sn (mg/m^3)
Area samples near millman/ formulator's breathing zone; fillingbarrel (heavy dusting) adjusting barrel weight (moderate dusting), positioning of raw materials for shaker/elevator	AE-18 (glass fiber filter)	6/26	2105-2116	16.5	190	71
	AA-09 (cellulose membrane filter)	6/26	2105-2116	16.7	190	32
Area samples near millman/ formulator's breathing zone; pouring TCHH with feed tray, pushing TCHH into feed elevator port and pouring additional TCHH into feed tray	AE-28 (glass fiber filter)	6/27	1245-1249	5.9	<20	6.6
	AA-03 (cellulose membrane filter)	6/27	1245-1249	6.6	20	3.3

LOD:

(1) Organotin by solvent extraction and flame AAS: 0.005 mg (as Sn) per sample, based on 195% recovery at the detection limit; equivalent to an airborne concentration of 0.01 mg/m^3 (assuming a 500-L air sample).
(2) Tin by acid digestion and flame AAS: 0.003 mg (as Sn) sample, equivalent to an airborne concentration of 0.006 mg/m^3 (assuming a 500-L air sample).
(3) Total particulate: 0.1 mg per sample, equivalent to an airborne concentraton of 0.2 mg/m^3 (assuming a 500-L air sample).

TABLE V

Summary of Breathing Zone Concentrations of Organotin by Job
(8-hour, Time-Weighted Averages)

Job	Number of Samples	Organotin Concentration Range* [mg/m^3 (as elemental Sn)]	[mg/m^3 (as TCHH)]
Filler-packaging machine	3	0.08-0.32	0.3-1.0
Bag seamer/sealer	2	0.17-0.61	0.54-2.0
Final weigh operator	3	0.07-0.30	0.2-1.0
Packer/boxer	2	0.1-0.14	0.4-0.46
Millman/formulator	2	0.39-3.4	1.3-11.
Forklift driver	1	< 0.006	< 0.02
Foreman	1	0.007	0.02

*Analytical results obtained using flame AAS.