Industrial Hygiene Survey Report of Worker Exposures to Organotins at M&T Chemicals, Inc. Axis Plant Axis, AL 36505

Survey Dates
March 14, 1984 and August 14, 1984

Survey Conducted By

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Report By

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Report Submitted To

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Contract No. 200-82-2521

PLACE VISITED:	M&T Chemicals, Inc. Axis Plant Axis, AL 36505
DATE(S) OF VISIT:	March 14 and August 14, 1984
PERSON MAKING VISIT:	Nam Won Paik, Ph.D., C.I.H. Clayton Environmental Consultants, Inc.
PERSON(S) CONTACTED AT FACILITY:	Richard M. Gioscia M&T General Offices Rahway, NJ J. Daniel Herzog Jr. Employee Relations M&T Axis Plant
UNION:	None
PURPOSE OF SURVEY:	To conduct an industrial hygiene survey of organotin exposures during organotin production as part of the current NIOSH-sponsored study of occupational exposures to organotins.
STANDARD INDUSTRIAL CLASSIFICATION:	2869 (Industrial Organic Chemicals, Not Elsewhere Classified)

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.

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Abstract

An industrial hygiene survey was conducted at the M&T Chemicals, Inc. Axis, Alabama plant to measure worker exposure to organotins at selected operations during the production of organotin compounds. 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. Two separate visits--on March 14, 1984, and on August 14, 1984--to the facility were made in connection with this survey.

Worker exposures to airborne organotins in organotin production areas were determined using M&T Chemical's Standard Test Method AA-62 (August 14, 1984 visit). This method allows for the determination of total organotins measured as tin.

Using M&T's Method AA-62, results of personal samples ranged from 0.02 to 0.05 mg/m^3 of total organotins; results of area samples generally ranged from 0.01 to 0.02 mg/m^3, although one sample indicated a total organotins concentration of 0.13 mg/m^3.

Based upon workplace exposure data collected and employment data provided by the company, there are presently 14 potentially exposed male employees available for inclusion in a possible reproductive effects study. Since the plant began production in 1981, the theoretical maximum length of exposure for any given employee is approximately four years. 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.

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.

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 organotin manufacturers and users

Task II. Walkthrough surveys of facilities using/producing organotin compounds

Task III. Detailed industrial hygiene surveys to document worker exposures

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

This survey of the M&T Chemicals, Inc. plant in Axis, Alabama was conducted as one of the Task III detailed industrial hygiene surveys. A walkthrough survey of this site was conducted on September 8, 1983.

1.1 USES

Occupational exposures to organotins may occur in the manufacture and use of these materials. Organotins are principally used as stabilizers for polyvinyl chlorides (PVCs), as catalysts in the plastics and rubber industries, and as biocides.

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 DESCRIPTION OF FACILITY

The M&T Chemicals, Inc. Axis plant was built in 1981. It is located approximately 10 miles north of Mobile, Alabama. The plant occupies approximately 200 acres and consists of two organotin production areas (the 200 and 300 areas), an administration building, and a maintenance building. The 100 area of the facility is an inorganic tin production area. The raw materials used in the production are alkyl aluminum compounds, tin tetrachloride, dibutyl ether, heptane, aluminum chloride, and butyl crudes. The final products are dibutyltin oxide (DBTO), tributyltin oxide (TBTO), butyl crudes, and tetrabutyltin. Dibutyltin dichloride (DBTC), tributyltin chloride (TBTC), tin tetrachloride, and butyl crudes are also produced and used in production processes.

4.0 DESCRIPTION OF WORKFORCE AND RECORDKEEPING SYSTEM

A total of 51 people are employed at the Axis plant, 32 of them (all males) directly involved in production. The average age is about 34 years. The total number of full-time production operators is 14. All employees were newly hired at the startup (1981) of the plant.

Workers work three consecutive 12-hour shifts over three days and change from day to night shift weekly. Employees work three 12-hour shifts one week, and four 12-hour shifts the following week.

There are two 12-hour shifts per day. Three operators (two butyl technicians and one butyl operator) work each day shift and two (one butyl technician and one operator) work each night shift in the 300 area. Two operators (one butyl technician and one butyl operator) work in 100/200 area. Activities associated with each job title, which have the potential for organotin exposure, are described below:

100/200 Area

- Butyl technician: Collect quality control samples routinely.
- Butyl operator: Collect quality control samples and monitor production processes of organotins.

300 Area

- o Butyl technician: Collect quality control samples.
- o Butyl operator: Collect quality control samples, monitor production processes of organotins, and perform drumming and packaging of TBTO. These drumming and packaging operations are performed once every two weeks. The operations were done during the August 14, 1984 survey.

There are several maintenance people in the plant.

Individual employee records are complete and have been retained to date. Records for terminated employees are also maintained. The personnel records contain the work history of each employee.

5.0 DESCRIPTION OF OPERATIONS

The aluminum alkyl process[6] of manufacturing organotins is currently used at the plant. This process is presented in Figure 1.

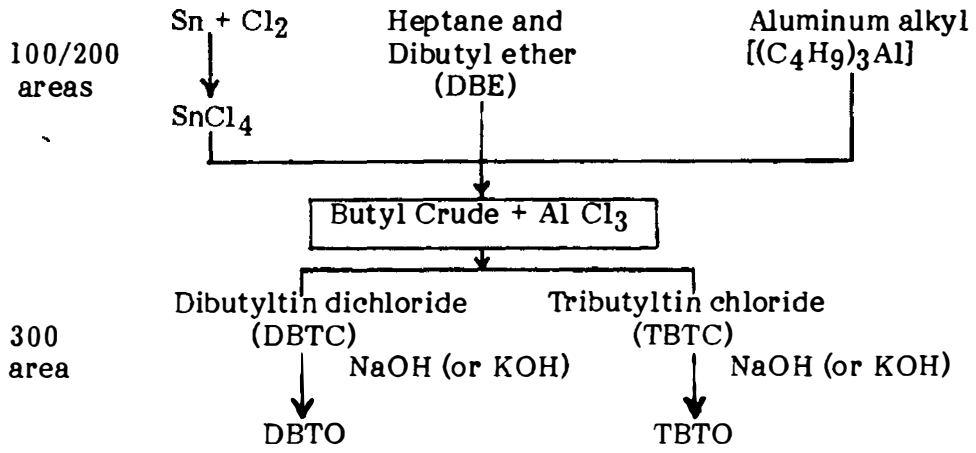

Figure 1. Aluminum alkyl process to manufacture butyl crudes which are used to manufacture DBTO and TBTO.

In the 100/200 area, butyl crude is produced from raw materials as indicated in Figure 1. Aluminum alkyl compounds are also produced as intermediate compounds. In the 100/200 areas, the operations are controlled from a control room and the process facilities, including pipelines, are located outdoors.

In the 300 area, the DBTC (or TBTC) and caustic material (potassium hydroxide or sodium hydroxide) are mixed and reacted in a reaction tank, and the final products, DBTO (powder) and TBTO (liquid), are collected in bags/fiber drums and 55-gallon drums, respectively, and stored in a warehouse prior to shipment.

6.0 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 typically the most toxic. Within a particular class, the lower alkyl groups are usually the most toxic, with the C_1 through C_3 groups significantly more toxic than the higher alkyl groups.[6,7]

Animal toxicity data, expressed as an LD_{50} (the dose that is lethal in 50% of the animals in a group of the same species when administered by the stated route) for five compounds which are used or produced at the M&T Axis plant are listed below. The indicated LD_{50} values were obtained from the 1983 Supplement to the 1981-82 Edition of the Registry of Toxic Effects of Chemical Substances (RTECS).[8] The RTECS is a compendium of toxicity 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.

Compounds	LD_{50}, mg/Kg
DBTC	100 (oral, mouse)[8]
DBTO	487 (oral, rat)[8]
TBTC	129 (oral, rat)[8]
TBTO	87 (oral, rat)[8]
Tetrabutyltin	1,389 (oral, mouse)[8]

Materials having LD_{50} values of 500 to 5,000 mg/Kg (single oral dose, rats) are classified as "slightly toxic" substances; materials with LD_{50} values of 50 to 500 mg/Kg are classified as "moderately toxic" materials; and chemicals with LD_{50} values of 1 to 50 mg/Kg are rated as "highly toxic" chemicals.[9]

Many organotin compounds are skin irritants and may be absorbed via the skin.[10]

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 diotcyltin 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.(7)

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.

7.0 OCCUPATIONAL EXPOSURE CRITERIA

Standards for occupational exposures to organotin compounds have been established or recommended by the Occupational Safety and Health Administration (OSHA) [Permissible Exposure Limits (PELs)], the American Conference of Governmental Industrial Hygienists (ACGIH) [Threshold Limit Values (TLVs)], and NIOSH, as follows:

OSHA[11]: PEL		0.1 mg/m^3 (as Sn); an 8-hour, time-weighted average (TWA)
ACGIH[12]: TLV	(1)	0.1 mg/m^3 (as Sn); an 8-hour, TWA
	(2)	0.2 mg/m^3 (as Sn); a short-term exposure limit (STEL) based on a 15-minute sample period
NIOSH[13]:	(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 total 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); no limits have been established for specific compounds. ACGIH has, however, separately adopted an 8-hour, TWA TLV, without a skin notation, of 5 mg/m^3 for cyhexatin (tricyclohexyltin hydroxide).[12]

8.0 DESCRIPTION OF INDUSTRIAL HYGIENE, MEDICAL, SAFETY, AND ENVIRONMENTAL PROGRAMS

8.1 MEDICAL PROGRAM

The medical program at the Axis plant is run by a local physician retained on contract by the plant. The medical program provides

pre-employment and annual physical examinations for production workers. Annual physicals are conducted by the physician at a local clinic.

The medical records are kept for 30 years after termination of employment.

8.2 INDUSTRIAL HYGIENE

The industrial hygiene program is supervised by an industrial hygienist from the corporate office. The program is supported by an air sampling program conducted by quality control employees. Sampling and analyses have been performed for airborne total organotins, dibutyl ether, and hydrogen chloride. Airborne organotin concentrations were determined in April and May 1982, and June and July 1983.

8.3 SAFETY PROGRAM

The facility has a comprehensive safety program which includes routine training, risk analysis and incident review. A full-time safety manager is in charge of the safety program. Program elements include a personal protective equipment program and a shoe cleaning program. Also there is a monthly meeting of a safety committee, consisting of representatives from management and engineering, office workers, and laborers. The security guard briefs all people who enter the plant on safety instructions. All are required to carry chlorine escape mouthpiece respirators. Visitors are required to follow all safety requirements and carry chlorine escape respirators.

8.3.1 Personal Protective Equipment Program

Use of personal protective equipment, including clothing, safety glasses, hard hats, shoes (rubber boots), and rubber gloves, is required in the production area. A shower facility is provided and it is reported that almost all production workers do shower after completion of work although it is not required.

The following types of respirators are currently provided:

(a) organic vapor/acid gas cartridge with half facepiece in the 100/200 and 300 areas.
(b) supplied air from a breathing air compressor is available in 300 area. All areas have bottled breathing air available.

(c) chlorine gas/escape mouthpiece in the 100/200 area.

(d) self-contained breathing apparatus is available in the 100, 200, and 300 areas.

(e) acid gas/organic vapor canisters with full facepiece in the 100/200 and 300 areas.

Air-supplied helmets are available for use with supplied air from the breathing air compressor in the 100/200 and 300 areas.

8.3.2 Shoe Cleaning Program

There is a facility for employees to wash shoes before entering the office building from production areas. The intent of the shoe cleaning facility is to prevent low level organotin contamination in the office building from contaminated shoes.

8.4 OTHER ENVIRONMENTAL PROGRAMS

Most tin waste is recycled; the sediments from the wastewater pond are transported to the M&T Chemicals Carrollton, Kentucky plant for tin reclamation.

9.0 HISTORICAL EXPOSURE DATA

Table I presents historical industrial hygiene sampling data. All samples were collected by M&T personnel during routine operations.

TABLE I
Historical Industrial Hygiene Sampling Data

Sampling Month	Number of Samples	Sampled Area	Chemicals Analyzed	Average Concentration (mg/m^3)
12/82	4	200	Dibutyl ether	None detected
12/82	2	100/200	Hydrogen chloride	None detected
4-5/82	10	100/200	Organotins	0.033 (as Sn)
6/83	4	100/200	Organotins	0.030 (as Sn)
7/83	4	300	Organotins	0.009 (as Sn)

10.0 DESCRIPTION OF ENGINEERING CONTROLS

A local ventilation system has been installed at the chemical reaction process in the 300 area; vapors exhaust through a caustic scrubber and solid materials exhaust to a baghouse for environmental protection. Three fans mounted in walls are used for general ventilation.

The 100/200 area is located outdoors; processes/operations are under the influence of natural ventilation.

11.0 EVALUATION SCOPE

On March 14, 1984, a personal sample was taken in the 100/200 area for measurement of dibutyl ether. Sampling was also conducted using NIOSH Method P&CAM 368 for specific organotins--tetrabutyltin, TBTO, TBTC, DBTO, and DBTC--and total organotins; however, problems encountered in analytical instrument set-up prevented successful analysis of the organotin samples. Area samples were collected in the 100/200 area for measurement of dibutyl ether, hydrogen chloride, and chlorine.

On August 14, 1984, samples were collected in the breathing zones of a butyl technician in the 100/200 area and a butyl technician and two butyl operators in the 300 area for measurement of exposure to total organotin. Area samples were also collected in both areas for total organotins measurement. Sampling and analyses for specific organotins were not undertaken for this survey. In connection with personal and area sampling, side-by-side samples were collected to allow for an inter- laboratory comparison of results using the M&T sampling and analytical method.

12.0 SAMPLING AND ANALYTICAL METHODS

A general summary of sampling and analytical methods used for determining airborne organotins, dibutyl ether, chlorine, and hydrogen chloride is shown in Table II.

TABLE II
Sampling and Analytical Methods

Compound	Method	Collection Method	Analytical Method
Total organotin	M&T Standard Method AA-62[14]	Glass fiber filter and XAD-2 tube in series	Solvent extraction/ desorption and AAS analysis
Dibutyl ether	NIOSH P&CAM 127[15]	150-mg activated charcoal	Gas chromatography
Chlorine	OSHA[16]	0.1% sulfamic acid solution	Specific ion electrode
Hydrogen chloride	NIOSH S-246[17]	0.5M sodium acetate solution	Specific ion electrode

Samples taken on August 14, 1984 were analyzed for total organotins using M&T Chemicals' Standard Test Method AA-62. Samples were collected using a glass fiber filter followed by an XAD-2 sorbent tube. Samples were extracted with acetic acid and toluene and analyzed for total organotins using graphite furnace AAS. The manufacturer has indicated that this method is in the process of being validated and that details of the method will be published in late 1985.

13.0 RESULTS AND DISCUSSION

Sampling and analytical results are presented in Appendix A, Tables III through VII.

Samples collected on August 14, 1984 were analyzed for total organotins using M&T Chemicals' Standard Test Method AA-62. The results are presented in Appendix A, Tables III-1 to III-4. All concentrations are expressed as milligrams of elemental tin per cubic meter of air sampled. Table IV summarizes the results.

13.1 ORGANOTINS

13.1.1 300 Area

Analytical results of personal samples for total organotins ranged from 0.02 to 0.05 mg/m^3. Results are presented in Table III-1. During this survey, a 2-1/2-hour personal sample was taken of the butyl operator during the drumming operation. The result was 0.03 mg/m^3; thus, there appeared to be no substantial difference in airborne total organotin concentrations between routine butyl operator activities and the drumming activity. It should be noted that air line respirators are worn during the drumming operation; therefore "actual" exposures very likely were lower than the sampling results would suggest.

Results of area samples are presented in Tables III-2 and III-3. The highest concentration of total organotin, 0.13 mg/m^3, was determined in the F301 area on the first floor. This concentration apparently resulted from the presence of organotin residues that were not cleaned up immediately after recent maintenance activities. Results at other monitored areas in the 300 area ranged from 0.01 to 0.02 mg/m^3. The airborne organotin concentration measured on the 2nd floor was 0.01 mg/m^3.

13.1.2 100/200 Area

Two samples, one personal (of a butyl technician) and one area, were taken from the 100/200 area during each survey. The results of personal and area samples analyzed by Clayton were 0.05 and 0.02 mg/m^3 for total organotins (as Sn) (see Table III-4).

During this survey, side-by-side samples were collected by M&T Chemicals and Clayton and analyzed by their respective laboratories (with both laboratories using the analytical procedure prescribed by M&T's AA-62 method). Additional details concerning the comparison of results of the side-by-side samples are presented in Section 13.3.

13.2 DIBUTYL ETHER, CHLORINE, AND HYDROGEN CHLORIDE

Tables V through VII present results of sampling for dibutyl ether, chlorine, and hydrogen chloride. A personal sample (approximately 7 hours) obtained from a butyl operator in the 200 area indicated that the airborne dibutyl ether concentration was 0.14 ppm. There is no standard for occupational exposure to dibutyl ether. An area sample obtained in the 100 area for chlorine indicated that the concentration was below the detection limit of the method used. The OSHA PEL for chlorine is 1 ppm. This PEL is for a ceiling concentration. An area sample (5-1/2 hours) obtained in the 100 area for hydrogen chloride indicated a concentration of 0.025 ppm. The OSHA PEL for hydrogen chloride is 5 ppm. This PEL is for a ceiling concentration.

Because the OSHA PELs for chlorine and hydrogen chloride are based upon shorter sampling times, the concentrations measured here are not directly comparable to these limits.

13.3 RESULTS OF ANALYSIS OF SIDE-BY-SIDE SAMPLES

The analytical results of side-by-side samples collected during the August 14, 1984 survey are presented and compared in Appendix B. There is a very good agreement between the results obtained from both laboratories (correlation coefficient (r) = 0.975).

13.4 OTHER OBSERVATIONS

Some of the workers reportedly occasionally experience skin and throat irritation.

13.5 WORKER POPULATION AVAILABLE FOR A REPRODUCTIVE EFFECTS STUDY

Based upon workplace exposure data collected and employment data provided by the company, there are presently 14 potentially exposed male employees available for inclusion in a possible reproductive effects study. Since the plant began production in 1981, the theoretical maximum length of exposure for any given employee is approximately four years.

14.0 CONCLUSIONS

14.1 WORKER EXPOSURES TO ORGANOTINS

Based on the results of the two surveys, worker exposures to organotins are summarized below:

(a) In the 300 area, the highest concentration of total organotins (0.13 mg/m^3) was measured at the F-301 area, i.e., at the southwest corner of the first floor of the building. Subjective observation indicated that the area was not well cleaned after recent maintenance activity. There was poor ventilation in this area during the survey and this is an area of infrequent worker activity. According to the corporate industrial hygienist of M&T, the area has since been cleaned, ventilation has been improved, and the area was remonitored. Remonitoring reportedly indicated a considerably lower concentration (0.02 mg/m^3).

(b) Personal sample results indicated that butyl technicians and operators were exposed to airborne total organotin concentrations of 0.02 to 0.05 mg/m^3. Butyl technician exposures as measured during the survey were slightly higher than those of the butyl operators.

(c) Total organotin concentrations in the general areas of the first floor of the 300 area were 0.01 to 0.02 mg/m^3 on August 14, 1984, as analyzed by M&T Chemical's Standard Method AA-62.

14.2 CHEMICALS OTHER THAN ORGANOTINS

Airborne concentrations of other chemical substances measured, including dibutyl ether in the 200 area, and chlorine and hydrogen chloride in the 100 area, were determined. Chlorine concentrations were below the detection limit of the method. Long-term area samples for hydrogen chloride and dibutyl ether indicated concentrations of 0.025 ppm and 1.42 ppm, respectively. The OSHA PEL for hydrogen chloride is 5 ppm (as a ceiling concentration); the OSHA PEL for chlorine is 1 ppm (as a ceiling concentration). No standard has been established for dibutyl ether. Because the OSHA PELs for chlorine and hydrogen chloride are based upon shorter sampling times, the concentrations measured here are not directly comparable to these limits.

15.0 RECOMMENDATIONS

(a) To reduce the potential for exposure to air- or surface- borne organotins, cleanup should be accomplished promptly after maintenance activity that results in visible contamination of surfaces, such as the situation observed in the F-301 area during the survey.

(b) Complaints of throat irritation can be minimized by increased use of the available respiratory protective equipment in activities where exposure to potentially irritating atmospheres may be anticipated.

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.

References

1. Iwamoto, I. Experimental Studies on the Influence of Butyltin Poisoning through the Respiratory Tract upon the Reproductive Function. J. Tokyo Med. Coll. 18: p. 1351-1376 (1960).

2. Nikonorow, M., H. Mazur, and H. Piekacz. Effect of Orally Administered Plasticizers and Polyvinyl Chloride Stabilizers in the Rat. Toxicol. Appl. Pharmacol. 26: p. 253-259 (1973).

3. Verschuuren, H.G., R. Kroes, H.H. Vink, and G.J. Van Esch. Short-Term Toxicity Studies with Triphenyltin Compounds in Rats and Guinea Pigs. Food Cosmet. Toxicol. 4: p. 35-45 (1966).

4. Pate, B.D., and R.L. Hays. Histological Studies of Testes in Rats Treated with Certain Insecticides. J. Econ. Entomol. 61: p. 32-34 (1968).

5. Newton, D.W., and R.L. Hays. Histological Studies of Ovaries in Rats Treated with Hydroxyurea, Triphenyltin Acetate, and Triphenyltin Chloride. J. Econ. Entolmol. 61: p. 1668-1669 (1968).

6. Malpass, D.L., L.W. Fannin, and J.J. Ligi. Organometallics in "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 16. p. 573-577. A Wiley-Interscience Publication, John Wiley & Sons, New York (1981).

7. Clayton, G.D., and F.E. Clayton (Editors). Patty's Industrial Hygiene and Toxicology, 3rd Revised Edition. Vol. 2A. Toxicology, p. 1940-1968. A Wiley-Interscience Publication, John Wiley & Sons, New York (1981).

8. NIOSH: Registry of Toxic Effects of Chemical Substances, 1983 Supplement, Volume 2, DHEW (NIOSH) Pub. No. 84-101, NIOSH, Cincinnati, Ohio (October 1984).

9. Hodge, H.C., and J.H. Sterner. Tabulation of Toxicity Classes. Am. Ind. Hyg. Assoc. Q. 10: p. 93-96 (1949).

10. Friberg, L., G.F. Nordberg, and V.B. Vouk. Handbook on the Toxicology of Metals. p. 614-623, Elsevier/North-Holland Biomedical Press, New York (1979).

11. Occupational Safety and Health Administration (OSHA). General Industry - OSHA Safety and Health Standards (29 CFR 1910) Subpart Z. Toxic and Hazardous Substances. OSHA, Washington, D.C. (1978).

12. American Conference of Governmental Industrial Hygienists (ACGIH). TLVs^{R} Threshold Limit Values for Chemical Substances in the Work Environment Adopted by ACGIH for 1984-1985. ACGIH, Cincinnati, Ohio (1984).

13. NIOSH. Criteria for a Recommended Standard . . . Occupational Exposure to Organotin Compounds. DHEW (NIOSH) Publication No. 77-115. NIOSH, Cincinnati, Ohio (November 1976).

14. M&T Chemicals, Inc. Determination of Butyl Organotin Compounds in Air Samples by AAS-Graphite Furnace Standard Test Method No. AA-62. Research Laboratory, Rahway, New Jersey (1984).

15. NIOSH. Organic Solvents in Air. Method No. P&CAM 127. NIOSH Manual of Analytical Methods, 2nd Edition, Vol. 1, NIOSH, Cincinnati, Ohio (1977).

16. OSHA. Industrial Hygiene Technical Manual. Appendix A. Chemical Information Table. Occupational Safety and Health Reporter, 77: 8716. The Bureau of National Affairs, Inc., Washington, DC (1984).

17. NIOSH. Hydrogen Chloride. Method No. S246. NIOSH Manual of Analytical Methods, 2nd Edition, Vol. 3, NIOSH, Cincinnati, Ohio (1977).

APPENDIX A

SAMPLING AND ANALYTICAL RESULTS

TABLE III - 1

Results of Organotin Analyses*
M & T Chemicals, Inc.
Axis Plant, Alabama

August 14, 1984

Sample Number	Description	Sampling Period Start	Stop	Sampled Air Volume (liters)	Airborne Organotin Concentrations (mg/m3 as Sn)
AE-36	300 Area, Personal sample, butyl technician 3	0817	1628	584	0.01
XAD-2-36	300 Area, Personal sample, butyl technician 3	0817	1628	584	0.04
	Total of above 2 samples	0817	1628	584	0.05
AE-14	300 Area, personal sample, butyl operator 3	1002	1530	423	0.01
XAD-2-14	300 Area, personal sample, butyl operator 3	1002	1530	423	0.01
	Total of above 2 samples	1002	1530	423	0.02
AE-16	300 Area, personal sample, butyl operator 3, during drumming operation	1532	1813	208	0.02
XAD-2-16	300 Area, personal sample, butyl operator 3, during drumming operation	1532	1813	208	0.01
	Total of above 2 samples	1532	1813	208	0.03

L.O.D.: 0.6 ug Sn per sample, equivalent to an airborne concentration of 0.0012 mg/m^3 (assuming a 500L air sample).

* Using M&T Chemicals Standard Test Method AA-62.

TABLE III - 2

Results of Organotin Analyses*
M & T Chemicals, Inc.
Axis Plant, Alabama

August 14, 1984

Sample Number	Description	Sampling Period Start	Stop	Sampled Air Volume (liters)	Airborne Organotin Concentrations (mg/m3 as Sn)
AE-06	300 Area, area sample, 2nd floor, behind R301	0857	1641	489	0.007
XAD-2-06	300 Area, area sample, 2nd floor, behind R301	0857	1641	489	0.004
	Total of above 2 samples	0857	1641	489	0.01
AE-40	300 Area, area sample, 1st floor, F351	0905	1539	500	0.008
XAD-2-40	300 Area, area sample, 1st floor, F351	0905	1539	500	0.003
	Total of above 2 samples	0905	1539	500	0.01
AE-18	300 Area, area sample, 1st floor, F-351 during drumming operation	1540	1826	212	0.008
XAD-2-18	300 Area, area sample, 1st floor, F-351 during drumming operation	1540	1826	212	0.004
	Total of above 2 samples	1540	1826	212	0.01

L.O.D.: 0.6 ug Sn per sample, equivalent to an airborne concentration of 0.0012 mg/m^3 (assuming a 500 L air sample).

* Using M&T Chemicals Standard Test Method AA-62.

TABLE III - 3

Results of Organotin Analyses*
M & T Chemicals, Inc.
Axis Plant, Alabama

August 14, 1984

Sample Number	Description	Sampling Period Start	Stop	Sampled Air Volume (Liters)	Airborne Organotin Concentrations (mg/m^3 as Sn)
AE-22	300 Area, area sample, 1st floor, F301	0911	1748	476	0.11
XAD-2-22	300 Area, area sample, 1st floor, F301	0911	1748	476	0.01
	Total of above 2 samples	0911	1748	476	0.13
AE-31	300 Area, area sample, 1st floor, P-341	0918	1744	549	0.01
XAD-2-31	300 Area, area sample, 1st floor, P-341	0918	1744	549	0.01
	Total of above 2 samples	0918	1744	549	0.02

L.O.D. = 0.6 ug Sn per sample, equivalent to an airborne concentration of 0.0012 mg/m^3 (assuming a 500 L air sample).

*Using M&T Chemical's Standard Test Method AA-62.

TABLE III - 4

Results of Organotin Analyses*
M & T Chemicals, Inc.
Axis Plant, Alabama

August 14, 1984

Sample Number	Description	Sampling Period Start	Stop	Sampled Air Volume (Liters)	Airborne Organotin Concentrations (mg/m^3 as Sn)
AE-21	100/200 Area, personal sample, butyl operator 4 (lunch time: 1341-1420)	1011	1756	498	0.007
XAD-2-21	100/200 Area, personal sample, butyl operator 4	1011	1756	498	0.040
	Total of above 2 samples	1011	1756	498	0.05
AE-09	100/200 Area, area sample, C-260, bottom sampling port	0847	1635	544	0.005
XAD-2-09	100/200 Area, area sample, C-260, bottom sampling port	0847	1635	544	0.02
	Total of above 2 samples	0847	1635	544	0.02

L.O.D. = 0.6 ug Sn per sample, equivalent to an airborne concentration of 0.0012 mg/m^3 (assuming a 500 L air sample).

*Using M&T Chemical's Standard Test Method AA-62.

TABLE IV
Summary of Organotin Results
of August 14, 1984 Survey

Sample Description	Airborne Organotin Concentration (mg/m^3 as Sn)
100/200 Area, personal samples, butyl technician/ operator	0.05
200 Area, area samples, C260 bottom sampling port	0.02
300 Area, personal sample, butyl technician	0.05
300 Area, personal sample, butyl operator	0.02-0.03
300 Area, area sample, F-301	0.13
300 Area, area sample, F-341 and F-351 filters	0.01
300 Area, area sample, 2nd level, behind R-301	0.01
300 Area, area sample, P-341	0.02

TABLE V
Airborne Dibutylether Concentrations: 200 Area
M&T Chemicals, Inc.
Axis Plant, Alabama
March 14, 1984

Sample Number	Description	Sampling Period Start	Sampling Period Stop	Sample Weight (mg)	Sample Volume (Liters)	Dibutylether Concentration (ppm)
C-1	Area sample at dibutylether sampling port (there was a small leak)	0954	1654	0.067	8.85	1.42
C-2	Personal sample, butyl operator	0946	1650	0.014	18.66	0.14

The limit of detection of dibutylether was 0.002 mg per sample.

No standard for occupational exposure to dibutylether has been established or recommended.

TABLE VI
Airborne Chlorine Concentrations: 100 Area
M&T Chemicals, Inc.
Axis Plant, Alabama
March 14, 1984

Sample Number	Description	Sampling Period Start	Sampling Period Stop	Sample Weight (ug)	Sample Volume (Liters)	Chlorine Concentration (ppm)
C12-1	Area sample, northside of 2nd level, above vent line to venturi scrubber	0933	1643	<4	447	< 0.003

The limit of detection of chlorine was 4 ug per sample.

OSHA PEL for chlorine is 1 ppm as a ceiling concentration as measured during any 15-minute sampling period.

TABLE VII
Airborne Hydrogen Chloride Concentrations at 100 Area
M&T Chemicals, Inc.
Axis Plant, Alabama
March 14, 1984

Sample Number	Description	Sampling Period		Sample Weight	Sample Volume	Hydrogen Chloride Concentration
		Start	Stop	(ug)	(Liters)	(ppm)
HCl-1	Area sample, northside of 2nd level, above vent line to venturi scrubber	0933	1500	12	325	0.025

American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for Ceiling Concentration: 5 ppm (not to be exceeded) as measured during any 15-minute sampling period.

Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for Ceiling Concentration: 5 ppm (not to be exceeded) as measured during any 15-minute sampling period.

The limit of detection (L.O.D.) of hydrogen chloride (HCl) was 23 ug. The sample was blank-corrected; weights of HCl in the sample and a blank were 35 ug and 23 ug, respectively. Thus, the net amount of HCl was 35 - 23 = 12 ug.

APPENDIX B

DUPLICATE SAMPLE RESULTS ANALYZED BY M&T CHEMICAL AND CLAYTON LABORATORIES USING M&T METHOD AA-62 ANALYTICAL PROCEDURE

Sample Description	Total Organotin Concentrations (mg/m^3 as Sn) M&T	Clayton
300 Area, personal samples, butyl technician 3	0.04	0.05
300 Area, personal samples, butyl operator 3	0.03	0.02
300 Area, personal samples, during drumming	0.04	0.03
300 Area, area samples, 1st floor F-301	0.09	0.13
300 Area, area samples 1st floor, P-341	0.04	0.03
300 Area, area samples 1st floor, F-351	0.02	0.01
300 Area, area samples 1st floor, during drumming	0.02	0.01
300 Area, area samples 2nd floor, behind R-301	0.02	0.01
100/300 Area, personal samples, butyl operator 4	0.04	0.05
200 Area, area samples, C-260	0.02	0.02

Correlation Coefficient (γ) = 0.975