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Evaluation of Employee Exposure to Organic Tin Compounds Used as Stabilizers at PVC Processing Facilities

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Organic tin compounds are primary substances used as heat stabilizers by the polyvinyl chloride (PVC) industry. The use of these compounds in the PVC industry is generally well controlled, usually by automated processes. This study was conducted to provide an overview of worker exposure to organic tin compounds at PVC processing facilities and to verify that these exposures are below the threshold limit value (TLV®) set by the American Conference of Governmental Industrial Hygienists for organic tin. The basis of the TLV indicates the principal concern is to minimize adverse effects on immune function and the central nervous system from airborne exposure to organic tin. The TLV has a skin designation based on 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.

Personal exposure monitoring was conducted following the National Institute for Occupational Safety and Health (NIOSH) 5504 sampling method and a modified version of the NIOSH analytical method. The results were reported as "total tin." The data indicated no average exposure levels for individual tasks exceeded the organic tin TLV, and 96% of results the samples were less than 20% of the TLV. Only 1 sample of 102 exceeded the TLV, and the individual was wearing appropriate respiratory protection. Subsequent investigation indicated the highest exposures occurred while the operators were conducting tasks that included manual handling of the organic tin compounds. These data suggest manual operations may have a greater potential for organic tin exposure.

Keywords NIOSH Method 5504, organic tin compounds, personal exposure monitoring, Tin Stabilizers Association

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The use of organic tin compounds in polyvinyl chloride (PVC) as stabilizer agents involves a potential risk of occupational exposure to organic tin compounds for employees in the manufacturing sector. To provide an overview of worker exposure to organic tin compounds used in the stabilizers for PVC processing, a series of personal samples was collected to assess the presence of tin in the breathing zone of the workers and to compare the study results with the threshold limit value (TLV®) for organic tin compounds of 0.1 mg/m^3,[1] as adopted by the American Conference of Governmental Industrial Hygienists (ACGIH®).

The hypothesis of this study was: Employee exposures during the use of organic tin stabilizers are well below the ACGIH TLV. Consequently, the objectives of this study were to conduct air sampling for organic tin and evaluate the data to provide an overview of worker exposure at PVC processing facilities in Canada and the United States.

Organic tin compounds are used in a wide variety of applications, including heat stabilizers, catalysts, antifouling agents, and biocides. The compounds evaluated in this study are nonpesticidal organic tin compounds. Maleate, laurate, carboxylate, and mercaptide derivatives of mono and dialkyltins are used as stabilizers for PVC plastics[2] to enhance performance. Stabilizers prevent PVC polymer degradation by combining with the hydrochloric acid produced during the processing operations. PVC stabilizers are comprised of only mono- and di-substituted organic tin compounds.

Organic tin materials have four substituents on the tin atom, with at least one of the substituents joined by a tin to carbon bond. They are typically represented as R_aSnX_b, where $a + b = 4$. R is usually a small linear alkyl group (typically methyl, butyl, or octyl) and X is a ligand. This ligand is a functional group that modifies the functionality and performance of the material. It could be small reactive groups like chloride, oxide, hydroxide—typical of materials used as catalysts or chemical intermediates—or larger functional ester, thioester, or mercaptan groups like 2-ethylhexylmercaptoacetate, 2-mercaptoethyltallate, or other larger substituents for materials used as PVC stabilizers.

The alkyl groups determine the toxicity of the materials. Typically, trialkyl-substituted tins are more toxic than disubstituted tins, while the monoalkyl-substituted tins are the least toxic.[3] The ligands also have a major influence on irritation/absorption. The stabilizers are much larger, less reactive, molecules. This results in a decrease of irritation and the level of toxicity; therefore, a longer contact time and/or higher dose of material is needed to cause adverse effects, such as irritant contact dermatitis and folliculitis.[4] Generally, the severity of the adverse effect is less for the stabilizers than for the intermediates used to produce the stabilizers.

In the case of repeated exposure, organic tin compounds generally affect the liver, kidneys, and urinary tract.[5] The chlorides and oxides are the most extensively studied of the compounds, and the No Observed Adverse Effect Levels (NOAEL) for target organ effects indicate all of these materials have some biological activity in the liver, bile duct, and the immune system after repeated exposure. The TLV for organic tin compounds was recommended "to minimize the potential for adverse effects on immune function and the CNS." It was based on a NOAEL from inhalation studies of 0.3–0.4 ppm of tri-n-butyl tin chloride or bromide based on changes in the liver, kidney, lungs, heart, nervous system, and reproductive system in rodents.[4]

In 1990, world consumption of organic tin was estimated by the World Health Organization to be 28,000 tons.[5] The total use was made up of:

- Plastic stabilizers and catalysts, approximately 20,000 tons
- Wood preservatives (tributyl) 3–4000 tons
- Antifouling paints (tributyl) 2–3000 tons
- Other uses of di- and tributyltins, <2000 tons

MATERIALS AND METHODS

Air monitoring surveys were conducted on day shift operators at seven Canadian and seven U.S. PVC processing facilities. Local and general exhaust and ventilation systems were operating during the monitoring periods. Where required by the employer, monitored employees wore protective gloves and National Institute for Occupational Safety and Health (NIOSH)-approved respirators during the monitoring periods.

To evaluate a wide scope of job functions at the PVC processing facilities, operators were included who were undertaking the following tasks: mixing/blending of PVC compound, milling of PVC compound, pelletizing, extrusion, and injection molding. Of these operations, the mixing/blending tasks can lack automated controls, where the other tasks are automated. The operators usually have a range of tasks they perform each day and are not limited to a single activity, and these activities could include working on both manual and automated processes.

The samples were collected at a sampling rate of one liter per minute (L/min) through an OSHA versatile sampler (OVS) sampling tube (SKC Part No. 226-30-16) using personal air sampling pumps. All sampling pumps were calibrated before and after each monitoring period. Personal air samples were collected in the employee's breathing zone during a variety of working activities. A total of 102 personal samples of air were collected during the 14 plant surveys (generally 7 to 8 hours of sampling time).

An American Industrial Hygiene Association (AIHA)-accredited laboratory performed sample analyses. The samples were analyzed following NIOSH Method 5504M (organic tin compounds, modified).[6] The 5504 (unmodified) method specifies sampling with a glass fiber filter cassette followed by an XAD 2 tube, desorption with acetic acid/acetonitrile, separation with high-performance liquid chromatography (HPLC; cation exchange), and final analysis with graphite furnace atomic absorption (GFAA). The sampling portion for this study used a single OVS tube consisting of a glass fiber filter followed by XAD-2 resin, eliminating the need for separate sampling media. The use of a single sampling device that contained the two individual components of the validated method was recommended by NIOSH. The use of the OVS tube was validated for butyltin compounds[7] and methyltin compounds.[8]

The analytical portion of the NIOSH 5504 method was also modified (as described in the Applicability section of the NIOSH 5504 method)[6] to delete the HPLC separation step. This modification provides results as total tin, separated by particulate and vapor. The analytical method used was modified due to the lack of AIHA-accredited labs available to conduct the unmodified version of the NIOSH 5504 method for organic tin compounds. After extensive research, it was found that this method, HPLC followed by a GFAA, is not used in commercial IH labs. This modification was appropriate for this study as speciation of the individual organic tin compounds was not required. As a result of this shortcoming in the available analytical methods, methods have now been developed that can distinguish between two of the primary organic tin compounds used in PVC compound production: butyltins and methyltins. The methyltin method is available from NIOSH, as #5526, Methyltin Chlorides. The butyltin (speciated) method is described elsewhere[7] and is available on the Organotin Environmental Programme Association (ORTEPA) website at www.ortepa.org.

The 8-hour time-weighted average monitoring results for total tin were compared with the ACGIH TLV for organic tin compounds of 0.1 mg/m^3 as tin.

RESULTS

The results from this study were classified by tasks for reporting purposes. Each operator performed a variety of different tasks each day. These tasks included working with processes that were manual (potentially had a higher chance of exposure) and automated processes. The data collected during the sampling did not include a listing of each individual task performed; only the general operation (blending, etc.) was listed.

The mean organic tin exposure level for each task was less than 10% of the TLV. There were two cases where the results were higher (>50% of the TLV) for processes that on subsequent investigation were found to involve multiple individual tasks and manual handling of the materials, as opposed to processes involving more automation and engineering controls. The manual operations included opening drums and pouring tin stabilizer into containers to be added manually (i.e., not through an automatic feed system). In these cases, the operators were further protected by the use of NIOSH-approved respirators, as manual handling of tin stabilizer was expected, and it was recognized that the potential for exposure could

TABLE I. Descriptive Statistics of Organic Tin Exposure to Individual PVC Processing Tasks

Task	N	Min	Max	Mean	Std. Deviation	Geometric Mean	Geometric Std. Deviation
Blending	28	<0.001	0.102	0.009	0.019	0.005	2.932
Extrusion	47	<0.001	0.034	0.005	0.007	0.003	2.512
Injection molding	9	<0.001	0.007	0.003	0.002	0.002	2.108
Milling	10	<0.001	0.064	0.011	0.019	0.005	3.681
Pelletizing	8	<0.001	0.006	0.003	0.002	0.003	1.805
Total	102						

Note: Results are presented as mg/m^3 of total tin.

exist during the performance of specific tasks. The other 100 results ranged from <0.001 to 0.034 mg/m^3, the latter still representing a threefold level below the TLV.

Table I presents the results of the descriptive statistics of the individual PVC processing tasks. The results are presented as mg/m^3 of total tin.

Thirty-seven percent of the results were below the laboratory's limit of detection (LOD). For the statistical analysis of the results, the <LOD was replaced with the LOD value divided by the square root of 2 as described by Hornung and Reed.[9]

DISCUSSION

The sampling results suggest several salient points. Although one of the data points was slightly higher than the TLV (0.102 mg/m^3), this work shift was later found to involve some infrequent manual handling of the stabilizer containing organic tin compounds. It was also noted that due to the difference in individual plant process designs, many of the operators conducted a variety of different tasks in an individual work shift, resulting in different exposure levels reported for similar tasks.

During this study, it was found that for the nonautomated processes (usually involving tasks conducted infrequently), personal protective equipment is generally used to reduce the operator's exposures. Respiratory protection is commonly used in the PVC processing industry during nonroutine or infrequent activities, such as the following, where there is a potential for exposure:

- Opening and closing of drums of tin stabilizer and connecting and disconnecting pumps to these drums
- Pouring of tin stabilizer into containers to be added manually (i.e., not through an automated, engineered feed system) to a batch of PVC being compounded
- Cleaning up small residuals from the tops of drums or from the dip pipe after removing the pump dip pipe from the drum
- Sampling of stabilizers for analysis at the time of bulk delivery
- Connecting and disconnecting hoses at the time of bulk delivery and cleaning up any small residuals remaining after delivery
- Cleaning mixing vessels or continuous lines after use for PVC compounding

Organic tin compounds have been assigned a "skin" notation by ACGIH. This notation is given to chemical agents that have the potential to significantly contribute to the overall exposure of the individual by direct skin contact with the substance. Field observations made by the technical field staff indicated that the employees who were monitored during this survey wore gloves when needed, thereby limiting their direct skin contact with the chemical agents used in the various processes in the monitored facilities.

CONCLUSIONS

The findings confirm that workers in organic tin manufacturing facilities may experience quantifiable exposures to organic tin compounds. However, the study results indicate that exposures to organic tin compounds can be controlled to well below the TLV during PVC processing. Although not part of the design of this study, investigations subsequent to the sampling seemed to indicate the primary means of exposure reduction was the use of automated systems for handling the tin-containing stabilizers. Automated systems are engineered to provide minimal potential for direct contact of operators with the tin stabilizers. When used in conjunction with personal protective equipment for the infrequent, manual, nonautomated tasks, it is expected that under routine operations, worker exposures can be maintained well below the TLV.

It is recommended that further studies be conducted to determine the precise effect of automated controls on the exposure to organic tin compounds. These studies should include a specific breakdown of each task performed during the sampling. If possible, task specific sampling should be done, insuring that both manual and automated tasks are included. The authors attempted to ascertain the reasons for the two sampling results that were above 50% of the TLV. Representatives from the manufacturing facilities that were sampled only had definitive information concerning the one exposure point, 0.0102 mg/m^3. They stated their records showed the tasks completed that day of sampling included manual handling of the organic tin stabilizer. The remaining sampling points could not be conclusively

linked to responsibilities associated with either manual or automated tasks.

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