

*GPEC 2004 Paper Abstract #47:*

**Title: Assessing the Workplace Environmental Performance of Organotin Stabilizers Used at PVC Processing Facilities**

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In addressing environmental performance of plastics, one needs to look at all phases of the lifecycle, including the workplace. Organotin compounds are used extensively in the PVC industry as heat stabilizers, and it is important to determine that they can, and are being used safely. The paper reports on studies performed regarding exposures related to skin contact and airborne vapors. For vapors a study was conducted to provide an overview of worker exposure to organotin at a variety of PVC processing facilities, and to verify that these exposures are below the TLV set by the ACGIH for organic tin. The results show that worker exposure for all but one instance was at safe levels, sufficiently below the TLV. In one case, where air levels were high, the use of appropriate personal protective equipment kept exposure of the worker at safe levels. There were no incidents of over exposure. For skin exposure we assessed the dermal penetration rates of organotins, comparing human skin with rat skin, the usual test medium. The data show that the stabilizers penetrate skin more slowly than other, similar organotins, and that human skin is less permeable than rat skin. These results are discussed in light of their support for worker safety.

# Assessing the Workplace Environmental Performance of Organotin Stabilizers Used at PVC Processing Facilities

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## **Abstract**

In addressing environmental performance of plastics, all phases of the lifecycle, including the workplace, should be examined. Organotin compounds are used extensively in the PVC industry as heat stabilizers, and it is important to determine that they can, and are being used safely. This paper evaluates the implications for workplace safety from studies related to dermal exposure from inadvertent skin contact and inhalation exposure from vapors. For vapors workplace exposure monitoring studies were conducted to measure organotin levels at a variety of PVC processing facilities. The results show that worker exposure for all but one instance was at safe levels, sufficiently below the TLV. In one case, where air levels barely exceeded the TLV, the use of appropriate personal protective equipment attenuated the exposure to a safe level. There were no incidents of over exposure. To evaluate dermal exposure we assessed dermal transmission rates of organotins using an *in-vitro* system, comparing human cadaver skin with rat skin. The organotin stabilizers penetrated skin more slowly than the chlorides, and human skin was less permeable than rat skin. These results are discussed in light of their support for worker safety.

## Introduction

In considering the potential environmental impact of materials, one needs to examine their performance in the workplace. This is important, since in most cases it is the people who work with these materials that will have the most potential for exposure. As suppliers of tin stabilizers to the PVC industry, the members of the Tin Stabilizers Association, along with other allied groups involved with organotin compounds, wanted to reaffirm that working with tin stabilizers was being done safely. For this reason we chose to examine the two most likely routes of exposure for workers, inhalation of vapors and exposure to skin.

## Background

Organotin compounds are a class of chemicals that are used in a wide variety of applications including heat stabilizers for PVC processing, catalysts for chemical reactions, antifouling agents, and biocides. Structurally these are tin compounds with four groups bonded to tin, and to be an organotin at least one of these groups must be bound to tin through a tin to carbon bond. These are usually represented by the formula:  $R_nSnX_{4-n}$ .

In this context then, one can have mono, di, tri, and tetra organotins, all of which are made industrially, and which have very different uses. In the case of PVC heat stabilizers, one must use mono and di organotins, sometimes as mixtures, since the tri and tetra organotins do not function as heat stabilizers. Regarding the organic group bound to tin, stabilizers are made with alkyl **R** groups methyl, butyl, or octyl. The other groups on tin, ligands **X**, can be either carboxylate ligands, or thioester ligands, depending on the exact performance required of the stabilizer. In addition, as the stabilizer performs its function it reacts chemically within the PVC to form the corresponding alkyltin chlorides,  $R_nSnCl_{4-n}$ . The work described here involved methyl, butyl, and octyltins with thioester ligands **X**, and chloride as ligand **X**.

The inherent toxicity of many organotins has been studied, work on the chlorides and oxides being the most extensive. One conclusion supported by this work is that the alkyl groups are a major controlling factor controlling the toxicity of the materials. While the critical target organ may vary based on the type of alkyl group, typically, trialkyl substituted tins are more toxic than di-substituted tins, while the monoalkyl substituted tins are the least toxic(1). In repeat dose exposure studies in rats, organotins produced treatment related effects on the nervous, immune, and reproductive systems, liver, kidneys, and urinary tract. The organotins can also produce effects from direct contact with skin, and in this case the ligands **X** can have a major influence on irritation, as well as absorption (see below).

Based on the toxicology the American Conference of Governmental Industrial Hygienists (ACGIH), established a Threshold Limit Value (TLV) related to inhalation exposure for all organotins in the workplace of  $0.1 \text{ mg Sn/m}^3$ , and a Short Term Exposure Limit (STEL) of  $0.2 \text{ mg Sn/m}^3$  (2). Note that these values apply to all

organotins in the workplace. This TLV is based partly on a Lowest Observed Effect Level (LOEL) for inhalation of 0.3-0.4 ppm in air based on changes in the liver, kidney, lungs, heart, nervous system and reproductive system in rodents (3). The basis of the TLV indicates the principle concern is to minimize adverse effects on immune function and central nervous system from airborne exposure to organic tin. Also, the TLV has a skin designation based on the potential for percutaneous absorption. It should be recognized that TLVs for inhalation exposures are based on the presumption that there is no concurrent exposure via the skin and oral ingestion routes.

With the above toxicology in mind, we wanted to address two issues of workplace safety for operations involving organotins. In one case we wanted to determine if workers might be exposed to levels of organotin in the air that were above the TLV. For this evaluation we made a survey of workplace personal exposure levels for a variety of PVC processing operations. In the second case we wanted to understand better the potential for transdermal exposure from unintended skin contact, and so we evaluated the dermal penetration (flux) properties of key organotin chemicals.

### **Workplace Exposure Monitoring**

To provide an overview of worker exposure to organic tins 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<sup>3</sup> (measured as tin), as adopted by the American Conference of Governmental Industrial Hygienists (ACGIH).

Air monitoring surveys were conducted on day shift operators at five Ontario, two Quebec, and 7 United States PVC processing facilities, covering a range of processes used to manufacture PVC articles, see Table I. In order to evaluate a range 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. It must also be noted that operators usually have a range of tasks and are not limited to a single activity. Local and general exhaust and ventilation systems were operating during the monitoring periods. Where required by the employer, usually based on recommendations in the specific MSD sheet, monitored employees wore protective gloves and National Institute for Occupational Safety and Health (NIOSH) approved respirators during the monitoring periods.

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 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 the NIOSH Method 5504M (organic tin compounds, modified)(4). The 5504 (unmodified) method specifies sampling with a XAD 2 tube followed by a glass fiber filter cassette, desorption with Acetic acid/Acetonitrile, separation with an HPLC (cation exchange), and final analysis with a graphite furnace atomic absorption (GFAA). The sampling portion of the NIOSH method was modified for this study: a single OVS tube consisting of a glass fiber filter followed by XAD-2 resin as recommended by NIOSH was used, eliminating the need for separate sampling media. The final method developed for this study utilized the sampling collection section based on the NIOSH 5504 method for organotins.

The analytical portion of the NIOSH 5504 method was also modified (as described in the "Applicability section" of the NIOSH 5504 method) 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 tins. After extensive research, it was found that this method, HPLC followed by a GFAA, is not used in commercial Industrial Hygiene labs. This modification was acceptable for this study as speciation of the individual organic tins was not required, and the assumption that all tin measured was organic tin represents a worst case exposure evaluation. It should be noted that methods are now available which 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 in the Journal of Occupational and Environmental Hygiene (5), and is available on the Organotin Environmental Programme Association (ORTEPA) web site at [www.ortepa.org](http://www.ortepa.org). The sampling method used with the speciated butyltin method is from NIOSH 5504, using the OVS tube.

Table I presents the collective results of the monitoring work, and the exposure measurements are presented as  $\text{mg}/\text{m}^3$  of total tin. The measurements have been collected into comparable tasks at the various processing facilities involved in the testing; blending/mixing, milling, pelletizing, extrusion, and injection molding. This provides an assessment of similar work at a variety of locations. The table also includes descriptive statistics: total number of employees samples by work task (N), minimum, maximum, mean, standard deviations, geometric mean, and geometric standard deviation for the samples. The detailed results of air monitoring for each individual involved in the study are presented in Table II.

When viewed as a whole, the results indicate that the mean average exposures of the separate tasks were at or below 10% of the TLV, with 96% of the individual samples measuring below 20% of the TLV, see Table II. One measurement deserves specific comment, the value under blending of 0.102, at the TLV. To understand this result it is

important to examine the exact nature of the exposure to organotins by job function. For some workers, specifically those involved with blending, the employees actually work with the stabilizers in preparing blends with PVC resin, and there is potential for direct contact with the organotins. All of the other job functions involve working with PVC that contains the stabilizers, as well as operations where heated PVC could release organotins vapors into the air. For these latter tasks, airborne exposure is mainly controlled by the ventilation systems used around the equipment and in the plants. As all of the measurements for these tasks were well below the TLV, it is apparent that the exhaust systems used in these operations sufficiently controls organotin vapors to keep exposure well below the TLV.

Regarding blending, many of the operations use automated systems to handle the stabilizers, and for these instances the measurements show the exposure is well below the TLV. The one value at the TLV involved a worker performing manual operations. Such manual operations include opening drums and pouring tin stabilizer into containers to be added manually (i.e. not through an automatic feed system) to the blenders. In these cases, the operators were using respiratory protection, as manual handling of tin stabilizer was expected and it was recognized that the potential for exposure above the TLV could exist during the performance of such tasks. In fact the MSD sheets for the compounds recommend the use of personal protective equipment in this kind of operation. Thus, although the value measured in the ambient air was high, the actual inhalation exposure of the worker was probably attenuated at least 10 fold due to due to the protective equipment being used; the worker was not overexposed.

Table I. Descriptive Statistics (all tin values in  $\text{mg}/\text{m}^3$  tin)

Job Task	N	Min	Max	Mean	Std. Deviation	Geometric Mean	Geo. Std Deviations
Blending	28	<0.001	0.102	0.009	0.019	0.004	0.179
Extrusion	47	<0.001	0.034	0.005	0.007	0.003	0.116
Inj. Molding	9	<0.001	0.007	0.002	0.002	0.002	0.067
Milling	10	<0.001	0.064	0.011	0.019	0.004	0.179
Pelletizing	8	<0.001	0.006	0.003	0.002	0.003	0.067
Total	102						

In summary, the data collected in this workplace exposure study (including the analytical results and the descriptions of personal protective equipment worn) showed that exposure for all workers was well below the TLV. Thus exposure via inhalation in these operations does not present a health risk. The low exposures resulted either because the standard ventilation and automated systems used provided adequate protection, or, in those instances where possible exposure was recognized, the workers were using appropriate protective equipment. Organotins can be used safely in the

workplace, in the presence of appropriate automated systems and ventilation, or with the use of appropriate protective equipment when manual operations are involved.

### **Dermal Penetration Studies**

Organotin compounds have the potential to cause irritation, if they come in contact with the skin. For this reason the MSD sheets recommend that appropriate skin protection be used, if manual handling of the materials is taking place. Furthermore, any organotin that gets on the skin should be washed off immediately. Thus, while skin contact should be avoided, and the material quickly removed, we wanted to understand the potential for the stabilizers to actually penetrate through the skin.

There are established *in-vitro* test procedures for comparing dermal penetration rates, and the usual test medium is isolated rat skin. Material is applied to one side of the skin and the amount passing through the skin is measured. Such measurements have been made for some organotins, and we wanted to extend these measurements to look more specifically at human skin and the stabilizers used by the PVC industry.

The results of the *in-vitro* dermal penetration studies are summarized in Table III. Penetration was measured for rat and human skin, using occluded and unoccluded methods. The chemicals tested were the methyl, butyl, and octyltin chlorides and thioester stabilizers.

Table III: Dermal Penetration values for organotins, % of applied material transmitted in twenty four hours.

Sample	Skin type, method			
	Rat		Human	
	Occluded	Unoccluded	Occluded	Unoccluded
Tin Chlorides				
Methyl	10	10	1.39	0.25
Butyl	15	16	6.58	0.247
Octyl	1.6	0.37	0.02	0.02
Thioester				
Methyl	0.21	0.14	0.0013	0.0004
Butyl	0.26	0.19	0.0004	0.001
Octyl	0.003	0.004	<0.0001	<0.0001

Two important conclusions are supported by these data. First, the higher molecular weight organotin stabilizers move through the skin in smaller amounts than the lower molecular weight chlorides. Second, transdermal penetration percentages are lower for human skin than rat skin. Both of these conclusions have important, and favorable implications in the workplace. The actual materials used by workers in PVC processing facilities are the stabilizers, not the chlorides, and the stabilizers have the lower transdermal penetration values. Risk assessments for these materials that base

exposure on transmission through rat skin, the standard medium for such tests, will overestimate the actual exposure through human skin, and are therefore a conservative assessment of exposure. On this particular point, the very low transmission rates for the stabilizers through skin means that in the event of inadvertent skin contact, employees have time to remove the stabilizer and minimize the potential for any overexposure.

### **Acknowledgements**

The authors would like to acknowledge Max Grasso of Reagens Canada Ltd and Graham Knowles of the Vinyl Council of Canada for their contributions to the initial portion of the exposure monitoring study. The authors thank all of the companies and the employees who participated in the monitoring study. The workplace exposure studies in Canada were funded by Atofina Canada and Reagens Canada. The other studies were designed and funded in association with the Organotin Environmental Programme Association (ORTEPA), the Tin Stabilizers Association (TSA), the European Tin Stabilizers Association (ETINSA), and the Vinyl Council of Canada (VCC). For further information on these groups please see:

[www.tinstabilizers.org](http://www.tinstabilizers.org), [www.tinstabilisers.org](http://www.tinstabilisers.org), and [www.cpia.ca](http://www.cpia.ca) (under PUBLIC).

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Table II. Detailed Sampling Data, Results As Total Tin (mg/m<sup>3</sup>)

Blending	Extrusion	Injection Molding	Milling	Pelletizing
0.001	0.001	0.004	0.001	0.001
0.001	0.001	0.004	0.001	0.002
0.001	0.001	0.005	0.001	0.002
0.001	0.001	0.005	0.001	0.003
0.001	0.001	0.005	0.002	0.004
0.001	0.001	0.005	0.002	0.004
0.003	0.001	0.005	0.004	0.005
0.003	0.001	0.005	0.004	0.015
0.004	0.001	0.005	0.007	0.015
0.004	0.001	0.006		0.064
0.004	0.001	0.006		
0.004	0.001	0.008		
0.004	0.002	0.009		
0.004	0.002	0.010		
0.004	0.002	0.011		
0.005	0.002	0.012		
0.006	0.003	0.013		
0.006	0.003	0.032		
0.006	0.003	0.034		
0.007	0.003			
0.008	0.004			
0.008	0.004			
0.010	0.004			
0.011	0.004			
0.013	0.004			
0.017	0.004			
0.019	0.004			
0.102	0.004			

< LOD values were replaced with the LOD value divided by the  $\sqrt{2} = 0.001$ . Thirty seven percent of the results were below the laboratory's limit of detection (LOD). These results are known as censored data in statistical terminology and are nonzero values that cannot be measured, but are known to exist at some level. In order to have a value 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 R. W. Hornung (6).