TIN STABILISERS
A HISTORY OF SAFE USE

John M. Batt
Director – Product Stewardship
Additives Division
ATOFINA Chemicals, Inc.

Tin stabilisers have been safely used for over fifty years as heat stabilisers in PVC processing technology. Suppliers and users of tin stabilisers continue their product stewardship efforts to promote and encourage the responsible handling of materials at PVC processing plants as well as continued product improvement. Considerable industrial experience and significant research supports the continued safe use of organotins as PVC stabilisers.

Use in the PVC manufacturing environment

Engineering and industrial hygiene practices continue in their efforts to reduce exposures to workers while limiting the possibilities for releases to the environment. Industrial automation has reduced the need for direct worker contact during many of the operations. Product transfer is generally automated at converter sites. During bulk deliveries, the product is pumped directly from delivery truck into a bulk storage tank; when delivered in totes, the product is usually directly pumped from the tote (which is used as storage) or discharged into a small storage tank with the tote being returned to the supplier for cleaning and re-use. Addition of the stabilisers to PVC is automated, which reduces direct human contact with the tin stabiliser.[1]

Larger facilities enable the more frequent use of bulk shipments. In high volume applications like pipe and siding, bulk deliveries account for about 25 % of total shipments to those applications in the US, while tote shipments (reusable 1 ton containers) account for the majority of the remainder. Returnable totes are preferred over drums by PVC converters in the US because totes have an environmental advantage over drums in the reduced need for cleaning and disposal. The returnable totes and bulk trucks are cleaned at controlled locations, usually the supplier's own facility.[2]

Worker Exposure

The Vinyl Council of Canada's Environmental Management Program's Ontario Leadership Group, determined that it would be appropriate to develop data with respect to worker exposure to tin based heat stabilisers. In order to provide an overview of worker exposure to butyltins at vinyl processing facilities in Canada, the VCC, working with the Organotin Environmental Programme (ORTEP) Association, conducted a study in which personal air samples were collected.[3] So that a broad range of job functions were checked at the vinyl processing facilities, operators were included who were undertaking the following tasks: mixing/blending of vinyl compound, pelletizing, extrusion and injection molding. Airborne exposure for employees who work with the tin stabiliser compounds was determined by assessing exposure to total tin. The Threshold Limit Value (TLV) for Organic Tin Compounds is 0.1 mg/m^3, as tin, as adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). This is also the Permissible Exposure Limit (PEL) set by OSHA in the US. The results showed that, even in the case where levels exceeded the TLV or PEL, when using proper respiratory protection, the workers were not exposed to total tin in amounts greater than the TLV or PEL.

Of the 34 samples taken, 20 samples or 59% did not detect any organotin at all in the breathing zone of the operators. The average of 12 of the remaining samples was less than 10% of the TLV. The results were higher than average in 2 cases, for processes which involved manual handling of the materials, as opposed to the more automated processes. In these cases, operators wore respiratory protection, as manual handling of tin stabiliser was expected and it was recognized that the potential for exposure could exist. The other 32 results, mostly with automated handling processes, ranged from none detected (below 0.005 mg/m^3) to 0.017 mg/m^3, representing more than a 5 fold level below the TLV. Under routine operations, these automated processes have minimal potential for direct contact of operators with the organotin products.

Respiratory protection is generally used in the vinyl processing industry during activities where exposure could be present such as the following:

- opening and closing of drums of tin stabiliser and connecting and disconnecting pumps to these drums
- pouring of organotin stabiliser into containers to be added manually (i.e. not through an automatic feed system) to a batch of vinyl being compounded
- cleaning up small residuals from the top of drums or from the dip pipe after removing the pump dip pipe from the drum
- sampling of stabilisers 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 vinyl compounding

The study points out the importance for all vinyl compounders and processors to examine any of their manual processes that involve the handling of organotin stabilisers in order to automate the processes as much as possible, to put in place operating procedures, training and appropriate respiratory protection where automation is not possible, and to routinely measure organotin exposures where manual handling continues.

The vinyl processing industry has been very responsible in addressing workplace exposures of their employees and it is the belief of the companies participating in the study that the results of this "snap-shot" of the industry are very positive. The results do, however, suggest that the more manual the design of the operation is, the more potential exists for exposure.

The results of the Canadian study indicate there does not appear to be a significant risk of exposure for the workers sampled. However, due to the limited number of facilities and processes involved in this study, the findings only have general applicability to the vinyl processing industry as a whole. In the United States, the Tin Stabilizers Association (TSA) has commissioned a similar, larger, study to be conducted in 2002 at US vinyl processing plants.

End User

Depending on the application and regional government regulations where the material is produced, there are a variety of regulations that apply to the use of tin stabiliser compounds. In Europe, the use of tin stabilisers in PVC toys is regulated by the European Union (EU) Toy Directives (88/378/EEC), which establish the permitted levels of materials allowable in PVC toys. The responsibility for enforcement lies with the EU Commissioner for Industrial Affairs. EU Directive 92/59 and the Scientific Committee for Food (SCF) establish migration limits for tin stabilisers in toy and food contact applications based on the tolerable daily intake (TDI) value. The tolerable daily intake represents the chemical dose that is unlikely to cause harm to human health if ingested on a regular (i.e., daily) basis (See Appendix A for Tolerable Daily Intake values for some of the common organotins associated with stabilisers). In the United States, octyl-, methyl- and dodecyltin compounds satisfy the requirements of the Food and Drug Administration (FDA) for use as stabilisers for certain indirect food contact applications (21 CFR 178.2650) such as packaging. Several European countries have also approved them for food packaging applications (Directive 90/128/EEC). Europe, the US, and Canada allow the use of tin stabiliser compounds in potable water pipes.

Drinking Water

Tin stabilisers are sanctioned in the U.S. and in several European countries for use in potable water pipes. In the U.S., butyltin and methyltin stabilisers are used, while in Europe octyltin and methyltin stabilisers are used. Tin stabilisers are particularly suitable for water pipes because authorities have concluded that significant leaching into the water does not occur after the initial surface layer of stabiliser has been washed off by the initial flush of water through the pipes.[4,5]

NSF International has been developing standards for the testing and certification of plastic plumbing components since 1965. The US EPA has recognized NSF Standard 61 as the criteria for determining health-effects acceptability of materials or products that convey potable water. NSF has concluded that the evaluation of PVC/CPVC pipe based upon the NSF standard is protective of human health and the presence of monoorganotin and diorganotin in potable water due to their use as heat stabilizers does not present a human health risk.[6]

Although the extraction of tin stabiliser compounds from new PVC pipe has been reported in the literature[7,8], this does not appear to raise any significant environmental or human health issues. Tin stabilisers can occur in new pipes because residual organotins are left on the pipe wall after manufacture. After the residual organotin is rinsed away, diffusion of organotin into the water declines dramatically and has been reported to be negligible after approximately 12 hours.[9] The fact that organotins may occur at extremely low levels does not suggest any potential risk from drinking water.

Several studies by Health Canada have been published documenting the measured concentrations of butyltins to which people could be exposed through their drinking water. In both PVC and CPVC pipe, levels of monobutyltin and dibutyltin in potable water have been noted in the parts per trillion (ppt) range after only a few liters of water have passed through the pipe, washing away any butyltin compounds from the surface of the pipe. One study[10] involved 45 municipalities and found butyltins detected at only six of these with a maximum concentration of 44 ppt. The values at most municipalities were below detectable levels (i.e., < 0.5 ppt). In another study[11], organotins were measured in the distribution (tap) water of five of these municipalities with butyltins being positively detected at only 1 of 22 homes sampled. The level of butyltins in water from freshly purchased CPVC pipe were found to drop very rapidly after a small amount of water washed the surface.[12] By the time a few liters of water had passed through the pipe, the level of butyltin in the water had already fallen into the parts per trillion range. In a more comprehensive study[13], Canadian drinking water distributed through recently installed PVC pipe was monitored and only a few positive detections of butyltins (dibutyltin maximum of 53 ppt, monobutyltin maximum of 28.5 ppt) were found although in most cases the concentrations were not detectable. The trace levels of butyltins measured (< 0.5 ppt to 53 ppt) are well within the range deemed safe for drinking water.

Using the predicted tolerable daily intake (pTDI) value for dibutyltin of 5 µg/kg (as tin)[14], an adult who weighs 60 kg and who consumes two liters of drinking water per day could safely ingest water with a butyltin concentration of 150 µg/L (as tin). This "safe" concentration is over 2,000 times greater than the highest dibutyltin concentration that was measured (53 ng/liter as tin) in drinking water from PVC piping. Furthermore, actual concentrations over the long-term (used pipes) can be expected to be lower, due to rinsing away of the initial organotins on the pipe surface. Thus, although organotins have been detected in water at extremely low levels, they are well below levels of concern for any effects on health.

Continued Product Improvement

Through continued product development, stabiliser products have become more efficient over the years, allowing for improved overall performance of the PVC (such as color of the finished article, outdoor weatherability and durability, and extrusion output rates) and use at lower concentrations in PVC. Over many decades, stabiliser producers have been able to meet customers' high expectations, while decreasing the total organotin used per kilogram of PVC.[15]

The first generation tin mercaptide stabilisers were dialkytin long chain mercaptans having an average tin content of 18%. Used at a use level of 2-3%, the tin content of the PVC was in the range of 3,000 to 5,400 ppm. Second generation products were mixed mono/di alkyltin long chain mercaptans. Although the tin content increased to about 22%, these products were often used in diluted form to aid in their handling while reducing losses. These second generation stabilisers were more efficient and only had to be used at a use level of about 1-2%, with the resulting tin content of the PVC decreased to 2,200 to 4,400 ppm. Recently, third generation stabilisers have been developed which are all monoalkytin, short chain, and/or functionalized mercaptans or sulfides. These increased efficiency stabilisers, available in diluted versions, contain around 24% tin, are used at 0.25 to 0.75% levels, and result in tin content of the PVC of about 900 to 1,800 ppm. There are even products available only in diluted form which have an increased tin content, are used at 0.04 to 0.08% levels, and result in PVC with only 172 to 344 ppm tin content.[16]

Environment

Lifecycle of PVC

The European Commission, in 1999, launched a comprehensive study program to assess the impact of PVC wastes on the environment and to be used to develop proposals to address issues that might arise in this regard. The EC recognized a need for an integrated approach to assess the whole life cycle of PVC in order to develop the necessary measures to address protection of human health and the environment. Five studies were commissioned dealing with landfill, recycling (chemical and mechanical), incineration, and economic evaluation of PVC waste management. A "Green Paper" was then drafted[17] in July, 2000 identifying and analyzing a number of issues regarding PVC and its impact on the environment; no issues or unresolved questions on tin stabilisers were raised in this paper. The two main issues brought up in the paper were the use of additives such as phthalate softeners and heavy metal stabilisers (lead and cadmium were singled out), and the waste management of PVC.

Industry challenged the Green Paper as an unsatisfactory review of the PVC lifecycle. They believe proposals in the paper go against the wealth of information collected by the Commission including the horizontal initiative studies themselves whose evident outcomes show that PVC-specific measures are unnecessary. Despite this, and in an effort of industry-wide product stewardship, the European PVC industry [made up of resin manufacturers, additive producers, and converters, represented by their European Associations: The European Council of Vinyl Manufacturers (ECVM), The European Council for Plasticisers and Intermediates (ECPI), The European Stabilisers Producers Association (ESPA), and the European Plastics Converters (EuPC)] signed a voluntary commitment on the sustainable development of PVC[18], which addresses the reduction of the use of cadmium stabilisers, conducting risk assessments on lead-based stabilisers, the mechanical recycling of certain post consumer wastes, and the development of further recycling technologies.

Landfill studies

The decomposition of PVC continues to be investigated to determine whether groundwater could potentially be affected from plastic deposited in landfills. Because of the leaching and biodegradation processes which take place there, landfills can present a "worst case" for environmental studies on PVC behavior. The findings have indicated that, even under aggressive soil conditions, PVC leaching results in a negligible amount of organotins in landfill leachate.[19,20] A three-year study[21] recently completed at universities in Germany and Sweden, in consultation with the Swedish EPA, concluded that PVC is resistant to breakdown under landfill conditions. Any release of tin stabilisers from PVC is subject to biological or abiotic dealkylation processes such that the mono and dialkyltin species from the tin stabilisers are successively transformed to inorganic tin. Naturally occurring methylation of tin by bacteria can also be a confounding factor[22] affecting background levels and analytical results obtained.

Landfills, under current technical regulations, are considered an appropriate disposal option for PVC. When the predicted no-effect concentrations (PNEC), derived from aquatic toxicity studies, are compared to the predicted environmental concentrations (PEC) of the various PVC additives, including tin stabilisers, indications are that they do not contribute significantly to any toxicity of leachate from the landfill.[23] Although negligible loss of stabilisers may occur, organotin in PVC in landfill sites does not appear to constitute a risk to the environment.

Conclusion

Tin chemicals have long been used in PVC as heat stabilisers and have become important, valued products for PVC processing. The processes in which they are used are designed to protect employees from exposure through the use of automation and personal protective equipment, and these processes are intended to maintain operating conditions within the exposure limit values for safety at the workplace.

The alkyltins used as stabilisers are bound into the PVC polymer matrix they are stabilising, and remain bound within the matrix – if they did not, they would not be useful as stabilisers.

Tin stabilisers can be used safely in the PVC industry when used in accordance with the Material Safety Data Sheet and in conjunction with adequate engineering controls and/or personal protective equipment.

For those applications where tin stabilisers have been found suitable in the past, they are still suitable and can continue to be used safely.

APPENDIX A

Tolerable Daily Intake (TDI) Values Of Common Organotins

Chemical	TDI[1]	Unit	Source / comment
Mono-methyltin tris (IOMA)	3	μg/kg BW/day	Commission of the European Communities; CEC - Synoptic Document N.7 - Draft of Provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs.
Dimethyltin S'-bis (IOMA)	3	μg/kg BW/day	Commission of the European Communities; CEC - Synoptic Document N.7 - Draft of Provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs.
Mono-n-octyltin-tris (2-EHMA)	20	μg/kg BW/day	Commission of the European Communities; CEC - Synoptic Document N.7 - Draft of Provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs.
Di-n-octyltin-bis (2-EHMA)	0.6	μg/kg BW/day	Commission of the European Communities (CEC) - Scientific Committee for Food (SCF). TDI is the same for all di-n-octyltin species[2]
Dibutyltin	5	μg/kg BW/day	Summer, K.H., K. Dominik, and H. Greim. 1996. Ecological and toxicological aspects of mono- and disubstituted methyl-, butyl-, octyl-, and dodecyltin compounds.
Di-n-octyltin	0.6	μg/kg BW/day	Commission of the European Communities (CEC) - Scientific Committee for Food (SCF), 1994. TDI is the same for all di-n-octyltin species[2]
Mono-n-octyltin tris(alkyl(C10-C16)MA)	20	μg/kg BW/day	Commission of the European Communities; CEC - Synoptic Document N.7 - Draft of Provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs.
Mono-n-octyltin tris(IOMA)	20	μg/kg BW/day	Commission of the European Communities; CEC - Synoptic Document N.7 - Draft of Provisional List of Monomers and Additives Used in the Manufacture of Plastics and Coatings Intended to Come into Contact with Foodstuffs.

[1] Tolerable daily intake

[2]-listed di-n-octyltin species in CEC - Synoptic Document N.7 are:-bis-(IOMA), -1,4-butanediol-bis-(MA), -dilaurate, -dimaleate, -ethyleneglycol-bis-(MA), -(MA), -benzoate-2-ethylhexyl-MA, -bis(n-alkyl(C10-C16)MA), bis-(7-ethylhexyl maleate), -bis-(2-ethylhexyl-MA), -bis-(ethyl-maleate), -bis-(isooctyl-maleate).

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