



# Rigid PVC Stabilization: Comparing Tin and Ca/Zn Stabilizers

Paul Lavallee  
Arkema Technical Service

PVC Andean Forum  
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## Key Question:

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- Little publicly available toxicity data on Ca/Zn Stabilizers.
- Methyl and Butyl Tins have been well-tested - - properties are well-known.

So, which performs most effectively in rigid PVC?



# Background: Heat Stabilizers

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## Mixed Metal Stabilizers

- Typically a powder, primarily Ca/Zn based.
- Complex mixtures of metal-fatty acids (stearates), carboxylates, salts, soaps, bases, and diluents.
- Earlier products, such as Ba/Cd, Cd/Zn, and Ba/Zn, are no longer widely used, primarily due to environmental reasons.

## Tin-based Stabilizers

- Typically liquid form.
- Based on alkyl tins compound. Alkyl groups can be methyl, butyl, or octyl
- Primarily mono-alkyl or di-alkyl (for example, mono-butyl-tin or di-butyl-tin).
- Tin stabilizer are not based on Tri-butyl-tin (more on that later)
- Other ingredients are added for stability, color benefits.

# Topics to be Covered

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- Elemental Zn, Sn Data
- Sn Data
  - Data Tri-Butyl Tins vs. Mono/Di Butyl Tins
  - Behavior of Organotins in PVC Pipe
  - Recent Testing & Employee Exposure
- Third Party Comparisons
- Stabilizer Comparison

# Ca/Zn Data

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- Elemental Zinc, Tin – Water limits

		<u>Zn</u>	<u>Sn</u>
● Mexico	River Water Limit	10 mg/L <sup>1</sup>	Not Listed <sup>1</sup>
● USA	Drinking Water Guidelines	5.0 mg/L <sup>2</sup>	Not Listed <sup>2</sup>
	Freshwater Discharge G/L	0.120 mg/L <sup>3</sup>	Not Listed <sup>3</sup>

- ZnStearate, Respirable

- USA Permissible Exposure Limit: 5mg/m<sup>3</sup><sup>4, 5</sup>
- Inhalation concern (ZnSt in talc) – issues with infants inhalation causing respiratory issues<sup>5</sup>
- ZnSt can form dust-air explosive mixtures<sup>6</sup>



# Sn Data: Tri-Butyl Tins vs. Mono/Di Butyl Tins

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## Tri-butyl Tins

- Tri-butyl tins historically used as a biocides
- Banned for use in Marine Anti-Foulant (MAF) paint (Sept., 2008)<sup>1</sup>
- No longer used in Europe, Americas, Japan in MAF applications (customer de-selected from 2003)
- Registered for wood preservative and cooling tower use

## Mono/Di Alkyl Tins

- Exhibit no biocidal properties
- Naturally breakdown into tin chlorides
- If incinerated, breakdown into tin oxides

**Mono/Di Alkyl Tins should not be grouped with Tri-butyl Tins!!**

“Tin Stabilizers are safe, for both processors and consumers.”

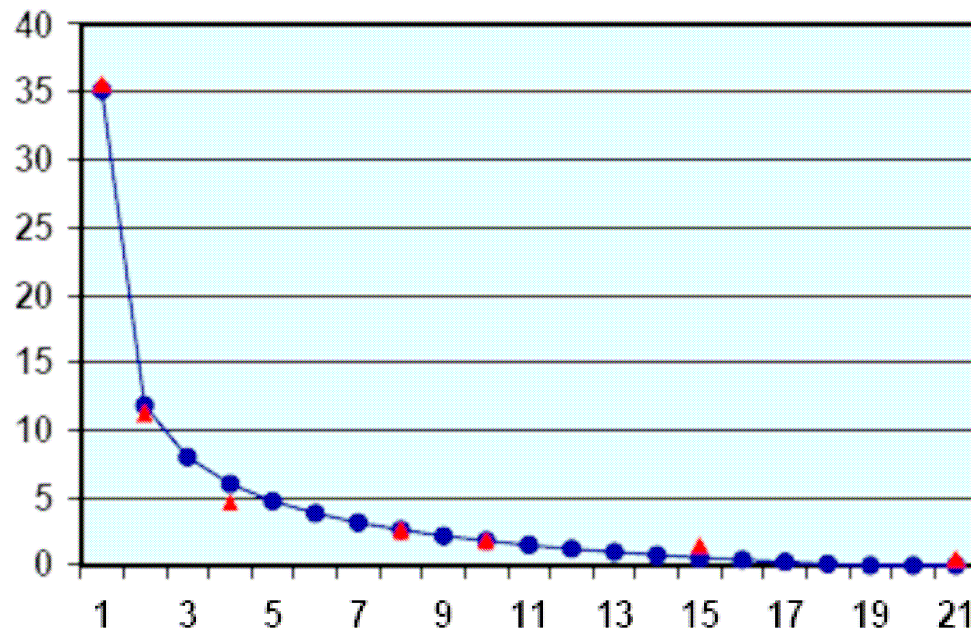
- FLUGS Institute, Nurnburg, Germany



# Behavior of Organotins in PVC Pipe<sup>1</sup>

- NSF International's Leaching Test

- 60 new PVC pipe samples: NSF 61's 3-week Water Extraction Testing
- Chart:  $\mu\text{g Sn} / \text{L water}$  plotted vs. Days



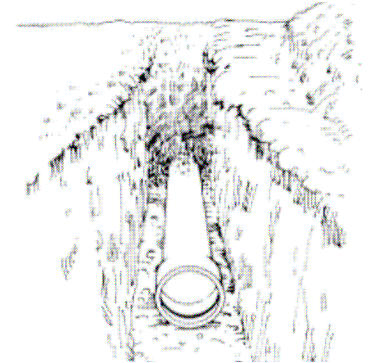
- Total extraction:  $< 100 \mu\text{g Sn} / \text{L}$

At 5  $\mu\text{g/L}$ , it would take 200,000 L to get 1 gram of Sn



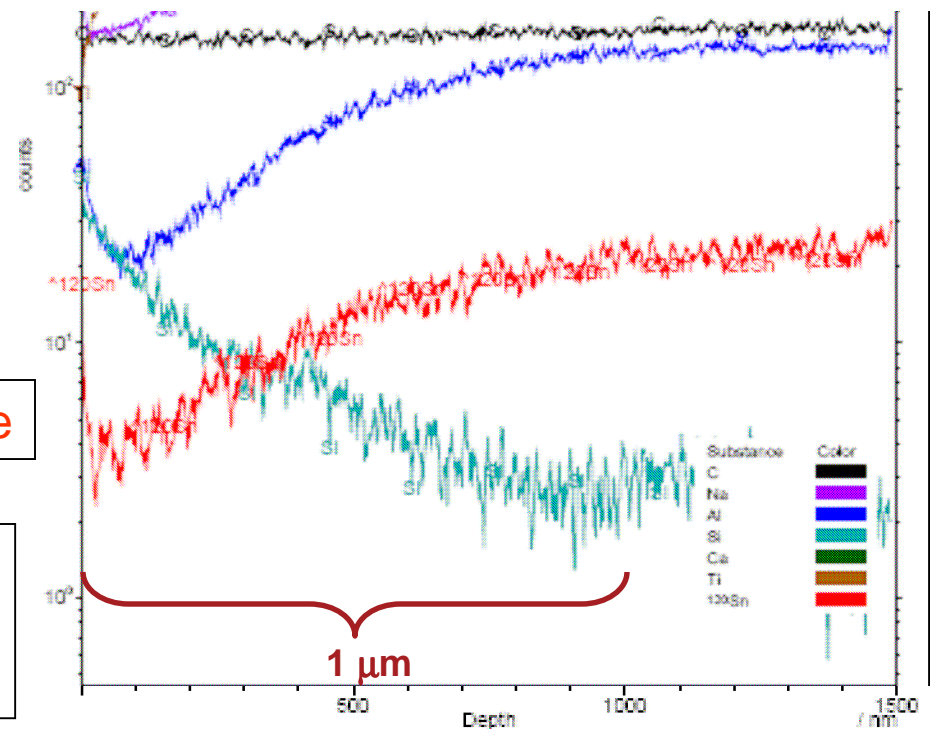
# Behavior of Organotins in PVC Pipe<sup>2</sup>

- PVC Pipe produced in 1964, in underground service for 22 years, analyzed in 2003
- SIMS measurement to measure tin level (red)
  - Outside pipe surface: No decrease in Sn Content => no Sn in Soil!
  - Inside pipe surface (pictured): tin content decrease is very small, limited to 0.000001 M from surface.



⇒ Very little tin lost over 22 years of service

Remaining tin stabilizer is still active:  
ground-up pipe had a normal BB Fusion  
curve, 40 years after initial extrusion!





# Recent Testing - USA

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## Consent Order

- 1999: U.S. EPA issued consent order restricting use of T340 (mono/di butyltin) Stabilizer
- Testing shows T340 stabilizer chemistry is NOT Persistent, Bio-accumulative, and Toxic (PBT).
  - EPA found T340 to be biodegradable
- 2007: Consent Order has been lifted!

## HPV

- 2000: US Environmental Protection Agency's High Production Volume (U.S. EPA HPV) initiative begun by manufacturers to generate data. Arkema co-sponsored testing.

# Employee Exposure to Organotin Stabilizers

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*Tin Stabilizer Association, in conjunction with Vinyl Council of Canada, sponsored testing....*

## Study Goal:

- Provide an overview of worker exposure to organotin compounds at PVC processing facilities
- Verify exposure below ACGIH Threshold Limit Value (TLV), without considering respiratory protection

## Test Results:

- No average exposure levels for individual tasks exceeded TLV
  - One sample of 102 exceeded TLV; employee wearing appropriate respiratory protection
- Manual operations may have a greater potential for exposure

# Recent Testing - Australia

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- In 2003, Australian Dept. of the Environment and Water Resources published “End-of-life Environmental Issues with PVC in Australia”

“Even if leached from PVC into the environment in the case of say, landfills, organotin stabilizers are not persistent in the environment on account of microbial activity. All organotin stabilizers eventually degrade into inorganic tins....the potential of mono and dialkyl tin compounds for ecotoxic effects is **low**.”



# Third-Party Comparisons

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- PVC Resin Manufacturer:
  - “The stabilization power of **Calcium-Zinc** in PVC is weak and, therefore, scrap rework capability is poor.
  - **Tin Mercaptides** – “give good heat, light, and color stability, and promote fusion and reduce melt viscosity.”
    - [www.oxyvinyls.com/LITERATURE/ovtr5.pdf](http://www.oxyvinyls.com/LITERATURE/ovtr5.pdf)
- Rigid PVC Extrusion Handbook
  - “**Calcium Zinc** stabilization is still marginal at best, providing minimal scrap rework capability.”
  - “**Tin Mercaptides** offer a unique set of properties for rigid PVC processing” classical vinyl stabilization and antioxidant functions combined with fusion promotion and melt viscosity reduction.”
    - [www.plastics.com/articlelive/articles/10/3/](http://www.plastics.com/articlelive/articles/10/3/)
- Compare amount of free metal content in Sn stabilizer to Ca/Zn stabilizer...

# Stabilizer Comparison: Tin, Ca/Zn, OBS

	Organotin based	Ca-Zn based	Organic based
Processing window	+	-	-
Recycling (rework)	+	-	-
Severe applications (big diameters & fittings)	+	-	-
NSF/PPI Approval	Yes	No	No

## Key Question:

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# Footnotes

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- 1 - Monthly Average permissible limit for public urban use & protection of aquatic life (NOM-001-ECOL-1996)
- 2 – US EPA. <http://www.epa.gov/safewater/contaminants/index.html>, List of Secondary Drinking Water Regulations
- 3 – National Recommended Water Quality Criteria, US EPA, 4303T, 2006. <http://www.epa.gov/waterscience/criteria/wqcriteria.html>. See item #13.
- 4- OSHA PEL (6/30/93, 29CFR 1910.1000)
- 5- Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5<sup>th</sup> Ed. Baltimore: Williams and Wilkins, 1984, pr. II-143.
- 6-ZnStearate MSDS: [www.jtbaker.com/msds/englishhtml/z4265/htm](http://www.jtbaker.com/msds/englishhtml/z4265/htm), AND International Programme on Chemical Safety Bulletin: Zinc Stearate, #0987