Highlights on PVC Stabilization for Pipes – Comparison and Trends

13 – 14 April 2015

Dr. Alexander Schmid
Agenda

- Overview PVC pipes, stabilizers and markets
- Worldwide trends for PVC pipes
- Comparison of Pb, Ca- and Sn-based stabilizer systems for PVC pipes
  - Performance
  - Properties
- Summary
Growth has come in the Developing Markets

Global PVC Consumption 2013 Pipes (Ktons)

- **Europe**: 1,500 Ktons (G.R. 2.9%)
  - West Eu: 1,200 Ktons (G.R. 8%)
  - Central Eu: 300 Ktons (G.R. 3.7%)
- **North America**: 2,300 Ktons (G.R. 2.9%)
- **South America**: 1,200 Ktons (G.R. 3.3%)
- **Middle East/Africa**: 1,200 Ktons (G.R. 6%)
- **India**: 1,700 Ktons (G.R. 7%)
- **Asia**: 1,200 Ktons (G.R. 5%)
- **China**: 3,800 Ktons (G.R. 5%)

**Total**: 12,900 Ktons

Source: Baerlocher Estimate/approximations
Increasing demand for stabilizers for PVC pipes

Global Stabilizer Consumption 2013
Pipes (Tons)

- **North America**: 67,900 Tons, G.R. 2.9%
- **South America**: 28,600 Tons, G.R. 3.3%
- **Europe**: 41,700 Tons
  - Western Eu: 6,700 Tons, G.R. 1%
  - Central Eu: 15,000 Tons, G.R. 3.7%
- **Middle East/Africa**: 33,600 Tons, G.R. 6%
- **Asia**: 45,200 Tons
  - India: 42,500 Tons, G.R. 7%
- **China**: 112,500 Tons, G.R. 5%

Total: 361,800 Tons

Source: Baerlocher Estimate/approximations
Pb stabilisation dominates for PVC pipe systems

Source: Baerlocher Estimate/approximations
Ca-based systems are now the standard in EU

Source: BAERLOCHER ESTIMATE
Tin stabilizers still dominate in North America

- Tin stabilizers
  - Best price/performance ratio for white colored pipes
- FDA regulates material for food contact application
  - NSF/PPI, UL, others: standard and certification for pipes
- Drinking water pipes: Max 1 part of Sn per 100 parts of resin
- California is the leader in material restriction
- Rarely tests with Ca-based pipe stabilizer systems
Pb-based systems dominating in Uruguay, Argentina, Paraguay, Bolivia → Clear trend to Ca/Zn

Columbia, Venezuela, Ecuador using Sn

Peru is using Pb, Ca/Zn as well as Sn depending on the company, but trend goes to Ca/Zn

Brazil: Ca/Zn-based systems already dominate
Pb dominates in Asia (but with some trends to Ca-based)

- Focus on Pb (small amounts on Sn, Ca-based, no regulation for Pb-free)
- China → Potable water pipe (Pb-free) (Goal: Pb-free for U-PVC)
- Korea/Australia/New Zealand → U-PVC pipe (Pb-free)
- Trend setters: China / Australia / New Zealand
- Main trend to Ca-based
Pb dominates in India
(limited volumes in Ca-based)

- Generally Pb-based, except for plumbing pipes small trend to Ca/Zn
- No regulations for drinking water application
  → Industry prefers Pb (cost-effective)
- Ca/Zn used by selected pipe producers but not promoted due to relative high costs
In general Pb stabilizers are used in M. East/Africa

- Pb-based stabilizer systems dominating for pipes
- Drinking water pipe has to be free of Pb, As, Cd, Cr (Ministry of Health, Iran)
- Sn and Ca-based systems on small usage level
- Slight trend towards Ca-based
- Ca-based systems present in Northern countries of Africa and South-Africa
Pb-based stabilizers ...

... provide:

→ Good initial color due to pigmenting properties of inorganic lead compounds

→ Good long-term stability

→ Broad processing window due to long experience of operating people

→ Metal content (Pb): 25 - 35%
Influence of dosage vs stability

linear correlation for Pb-based systems

<table>
<thead>
<tr>
<th>Dosage</th>
<th>HCL [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,8 phr</td>
<td>17</td>
</tr>
<tr>
<td>2,3 phr</td>
<td>23</td>
</tr>
<tr>
<td>2,8 phr</td>
<td>27</td>
</tr>
</tbody>
</table>
→ Linear correlation between lead content and thermostability over a wide range
→ Thermostability can simply be boosted by addition of lead sulfate
→ Increased lubrication by increased stabilizer dosage
→ Variation of dosage allows many adjustments
Ca-based core stabilizers

... provide:

→ Initial color sufficient for brown / dark colored applications

→ Thermostability sufficient for standard pipe extrusion or injection moulding processes

→ Co-Stabilizers, either organic or inorganic, are applied for purposes such as better initial color, improved thermostability, light stability, ...

→ Metal content (Ca, Zn): 1 - 2,5%
# Influence of co-stabilisers

<table>
<thead>
<tr>
<th>Formulation</th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Filler</td>
<td>7 phr</td>
<td>7 phr</td>
<td>7 phr</td>
</tr>
<tr>
<td>Ca-based</td>
<td>2 phr</td>
<td>2 phr</td>
<td>2 phr</td>
</tr>
<tr>
<td>Core Stabilizer</td>
<td>2 phr</td>
<td>2 phr</td>
<td>2 phr</td>
</tr>
<tr>
<td>Zn-soap</td>
<td>-----</td>
<td>0.2 phr</td>
<td>-----</td>
</tr>
<tr>
<td>Organic Co-Stabilizer</td>
<td></td>
<td>0.2 phr</td>
<td></td>
</tr>
<tr>
<td>Congo-Red-Test</td>
<td>20</td>
<td>20</td>
<td>20 min</td>
</tr>
</tbody>
</table>

Mathis-Oven-Test
200°C, 5 min

![Test samples](image)
Influence of dosage vs stability

Ca-organic core stabilizer

<table>
<thead>
<tr>
<th>Dosage</th>
<th>HCl [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,8 phr</td>
<td>11</td>
</tr>
<tr>
<td>2,3 phr</td>
<td>14</td>
</tr>
<tr>
<td>2,8 phr</td>
<td>16</td>
</tr>
</tbody>
</table>
Influence of Dosage vs Stability

Ca-organic core stabilizer + co-stabilizer

Dosage | HCl [min]
--- | ---
1.8 phr | 11
2.3 phr | 16
2.8 phr | 16
## Influence of dosage vs stability

### Basic Ca/Zn stabilizer + co-stabilizer

<table>
<thead>
<tr>
<th>Dosage (phr)</th>
<th>HCl [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>13</td>
</tr>
<tr>
<td>2.8</td>
<td>12</td>
</tr>
</tbody>
</table>
→ Due to use of different Co-Stabilizers more complex systems
→ Increase of stabilizer dosage doesn’t always give linear increase of thermostability
→ Often improvement of color goes parallel with a decrease in stability
→ Variation of dosage is more critical
Sn-based systems ...  

... provide:

→ Formulation concept: Single Components
  → Sn-based component + Calcium Stearate
  → + Lubricants (oxidized waxes, paraffins)

→ Relative fast fusion behavior of Sn-based formulations compared to Ca-based formulations
  → Adaption of rheology/stability

→ Metal content (Sn): 1 - 5% based on overall composition
  (~17% based on Sn-stabilizer)
Influence of dosage vs stability

<table>
<thead>
<tr>
<th>Dosage</th>
<th>Sn-based stabilizer</th>
<th>HCl [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,1 phr</td>
<td><img src="image1" alt="Image of stability for 2.1 phr" /></td>
<td>8</td>
</tr>
<tr>
<td>2,3 phr</td>
<td><img src="image2" alt="Image of stability for 2.3 phr" /></td>
<td>10</td>
</tr>
<tr>
<td>2,7 phr</td>
<td><img src="image3" alt="Image of stability for 2.7 phr" /></td>
<td>17</td>
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Sn-based stabilizers, properties

→ Sn-based stabilisers are typically applied in liquid form
→ Good initial color
→ Good long-term stability
Comparison of Ca/Pb/Sn-based pipe stabilisers

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<tr>
<th>Stabilizer system</th>
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<th>HCl [min]</th>
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<tbody>
<tr>
<td>Pb</td>
<td>2,3</td>
<td>23</td>
</tr>
<tr>
<td>Ca-org (dark colour)</td>
<td>2,3</td>
<td>20</td>
</tr>
<tr>
<td>Ca-org (light colour)</td>
<td>2,4</td>
<td>16</td>
</tr>
<tr>
<td>Ca/Zn</td>
<td>2,3</td>
<td>13</td>
</tr>
<tr>
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<td>2,3</td>
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<table>
<thead>
<tr>
<th>Stabilizer system</th>
<th>[phr]</th>
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<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
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<td>Pb</td>
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Europe is focused on Ca-based stabilisers

- Pb-based stabilizers still dominating worldwide
- North-America focused on Sn-based stabilizers
- Ca-based stabilizers dominating in Europe and South-America

- Critical driver: Cost
- Solutions to reduce cost:
  - High filler level
  - Multi-layer pipe
  - More effective use of stabiliser one-packs
Baerlocher provides tailor-made solutions for your pipe application

- static/dynamic thermostability
- rheology
- initial color
- color hold

... from dark ...

... to light colored applications ...

Baerlocher