Managing the Change –
From Lead-based to Calcium-based
Stabilisation in PVC Cables & Wires,
Pipes & Fittings and Rigid Profiles

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Technical Product Manager
PVC Additives for Window and Technical Profiles
Overview

- PVC stabilisation – the change from Pb-based to Ca-based
- PVC Cables & Wires – correct recipe design for maximum performance
- PVC Pipes & Fittings – trend towards highly filled pipe formulations
- PVC Profiles – outdoor weathering performance is key
PVC stabilisers: Where was Europe 10 years ago?

- Lead (Pb) stabilisers dominated the European PVC stabiliser market in the early 2000s
- Extruded rigid PVC was nearly completely Pb-stabilised
- Injection moulding and foam profile extrusion used Sn stabilisers
- First attempts to introduce Ca-based stabilisers for plasticised PVC extrusion (e.g. cables, tubes) had been made
What happened in the meantime?

- several initiatives paved the way to Lead-free:
  - whole PVC industry has committed itself to lower the use of Pb stabilisers in the “Vinyl 2010” initiative
  - TEPPFA discussed a voluntary switch away from lead stabilisers in pipes until end of 2010
  - automotive industry lowered the limits for heavy metals in cables
- REACH legislation was expected to come into force, details not clear in the beginning
  - Lead-containing chemicals are classified as hazardous substances
A change has taken place in Europe

- increasing Pb prices rather than regulatory pressure were accelerating the switch

- current usage of Ca-based PVC stabilisers:
  - Cable & Wire: 100%
  - Profile: 75%
  - Pipe & Fitting: 66%

Source: ESPA
**Chemical background: Thermal Degradation of PVC**

- hydrogen chloride (HCl) is split off when PVC is heated above 150°C
- the formed HCl acts as a catalyst and accelerates the degradation of the PVC (zipping mechanism)
- the formation of **conjugated C=C double bonds** leads to yellow discolouration and crosslinking of the PVC
Two ways of action for PVC heat stabilisers

- certain chemical substances are able to prevent the thermal degradation of PVC by …
  - preventing the formation of hydrogen chloride (primary stabilisers)
  - neutralising the hydrogen chloride formed (secondary stabilisers)

- these substances are called **heat stabilisers**

- Baerlocher provides heat stabilisers as part of tailor-made one-packs for various PVC applications
Heat stabilisers are part of tailor-made one-packs

- one-packs for the production of PVC articles combine stabilisers, lubricants and more:

- Pigment Toners
- Processing Aid
- External Lubricants
- Internal Lubricants
- Co-Stabilisers
- Metal Soaps
- Acid Scavengers
Pb-based stabiliser one-packs are complex mixtures

- Pb one-packs contain inorganic acid scavengers, such as tri-basic Lead sulfate (TBLS) or di-basic Lead phosphite (DBLP)
- additional Lead stearate acts as heat stabiliser and lubricant
- Lead metal content ca. 25 - 45%
- linear correlation between Lead content and thermostability
- increased lubrication by increased stabiliser dosage

→ Variation of dosage allows many adjustments!
High performance of Pb-based stabilisers

- good initial colour due to pigmenting properties of inorganic Lead compounds
- excellent long-term thermostability
- broad processing window
- high weathering performance when formulated correctly
Composition of Calcium-based stabiliser systems

Calcium-based stabilisers
… is a general term for all stabilisers without Lead, Barium, Cadmium and Tin

- current systems are based…
  - on Calcium and Zinc metal soaps
  - on Layered Double Hydroxides
  - on Zeolite

- Calcium-based stabiliser systems comprise
  - Calcium/Zinc stabilisers
  - Calcium-Organic stabilisers
Ca-based systems are fine-tuned with co-stabilisers

- Calcium compounds provide thermostability (acid scavengers)

- Zinc compounds or organic co-stabilisers provide good early colour (primary stabilisers) – they can be used alternatively or in combination
  
  → Calcium/Zinc or Calcium-Organic systems

- co-stabilisers also help with colour hold and weatherability

- metal content (Ca, Zn): 1 - 5 % each
  
  → Complex interaction of components – variation of dosage allows only minor adjustments!
Stabilisation synergism of Calcium and Zinc soaps

\[ \text{PVC} + \text{Zn stearate} \rightarrow \text{replacement of labile chlorine atoms} \]
Stabilisation synergism ... continued

ZnCl₂ → replacement of labile chlorine atoms

ZnCl₂ + Ca(OCO-C_{17}H_{35})₂ → recovery of Zn stearate with Ca stearate
Cable stabilisation is switched to Ca/Zn systems

- modern Ca-based cable stabilisers provide comparable properties to conventional Lead stabilisers regarding ...
  - dosage
  - thermostability
  - mechanical properties
  - electrical properties
Adjustments are necessary with Ca/Zn stabilisation

it is important to know about general properties and necessary changes when switching to Ca/Zn cable stabilisation:

- underdosing or overdosing of Ca/Zn stabiliser will reduce its performance
- influence on Ca/Zn stabiliser performance by additional components: Ca stearate, CPE, CPW, stearic acid
- heavy metal pigments have to be replaced completely to be “heavy-metal-free”
- shorter storage stability of Ca/Zn stabiliser and cable compound
Choosing the right product is the key to success

<table>
<thead>
<tr>
<th>Ca/Zn stabilisers</th>
<th>Cable Operating Temperature [°C]</th>
<th>Dosage [phr]</th>
<th>Application Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP MC 91535 KA</td>
<td>60 - 80</td>
<td>3 - 6</td>
<td>dark pigmented cables</td>
</tr>
<tr>
<td>BP MC 90224 KA</td>
<td>80 - 90</td>
<td>4 - 8</td>
<td>dark pigmented cables</td>
</tr>
<tr>
<td>BP MC 90827 KA</td>
<td>80 - 90</td>
<td>4 - 8</td>
<td>light pigmented cables</td>
</tr>
<tr>
<td>BP MC 8656 KA-ST</td>
<td>90 - 105</td>
<td>4 - 8</td>
<td>light pigmented cables</td>
</tr>
<tr>
<td>BP MC 225 KA/1</td>
<td>80 - 90</td>
<td>3 - 6</td>
<td>white cables</td>
</tr>
</tbody>
</table>

- the exact stabiliser dosage is depending on the overall cable compound formulation
Pipe stabilisation still dominated by Lead systems

- General focus for pipes on Lead (small amounts on Sn, Ca-based) – no regulation to push for Lead-free
- Main trend to Ca-based in China / Australia / New Zealand
  - China → potable water pipe (Pb-free)
  - Korea / Australia / New Zealand → all U-PVC pipe (Pb-free)
## Formulation guide for Pipe & Fitting applications

<table>
<thead>
<tr>
<th>[phr]</th>
<th>Pressure Pipes</th>
<th>Sewer Pipes</th>
<th>Injection Moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-PVC</td>
<td>100 (k 68)</td>
<td>100 (k 68)</td>
<td>100 (k 57)</td>
</tr>
<tr>
<td>Coated Filler</td>
<td>max. 5</td>
<td>20 - 50</td>
<td>0 - 2</td>
</tr>
<tr>
<td>Ca-based Stabiliser</td>
<td>2.0 - 3.0</td>
<td>2.0 - 3.0</td>
<td>4.0 - 6.0</td>
</tr>
<tr>
<td>Processing Aid</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
</tr>
<tr>
<td>Pigment</td>
<td>as desired</td>
<td>as desired</td>
<td>as desired</td>
</tr>
</tbody>
</table>
Cost is driving development in PVC pipes

- worldwide trend to more cost-efficient production of PVC pipes
- possibilities for cost reduction lie in use of higher filler levels
Increased filler content can reduce costs

Pipe markets with high filler level applications:

- **Europe**
  - e.g. Italy: up to 60 phr

- **ME/A**
  - Middle East: up to 50 phr
  - Africa: up to 30 phr

- **China**
  - up to several hundred phr !?!
Increased filler levels affect PVC processing

- preparation of dryblend
  - flow properties / homogeneity / deposits

- processability
  - bridging / fusion behaviour / abrasion

- final products
  - mechanical properties / colour / surface appearance / costs
Type of filler affects performance

- Effects of finer filler grades
  - ✔️ faster gelation
  - ✔️ better surface appearance
  - ❌ lower maximum loading level

- Effects of coated filler
  - ✔️ improved flow
  - ✔️ lower abrasion

- Effects on mechanical properties
  - Increased stiffness with higher filler loading
  - Stiffness (but not toughness) independent of filler grade
Specific stabilisers allow for increased filler levels

Development of stabiliser systems for highly filled formulations:

- Internal / external lubricants
  (e.g. PE waxes, paraffins, ester waxes)
  → incorporation of filler
  → improved processing
  → required gloss level
- pigmentation is adapted for correct colour
Ca-based stabilisers will dominate in PVC pipes

- Solutions in Ca/Zn and Ca-Organic stabilisation are available for all pipe applications
- Ca/Zn or Ca-Organic stabilisers can be used for dark coloured pipe applications
- For colour demanding applications Ca/Zn stabilisers show a better price/performance ratio
- Cost-effective Ca-based stabiliser systems will facilitate the change
Profile stabilisation still dominated by Lead systems

- General focus for profiles on Lead (small amounts already Ca-based)
- No general regulation to push for Lead-free
  - Korea and Japan will go Lead-free
  - Rumours for China to become Lead-free
- Some Europe-based companies roll out Ca/Zn worldwide
# Formulation guide for PVC Profile applications

<table>
<thead>
<tr>
<th>[phr]</th>
<th>Window profile</th>
<th>Rain gutter</th>
<th>Roller shutter</th>
<th>Cable duct</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-PVC</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Coated Filler</td>
<td>10 - 18</td>
<td>5 - 10</td>
<td>10 - 20</td>
<td>15 - 45</td>
</tr>
<tr>
<td>Ca/Zn Stabiliser</td>
<td>3.5 - 4.0</td>
<td>2.5 - 4.0</td>
<td>2.5 - 4.0</td>
<td>2.5 - 4.0</td>
</tr>
<tr>
<td>Processing Aid</td>
<td>0.5 - 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Impact Modifier</td>
<td>5.0 - 9.0</td>
<td>0 - 5.0</td>
<td>0 - 5.0</td>
<td>0 - 2.0</td>
</tr>
<tr>
<td>Pigment</td>
<td>min. 3.0</td>
<td>as desired</td>
<td>as desired</td>
<td>as desired</td>
</tr>
</tbody>
</table>
Regional climate influences profile formulations

Radiation in W/m² per year

Precipitation in mm per year

Source: IPCC Intergovernmental Panel on Climate Change
Weathering is key for outdoor installed profiles

- proper processing and correct appearance of profiles is fine-tuned with stabiliser adjustments

- weatherability is governed by stabiliser and pigment

- weathering performance needs to match requirements of respective service climate

- Baerlocher is running extensive trials to improve weatherability
  → similar performance of Pb and Ca/Zn systems
White window profiles in natural weathering

<table>
<thead>
<tr>
<th>[phr]</th>
<th>Lead-based Profile</th>
<th>Ca/Zn Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-PVC</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Coated Filler</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Pb-based Stabiliser</td>
<td>5.3</td>
<td>–</td>
</tr>
<tr>
<td>Ca/Zn Stabiliser</td>
<td>–</td>
<td>4.4</td>
</tr>
<tr>
<td>Impact Modifier</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>TiO₂ Pigment</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Pb vs. Ca/Zn: $\Delta L^*$ (Bandol, 45° south-facing)
Pb vs. Ca/Zn: $\Delta a^*$ (Bandol, 45° south-facing)
Pb vs. Ca/Zn: $\Delta b^*$ (Bandol, 45° south-facing)
Pb vs. Ca/Zn: Gloss (Bandol, 45° south-facing)
PVC profiles will be changed to Ca/Zn stabilisation

- Importance of PVC profile extrusion is growing in Asia

- Europe has changed to Ca-based stabilisation, other regions will follow

- technically sound solutions in Ca/Zn for profiles already exist

- critical driver: costs
Baerlocher can be of help

- Baerlocher offers optimised stabiliser/lubricant packs tailor-made for every application
  - desired early colour and colour hold
  - high weathering resistance
  - required thermostability
  - adjusted lubrication

specific one-pack design for each purpose
Various tailor-made Baerlocher products available

- **BAEROPAN SMS 355**
- **BAEROPAN R 91605 FP**
- **BAEROPAN MC 8656 KA-ST**
- **BAEROPAN TX 9502 R**
- **BAEROPAN MC 91684 P**

- tailor-made for all applications (pipe, fitting, profile, cable etc.)
- adapted to the specific processing units and raw materials used
- formulated according to the customer’s requirements regarding the final product