Update on PVC Stabilisers

PVC Network

22-23 February 2012 – Ferrara (Italy)

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European Stabiliser Producers Association

§ Pan-European trade association representing more than 95% of the PVC stabiliser industry across Europe

§ Affiliated to Cefic - the European Chemical Industry Council

§ Member of VinylPlus (www.vinylplus.eu)

§ A unique organisation representing four sub-groups:
  • ECOSA – Calcium organic stabilisers for food contact & medical applications, plus all lead replacement systems
  • ETINSA – Tin stabilisers used primarily in rigid applications including food contact use
  • ELISA – Liquid stabilisers used in a wide range of flexible PVC, calendered sheets, flooring
  • ELSA – Lead stabilisers major use in pipes and profiles
2011 consumption by stabiliser type
Western + Eastern Europe

<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>Tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>66.100</td>
</tr>
<tr>
<td>Ca-based</td>
<td>95.800</td>
</tr>
<tr>
<td>Liquid MM</td>
<td>15.200</td>
</tr>
<tr>
<td>Tin</td>
<td>12.800</td>
</tr>
<tr>
<td>TOTAL</td>
<td>189.900</td>
</tr>
</tbody>
</table>
ESPA 2012: 11 Members
Communication: website

§ New ESPA website launched in July 2011
  – www.stabilisers.eu
  – Accurate information on stabilisers & applications
  – Information on VinylPlus + direct link to www.vinylplus.eu
Communication: activities

§ Active participation in VinylPlus Communication Committee

§ Promotion of VinylPlus via ESPA website/meetings & ESPA members (roll-ups, members website, etc.)

§ ESPA presentations at key PVC conferences / PVC Network meetings
   - PVC Additives: Developments & Trends, Global Vinyl Council, Jakarta, October 2011 – B. Dero
   - The future of tin stabilisers in PVC Applications, 11th International PVC Conference, April 2011 - A. Cavallero
Classification & labelling
**CMR classifications under CLP (GHS)**

<table>
<thead>
<tr>
<th>CMR classification : Comparison with GHS</th>
<th>GHS</th>
<th>Signal Word</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMR (DSD*)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Repro Cat 2</em></td>
<td><em>Repro cat 1.B</em></td>
<td><strong>Danger</strong></td>
</tr>
<tr>
<td><em>Repro Cat 3</em></td>
<td><em>Repro cat 2</em></td>
<td><strong>Warning</strong></td>
</tr>
</tbody>
</table>

*Always specify to which legislation “cat. 2“ refers to avoid confusion*

*DSD = Directive 67/548 EEC  (Dangerous Substances Directive)*
Interplay between CLP and REACH
CMR cat 1-2 and PBT / Substances of Very High Concern (SVHC) under REACH

CMR 1-2 (CLP*)

- **CMR**: substances which are **C**arcinogenic, **M**utagenic, or toxic for **R**eproduction
- CMR classification is split as follows:
  - cat. 1a -1b → qualifier for potential identification as SVHC
  - cat 2

PBT/vPvB

- **PBT**: substances which are **P**ersistent, **B**ioaccumulative and **T**oxic
- **vPvB**: substances which are very **P**ersistent and very **B**ioaccumulative

Inclusion of an SVHC substance in Reach Annex XIV triggers specific processes under REACH (Authorisation/Restriction)

*CLP: Regulation (EC) N° 1272/2008*
Tin Stabilisers
Tin stabilisers: chemistry

Similar structures based on the following combinations of 4 organic groups (R1 to R4) attached to a central tin atom by a C-Sn bond:

- one [two] alkyls (methyl, butyl or octyl) with
- three [two] esters (e.g., a thioglycolate)

→ 3 main families of tin stabilisers:

- **Methyltins**
- **Butyltins**
- **Octyltins**

Each family is split in *mono-alkyl* and *di-alkyl*, with reference to the major constituent (the commercial substances usually contain both in variable proportions)
Mono-methyltins

- Reprotoxic cat. 2 – endorsed by ECHA*

REACH

(√)**

* at the 17th RAC meeting
** on CoRAP list for Evaluation

Di-methyltins

- Reprotoxic cat. 2 - endorsed by ECB***

REACH

√

*** and CLH public consultation initiated this Feb. by France
Mono-butyltins

- No C, M, R classification

Di-butyltins

- Reprotoxic cat. 1b
- Mutagenic cat. 2

Butyltins

REACH

- Restrictions in Reach Annex XVII
- The first restrictions apply 1 January 2012
- Additional restrictions apply 1 January 2015
Tin stabilisers: Classification & REACH

- Mono-octyltin
  - No C, M, R classification
  - Not PBT/vPvB **

- Octyltins
  - Reprotoxic cat.2 *
  - Not PBT/vPvB **

- Di-octyltins
  - REACH (√)

* ETINSA group-classification. The classification of the stabiliser DOT (EHTG)2, registered in 2010 is currently reviewed by ECHA’s Risk Assessment Committee.
** Testing completed in 2009 in accordance to Commission Regulation 465/2008
Tin Stabilisers

Restrictions for use and placing on the market imposed by REACH Annex XVII


( based on the Restrictions on Marketing and Use initially issued in Commission Decision 2009/425/EC)
Use of dibutyl and di-octyltins: flow-sheet through REACH Annex XVII restrictions

The sole purpose of this document is to help Downstream Users to find their way through the COM Decision 2009/425/EC of 28 May 2009. The DU shall refer to the legal text (REACH Annex XVII) before taking any decision.
Several tin stabilisers registered in Tier 1

The Organotin Reach Consortium continues for additional registrations
Occupational exposure limits for tin stabilisers

- The MAK Commission has been reviewing OELs for organic tin compounds since several years.
- OELs for butyltins and dioctyltin compounds have been revised/issued.
- MAK are currently reviewing the toxicological information for dimethylnltins.
- Compounds not specified elsewhere fall under a generic OEL for organic tin compounds.
- ETINSA is in direct contact with MAK to ensure that they have access to the available information.
Tin stabilisers summary

Organotins constitute a group of substances presenting widely different toxicological properties. Organotins does not equate « TBT ».

The Restrictions on Marketing and Use resulting from the risk assessment have been included in REACH Annex XVII, providing Regulatory certainty: the dates by which the use of some organotins in specific applications have to be discontinued are known.

Many stabilisers of the organotins family have already been registered.

With the switch to CLP there is a risk of confusion concerning the CMR classification “cat. 2” → always specify to which legislation it refers (DSD or CLP).

Under CLP the scull and crossbones label has disappeared for many tin stabilisers.
Lead Stabilisers
Lead stabilisers and Reach

Registration

§ Lead stabilisers had to be registered by December 2010, regardless to the volume band of the manufacturer/importer owing to their CMR cat 1 classification.

§ The stabilisers which have a commercial relevance have all been registered.

Restrictions

§ All lead compounds are under scrutiny by MS, Commission, ECHA:
  – Several compounds are listed in Annex XIV or on the candidate list;
  – More compounds are being investigated.

§ Lead monoxide, the raw material to prepare stabilisers, is investigated by ECHA upon a request from the Commission.
ELSA engaged with other stakeholders of the lead compounds supply chain:
- ELOA (European Lead Oxides Manufacturers Association)
- ILA (International Lead Association, Europe)

ELSA met with the Commission to emphasize the following:
- lead oxide is an intermediate in the production of lead stabilisers → out of scope of Authorization;
- there is a Voluntary commitment to phase out lead-based stabilisers by end 2015
- the replacement of lead stabilisers is visible in the audited statistics → no additional restrictions measures appear to be needed.

No question was raised concerning any possible earlier phase-out
Other Stabilisers
Other Stabilisers and Reach

§ **Liquid stabilisers** (for flexible PVC, calendered sheets, flooring)
  – several reformulations over the past years to adapt to the changes of classifications of some components
  – on schedule to complete 2013 registrations

§ **Calcium-organic** based stabilisers (food contact & medical applications, plus all lead replacement systems)
  – No Reach registration issues
Conclusion

§ PVC Stabilisers are present in a PVC compound at a low percentage only but they are crucial ingredients without which PVC cannot be processed.

§ ESPA is contributing in a decisive way to address the challenge of sustainability of PVC through the Voluntary phase out of lead-based stabilisers.

§ ESPA members are constantly devoting important resources to R&D, in order to provide the market with the most sustainable additives, in line with the VinylPlus criteria.

§ ESPA members are continuously adapting the stabilisers to address the new regulatory constraints.

§ This allows ESPA members to continue to supply performant and Reach-compliant solutions to the PVC chain.
Thank you for your attention

For more information on stabilisers:

§ Alain Cavallero, Secretary General – aca@cefic.be

§ Sylvie Famelart, Communication Counsellor – sfa@cefic.be
End
Back-up slides
DIBUTYLTINS

Dibutyltin compounds shall not be used in articles* for supply to the general public after 1 January 2012, with derogations until 1 January 2015 for the following articles:

- soft PVC profiles whether by themselves or coextruded with hard PVC
- fabrics coated with PVC containing DBT compounds as stabilisers when intended for outdoor applications
- outdoor rainwater pipes, gutter and fittings, covering material for roofing and façades

* excluding articles covered under Reg. (EC) 1935/2004 (food contact)
REACH Annex XVII restrictions impacting use of tin stabilisers in articles

**Dioctyltins**

All Dioctyltin applications allowed, except in a short list of articles for supply or use by the general public after 1 January 2012. In particular for stabilisers:

- textile articles intended to come in contact with the skin
- gloves
- footwear intended to come into contact with the skin
- wall and floor coverings*

*wall covering means “wall paper” (E-PVC) and does not include *sidings* (U-PVC).

The EU Industry (ETINSA) already proactively phased out any organotin from the above-mentioned article categories; they were the ones individuated in the Risk Assessment as showing a potential risk.
CMR classifications under CLP

- CMR cat. 1, 2 and 3 (DSD*) are translated in CLP as C, M, R cat. 1a, 1b and 2
- CMR cat. 3 being translated in CLP as cat. 2 → always specify to which legislation “cat. 2” refers to avoid confusion on this important point!
- In CLP the pictogram Skull & cross-bones becomes associated only to acute toxicity (instead of both acute and chronic under DSD)
- In contrast an additional pictogram appears to reflect chronic toxicity: (GHS 08). Hence only this new symbol is associated to C, M and R classifications under CLP

The next slide shows the labels for CMR hazard under the DSD and CLP

*DSD = Directive 67/548 EEC (Dangerous Substances Directive)