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EUROPEAN STABILISER PRODUCERS ASSOCIATION

The Future of Tin Stabilisers in PVC Applications: *Update after Tier 1 Reach Registration*

**11th International PVC conference
12-14 April 2011, Brighton (UK)**

Alain Cavallero ; B. Dero

- ESPA – ETINSA mission and objectives
- Tin Stabilisers: market trends and applications
- Classification of tin Stabilisers and Reach
- Classification & Labelling of tin stabilisers
- Restrictions on the marketing and use of organotins
- Summary

- 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 **Vinyl 2010** (www.vinyl2010.org)
- A unique organisation representing four sub-groups:
 - **ELSA (~97%)** – **Lead** stabilisers major use in pipe and profiles
 - **ECOSA (~90%)** – **Calcium organic** stabilisers for food contact & medical applications, plus all lead replacement systems
 - **ETINSA (~100%)** – **Tin** stabilisers used primarily in rigid applications including food contact use
 - **ELISA (~95%)** – **Liquid** stabilisers used in a wide range of flexible PVC, calendered sheets, flooring

- Promote the use of PVC stabilisers
- Provide information to users, legislators and other interested parties on safety, health and environmental issues related to PVC stabilisers
- Work with industry partners, associations and other stakeholders to support the safety and sustainability of stabilisers and PVC
- Carry out research relevant to safety and sustainability
- To be an active partner in Vinyl 2010 (www.vinyl2010.org)

ESPA - *sub group ETINSA*

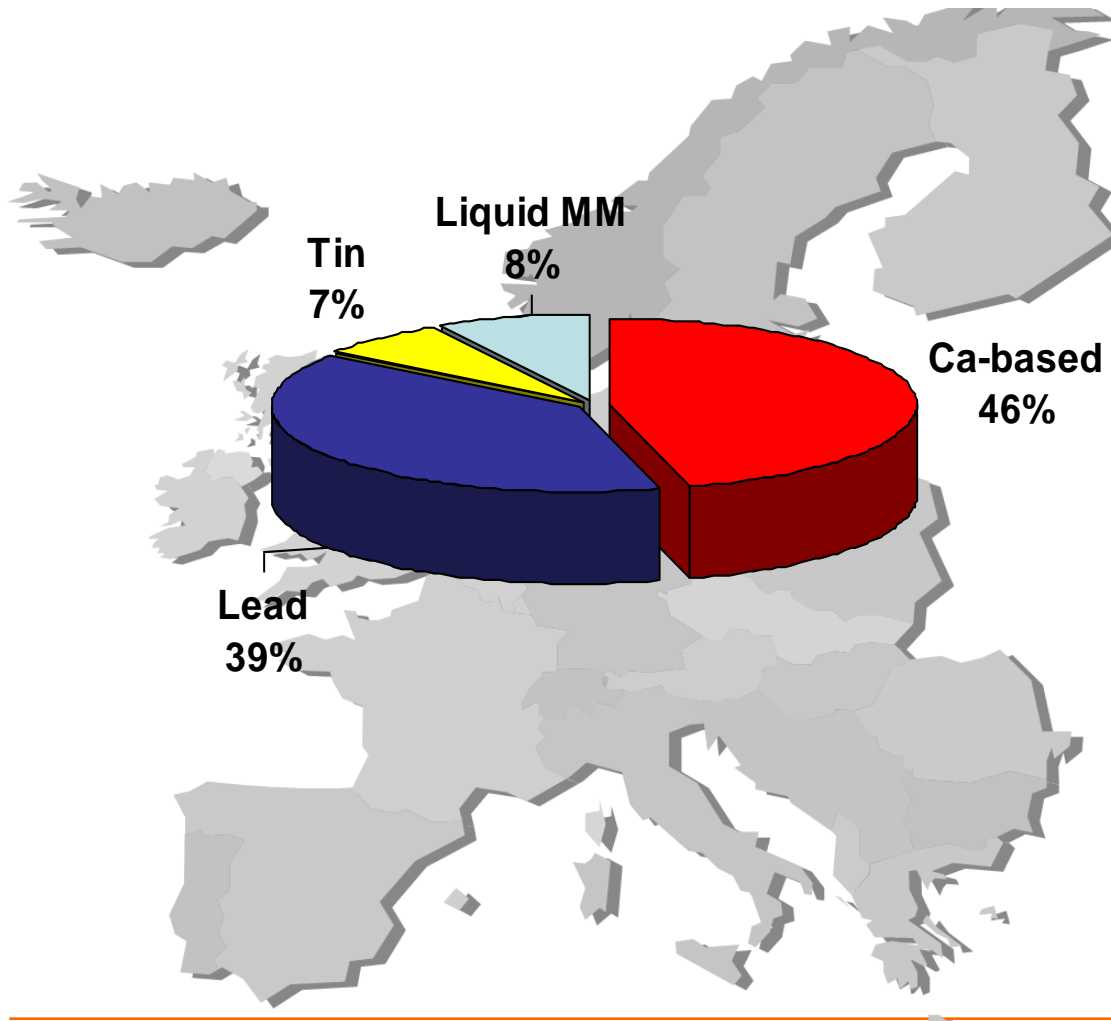
- *Akcros*
- Akdeniz Kimya
- *Arkema*
- Asua
- *Baerlocher*
- Chemson
- *Dow*
- Floridienne Chimie
- *Galata Chemicals*
- Lagor
- *Reagens*

Tin Stabilisers

Market trends & applications

2010 consumption by stabiliser type

Western + Eastern Europe



Total 204.300 tons

Stabiliser	Tons
■ Lead	80.300
■ Ca-based	93.500
■ Liquid MM	16.400
■ Tin	14.100
TOTAL	204.300

Being Tin stabilisers typically used at lower phr than the other ones, they contribute to the stabilisation of an higher % of the total PVC volume.



- Calendered rigid films

- Extruded rigid sheets and profiles (compact and foamed)



- Others, such as pipes and fittings

Tin stabilisers main applications in the EU



Western Europe - 2010

Type	Application	Total Tin Stab. %	Total Tin Stab. tons
Rigid	Calendered film	84	11.500
Rigid	Sheets & profiles	12,4	1.700
Rigid	Others	3,6	500
Flexible	Flooring,wall covering	0	0
Total rigid			13.700
Total flexible			0
Total		100	13.700

Classification & REACH

CMR cat 1-2 and PBT: Substances of Very High Concern (SVHC) under REACH



CMR 1-2 (DSD*)

- **CMR:** substances which are **C**arcinogenic, **M**utagenic, or toxic for **R**eproduction
- CMR classification is split as follows:
 - **cat. 1** and **2** → trigger SVHC status
 - **cat 3** (does not trigger SVHC status)

PBT/vPvB

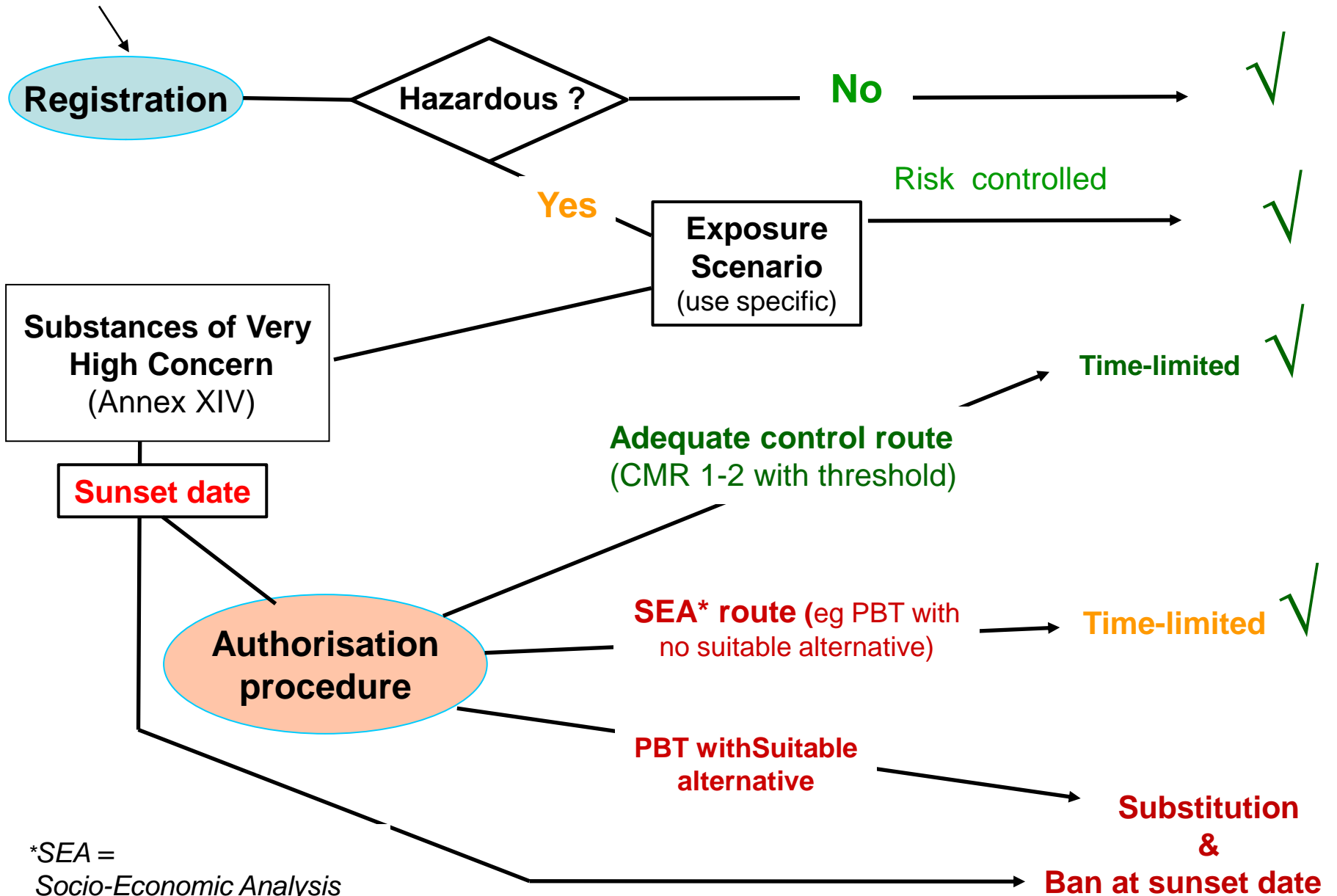
- **PBT:** substances which are **P**ersistent, **B**ioaccumulative and **T**oxic
- **vPvB:** substances which are **v**ery **P**ersistent and **v**ery **B**ioaccumulative

The **SVHC** status triggers specific processes under REACH
(outlined on the next slide)

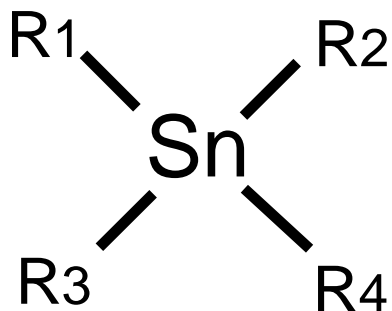
**DSD: Dangerous Substances Directive*

How REACH rules future uses of substances

~ 30,000 substances



*SEA = Socio-Economic Analysis



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 (eg a thioglycolate)

→ 3 main families of tin stabilisers:

Methyltins

Butyltins

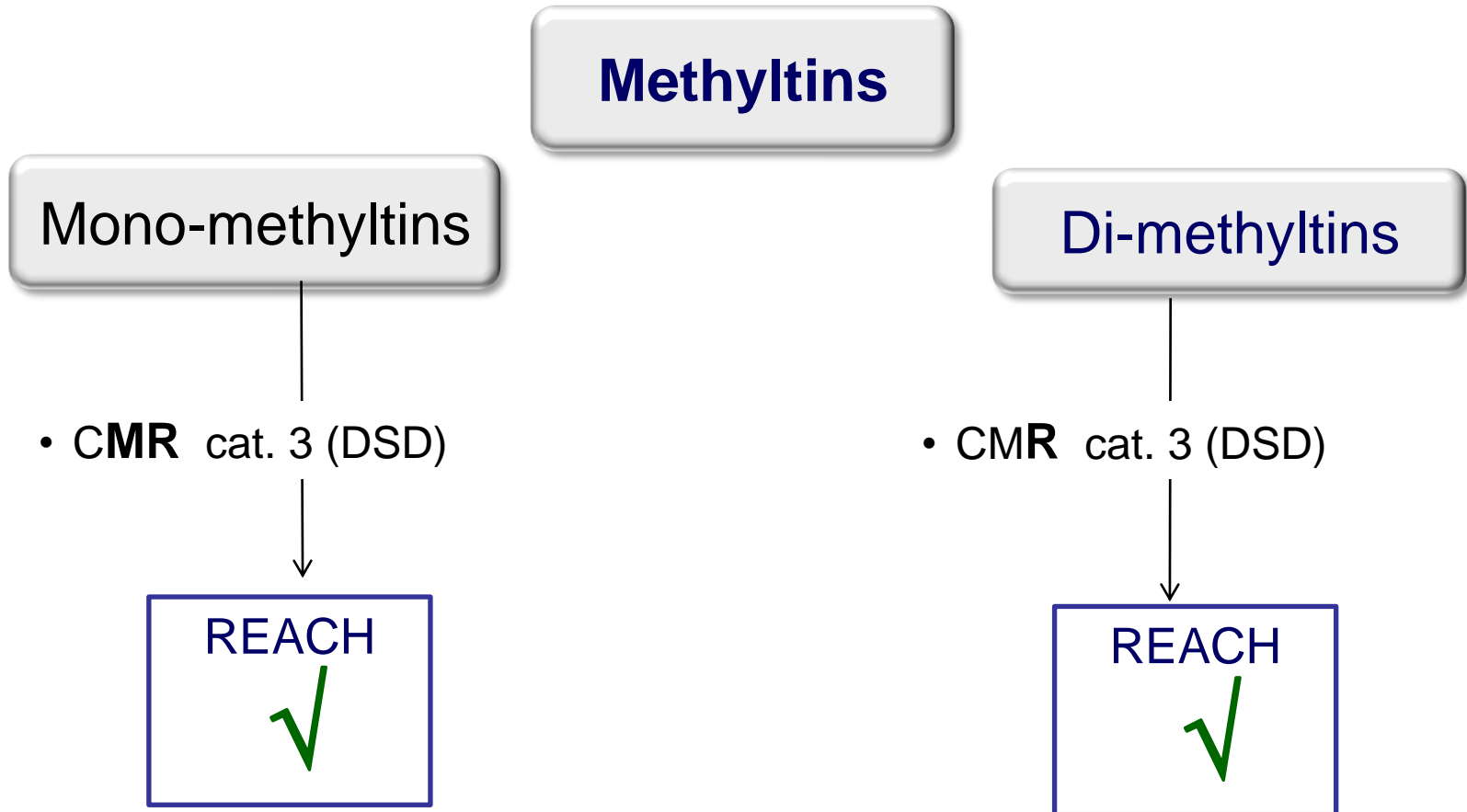
Octyltins

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)

Methyltins

Butyltins

Octyltins



Butyltins

Methyltins

Octyltins

Butyltins

Mono-butyltins

- No CMR classification

REACH



Di-butyltins

- **CMR** cat. 2 (DSD)
- **CMR** cat. 3

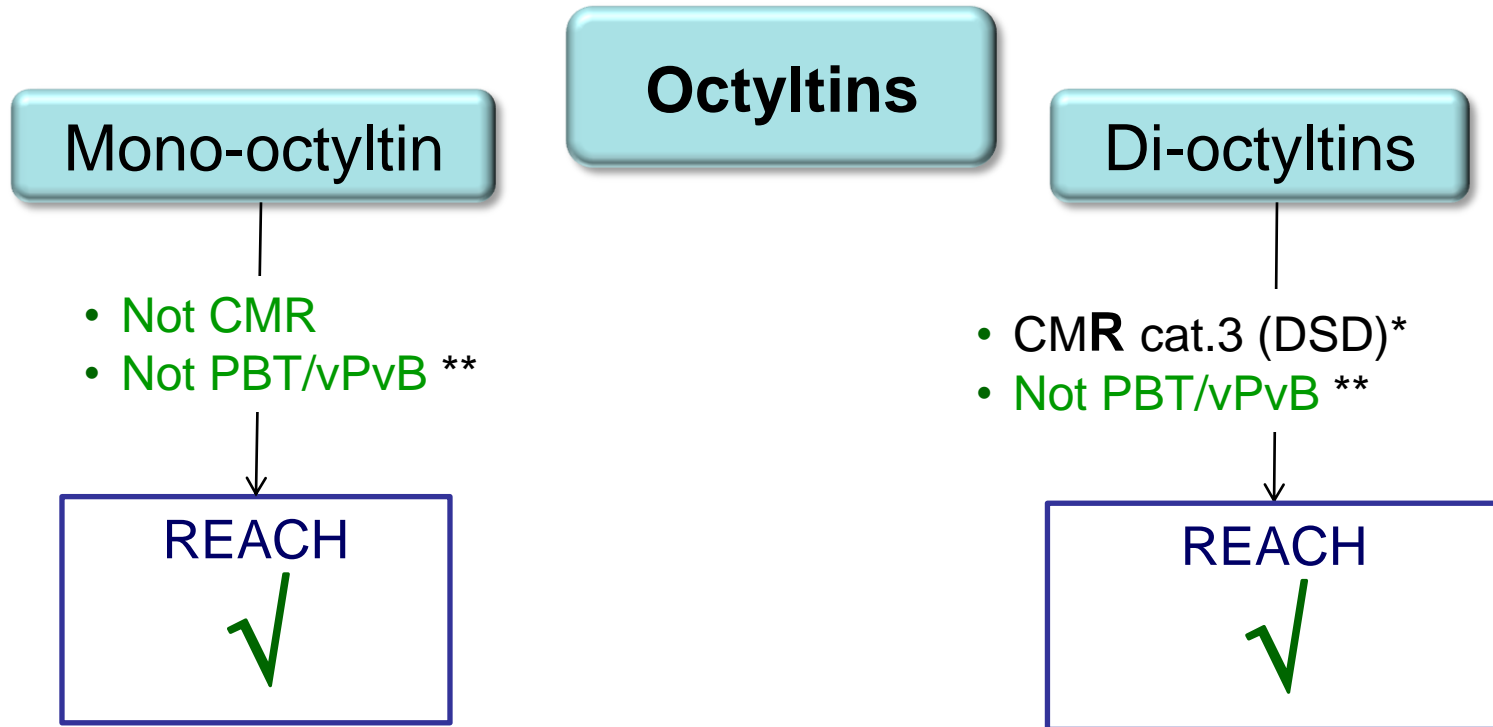
REACH

- **The *Restrictions on Marketing & Use* with phase-out dates have now been included in Reach Annex XVII**
- The Authorisation route might be initiated
- The process will be triggered by inclusion in Reach Annex XIV, if and when it happens

Methyltins

Butyltins

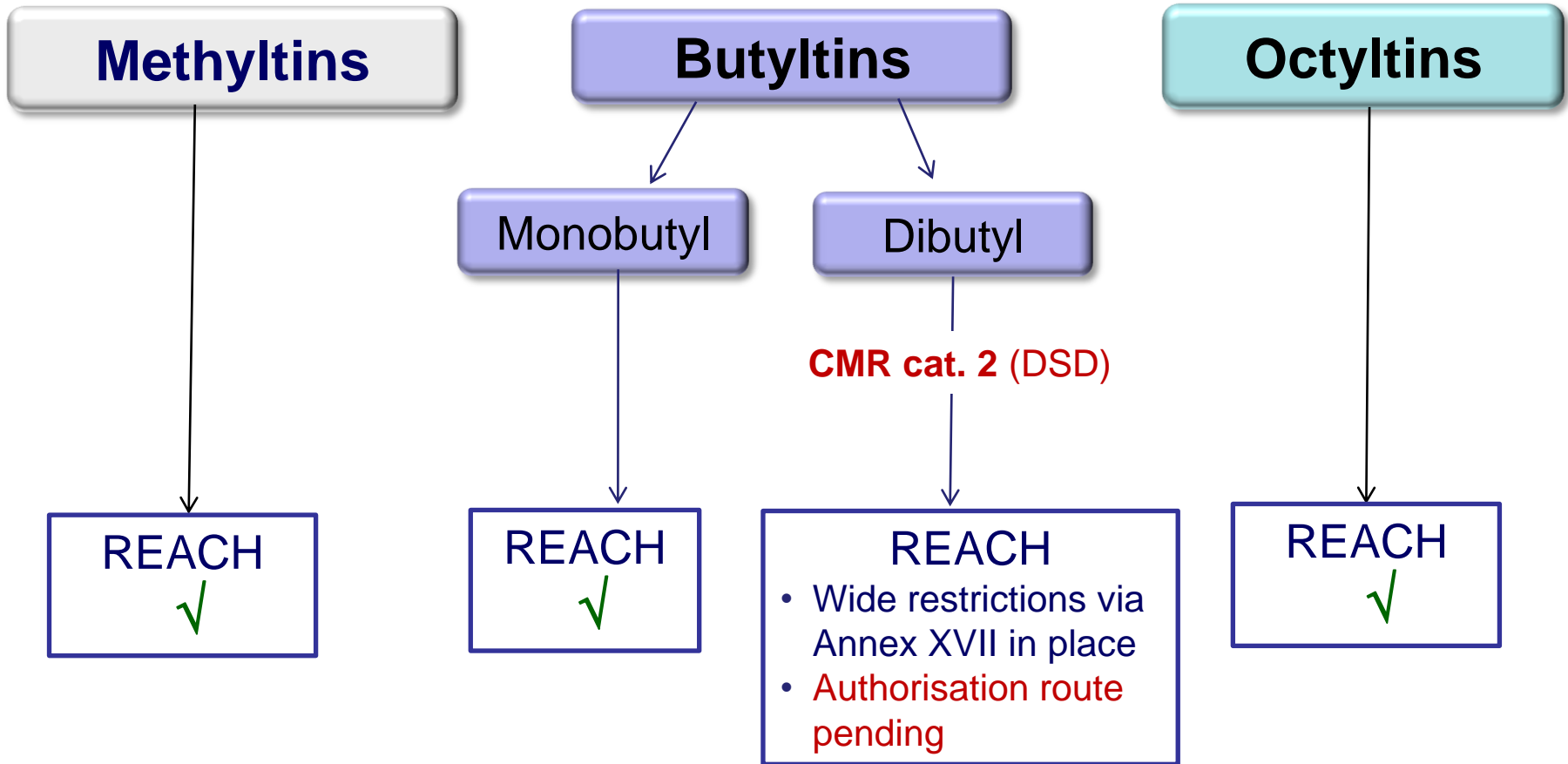
Octyltins



* *ETINSA voluntary classification and Reach registration dossier 2010*

** *Testing completed in 2009 in accordance to Commission Regulation 465/2008 concluded that MOT and DOT esters do not meet the Reach Annex XIII bioaccumulation criterion (B)*

Tin stabilisers under REACH - SVHC issue: status overview



Tin Stabilisers

Classification & labelling

Classification & Labelling

- Some confusion among Downstream Users:
 - Official \leftrightarrow voluntary classifications
 - CMR cat 1-2-3 \leftrightarrow GHS cat 1a, -1b, -2
 - Current labels \leftrightarrow GHS labels
- The CLP regulation (*Classification Labelling and Packaging*), together with the *Notification* process, will contribute to enhance clarity in the longer term.



Classification Labelling Packaging Regulation “CLP” (EC) 1272/2008



- CLP implements the *Globally Harmonised System of classification and labelling* (GHS) into EU law
- Replaces the DSD* and the DPD** in a stepwise approach:
 - substances: CLP mandatory as from 1 Dec. 2010
 - mixtures: CLP mandatory as from 1 June 2015
- Both classifications may co-exist during the transition period but labelling will be unique to avoid confusion.
(details on next slide)
- Frequently Asked Questions brochure and in depth guidances available on ECHA's website at <http://echa.europa.eu/>

* *DSD: Dangerous Substances Directive 67/548/EEC*



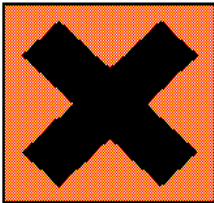

** *DPD: Dangerous Preparations Directive 1999/45/EC*

Deadline	The Safety Data Sheet ...
until 1 December 2010	... shall contain the classification of a substance according to DSD. However, if a substance is already classified, labelled and packaged according to CLP, the Safety Data Sheet for the substance shall also contain the CLP classification of the substance.
until 1 June 2015	... shall contain the classification of a substance according to DSD. After 1 December 2010 the CLP classification shall also be provided.
until 1 June 2015	... shall contain the classification of a mixture according to DPD. However, if a mixture is already classified, labelled and packaged according to CLP, it shall also contain the CLP classification of the mixture .
from 1 June 2015	... shall contain substance and mixture classifications according to CLP

CMR classifications under CLP (GHS)

- CMR cat. 1, 2 and 3 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). This new symbol becomes now the only one associated to all C,M and R classifications
- The next slide shows the labels for CMR hazard under the DSD and CLP



Classification : Comparison with GHS CMR		
CMR (EU now)	GHS	Signal Word
 Repto Cat 2	 Repto cat 1.B	Danger
 Repto Cat 3	 Repto cat 2	Warning

Tin Stabilisers

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

Com. Regulation EU 276/2010 in Official Journal of 31 March 2010

(based on the *Restrictions on Marketing and Use* initially issued in
Commission Decision 2009/425/EC)

From *Marketing & Use* to REACH *Annex XVII* restrictions



- Environmental concern with tributyltin-based antifouling paints for ships lead to first restrictions on TBT. This acronym started to be misused to mean « organotins » -covering a wider family of substances with different toxicological profiles
- Risk Assessment on several organotins commissioned by DG Enterprise in 2002 and finalised with an Impact Assessment in 2007. No specific risks identified for the use of **DBT & DOT** stabilisers in rigid PVC (**Methyltins** were not evaluated)
- Considering the global exposure to organotins from various sources (with sea-food as a major contributor) some restrictions on various uses of DBT and DOT compounds were put forward.
- Those restrictions were implemented in the framework of Dir. 76/769 (*Restrictions on Marketing & Uses*) and made formal by Com. Decision 2009/425/EC
- Those restrictions were subsequently integrated into REACH Annex XVII by Com. Regulation EU 276/2010 (in Official Journal of 31 March 2010)

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)

Diocetylins

All Diocetyl tin 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:

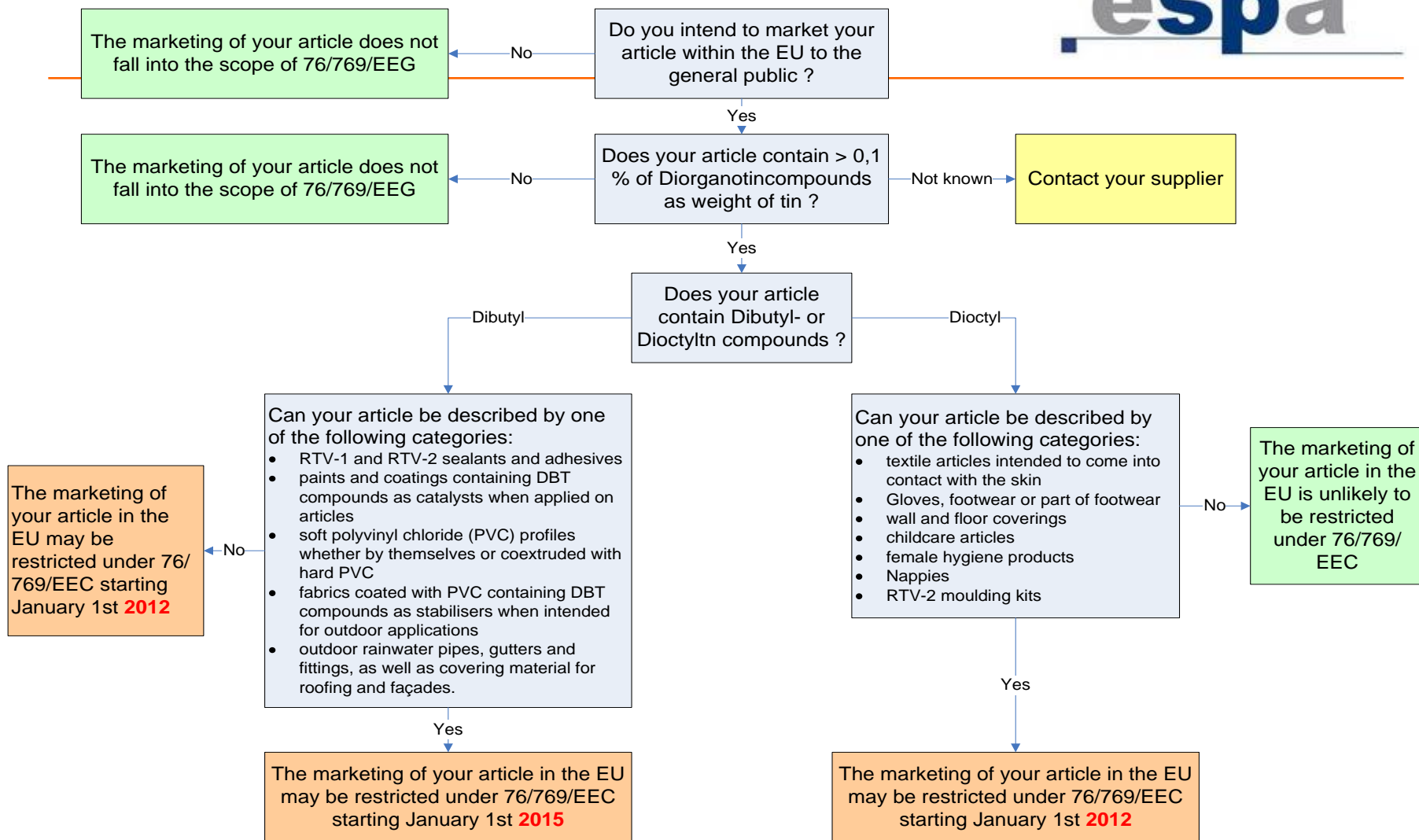
- textile articles intended to come in contact with the skin
- gloves
- footwear intended to come into contact with the skin
- wall and floor coverings*

*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.**

- To be judged from the questions raised by DU it appears that a thorough reading of the restriction is needed to avoid misunderstandings
- Misunderstanding leads to over-simplification (“*tin stabilisers are banned*”) and result in “green marketing” initiatives
- **ETINSA** prepared a **flow-sheet** to help Downstream Users to find their way through the restriction (next slide – and available upon request*)

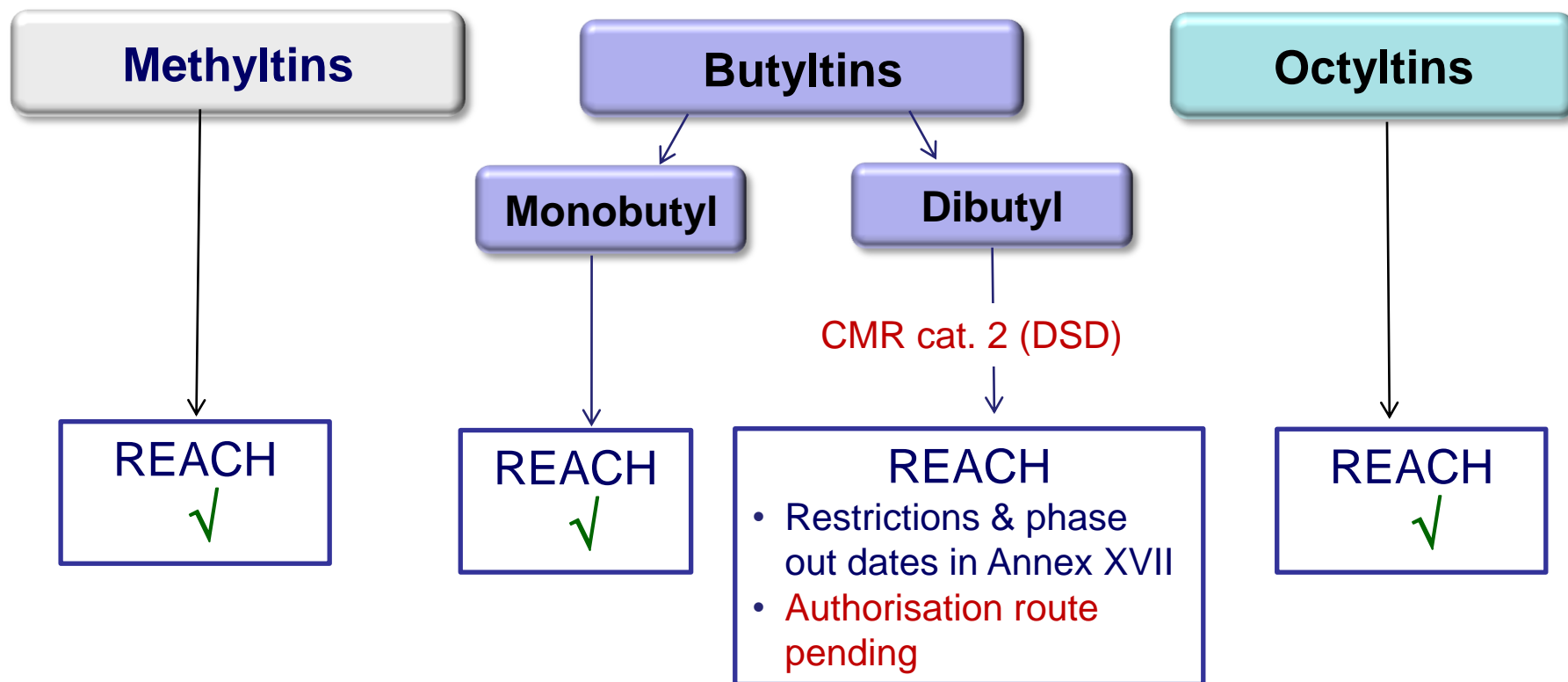
* Disclaimer: this flow sheet aims only at helping the reader to navigate through the regulation and does not replace the legal text (now in REACH Annex XVII) which remains the only legal document.

Use of dibutyl and di-octyltins: flow-sheet through “M & Use”



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.

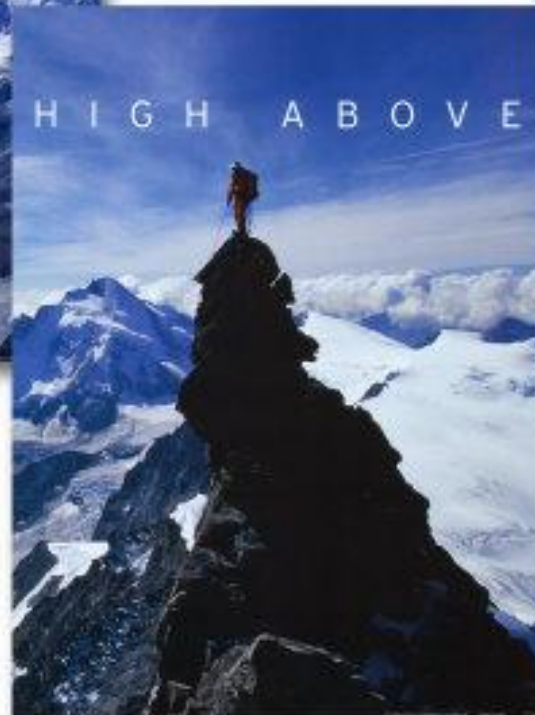
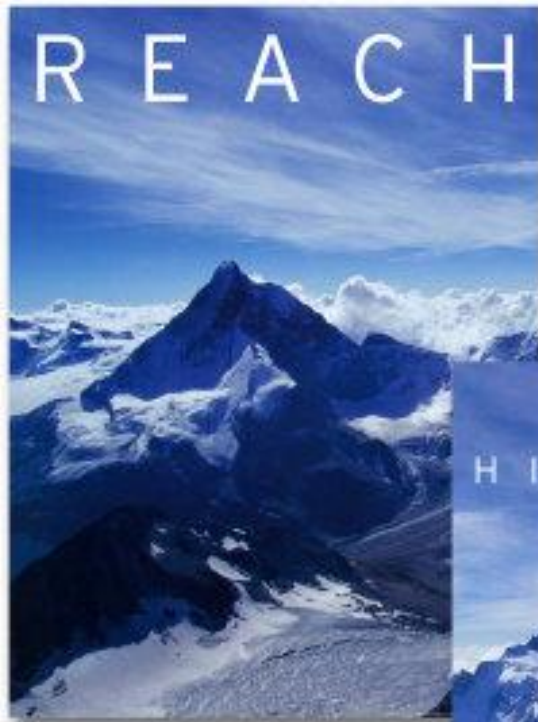
Use of tin stabilisers under REACH: status overview (including Annex XVII specific restrictions)



The Organotin Reach Consortium was formed in 2008 with all the major EU Manufacturers/ Importers of organotins compounds. Several “Tier 1” substances have been registered by Dec. 2010 and the consortium is preparing the registrations of the substances due in the next tiers.

- Organotins constitute a group of substances presenting widely different toxicological properties. Organotins does not equate « TBT ».
- The risk assessment and the resulting restrictions, now in REACH Annex XVII, clarified the situation.
- Regulatory certainty: the dates by which the use of some Organotins in specific applications have to be discontinued are already known.
- Many stabilisers of the organotins family have already been registered.
- The switch to GHS (CLP) might introduce confusion concerning the CMR classification → always specify to which legislation it refers (*DSD* CMR cat. 3 = *GHS* cat. 2).
- The *skull and crossbones* label will disappear for many tin stabilisers.

As a result of the above octyltins and methyltins will continue to be used in all the applications where organotins are currently in use



Thank you

For further information
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*Acknowledgment to the ETINSA
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set-up this presentation*