Meeting the Restrictions and Certifications for Today and the Future.

ABICOL – Associação Brasileira da Indústria de Colchões

23.11.2018 | C.Toyoshima

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Emissions in the PU Industry

Automotive

Markets:
Seating, instrument panels, steering wheels, headliners, NVH

Key influencers:
- VDA – German Association of the Automotive Industry
- GMW
- UL VIAQ – Vehicle Interior Air Quality
- OEM-specific Requirements

Insulation

Markets:
Spray foam

Key influencers:
- SPFA – Spray Polyurethane Foam Alliance
- EPA (HFOs, halogenated flame retardents, etc.)
- UL GREENGUARD

Comfort

Markets:
Mattresses, furniture, pillows, carpet backing

Key influencers:
- CertiPUR-US
- State and Federal Regulations

Global community is discussing product properties …

…it‘s not all scientific, but certainly driving the market!

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Certificates (Specifications & Labels) can help address misconceptions

Not legal regulations, but may become legally binding if used for advertisement or if included in supply agreements.

Specification
Chemical compounds and substances

Spec. no: **IOS-MAT-0010**
Date: 2015-11-13
Version no: AA-10911-13

Issued by
Ralph Nussbaum
Product Requirements and Compliance/ Product Laws and Standards specialist

Signature

Authorised by
Pär Stenmark
Manager Product Requirements & Compliance/IKEA of Sweden

Signature

Replaces:
AA-10911-11

Chemical compounds and substances

https://industries.ul.com/environment/certificationvalidation-marks/greenguard-certification-program

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Typical Criteria for Foam Certificates

CONTENT

What goes <u>into</u> the foam?

$MeCl_2$ – Europe / USA
Flame Retardants – California / *Massachusetts…*

Restrictions on:
Hazardous blowing agents,
Certain flame retardants,
Phthalates, etc.

QUALITY

Physical Property Specifications

Density and Hardness Variation
Support & Resiliency
Compression Set Limits

EMISSION

What comes <u>out of</u> the foam?

Volatile Organic Compounds
- Consumer exposure by inhalation

Extractable Substances
- Consumer exposure by dermal contact

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CertiPUR-US – Emissions Specifications

Independent Laboratory Emissions Testing[7]

Substance	CAS-No.	Guideline Limit [mg/m³]
Formaldehyde	50-00-0	<0.1
Benzene	71-43-2	<0.5
Toluene	108-88-3	<0.5
Styrene	100-42-5	<0.3
Vinylcyclohexene	100-40-3	< LOD*
4-Phenylcyclohexene	4994-16-5	< LOD*
Butadiene	106-99-0	< LOD*
Vinyl Chloride	75-01-4	< LOD*
Aromatic hydrocarbons		< 0.5
TVOC Emissions		< 0.5

[7] Average Density and Average 25% IFD measured using procedures in Section 1 must be reported for the foam production used in Analytical Testing.

* Below the Limit of Detection

Test Method: ISO 16000-Parts 3, 6, 9, & 11 – with chamber volume of 0.5 or 1 m³. The foam sample is placed on the bottom of an emission test chamber and is conditioned for 72 hours at 23°C/50%RH, applying an air exchange rate n of 0.5 per hour and a chamber loading L of 0.4 m2/m³ (=total exposed surface of sample in relation to chamber dimensions without sealing edges and back) in accordance with ISO 16000-9 and ISO 16000-11.

http://certipur.us/

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CertiPUR-US – Extraction Specifications

Tributyltin

Substance	CAS-No.	Guideline Limit [ppm]
Tributyltin (TBT)	688-73-3	0.5

Phthalates

Substance	CAS-No.	Guideline Limit
Sum of 7 phthalates*		≤ 0.01 wt %

TDA/MDA

Substance	CAS-No.	Guideline Limit
2,4 – Toluenediamine (TDA)	95-80-7	≤ 5.0 ppm
4,4' – Diaminodiphenylmethane (MDA)	101-77-9	≤ 5.0 ppm
Sum of TDA (2,4) plus MDA (4,4')	95-80-7 + 101-77-9	≤ 5.0 ppm

Polybrominated (PBDE) Flame Retardant Additives

Substance	CAS-No.	Guideline Limit
pentabromodiphenyl ether	32534-81-9	≤ 0.01 wt %
octabromodiphenyl ether	32536-52-0	≤ 0.01 wt %
decabromodiphenyl ether	1163-19-5	≤ 0.01 wt %

http://certipur.us/

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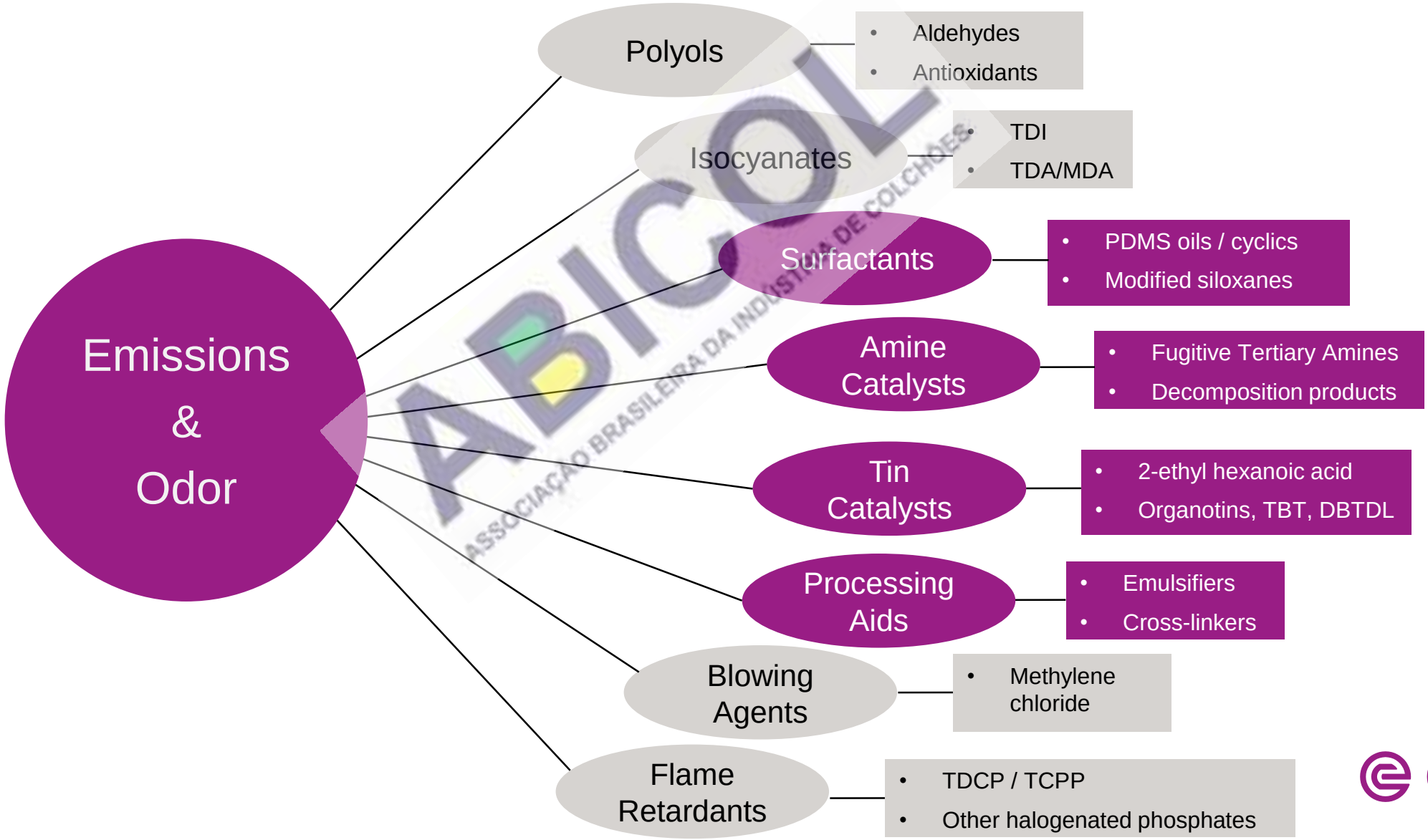
Emissions and Odor Sources by Component



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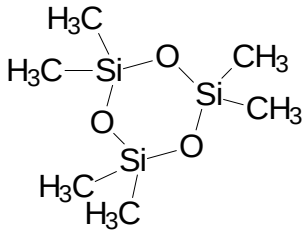
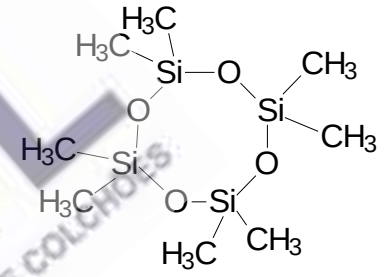
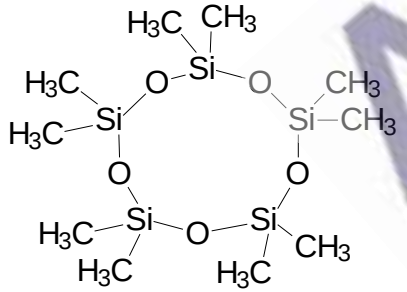
Cyclic Low MW Siloxanes – Residual Components in Surfactants



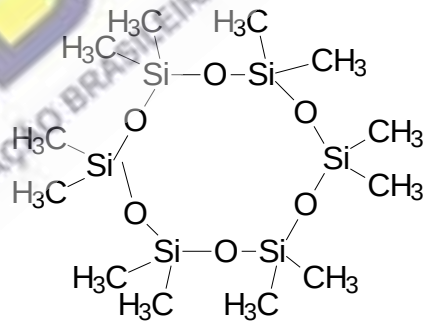
D3
bp: 134 °C
CAS-No.: 541-05-9



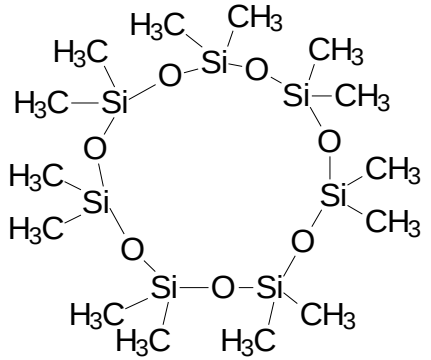
D4
bp: 175 °C
CAS-No.: 556-67-2
Reprotoxic, cat. 2



D5
bp: 210 °C
CAS-No.: 541-02-6
discussions about PBT listing



D6
bp: 245 °C
CAS-No.: 540-97-6



D7
bp ≈ 265 °C
CAS-No.: 107-50-6

→ **Siloxanes do not have an odor. For VOC testing D4, D5, D6, D7 are of relevance.**

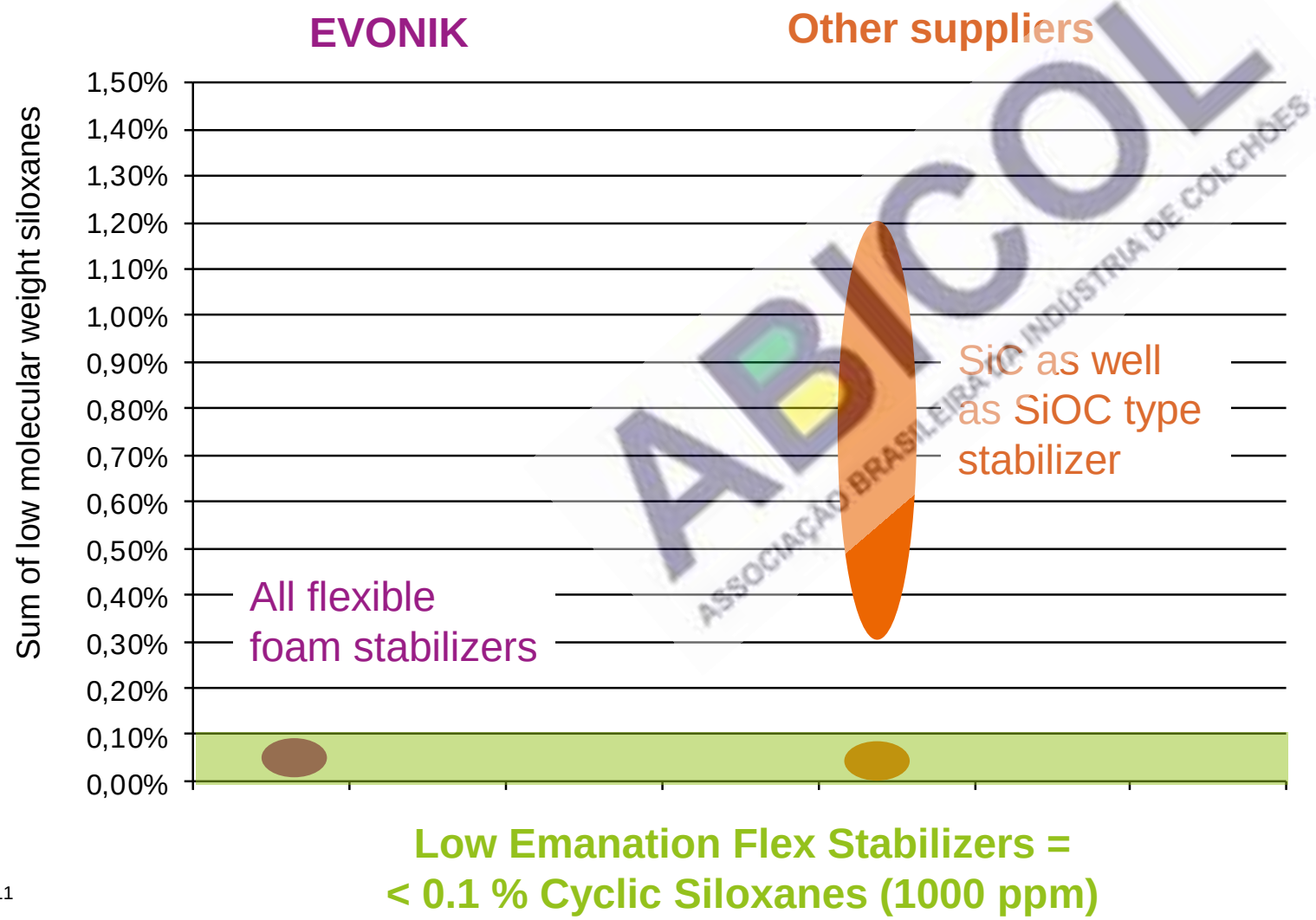
Regulatory situation D4, D5, D6

- In Feb. 2018, Germany and ECHA proposed inclusion on the list of substances of very high concern („SVHC list“) for
  - Octamethylcyclotetrasiloxane (D4) based on its Persistent, Bioaccumulative and Toxic* (PBT) properties
  - Decamethylcyclopentasiloxane (D5) and Dodecamethylcyclohexasiloxane (D6) based on their very Persistent, very Bioaccumulative (vPvB) properties
- **On June 27th 2018, D4, D5 and D6 have been included in the SVHC list.**
- Inclusion on the list was based on environmental concerns, not on human health concerns
- **Consequence of the SVHC listing:**

  D4, D5 and D6 have to be on the SDS (incl. a reference to SVHC) if present at or above 0.1 % (each)

* D4 is classified as toxic to reproduction category 2 (H 361)

Content of Cyclic Siloxanes in Flexible Foam Stabilizers



Low Emanation Flex Stabilizers =
< 0.1 % Cyclic Siloxanes (1000 ppm)

2008 – Evonik started offering low VOC surfactants for flexible slabstock foam.

2010 – Evonik completed conversion to of all flexible slabstock surfactants to low VOC quality (< 0.1% cyclic siloxane)

2018 – Evonik to initiate cyclic siloxane testing of all production batches of flexible slabstock surfactants, and report measured value on Certificate of Analysis to confirm that reportable limit of 0.1% D4, D5 and D6 is not exceeded and hence can be excluded from SDS.

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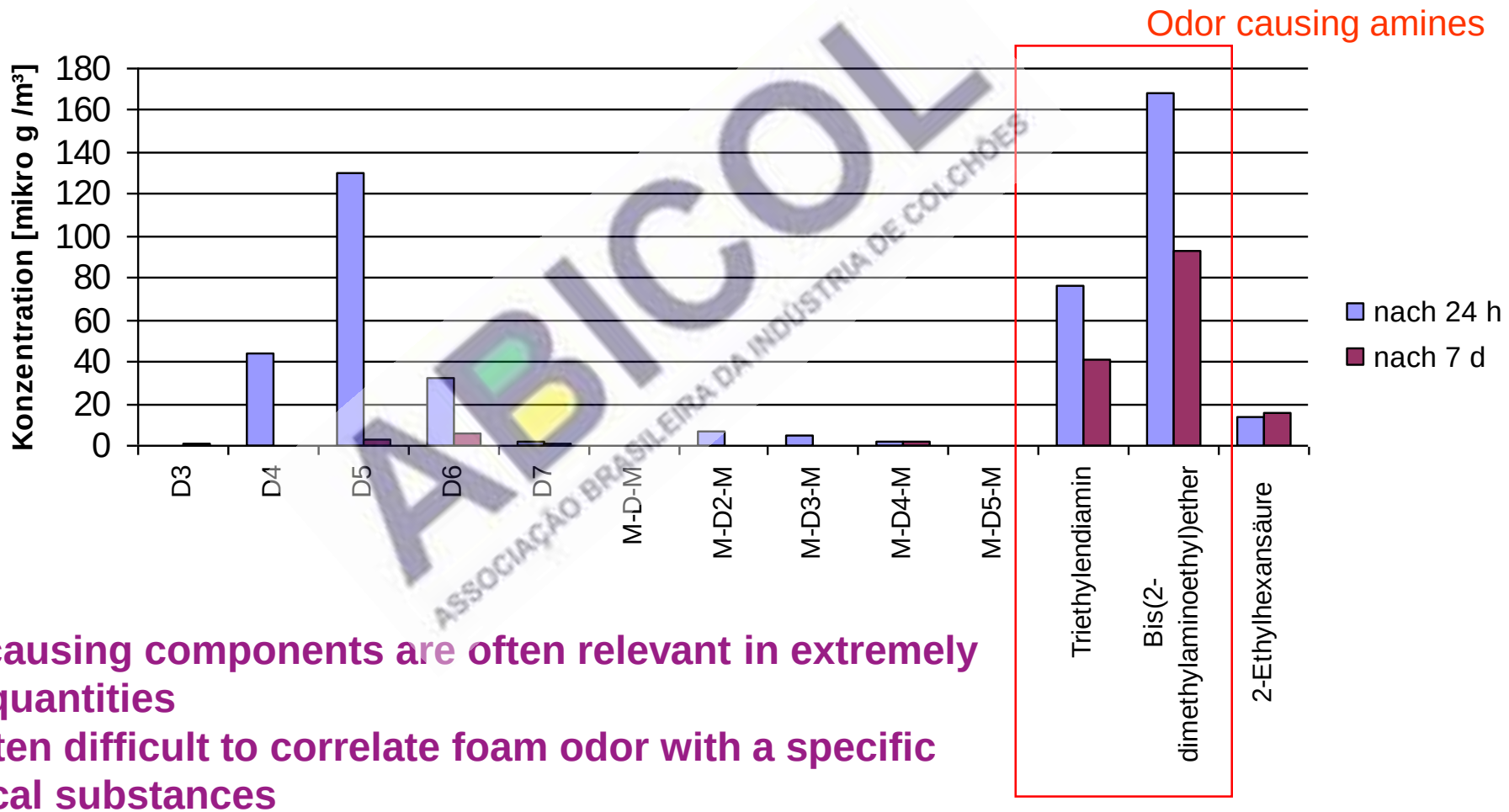
Standard Amines – significant Sources of Odor and VOC in foam



- **Odor causing components are often relevant in extremely small quantities**
- **It is often difficult to correlate foam odor with a specific chemical substances**
- **Odor causing components exhibit often slow release (high boiling point)**

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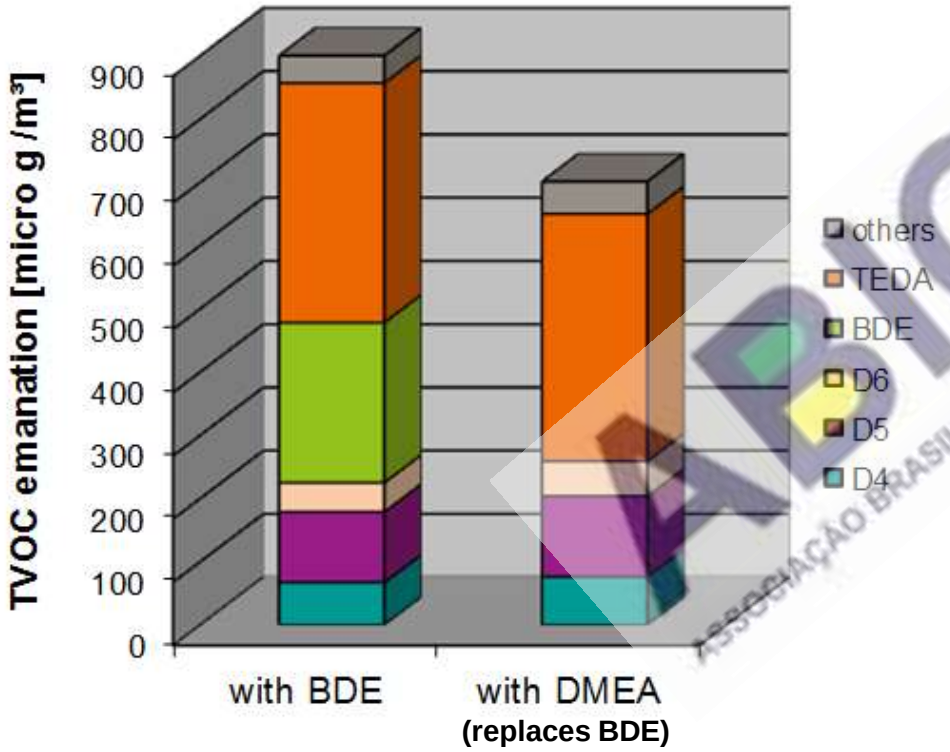
Standard Fugitive vs. Basic Reactive Amine Catalysts



Boiling points of amines:

NMM [N-methylmorpholin]	113 °C
DMP [dimethylpiperazin]	132 °C
DMEA* [dimethylethanol amine]	135 °C
NEM [N-ethylmorpholin]	138 °C
DMCHA [dimethylcyclohexyl amine]	163 °C
TEDA [triethylen diamine]	174 °C
DMBA [dimethylbenzyl amine]	182 °C
BDMAEE [bis(dimethylaminoethyl)ether]	189 °C
PMDETA [pentamethyldiethylene triamine]	200 °C
DEOA* [diethanol amine] or Dabco NE1050	270 °C
DMDEE [N,N-dimorpholinodiethylether]	309 °C
TEOA* [triethanol amine]	310 °C

Typical foaming temperature

*= reactive amine

Flexible Foam with Index > 100: BDE > TEDA >>>> DMEA > No Emission catalysts

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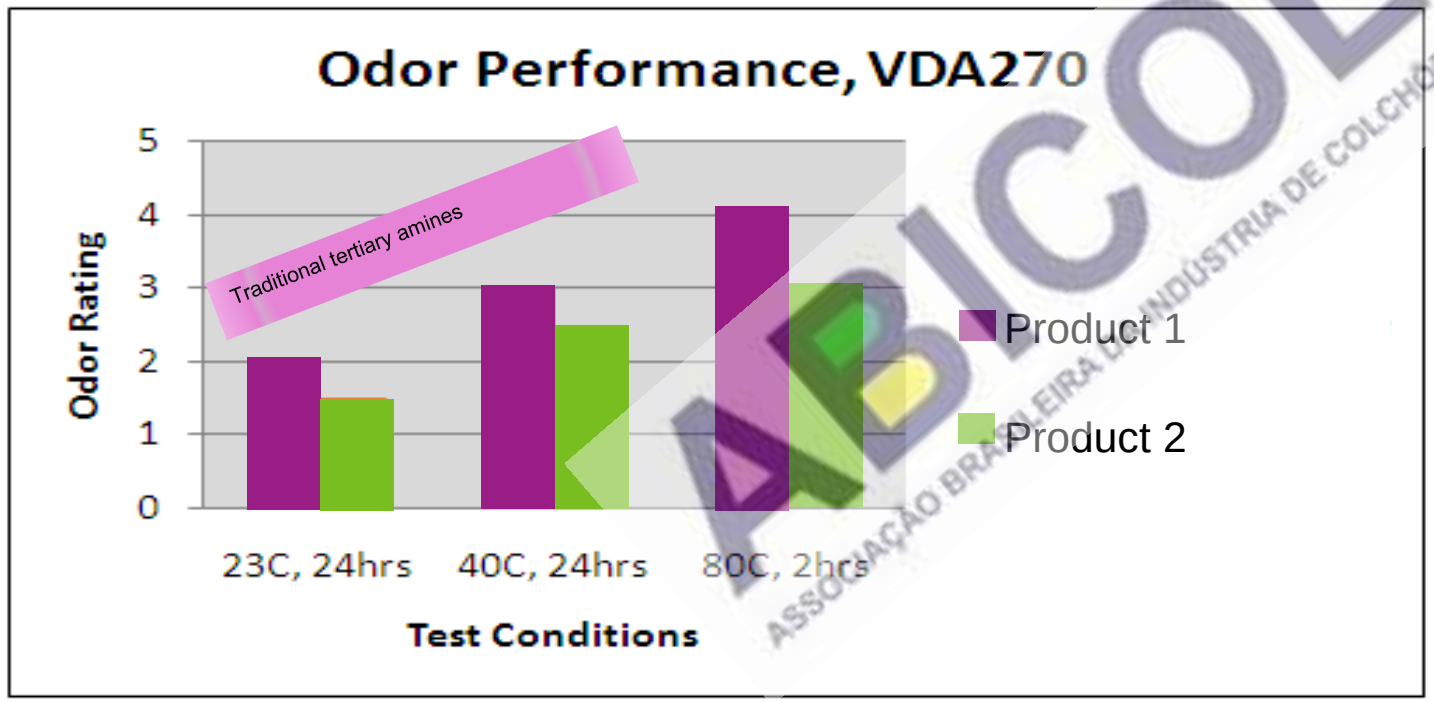
Special Reactive Blow Amine –Low Odor Results

- Odor testing confirms difference between existing reactive blow catalysts.



Rating System

1. Imperceptible
2. Perceptible, undisturbing
3. Clear perceptible, undisturbing
4. Disturbing
5. Strongly disturbing

- The higher the temperature, the more differentiated the odor performance.
  - ➢ Critical factor in the production environment.

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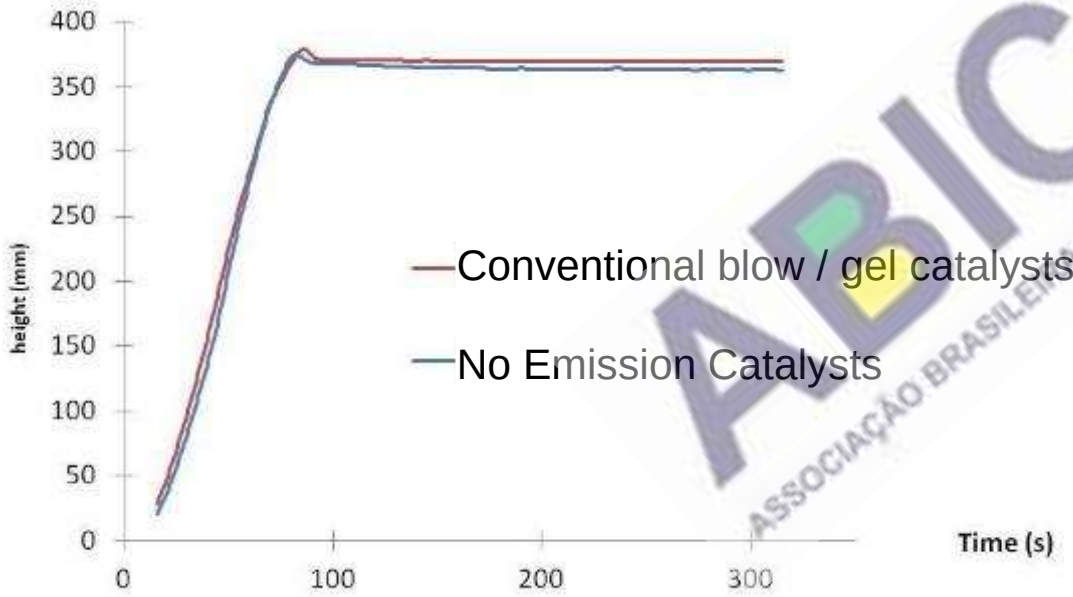
No Emission Catalysts: Replacement of Standard Catalysts

- There are reactive catalysts that provide similar activity and foam physical properties to conventional catalysts.



TDI-based formulation		
Polyol A [parts]	100	100
Water [pphp]	4.8	4.8
Standard surfactant [pphp]	1	1
Conventional gel [pphp]	0.14	-
Conventional blow [pphp]	0.05	-
No Emission gel [pphp]	-	0.17
No Emission blow [pphp]	-	0.06
Tin Octoate [pphp]	0.28	0.28
CH_2Cl_2 [pphp]	7	7
TDI 80 Index	<110>	<110>
Density [kg/m³]	19	19

- **No Emission blow used at 1.1 : 1 replacement for conventional blow**
- **No Emission gel used at 1.2 : 1 replacement for conventional gel**

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Organotin & Stannous Salt Catalysts – Toxicology

	Dibutyl**T**in**Di**laurate	**S**tannous **O**ctoate	**E**mission **F**ree **T**in **C**atalyst	2-EHA free **T**in **C**atalyst
Substance Class	**Tin organic compound!**	Stannous salt	Stannous salt	Stannous salt
Labeling	Danger 	Danger 	Warning 	Danger 
Classification	Skin Corrosion (Cat.1C, H314) Skin Sensitation (Cat.1, H317) **Cell mutagenicity (Cat.2, H341)** **Reprod. tox. (Cat.1B, H360)** **Organ Tox. (Cat.1,H370/ H372)** Acute aquatic toxicity (Cat.1, H400) Chronic aquatic toxicity (Cat.1, H410)	Serious Eye Damage (Cat.1, H318) Skin Sensitation (Cat.1, H317) **Reproductive toxicity (Cat.2, H361)** Chronic aquatic toxicity (Cat.3, H412)	Skin irritation (Cat.2, H315) Skin Sensitation (Sub-Cat.1A, H317) Chronic aquatic toxicity (Cat.2, H411)	Serious Eye Damage (Cat.1, H318) Skin Sensitation (Sub-Cat.1B, H 318) Acute toxicity (Cat.4, H302)
Additional Information	DBTDL is under discussion for TBT and DBT DBTDL use leads to the failure of specific labels (IKEA, LGA, CertiPUR)	2-Ethyl hexanoic acid: Reproductive toxicity (Cat. 2, H361) ⇓ Volatile compound	Ricinoleic acid: **No** Reproductive toxicity ⇓ Non-volatile compound	Neodecanoic acid: **No** Reproductive toxicity ⇓ Volatile compound

Stannous Salt Catalysts – Property & Performance

	Stannous Octoate	Emission Free Tin Catalyst	2-EHA free Tin Catalyst
Chemical Description	Stannous octoate - tin(II) salt of 2-ethylhexanoic acid	Stannous ricinoleate - tin(II) salt of ricinoleic acid	Stannous neodecanoate - tin(II) salt of neodecanoic acid
Appearance	slightly yellow liquid	clear, yellow to slightly turbid liquid	slightly yellow liquid
Tin Content	28.0 – 29.3 % tin(II)	12.5 – 13.5 % tin(II)	≥ 19.0 (up to 21.0) % tin(II)
Stannous Content	96 % minimum in relation to the tin content		
Viscosity (20 °C)	approx 350 mPas	700 – 3500 mPas	200 – 800 mPas
Specific Gravity (20 °C)	approx 1.25 g/ml	1.075 ± 0.025 g/ml	1.13 ± 0.03 g/ml
Solubility	Soluble in polyols and most organic solvents, insoluble in water and alcohols		
Emission profile*	Emanation of 2-Ethylhexanoic acid (2-EHA)	**No emanations!**	Emanation of Neodecanoic acid (less acid emanation than K 29)
KOSMOS 29 Replacement	**Common Stannous Octoate use levels:** Low Density (MC): up to 0.70 pphp Medium Density: 0.15 – 0.25 pphp High Density: 0.10 – 0.15 pphp	Use level **2.7 times higher compared to S.O.** to achieve same airflow. **Small amine reduction** necessary – about 20% less to achieve similar rise profile	Use level **similar to Stannous Octoate** to achieve same airflow. **Higher amine level** needed – about 20% more to achieve same rise profile
Special Performance	Degrades to SnO and emissive 2-EHA during the PU formation	**Emission-free alternative to Stannous Octoate**	**2-Ethyl-hexanoic acid free alternative to Stannous Octoate**

*Emanation of the acid depends also on the foam type and the choice of the corresponding amine catalyst (pH of the foam).

Tin Catalyst Summary

Product	Regulatory Concern	Emissions / Extractions Issues	Performance
DBTDL	Reproductive & Organ Toxicity Cell Mutagenicity Acute & Chronic Aquatic Toxicity	Extraction of Tributyl Tin (TBT)	- used to reduce densification from cold flow - replace with stannous salt + Ortegol 204
STANNOUS OCTOATE	Reproductive Toxicity	Emission of 2-Ethyl Hexanoic Acid (2-EHA)	- standard tin catalyst for conventional foam
2-EHA FREE TIN CATALYST	**Not significant**	**Emission of Neo Decanoic Acid (less than 2-EHA)**	- eliminates emissions of 2-EHA - same rise profile & airflow as T 9 / K 29 achieved with = tin level and +20% amine
EMISSION FREE TIN CATALYST	**Not significant**	**No Emissions**	- eliminates all tin catalyst emissions - same rise profile & airflow as T 9 / K 29 achieved with 2.7x tin level and -20% amine

The merger of Evonik and Air Products' PMD has provided new capabilities

PU foam stabilizers

PU foam catalysts

Release agents and other

Innovation	Product need	Market trends	
Novel combination of catalysis & interfacial chemistry	Finer foam cells	**Super insulation**	
New additive packages to prevent VOC formation	**Emission-free foams**	**Highest consumer safety**	
Better breathability via additives allow for more cell opening	Improved heat management	**High comfort mattress**	

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