

**Minimierung der Fogging & VOC-Emissionen  
von PU-Schaum durch geeignete Rohstoffe**

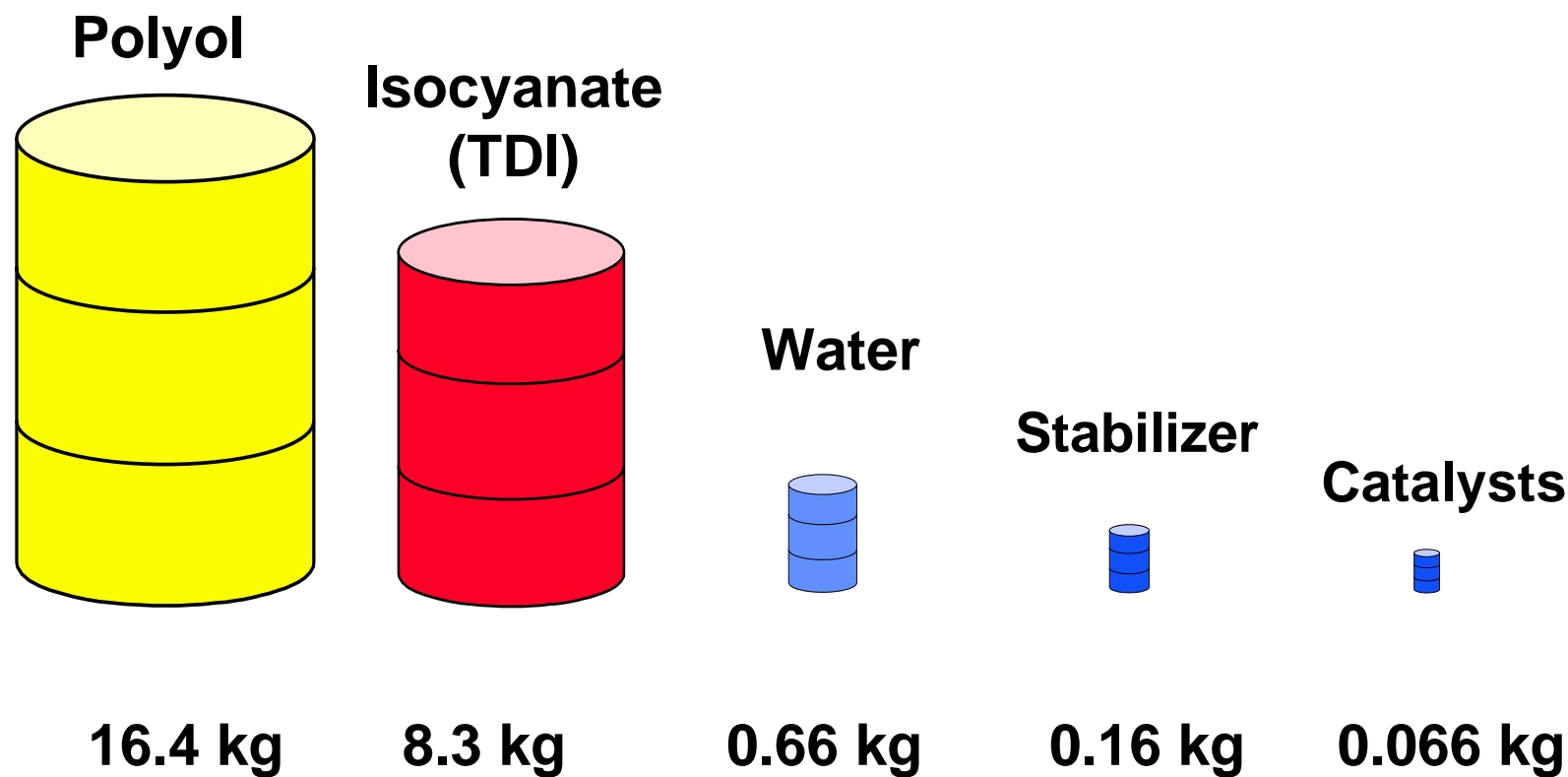
**Dr. Rüdiger Landers**

**28.11.2006**



*Goldschmidt Polyurethane Additives*

# Raw Materials Required to Produce a Polyurethane Flexible Foam



Quantities being required to produce 1 m<sup>3</sup> of flexible foam with a density of 24 kg/m<sup>3</sup>

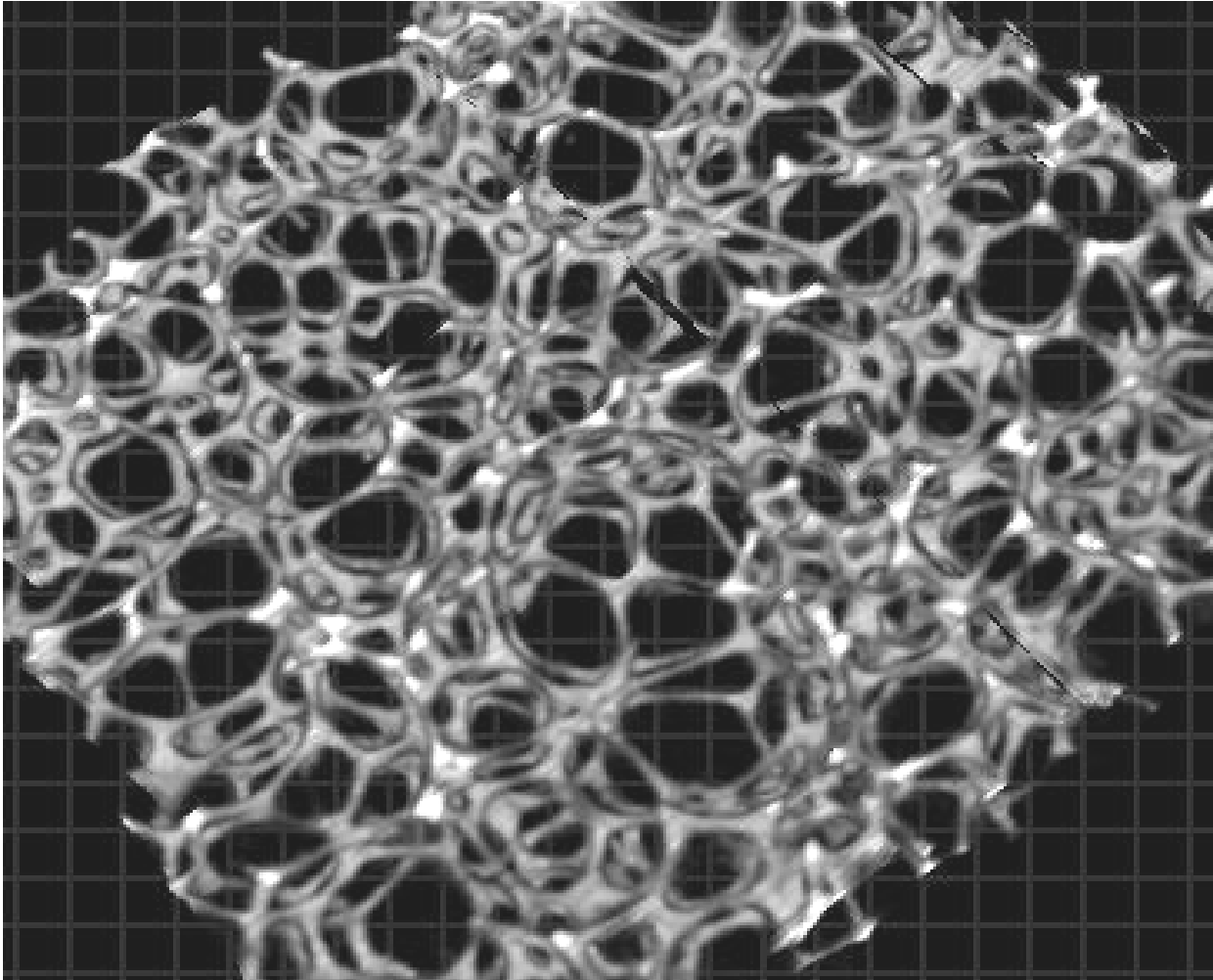


# Goldschmidt's Additive Portfolio for the Polyurethane Foam Industry

- **Foam Stabilizers**
- **Tin Catalysts**
- **Amine Catalysts**
- **Release Agents**
- **Antioxidants**
- **Cross Linkers**
- **Colour Pastes**
- **Softening Agents**
- **Antistatic Agents**
- **UV-Stabilizers**



# Why is a PU Foam Critical Regarding Emanations ?



μCT-reconstruction of a HR slabstock foam



# VOC / FOG Definition's

VVOC: < 0 ... 50-100°C

VOC : 50 - 250 °C

SVOC: 240 - 400°C

POM : >380°C

WHO

VOC

FOG

VVOC: Very Volatile Organic Compounds

VOC: Volatile Organic Compounds

SVOC: Semi Volatile Organic Compounds

POM: Particulate Organic Matter

## EU definition:

substances with a vapor pressure of  
> 0.01 kPa at 293.15 K



# Emanations of PU Foam

Comfort  
Market



Automotive  
Market



# Automotive Test Methods

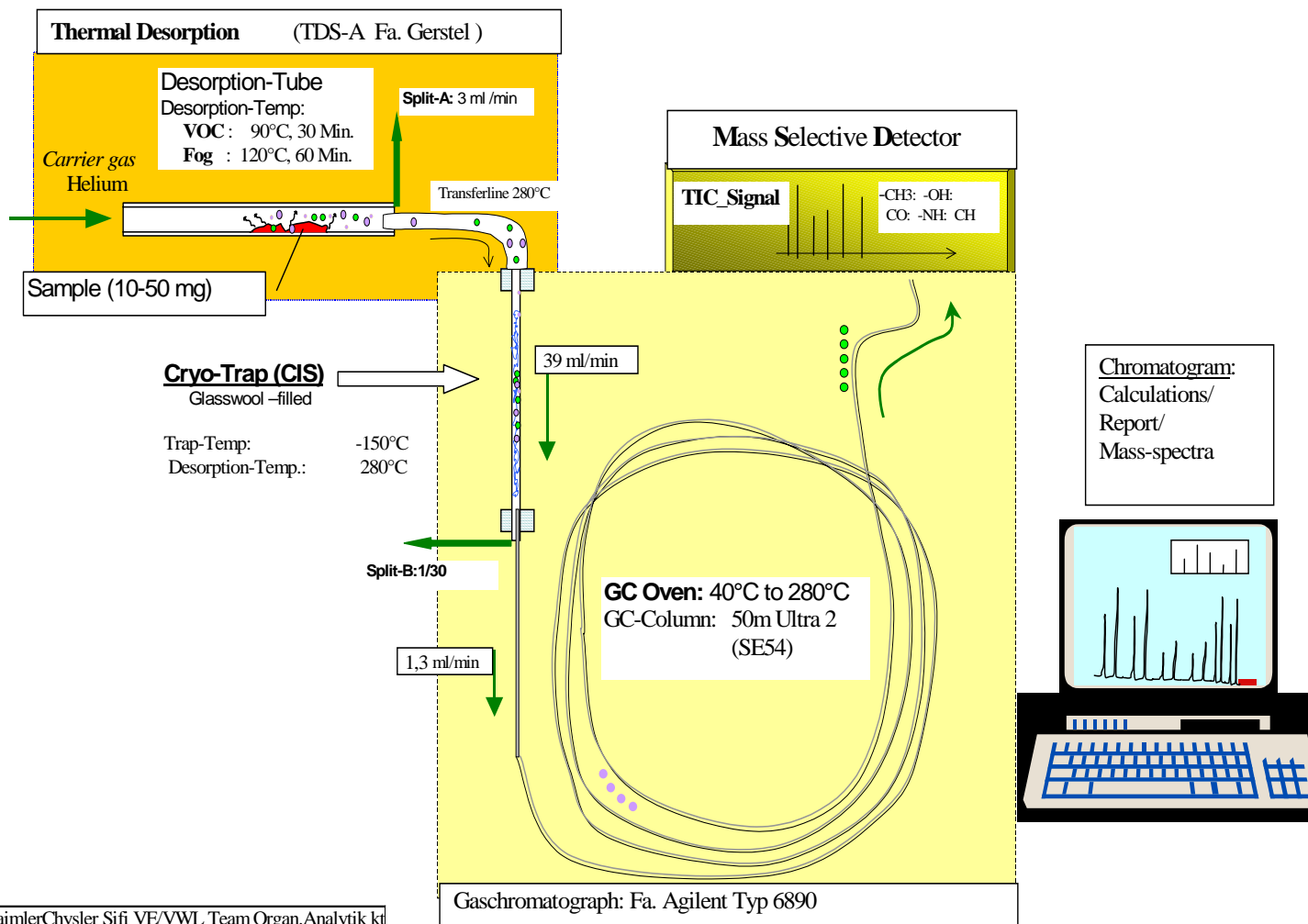


	test:	assessment:	conditions applied:	remarks:	results given in:
Fogging	DIN 75 201	gravimetric	100 °C /16 h	closed vessel	mg abs.
Staining	PV 3937	colour detection	100 °C /72 h	evaluation of PVC for amines	red colour
VOC	VW 55 031 (VDA 277)	GC	120 °C / 5h	Head Space Chromatography closed vessel	µg C / g foam
<b>VOC</b>	<b>DaimlerChrysler PB VWL 709 (VDA 278)</b>	<b>GC/MS</b>	<b>90°C / 30 min</b>	<b>thermodesorption atmosphere exchange</b>	<b>µg/g foam ( toluene equivalent )</b>
<b>FOG</b>	<b>DaimlerChrysler PB VWL 709 (VDA 278)</b>	<b>GC/MS</b>	<b>120°C / 1.5 h</b>	<b>thermodesorption atmosphere exchange</b>	<b>µg/g foam ( hexadecane equivalent )</b>
VOC	Toyota (TSM0510G)	GC/MS	65 °C / 13 min	thermodesorption atmosphere exchange	µg/g foam (reference substances)
VOC	Test Chamber (VDA 276)	GC/MS	65/80 °C / 2-4.5 h	atmosphere screening/ fogging	µg/m3 atmosphere ( toluene equivalent)
formaldehyde	Test Chamber (VDA 275)	photometer	60 °C / 3 h	emission into water	µg/g formaldehyde



# Daimler Chrysler PB VWL 709

## (Organic Emanation Analysis for Characterisation of non-Metal Material) (09/2002)



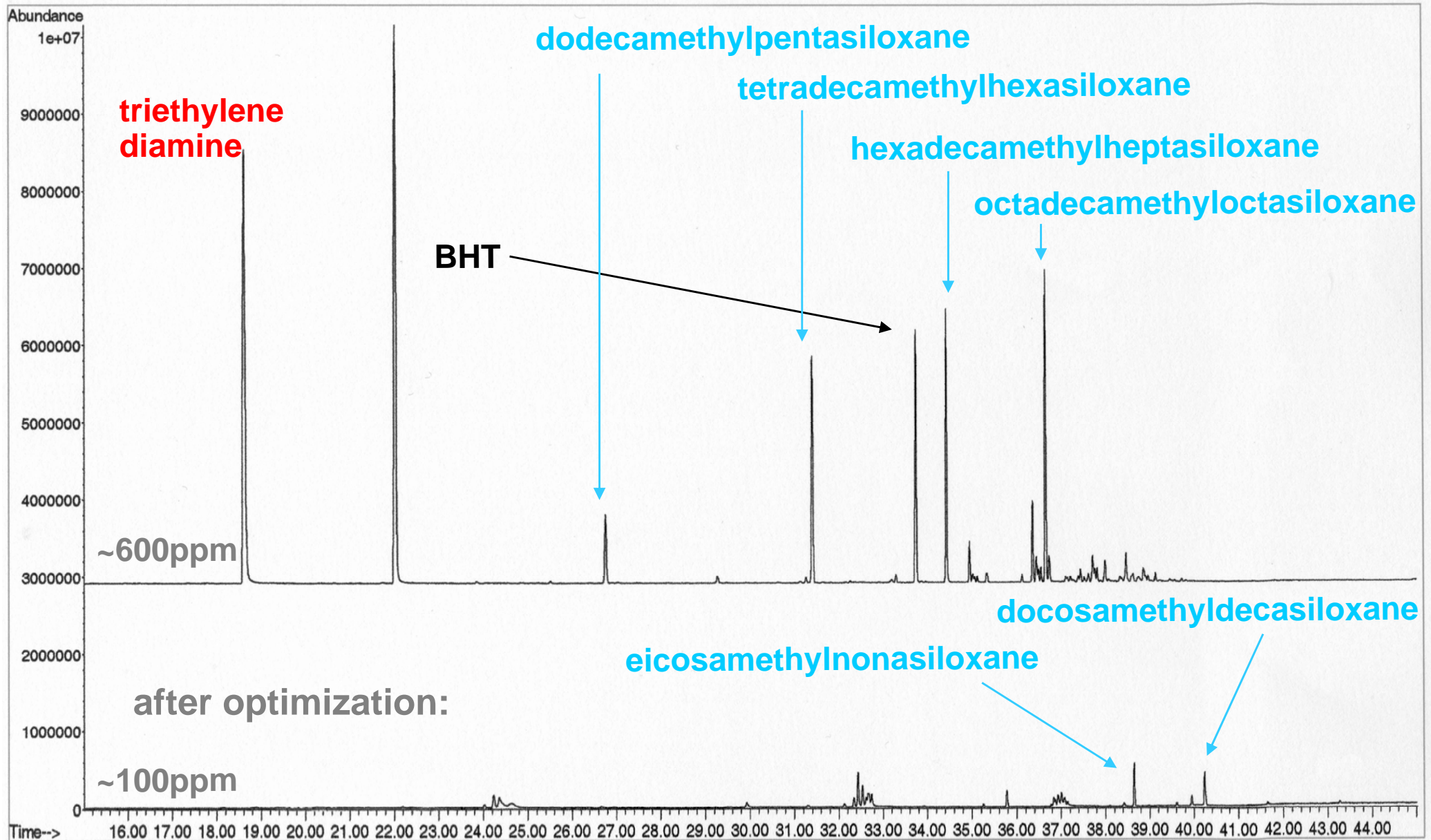


# Daimler Chrysler PB VWL 709 typical VOC- Chromatograms

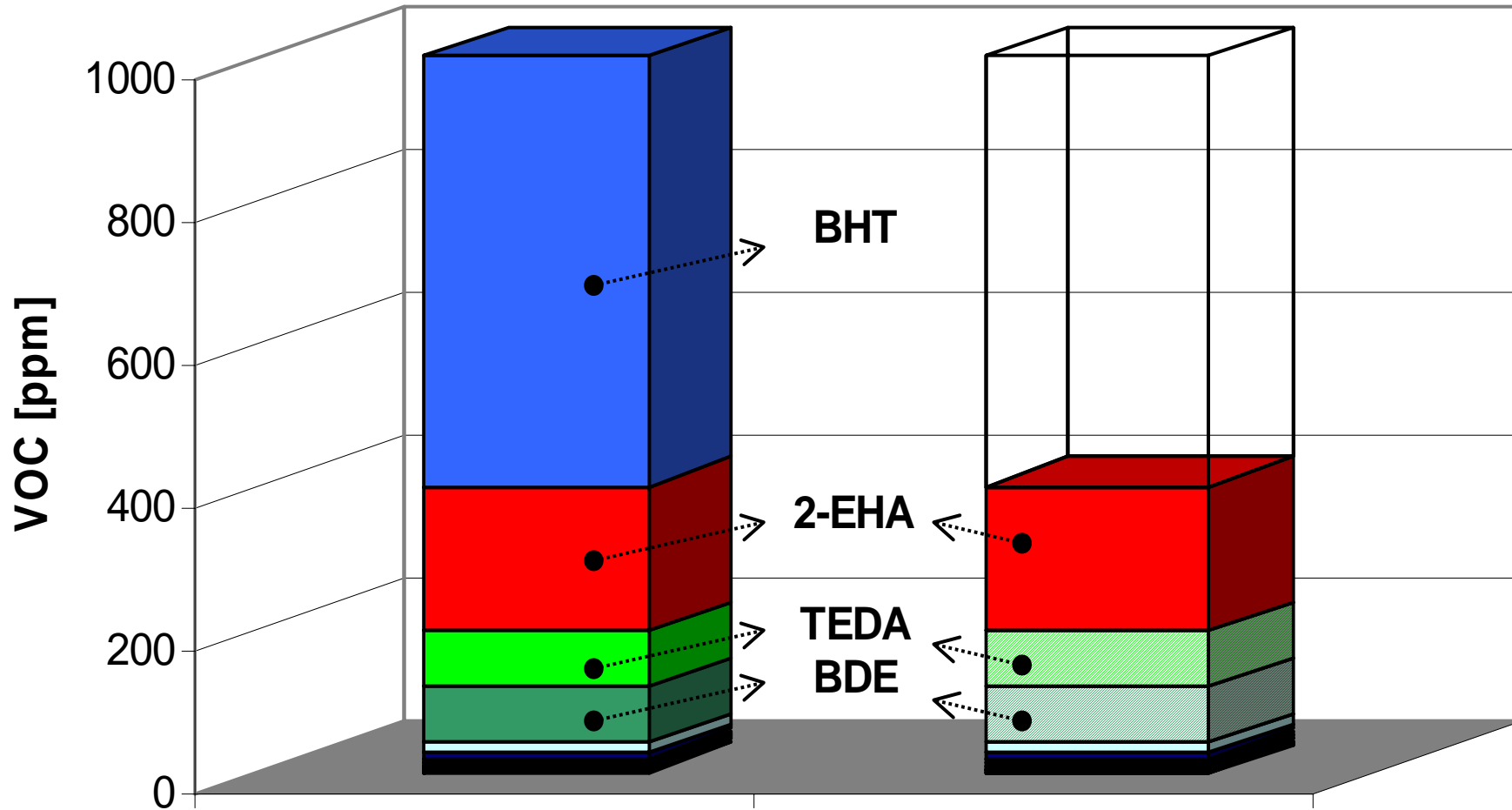
degussa.

creating essentials

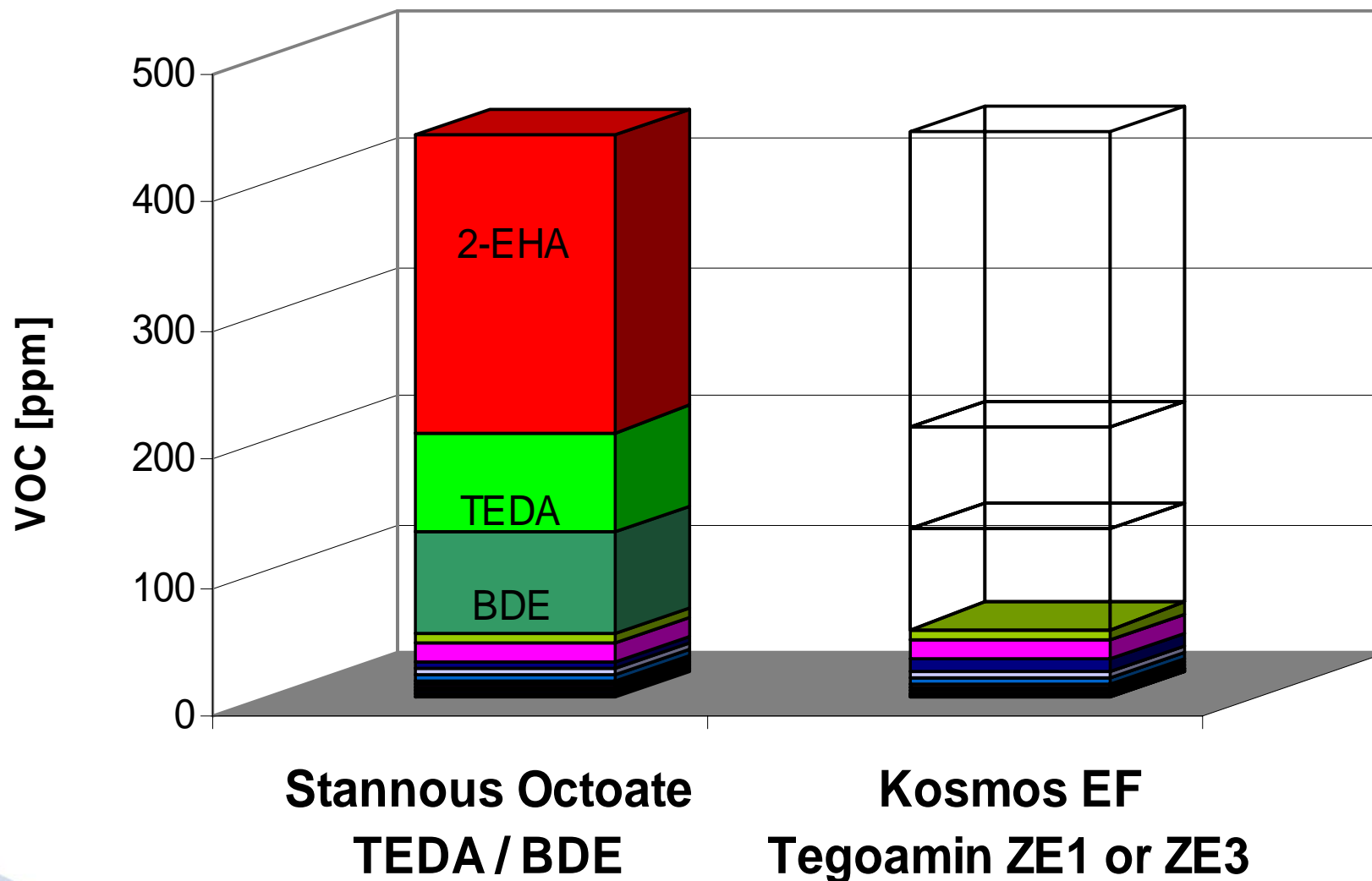
**bis-(dimethyamoethyl) ether**



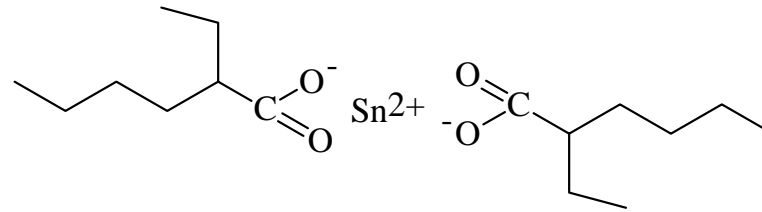
# Step-by-Step Reduction of VOC Level



# Further Reduction Using the Emanation Free Catalyst System



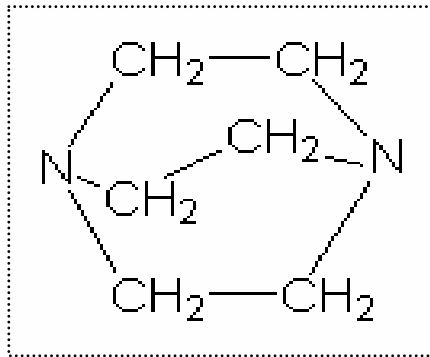
# Alternative, Low Emanation Alternatives for Established PU Catalysts



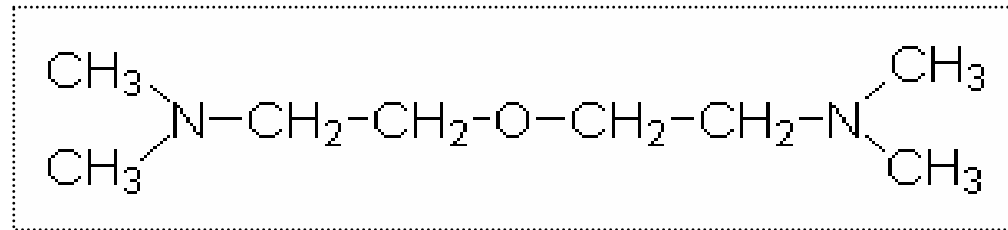
Tin octoate  
(Kosmos<sup>®</sup> 29)



Sn (II) ricinoleate (Kosmos<sup>®</sup> EF)



Triethylendiamin (TEDA)



Bis(dimethylaminoethyl)ether (BDE)



Reactice amins with higher molecular mass



# Emanations of PU Foam

**Comfort  
Market**



**Automotive  
Market**



# Why Talking About PU Foam Emanations ?

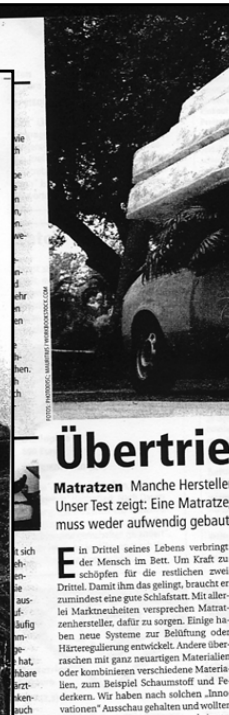
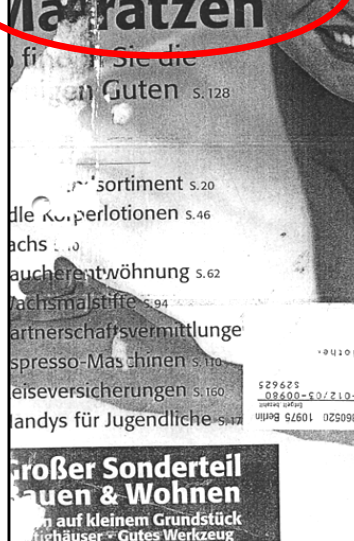
degussa.

creating essentials



Nightmare  
mattresses

Lying on toxic  
chemicals



→ It's a hot topic in European  
PU Foam Industry !

# Relevance for PU Foam Industry

Testing by Newspapers,  
Non-Governmental-  
Organisations, ...

STIFTUNG WARENTEST							
test	Matratzen	Schaumstoff					
	Gewichtung						
Gewicht in kg / Höhe in cm ca.		9,8/14	8,4/14,5	6,5/12,5	10,7/16	11,1/16,5	9,1/16
Mittlerer Preis (0,90 m x 2 m) in Euro ca.		159 <sup>9)</sup>	129	59	179 (Einkaufspreis)	149	159
Mittlerer Preis für Größe 1,40 x 2,00 m in Euro ca.		259	179	100		249	259
<b>test-QUALITÄTSURTEIL</b>	<b>100 %</b>	<b>GUT (2,2)</b>	<b>BEFRIEDIGEND (2,8)</b>	<b>AUSREICHEND (4,0)</b>	<b>AUSREICHEND (4,0)</b>	<b>AUSREICHEND (4,0)</b>	<b>MANGELHAFT (5,0)</b>
<b>LIEGEEIGENSCHAFTEN</b>	<b>35 %</b>	gut (2,4)	befriedigend (2,6)	gut (2,5)	gut (2,4)	gut (2,4)	befriedigend (2,7)
<b>HALTBARKEIT</b>	<b>20 %</b>	gut (1,9)	gut (1,8)	gut (1,7)	gut (1,9)	ausreichend (4,0) <sup>*) 11)</sup>	mangelhaft (5,0) <sup>*) 11)</sup>
<b>BEZUG</b>	<b>15 %</b>	sehr gut (1,4)	ausreichend (4,5)	ausreichend (4,5)	sehr gut (1,4)	befriedigend (2,6)	sehr gut (1,4)
Washbarkeit		++	- <sup>*)</sup>	- <sup>*)</sup>	++	⊖ <sup>7)</sup>	++
Beeinträchtigung durch Nässe		++	+	++	++	++	++
Verarbeitung		+	+	+	+	+	+
<b>GESUNDHEIT UND UMWELT</b>	<b>10 %</b>	gut (1,7)	gut (1,6)	ausreichend (4,5) <sup>*)</sup>	ausreichend (4,5)	sehr gut (1,5)	gut (1,6)
Raumluftbelastung <sup>2)</sup>		++	++	++	++	++	+
Geruchsbelästigung		+	+	++	⊖	++	+
Schadstofffreiheit <sup>3)</sup>		○	○	- <sup>*) 6)</sup>	- <sup>*) 5)</sup>	++	++
Entsorgung (Trennbarkeit der Materialien)		++	++	++	++	++	++

VOC chamber test emanations

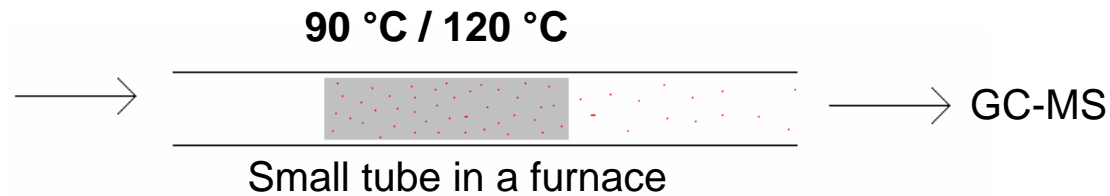


(test magazin, 3/2006)

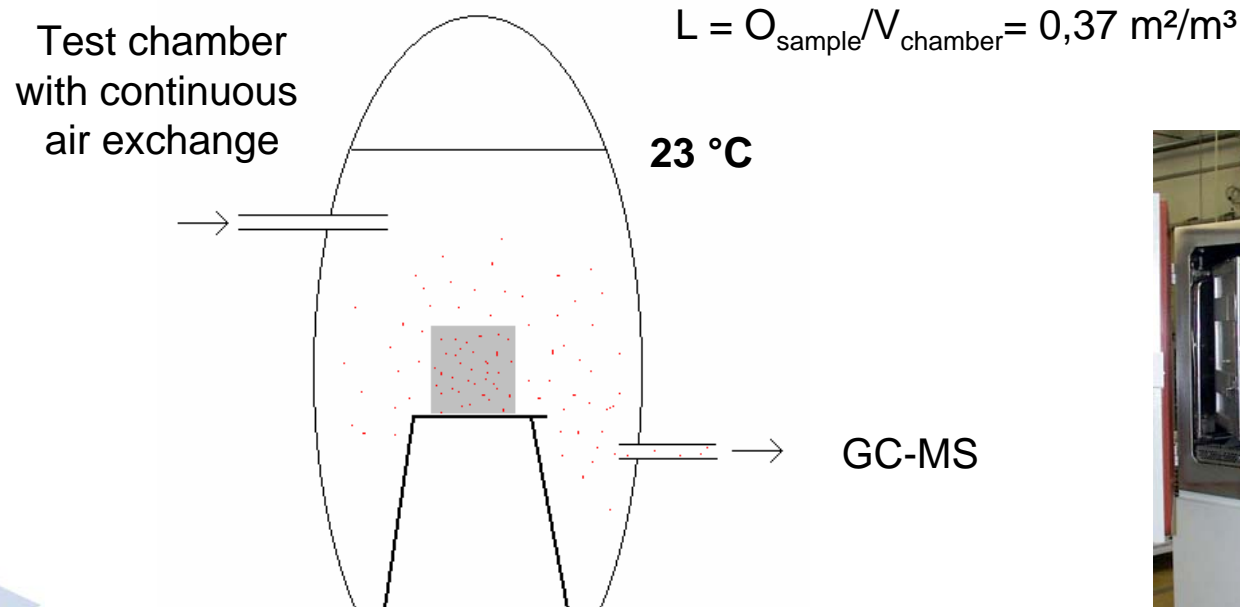
- VOC chamber tests are included in many consumer goods tests !
- Mattress market is significantly affected !



## 1. VOC-Test Automotive (Daimler Chrysler)









## 2. VOC-chamber test for furniture/fabrics (Mattress/Upholstered Furniture)



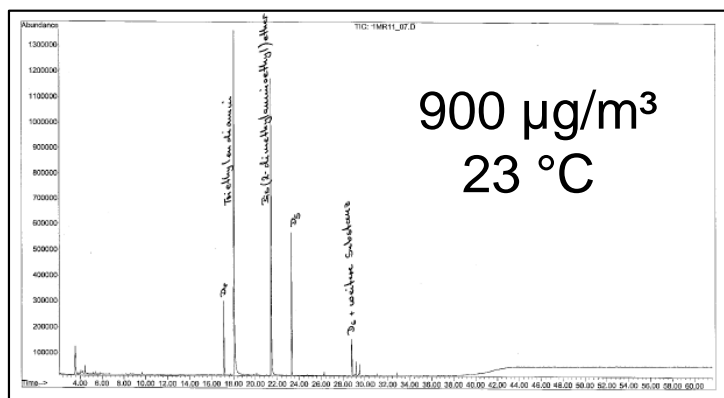


# ECO-Labels Related to VOC

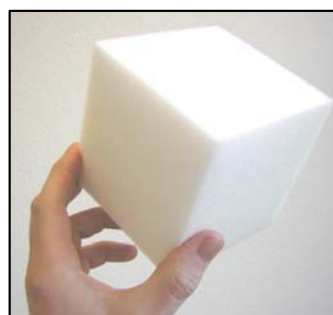
## Chamber Tests

Subject	Difficulty to pass	Criterion VOC chamber test
	easier	TVOC : < 500 µg/m <sup>3</sup> (7 days) + 300 µg/m <sup>3</sup> siloxanes
	medium	TVOC : < 500 µg/m <sup>3</sup> (7 days) and < 200 µg/m <sup>3</sup> (28 days)
	severe	TVOC < 500 µg/m <sup>3</sup> (24 – 30 hours)
	severe	TVOC < 500 µg/m <sup>3</sup> (16 hours)
	severe	TVOC : < 500 µg/m <sup>3</sup> (16 hours)
	most severe	TVOC < 300 µg/m <sup>3</sup>

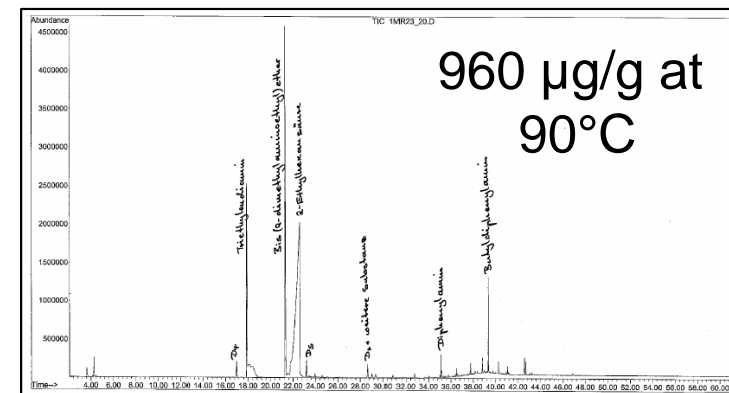
# Examination of a PUR Foam by Different VOC Emanation Tests



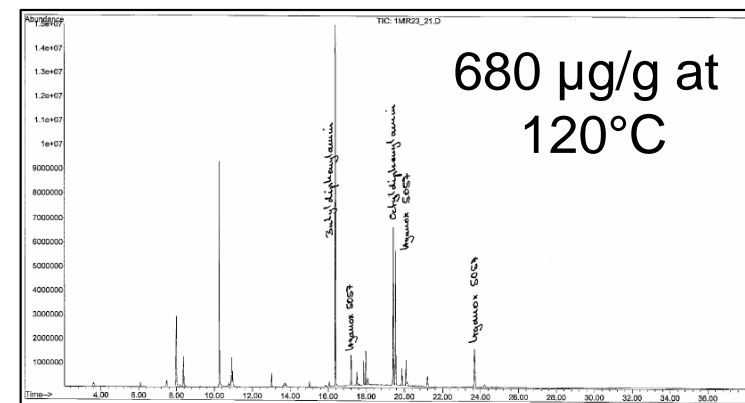
VOC chamber test  
room temperature



Standard  
PU Foam

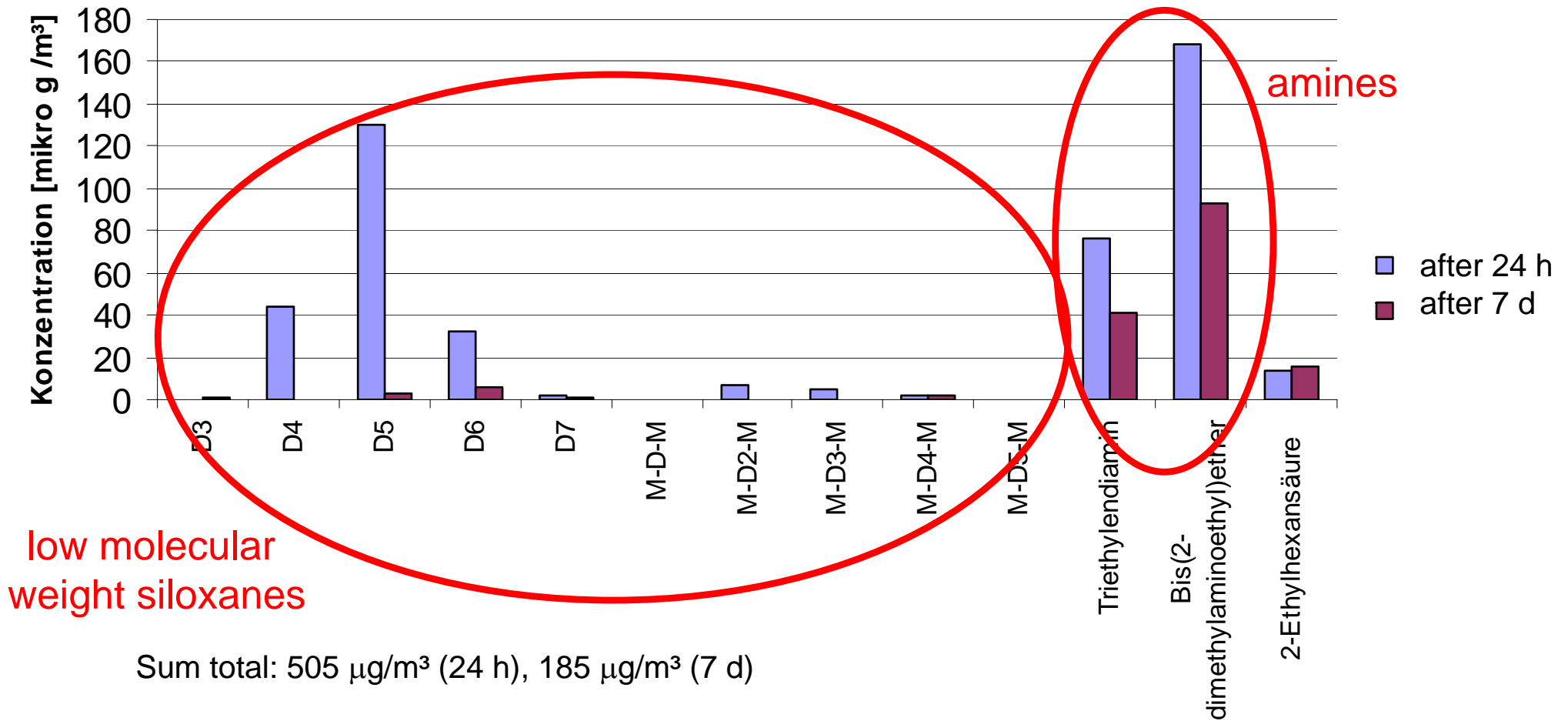


Daimler Chrysler  
VOC test  
elevated temperature



# Typical Results of VOC Test Chamber Measurements

Emissions from a standard flex foam (TEGOSTAB<sup>®</sup> B 8080) from production run

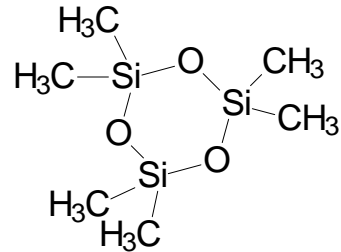


low molecular weight siloxanes

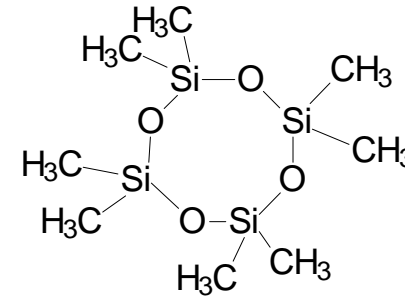
Sum total: 505 µg/m³ (24 h), 185 µg/m³ (7 d)



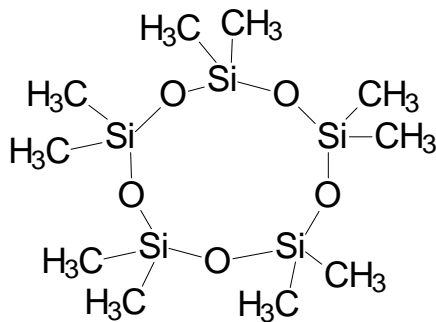
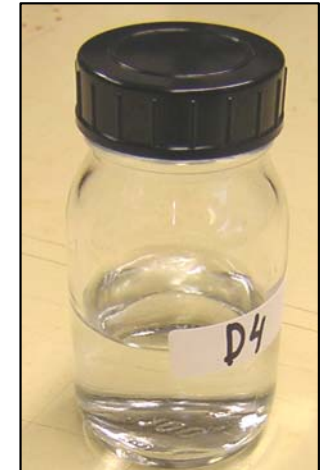
# Cyclic Low Molecular Weight Siloxanes



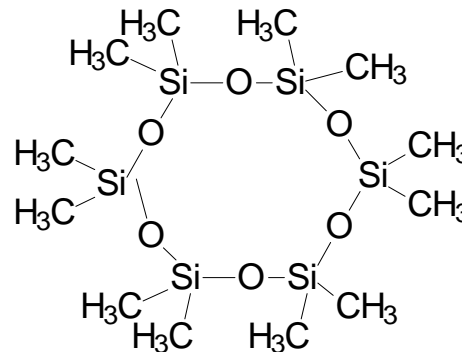
**D3**  
**134 °C**



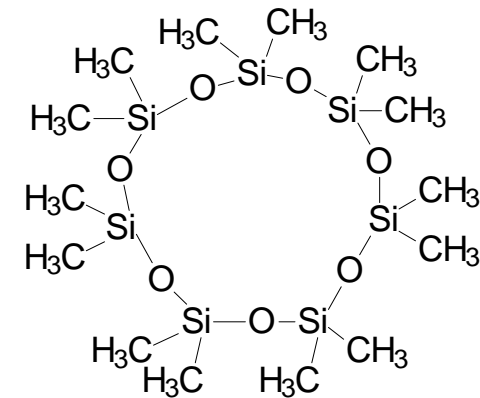
**D4**  
**175 °C**



**D5**  
**210 °C**



**D6**  
**245 °C**



**D7**  
**≈ 265 °C**

# Types of Goldschmidt Flexible Foam Stabilizers

**SiOC type:** BF 2370, B 4900, B 8002, B 8040, B 8050,  
< 0.1 % cyclic siloxanes  
B 8036, BF 2270, B 8014, B 8035, B 8021

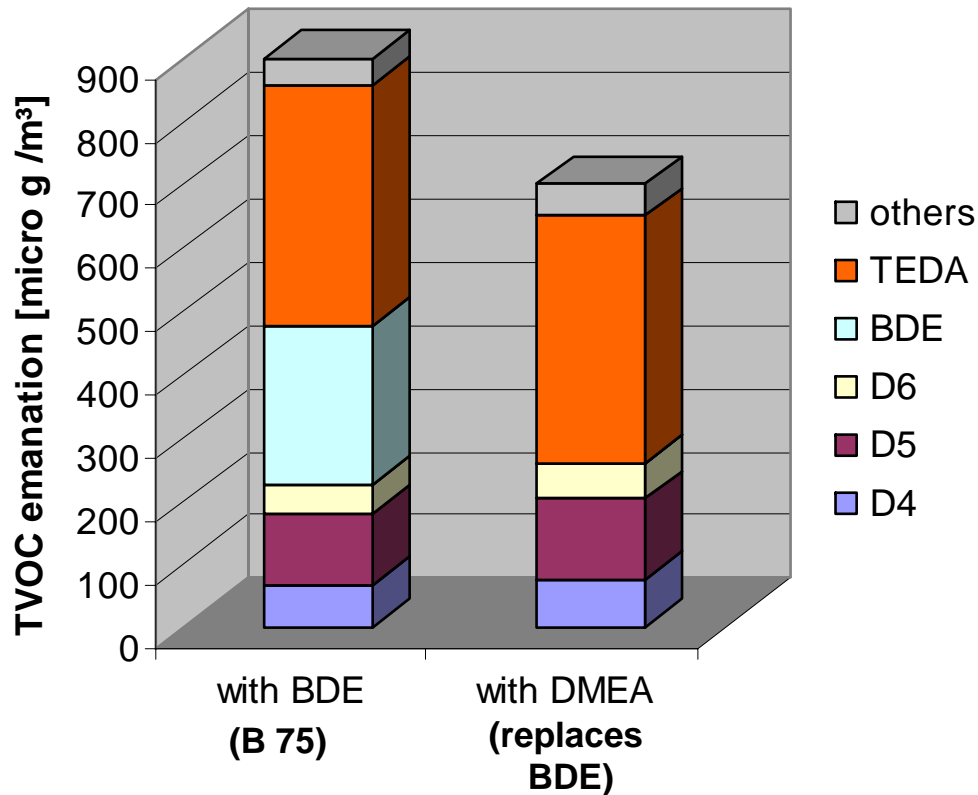
**SiC type:** B 8080, BF 2470, B 8110, B 8221, B 8228, B 8229,  
0.5 – 1.1% cyclic siloxanes  
B 8232, B 8240, B 8250, B 8255, B 8125, B 8233,  
B 8124, B 8238, B 8236, B 8032, B 8241



**Special low emission SiC stabilizers:** B 8239, B 8256,  
< 0.1 % cyclic siloxanes  
B 8285, B 8080D,  
EP-H-150

(status 11/2006)

# Emanation from Amines



## Boiling points of amines:

NMP [N-methylmorpholin]:	113 °C
DMP [dimethylpiperazin]:	132 °C
<b>DMEA* [dimethylethanol amine]:</b>	<b>135 °C</b>
NEP [N-ethylmorpholin]:	138 °C
DMCHA [dimethylcyclohexyl amine]:	163 °C
TEDA [triethylen diamine]:	174 °C
DMBA [dimethylbenzyl amine]:	182 °C
BDE [bis(dimethylaminoethyl)ether]:	189 °C
PMDETA [pentamethyldiethylene triamin]:	200 °C
<b>ZE 1* [reactive amine]:</b>	<b>212 °C</b>
<b>ZE 3* [reactive amine]:</b>	<b>255 °C</b>
<b>DEOA* [diethanol amine]:</b>	<b>270 °C</b>
DMDEE [N,N-dimorpholinodiethylether]:	309 °C
<b>TEOA* [triethanol amine]:</b>	<b>310 °C</b>

\* = reactive amine

➔ Flexible Foam with Index > 100:  
BDE > TEDA >> DMEA > ZE 3



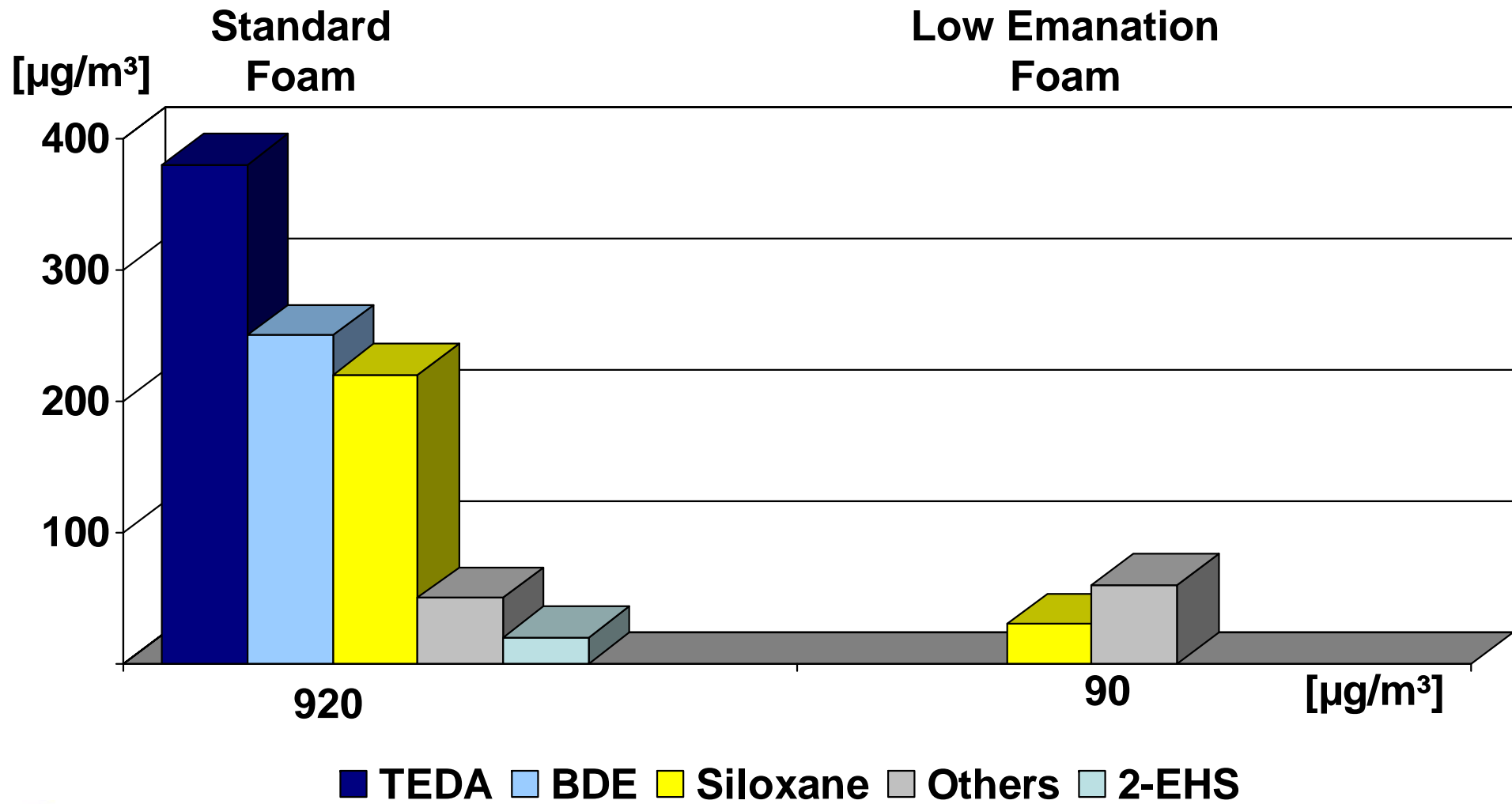
# VOC Chamber Test

## Low Emanation Flexible Foam

Standard Polyol OHN: 47	100	100
H <sub>2</sub> O	2.5	2.5
<b>TEGOSTAB<sup>®</sup> B 8080</b>	<b>0.8</b>	-
<b>TEGOSTAB<sup>®</sup> B 8080 D</b>	-	<b>0.8</b>
<b>TEGOAMIN<sup>®</sup> B 75</b>	<b>0.25</b>	-
<b>TEGOAMIN<sup>®</sup> ZE 3</b>	-	<b>0.15</b>
<b>KOSMOS<sup>®</sup> 29</b>	<b>0.15</b>	-
<b>KOSMOS<sup>®</sup> EF</b>	-	<b>0.42</b>
<b>T 80 &lt;108&gt;</b>	<b>34.0</b>	<b>34.0</b>



# VOC Chamber Test Low Emanation Foam





# Actual Test Results

## STIFTUNG WARENTEST

test Matratzen		Schaumstoff						
Gewichtung								
Gewicht in kg / Höhe in cm ca.		9,8/14	8,4/14,5	6,5/12,5	10,7/16	11,1/16,5	9,1/16	
Mittlerer Preis (0,90 m x 2 m) in Euro ca.		159 <sup>9)</sup>	129	59	179 (Einkaufspreis)	149	159	
Mittlerer Preis für Größe 1,40 x 2,00 m in Euro ca.		259	179	100		249	259	
<b>test-QUALITÄTSURTEIL</b>	<b>100 %</b>	<b>GUT (2,2)</b>	<b>BEFRIEDIGEND (2,8)</b>	<b>AUSREICHEND (4,0)</b>	<b>AUSREICHEND (4,0)</b>	<b>AUSREICHEND (4,0)</b>	<b>MANGELHAFT (5,0)</b>	
<b>LIEGEEIGENSCHAFTEN</b>	<b>35 %</b>	gut (2,4)	befriedigend (2,6)	gut (2,5)	gut (2,4)	gut (2,4)	befriedigend (2,7)	
<b>HALTBARKEIT</b>	<b>20 %</b>	gut (1,9)	gut (1,8)	gut (1,7)	gut (1,9)	ausreichend (4,0) <sup>*) 11)</sup>	mangelhaft (5,0) <sup>*) 11)</sup>	
<b>BEZUG</b>	<b>15 %</b>	sehr gut (1,4)	ausreichend (4,5)	ausreichend (4,5)	sehr gut (1,4)	befriedigend (2,6)	sehr gut (1,4)	
Washbarkeit		++	- <sup>*)</sup>	- <sup>*)</sup>	++	⊖ <sup>7)</sup>	++	
Beeinträchtigung durch Nässe		++	+	++	++	++	++	
Verarbeitung		+	+	+	+	+	+	
<b>GESUNDHEIT UND UMWELT</b>	<b>10 %</b>	gut (1,7)	gut (1,6)	ausreichend (4,5) <sup>*)</sup>	ausreichend (4,5)	sehr gut (1,5)	gut (1,6)	
Raumluftbelastung <sup>2)</sup>		++	++	++	++	++	+	
Geruchsbelastung		+	+	++	⊖	++	+	
Schadstofffreiheit <sup>3)</sup>		○	○	- <sup>*) 6)</sup>	- <sup>*) 5)</sup>	++	++	
Entsorgung (Trennbarkeit der Materialien)		++	++	++	++	++	++	

Rating is + or ++



(test magazin, 3/2006)

➔ PU Flexible Foam Industry has taken actions



# Conclusion Regarding PUR Foam

- Fogging Problem: - driven by technical / scientific considerations
  - many solutions have been developed during the last years
- VOC discussion in Comfort Market: - driven by external factors, not necessarily scientific
  - technical solutions for current labels / limit values are available
- Focus on toxicological & scientific evidence would be really helpful
- PUR foam producers & raw material suppliers were able to reduce emanations significantly
- Often is the usage of low-emanation raw materials also a question of commercial considerations. „Is the customer willing to pay for it ?“
- Low emanation PUR foam is able to compete in respect of VOC with many natural products

