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

Dr. Rüdiger Landers

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Raw Materials Required to Produce a Polyurethane Flexible Foam

Quantities being required to produce 1 m$^3$ of flexible foam with a density of 24 kg/m$^3$
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

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>VVOC</td>
<td>&lt; 0 ... 50-100°C</td>
</tr>
<tr>
<td>VOC</td>
<td>50 - 250 °C</td>
</tr>
<tr>
<td>SVOC</td>
<td>240 - 400 °C</td>
</tr>
<tr>
<td>POM</td>
<td>&gt;380°C</td>
</tr>
</tbody>
</table>

**WHO**

**EU definition:**
substances with a vapor pressure of > 0.01 kPa at 293.15 K

**Definitions:**
- **VVOC:** Very Volatile Organic Compounds
- **VOC:** Volatile Organic Compounds
- **SVOC:** Semi Volatile Organic Compounds
- **POM:** Particulate Organic Matter

Goldschmidt Polyurethane Additives
Emanations of PU Foam

Comfort Market

Automotive Market

Goldschmidt Polyurethane Additives
## Automotive Test Methods

<table>
<thead>
<tr>
<th>Test</th>
<th>Assessment</th>
<th>Conditions Applied</th>
<th>Remarks</th>
<th>Results Given In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fogging</td>
<td>DIN 75 201</td>
<td>Gravimetric</td>
<td>100 °C / 16 h closed vessel</td>
<td>mg abs.</td>
</tr>
<tr>
<td>Staining</td>
<td>PV 3937</td>
<td>Colour detection</td>
<td>100 °C / 72 h evaluation of PVC for amines</td>
<td>Red colour</td>
</tr>
<tr>
<td>VOC</td>
<td>VW 55 031 (VDA 277)</td>
<td>GC</td>
<td>120 °C / 5 h Head Space Chromatography closed vessel</td>
<td>µg C / g foam</td>
</tr>
<tr>
<td>VOC</td>
<td>DaimlerChrysler PB VWL 709 (VDA 278)</td>
<td>GC/MS</td>
<td>90 °C / 30 min thermodesorption atmosphere exchange</td>
<td>µg/g foam (toluene equivalent)</td>
</tr>
<tr>
<td>FOG</td>
<td>DaimlerChrysler PB VWL 709 (VDA 278)</td>
<td>GC/MS</td>
<td>120 °C / 1.5 h thermodesorption atmosphere exchange</td>
<td>µg/g foam (hexadecane equivalent)</td>
</tr>
<tr>
<td>VOC</td>
<td>Toyota (TSM0510G)</td>
<td>GC/MS</td>
<td>65 °C / 13 min thermodesorption atmosphere exchange</td>
<td>µg/g foam (reference substances)</td>
</tr>
<tr>
<td>VOC</td>
<td>Test Chamber (VDA 276)</td>
<td>GC/MS</td>
<td>65/80 °C / 2-4.5 h atmosphere screening/ fogging</td>
<td>µg/m³ atmosphere (toluene equivalent)</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Test Chamber (VDA 275)</td>
<td>Photometer</td>
<td>60 °C / 3 h emission into water</td>
<td>µg/g formaldehyde</td>
</tr>
</tbody>
</table>
Daimler Chrysler PB VWL 709
(Organic Emanation Analysis for Characterisation of non-Metal Material) (09/2002)
bis-(dimethyaminoethyl) ether

dodecamethylpentasiloxane
tetradecamethylhexasiloxane
hexadecamethylheptasiloxane
octadecamethyloctasiloxane
docosamethyldecasiloxane
eicosamethylnonasiloxane
Step-by-Step Reduction of VOC Level

- BHT
- 2-EHA
- TEDA
- BDE
Further Reduction Using the Emanation Free Catalyst System

Goldschmidt Polyurethane Additives
Alternative, Low Emanation Alternatives for Established PU Catalysts

Sn²⁺ C

O

- C

O

- C

O

Sn (II) ricinoleate (Kosmos® EF)

Triethylendiamin (TEDA)

Bis(dimethylaminoethyl)ether (BDE)

Reactice amins with higher molecular mass
Emanations of PU Foam

Comfort Market

Automotive Market

VOC  FOG

Goldschmidt Polyurethane Additives
Why Talking About PU Foam Emanations?

Nightmare mattresses

Lying on toxic chemicals

→ It’s a hot topic in European PU Foam Industry!
Testing by Newspapers, Non-Governmental Organisations, ...

VOC chamber test emanations

VOC chamber tests are included in many consumer goods tests!

Mattress market is significantly affected!
Emanation Tests

1. VOC-Test Automotive (Daimler Chrysler)

- 90 °C / 120 °C
- Small tube in a furnace
- GC-MS

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

- Test chamber with continuous air exchange
- L = O_{sample} / V_{chamber} = 0.37 m²/m³
- 23 °C
- GC-MS
<table>
<thead>
<tr>
<th>Subject</th>
<th>Difficulty to pass</th>
<th>Criterion VOC chamber test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>easier</td>
<td>TVOC : &lt; 500 µg/m³ (7 days) + 300 µg/m³ siloxanes</td>
</tr>
<tr>
<td></td>
<td>medium</td>
<td>TVOC : &lt; 500 µg/m³ (7 days) and &lt; 200 µg/m³ (28 days)</td>
</tr>
<tr>
<td></td>
<td>severe</td>
<td>TVOC &lt; 500 µg/m³ (24 – 30 hours)</td>
</tr>
<tr>
<td></td>
<td>severe</td>
<td>TVOC &lt; 500 µg/m³ (16 hours)</td>
</tr>
<tr>
<td></td>
<td>severe</td>
<td>TVOC : &lt; 500 µg/m³ (16 hours)</td>
</tr>
<tr>
<td></td>
<td>most severe</td>
<td>TVOC &lt; 300 µg/m³</td>
</tr>
</tbody>
</table>
Examination of a PUR Foam by Different VOC Emanation Tests

VOC chamber test room temperature

Standard PU Foam

Daimler Chrysler VOC test elevated temperature

900 µg/m³ at 23 °C

960 µg/g at 90°C

680 µg/g at 120°C
Typical Results of VOC Test
Chamber Measurements

Emissions from a standard flex foam (TEGOSTAB® B 8080) from production run

Konzentration [mikro g/m³]

- D3
- D4
- D5
- D6
- D7
- M-D-M
- M-D2-M
- M-D3-M
- M-D4-M
- M-D5-M

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

low molecular weight siloxanes

amines

after 24 h
after 7 d

Goldschmidt Polyurethane Additives
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, B 8036, BF 2270, B 8014, B 8035, B 8021

**SiC type:** B 8080, BF 2470, B 8110, B 8221, B 8228, B 8229, 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, 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
- DMEA* [dimethylethanol amine]: 135 °C
- 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
- ZE 1* [reactive amine]: 212 °C
- ZE 3* [reactive amine]: 255 °C
- DEOA* [diethanol amine]: 270 °C
- DMDEE [N,N-dimorpholinodiethylether]: 309 °C
- TEOA* [triethanol amine]: 310 °C

* = reactive amine

Flexible Foam with Index > 100:
BDE > TEDA >> DMEA > ZE 3
## VOC Chamber Test
### Low Emanation Flexible Foam

<table>
<thead>
<tr>
<th>Component</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Polyol OHN: 47</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>TEGOSTAB® B 8080</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>TEGOSTAB® B 8080 D</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>TEGOAMIN® B 75</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>TEGOAMIN® ZE 3</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>KOSMOS® 29</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>KOSMOS® EF</td>
<td>-</td>
<td>0.42</td>
</tr>
<tr>
<td>T 80 &lt;108&gt;</td>
<td>34.0</td>
<td>34.0</td>
</tr>
</tbody>
</table>
VOC Chamber Test
Low Emanation Foam

[Graph showing emissions from Standard and Low Emanation Foam]

- TEDA
- BDE
- Siloxane
- Others
- 2-EHS

Goldschmidt Polyurethane Additives
### Actual Test Results

**Stiftung Warentest**

<table>
<thead>
<tr>
<th>Gewicht in kg / Höhe in cm</th>
<th>9,8/14</th>
<th>8,4/14,5</th>
<th>6,5/12,5</th>
<th>10,7/16</th>
<th>11,1/16,5</th>
<th>9,1/16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mittlerer Preis (0,90 m x 2 m) in Euro</td>
<td>159</td>
<td>129</td>
<td>59</td>
<td>179 (Einkaufspreis)</td>
<td>149</td>
<td>159</td>
</tr>
<tr>
<td>Mittlerer Preis für Größe 1,40 x 2,00 m in Euro</td>
<td>100</td>
<td>100</td>
<td>249</td>
<td>249</td>
<td>259</td>
<td>259</td>
</tr>
</tbody>
</table>

**Rating is + or ++**

**PU Flexible Foam Industry has taken actions**

(test magazin, 3/2006)
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-emantion 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