Low emanation amine catalyst for DMF-free PU foams

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1. Emanation of PU Foam

2. Experimental Results
   - Conventional Slabstock Foam -

3. Experimental Results
   - High Resilience Slabstock Foam-

4. Summary

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Application fields where low emanation is mandatory

Automotive Industry

	Test	Assessment	Conditions applied	Remarks	Results given in
Fogging	DIN 75 201	Gravimetric	100°C/16h	Closed vessel	mg abs.
Staining	PV3937	Colour Detection	100°C/72h	Evaluation of PVC for amines	Red colour
VOC	VW55 031 (VDA 277)	GC	120°C/5h	Head Space Chromatography closed vessel	µg C/g foam
VOC	**DaimlerChrysler PB VWL709 (VDA 278)**	**GC/MS**	**90°C/30min**	**Thermodesorption atmosphere exchange**	**µg/g foam (toluene equivalent) limit: 100 ppm total VOC**
FOG	**DaimlerChrysler PB VWL709 (VDA 278)**	**GC/MS**	**120°C/1.5 h**	**Thermodesorption atmosphere exchange**	**µg/g foam (hexadecane equivalent)**
VOC	Toyota (TSM0510G)	GC/MS	65°C/13min	Thermodesorption atmosphere exchange	µg/g foam (reference substances)
VOC	Test Chamber (VDA 276)	GC/MS	65/80°C/2-4,5h	Atmosphere screening / fogging	µg/m^3 atmosphere (toluene equivalent)
Formalde-hyde	Test Chamber (VDA 275)	Photometer	60°C/3h	Emission into water	µg/g formaldehyde

Application fields where low emanation is mandatory

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Bedding Industry

Label	Criterion VOC chamber test – Total Emanation
IKEA	TVOC < 1200 µg/m³ (2d), < 600 µg/m³ (28d)
schadstoff-geprüft LGA	TVOC < 500 µg/m³ (7 days) + 150 µg/m³ siloxanes
Der Blaue Engel	TVOC < 500 µg/m³ (7 days) and < 200 µg/m³ (28 days)
Eco-label	TVOC < 500 µg/m³ (24 – 30 hours)
Textiles Vertrauen – Schadstoffgeprüfte Textilien nach Öko-Tex Standard 100	TVOC < 500 µg/m³ (16 hours)
CertiPUR	TVOC < 500 µg/m³ (16 hours)
CertiPUR-US	TVOC < 500 µg/m³ + 300 µg/m³ for siloxanes (16 hours)

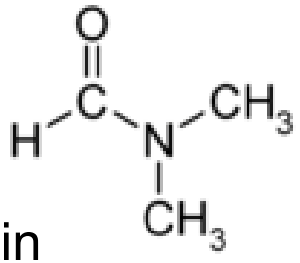
Application fields where low emanation is mandatory

Bedding Industry

Criterion VOC chamber test for CMT Materials

Category	After 3 days	After 7 days
K1	< 2 µg/m³	< 1µg/m³
K2	< 5 µg/m³	< 1 µg/m³
M1, M2, R1, R2	Each < 10 µg/m³	Each < 2µg/m³

Toxicity of Dimethylformamide (DMF)



R 61: Teratogenic nature

R 20,21: Harmful by inhalation and in contact with skin

R 36: Irritating to eyes

Toxic

DMF emanation of PU foams

What is the origin of DMF in flexible PU foam?

Assumption:

DMF originate as a contaminant of certain amine catalysts in particular those containing the ***dimethylamino-moeity.***

⇒ **Analytic studies of several amine catalysts**

DMF emanation of PU foams

Content of dimethylformamide (DMF) in different amine catalysts

Amine Catalyst	DMF content in ppm*)
70% Bis(dimethylaminoethyl)ether (BDE) in DPG	150
Pentamethyldiethylenetriamine (PMDETA)	240
Dimethylethanolamine (DMEA)	95
TEGOAMIN® ZE3	150
Diethylethanolamine	not detectable
Triethanolamine	not detectable

**) The content of DMF in amines was determined by an in-house developed analytical method based on GLC/MSD by using deuterated DMF as internal standard.*

Low emanation amine catalyst for DMF-free PU foams

DMF emanation of flexible slabstock foams for different catalysts

100	pphp	Polyol, VORANOL® CP 3322 (Dow Chemical)
2,5	pphp	Water
0,8	pphp	TEGOSTAB® BF2470
0,18	pphp	KOSMOS ® 29
34,0	pphp	Isocyanat (TDI T80), <108>
varied		catalyst

Catalyst	Rise Time	VOC Emanation according to the chamber test at room temperature (24h)		
	[s]	DMF [µg/m³]	Amines [µg/m³] (as Toluene Equivalent)	Total VOC [µg/m³] (as Toluene Equivalent)
0.10 p TEGOAMIN® BDE	**174**	**4**	**198**	**270**
0.10 p TEGOAMIN® ZE3	**206**	**3**	**<1*)**	**50**

*) below the detection limit

Novel amine catalyst for low emanation and DMF-free flexible polyurethane foam

Amine catalyst requirements

- Low emanation
- DMF-free PU Foams
- No negative influence on physical properties such as hardness, elongation, compression sets etc.
- No negative impact on critical aging tests (hydrolysis, thermal aging)
- No delay of the postcuring process
- Acceptable catalytic activity

⇨ **Novel Amine Catalyst TEGOAMIN® ZE 4**

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Catalyst	Rise Time	VOC Emanation according to the chamber test at room temperature (24h)		
	[s]	DMF [µg/m³]	Amines [µg/m³] (as Toluene Equivalent)	Total VOC [µg/m³] (as Toluene Equivalent)
0.10 p TEGOAMIN® BDE	**174**	**4**	**198**	**270**
0.10 p TEGOAMIN® ZE3	**206**	**3**	**<1*)**	**50**
0.30 p TEGOAMIN® ZE4	**212**	**<1*)**	**<1*)**	**50**

*) below the detection limit

Low emanation amine catalyst for DMF- free PU foams

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Foam physical properties for different amine catalysts in conventional flexible slabstock foams – 4 parts of water formulation

100 pphp	Polyol, VORANOL® CP 3322
4.0 pphp	**Water**
1.0 pphp	TEGOSTAB®BF2370
0.20 pphp	KOSMOS®29
50.6 pphp	Isocyanat (TDI T80), **index 110**
varied	**amine catalyst**

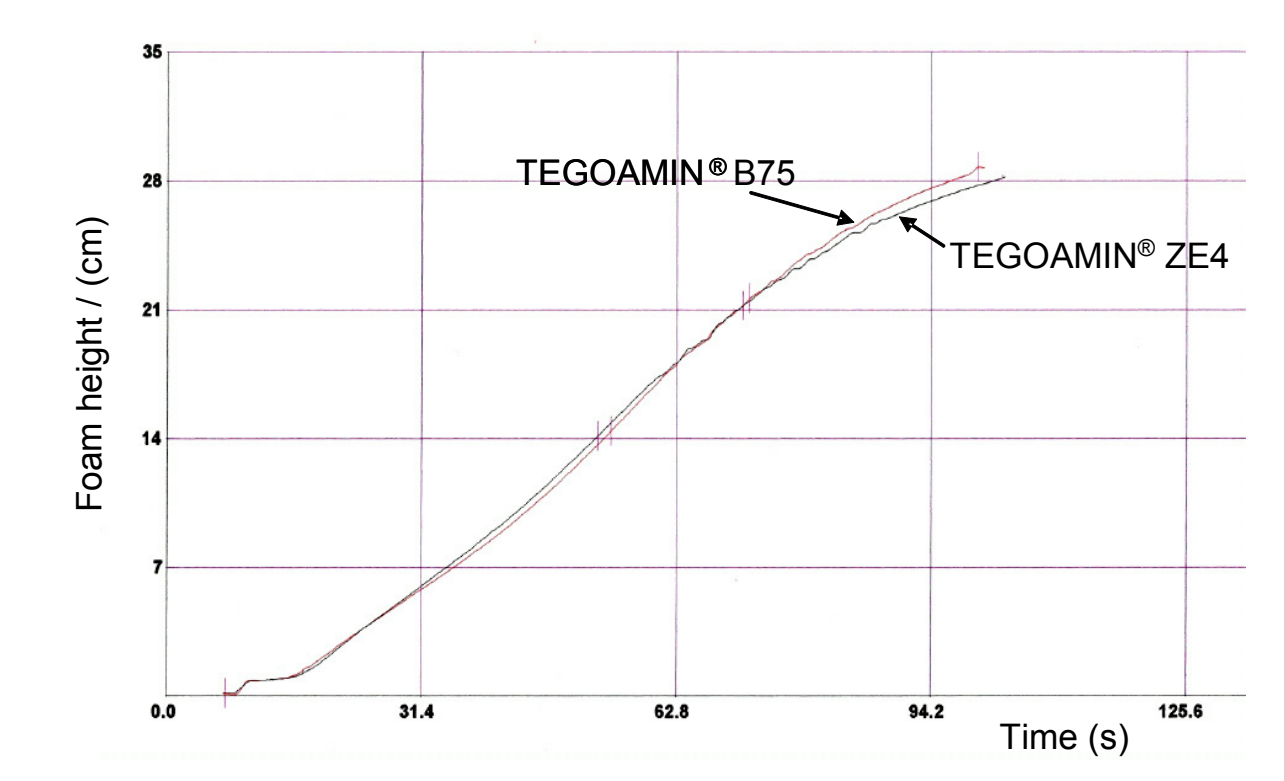
Amine	Rise time [s]	Foam height [cm]	Foam settling [cm]	Density [kg/m³] *(pcf)*	Air permea-bility*	CLD hardness 40% comp. [kPa]	Tensile strength [kPa]	Elongation [%]	Comp. set 22 h, 70°C, 90% comp. [%]	Ball Rebound [%]
0.075 pphp TEGOAMIN® B75	**100**	**28.7**	**0.3**	**25.4** *(1.6)*	**8**	**3.3**	**125**	**225**	**4**	**39**
0.25 pphp TEGOAMIN® ZE4	**103**	**28.1**	**0.3**	**25.3** *(1.6)*	**9**	**3.5**	**165**	**315**	**4**	**37**

**Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the given value, the more open celled is the foam structure.*

Low emanation amine catalyst for DMF- free PU foams

Rise profile for different amine catalysts in conventional flexible slabstock foams – 4 parts of water formulation

100 pphp	Polyol, VORANOL® CP 3322
4.0 pphp	**Water**
1.0 pphp	TEGOSTAB®BF2370
0.20 pphp	KOSMOS®29
50.6 pphp	Isocyanat (TDI T80), **index 110**
varied	**amine catalyst**



Low emanation amine catalyst for DMF- free PU foams

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Influence of the amine catalyst on the **HYDROLYSIS RESISTANCE** (5h, 120°C, 100% humidity, 3 cycles) of **flexible slabstock foams**

100 pphp	Polyol, VORANOL® CP 3322
2.0 pphp	Water
0.8 pphp	TEGOSTAB® B8002
0.14 pphp	KOSMOS® 29
29.3 pphp	Isocyanat (TDI T80), index 110
varied	**amine catalyst**

Amine Catalysts & Use Level	Rise time [s]	Density [kg/m³] *(pcf)*	Air permea-bility*	CLD hardness 40% comp. [kPa]		Comp. set 22 h, 70°C, 50% comp. [%]		Tensile strength [kPa]		Elongation [%]	
				Initial	After aging	Initial	After aging	Initial	After aging	Initial	After aging
0.10 pphp TEGOAMIN® B75	261	45.9 *(2.9)*	10	4.6	2.5	3	3	100	120	230	310
0.25 pphp TEGOAMIN® ZE4	270	46.0 *(2.9)*	15	4.7	3.1	4	6	110	155	220	345

**Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the given value, the more open celled is the foam structure.*

Low emanation amine catalyst for DMF- free PU foams

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Influence of the amine catalyst on the **THERMAL RESISTANCE** (2h at 180°C) of **flexible slabstock foams**

100 pphp	Polyol, VORANOL® CP 3322
4.0 pphp	Water
1.0 pphp	TEGOSTAB® BF 2370
0.2 pphp	KOSMOS® 29
50.6 pphp	Isocyanat (TDI T80), index 110
varied	**amine catalyst**

Amine Catalysts & Use Level	Rise Time [s]	Density [kg/m³] *(pcf)*	Air Permea-bility[1]	CLD Hardness 40% Deflection [kPa]		Compression Set 22 h, 70°C, 90% Compression [%]		Tensile Strength [kPa]		Elongation [%]		Ball Rebound [%]	
				Initial	After Aging	Initial	After Aging	Initial	After Aging	Initial	After Aging	Initial	After Aging
0.15 p TEGOAMIN® 33	108	24.9 *(1.6)*	14	3.1	2.0	8	13	135	125	360	370	35	36
0.08 p TEGOAMIN® B75	113	25.0 *(1.6)*	19	3.1	2.8	4	6	145	150	365	365	35	35
0.25 p TEGOAMIN® ZE4	106	24.8 *(1.6)*	19	2.9	2.4	4	6	155	125	370	360	35	34

**Air permeability has been measured as back pressure (mm water column) which is obtained by an air stream passing the foam with constant speed. The lower the given value, the more open celled is the foam structure.*

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   - Conventional Slabstock Foam -

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Comparison of foam physical properties for different amine catalysts in HR slabstock foams

Before and after **HUMID AGING** (3 cycles at 120°C and 100% relative humidity for 5 h per cycle)
2.5 parts of water formulation

60	pphp	VORALUX® HF 505
40	pphp	VORALUX® HL 400
1.0	pphp	VORANOL® CP1421
2.5	**pphp**	**Water total**
0.5	pphp	DEOA
0.4	pphp	TEGOSTAB® B 8716 LF2
0.12	pphp	KOSMOS® 29
31.25	pphp	Isocyanat (TDI T80), index 103

Amine Catalyst & Use Level	Cream Time [s]	Rise Time [s]	Blow Off	Core Density [kg/m³] *(pcf)*	CLD Hardness 40% Deflection [kPa]		Tensile Strength [kPa]		Elongation [%]		Ball Rebound [%]	
					Initial	After Aging	Initial	After Aging	Initial	After Aging	Initial	After Aging
0.10 p TEGOAMIN® 33 0.03 p TEGOAMIN® BDE	5	148	1	41.6 *(2.6)*	5.2	3.7	150	140	110	150	50	47
0.48 p TEGOAMIN® ZE1	5	146	0-1	38.0 *(2.4)*	3.6	2.3	125	110	110	165	55	47
0.40 p TEGOAMIN® ZE4	5	148	1	42.0 *(2.6)*	5.5	3.7	150	130	115	155	50	46

Comparison of foam physical properties for different amine catalysts in HR slabstock foams

Before and after **THERMAL AGING** (140°C for 7 days) – **2.5 parts of water formulation**

60	pphp	VORALUX® HF 505
40	pphp	VORALUX® HL 400
1.0	pphp	VORANOL® CP1421
2.5	**pphp**	**Water total**
0.5	pphp	DEOA
0.4	pphp	TEGOSTAB® B 8716 LF2
0.12	pphp	KOSMOS® 29
31.25	pphp	Isocyanat (TDI T80), index 103

Amine Catalyst & Use Level	Cream Time [s]	Rise Time [s]	Blow Off	Core Density [kg/m³] *(pcf)*	CLD Hardness 40% Deflection [kPa]		Tensile Strength [kPa]		Elongation [%]		Ball Rebound [%]	
					Initial	After Aging	Initial	After Aging	Initial	After Aging	Initial	After Aging
0.10 p TEGOAMIN® 33 0.03 p TEGOAMIN® BDE	5	148	1	41.6 *(2.6)*	5.3	4.1	150	140	110	110	50	50
0.48 p TEGOAMIN® ZE1	5	146	0-1	38.0 *(2.4)*	3.7	2.8	125	120	110	130	55	46
0.40 p TEGOAMIN® ZE4	5	148	1	42.0 *(2.6)*	5.6	4.2	150	145	115	120	50	50

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Novel amine catalyst for low emanation flexible polyurethane foam

Summary

- Novel amine catalyst which allows for the production of low emanation and DMF-free flexible foams (conventional as well as HR slabstock foam)
- Similar physical properties to foams made with conventional amine catalysts like e.g. TEGOAMIN® 33 and TEGOAMIN® B 75
- TEGOAMIN® ZE4 shows no evidence of promoting reverse catalysis
  - ⇨ maintaining good foam quality under humid and thermal aging conditions
- TEGOAMIN® ZE4 provides improved skin curing over other typical reactive amines


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