

Zero Emission Polyurethane Catalyst

— Reactive Strong Gelling Amine —

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TOSOH Corporation has developed a novel reactive amine catalyst (RZETA) for Polyurethane (PU) foam production, which contains a TEDA molecule with a reactive site toward isocyanate. Various kinds of non-fugitive amine catalysts, including RZETA, were evaluated in flexible slabstock as well as HR-Molded foam systems. In both systems, RZETA exhibited higher catalytic activity and better physical foam properties, including durability performance, while lowering the VOC emissions of the system.

This paper will describe the performance of TOSOH's newly developed catalyst, and also propose a new catalyst package for the reduction of VOC using non-fugitive catalysts.

1. Introduction

Polyurethane (PU) has various commercial uses, including but not limited to automotive interior parts, residential upholstered furniture and bedding, shoe sole and rigid spray. Within certain applications, reducing the Volatile Organic Compound (VOC) content in PU systems continues to be an important factor in improving product performance and user safety. The choice of PU catalysts plays a role in the VOC issue [1, 2].

Tertiary amines have been used to catalyze the reaction of isocyanates with water (blowing reaction) and polyols (gelling reaction). The amines control the relative reaction rates of the blowing and gelling reaction depending on the specific amine catalyst structure or other factors such as steric and electronic effects. The ability of a catalyst to promote side reactions, such as allophanate, biuret or isocyanurate, is

also important as these reactions affect the final physical properties of the foams.

Generally, Triethylenediamine (TEDA) and Bis (dimethylaminoethyl) ether (BDMAEE) are used for flexible polyurethane foam to activate the gelling and blowing reaction, respectively. However, these are fugitive compounds with noticeable volatility; therefore the contribution of these catalysts to VOC emissions and associated odor is significant.

In order to overcome the emissions problem, a wide variety of non-fugitive amines containing hydroxyl or reactive amino functional groups as a reaction site with isocyanates have been proposed and evaluated [3-13]. Incorporation of the amine into the polymer network has shown improvement in the areas of worker exposure, air quality, fogging and odor problems in the plant. However, a fully adequate replacement catalyst system has yet been found.


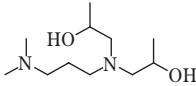

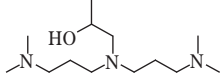
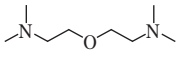
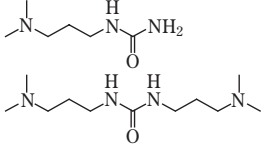
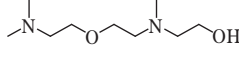
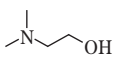
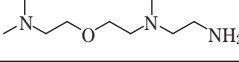
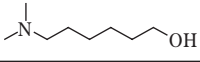
The catalytic activity of these non-fugitive catalysts is lower than conventional catalysts. Additionally, the foam properties, curing function and durability performance,

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Table 1 Evaluated Tertiary Amine Catalysts

Abbreviation	Chemical Structure	Abbreviation	Chemical Structure
TEDA-L33	 : 33% DPG : 67%	Catalyst-C	
RZETA	 : 33% DPG : 67%	Catalyst-D	
TOYOCAT-ET	 : 70% DPG : 30%	Catalyst-E	 : 75% (as Mixture)
TOYOCAT-RX24	Special Reactive Amine	Catalyst-F	
Catalyst-A		Catalyst-G	
Catalyst-B			

when utilizing these catalysts tend to worsen due to the lack of gelling activity. Fundamentally, reactive amine catalysts are incorporated into the polymer network and lose their catalytic activity during the latter stages of the foaming process. Typical reactive amine catalysts can also work as chain terminators, thus hindering the growth of the polymer structure. This can result in inferior foam properties.

Since most reactive catalysts available today demonstrate blowing or balanced catalytic activity, the need for a strong gelling reactive catalyst remains present in the marketplace. For this reason, amine catalysts that have high gelling activity similar to TEDA with reduced emissions are a consistent demand from the market.

Previously, Tosoh has reported the gelling properties and potential of reactive-TEDA by comparison of various kinds of reactive amines [14-17]. It was proved that the advantages of reactive-TEDA over other reactive amine catalysts for flexible foam applications thanks to its comparably strong gelling activity similar to that of TEDA.

In this paper, we will review the catalytic performance in flexible foam while also comparing it to conventional non-reactive and commercially available reactive amine catalysts. The solution we have developed will provide a feasible alternative to the flexible foam industry by providing the novel reactive gelling catalyst that

will meet stringent VOC emission standards while maintaining excellent foam quality.

2. Experimental

2.1 Tertiary Amine Catalysts

The list of amine catalysts evaluated in this paper and their abbreviations are shown in **Table 1**. TEDA-L33, a strong gelling catalyst, and TOYOCAT®-ET¹⁾, a strong blowing catalyst, have long been standard tertiary amine catalysts for flexible polyurethane foams.

RZETA contains hydroxymethyl-TEDA as a major reactive amine ingredient and 66.7% of DPG in the same manner as TEDA-L33. TOYOCAT-RX24 and Catalysts A to G are conventional non-fugitive type amine catalysts used in flexible foam production.

2.2 Chemical Properties

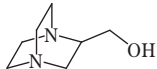

Table 2 shows the chemical properties of RZETA and TEDA. Hydroxymethyl-TEDA has a higher boiling point and a lower vapor pressure than TEDA. In addition, it has high LD50 value. These values show RZETA is safer for end-products and users in terms of lower volatility and lower toxicity.

2.3 Formulation and Foam Preparation

Flexible slabstock and molded foam formulations evaluated in this study are shown in **Table 3**, **4** and **5** respectively. The foaming conditions are given in **Table**

1) TOYOCAT® is Trademark of TOSOH CORPORATION

Table 2 Chemical Properties

		RZETA	TEDA
Amine compound			
aspect		white crystal	white crystal
Mw		142.2	112.2
m.p. (°C)		72	160
b.p. (°C)		281	174
Vapor Pressure (kPa)	100°C	0.076	7.8
	150°C	1.97	52.1
LD ₅₀ (mg/kg)		>2,000	1,700

6.

The flexible slabstock foams were prepared using an aluminum open mold (25×25×25cm) or wooden open mold (50×50×50cm) by hand mixing methods. The concentration of amine catalyst was adjusted to give

similar rise times at approximately 100 seconds (A) or 150 seconds (B) in order to evaluate each catalyst system on the same criteria. Formulation A and B were applied to evaluate the physical property and emission performance, respectively. The level of SDO was minimized in order to investigate the influence of amine catalysts on both VOC emission and foam performance more clearly.

Molded foams were prepared using an aluminum mold (25×25×8cm) which was preheated in an oven prior to molding (from 60±1°C). Over-all foam density was adjusted to 52kg/m³. All chemical components were conditioned at a temperature of 20±1°C. The concentration of each catalyst was adjusted to give an identical gelling time at approximately 60 seconds. The demolded time was fixed at 8 minutes.

Table 3 Formulations for Flexible Slabstock Foam

		A (Physical property)	B (Emission)
OHV (mgKOH/g)		pbw	pbw
Tri-functional Polyether Polyol	57	100	100
Water	6228	5	3
Silicone Surfactant	—	1	1.15
SDO	—	varied	0.16
Amine Catalysts	varied	varied	varied
NCO content (wt%)		Index	Index
Isocyanate (TDI, T-80)	48	110	110

Table 4 Formulations for HR Molded Foam (All-MDI Formulation)

	OHV (mgKOH/g)	pbw
Tri-functional Polyether Polyol	34	92.6
Cell Opener	35	1.9
Water	6228	3.2
Diethanolamine	1601	0.65
Silicone Surfactant	—	1
Amine Catalysts	varied	varied
NCO content (wt%)		Index
Isocyanate (p-MDI)	32	100

Table 5 Formulations for HR Molded Foam (TM80 Formulation)

	OHV (mgKOH/g)	pbw
Tri-functional Polyether Polyol	34	60
Polymer Polyol	21	40
Water	6228	3
Triethanolamine	1128	4
Silicone Surfactant	—	0.7
Amine Catalysts	varied	varied
NCO content (wt%)		Index
Isocyanate (TDI/MDI=80/20)	45	105

Table 6 Forming Conditions

		Slabstock	HR Molded	
			All-MDI	TM80
Liquid Temp.	(°C)	20°C	20°C	25°C
Mixing speed	(rpm)	3,500	6,000	
Mixing Time	(sec.)	10	5	
Mold-A (Aluminum)	(cm)	25×25×25cm	25×25×8cm	
Mold-B (Wooden)	(cm)	50×50×50cm	—	
Demolded Time	(min.)	—	8min	10min

2.4 Evaluation

(1) Rise Profiles

The evaluation of the rise profile during foaming has been considered an important parameter for the development of polyurethane systems as well as quality control for the production. The rise profiles were measured by using the long-range laser displacement apparatus (LF-2510, KEYENCE Corp.). The profile data was collected every second.

(2) Foam Physical Properties

After 7 days at ambient conditions ($23 \pm 0.3^\circ\text{C}$ and $50 \pm 2\%$ RH), physical foam properties, such as foam density, CLD (compression load deflection), and air flow, were measured according to the following test method: CLD: ISO 2439.

(3) Foam Durability Tests

Different static compression set and load loss tests were performed for durability testing. Dry compression sets were conducted with method A (70°C , 22hrs, 50% compression) and method B (70°C , 72hrs, 50%compression). Wet compression sets were determined at conditions of 50°C , 95% RH, 22hrs and at 50% compression.

(4) Amine Emission Tests

Certipur® method

Volatile emission from the flexible slabstock foam samples was determined through a large scale chamber test utilizing thermal desorption GC analysis, generally recognized as CertiPUR® method [18]. CertiPUR® is a standard for the environmental properties of flexible slabstock foams used in bedding and upholstered furniture applications. The tests were performed in house and not by a certified laboratory. Two foam samples ($25 \times 20 \times 15\text{cm}$), cut out of the center of a $50 \times$

$50 \times 50\text{cm}$ block, were placed into a 1 m^3 test chamber standing vertically on one $20\text{ cm} \times 15\text{ cm}$ side; both samples were placed in the test chamber with 15 cm distance in between.

The foam samples were conditioned for 3 days at $23^\circ\text{C}/50\%$ RH, applying an air exchange rate n of 0.5 per hour and a chamber loading L of $0.4\text{ m}^2/\text{m}^3$ in accordance with ISO 16000-9 and ISO 16000-11.

The emissions of VOC were trapped on Tenax TA sorbent tubes and subsequently analyzed by means of thermo-desorption-GC-MS in accordance to ISO16000-6. Results are semi-quantitatively expressed as toluene equivalents. TVOC value is the sum of all components with a concentration $\geq 1\text{ }\mu\text{g}/\text{m}^3$ and eluting within the retention time window from n -hexane (C6) to n -hexadecane (C16) inclusive. Aldehydes can be determined by collection of the sampled air onto a DNPH cartridge and subsequent analysis by HPLC/UV in accordance to ISO16000-3.

VDA 278 method

Volatile emission from the HR molded foam was determined through a dynamic headspace test utilizing thermal desorption method (VDA 278 method). VDA 278 has been recognized as a standard emission test in

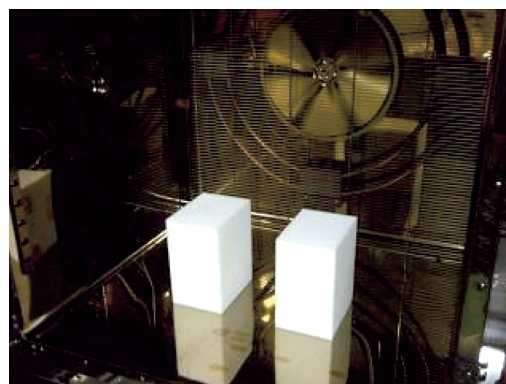


Fig. 1 Emission test chamber and foam samples

the German automotive industry to evaluate emissions from polyurethane foam under aggressive conditions [19]. A small section of the material was placed inside of a headspace vial. The vial was analyzed by the VOC GC-MS headspace method which was heated at 90°C for 30 minutes. The vial was then re-analyzed by the FOG headspace method which was heated at 120°C for 60 minutes.

VDA 278 utilizes thermal desorption technique which requires a second cold trap. In this study, the column and oven were cooled at -40 degree C by liquid CO₂ prior to the introduction into column for separation and analysis instead of using a cold trap.

3. Results and Discussion

3.1 Flexible slabstock foam

(1) Reactivity

In general, amine catalysts are used in conjunction with a tin compound for flexible polyether slabstock foams. The amine catalyst used in producing flexible slabstock foams plays a very important role because it accelerates both urethane and urea reactions and directly affects the foam physical properties. TEDA-L33 has been widely used as a standard amine catalyst for flexible polyether slabstock foams.

Water dosage was fixed to 5 parts by weight to compare the catalytic activity performance and foam formability among the evaluated catalysts. As shown in Fig.2, RZETA exhibited an almost identical foam height to TEDA-L33, although RZETA provided relatively faster initial reaction. However, other Non-fugitive amine catalysts exhibited much faster rise profile as shown in Fig.3. These results indicate that RZETA exhibits

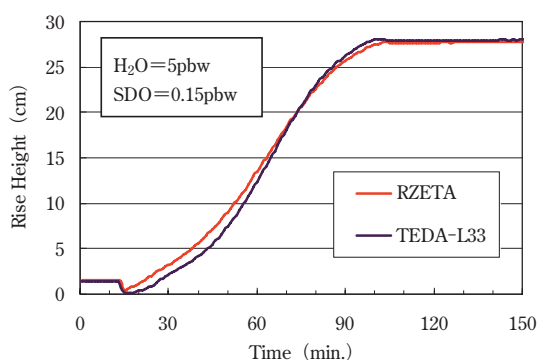


Fig. 2 Comparison of Rise Profiles-1

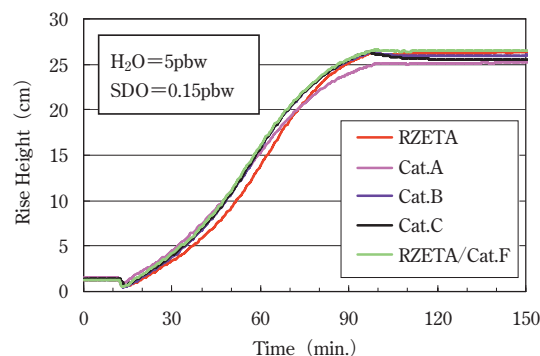


Fig. 3 Comparison of Rise Profiles-2

higher gelling ability compared to other non-fugitive amine catalysts.

(2) Catalytic activity

Fig. 4 is a comparison of required catalyst dosage to have a similar reaction time among the evaluated catalysts under variable quantities of SDO.

RZETA required about as twice the dosage as compared with TEDA-L33. There are 3 factors that contribute to the reduced catalytic activity of RZETA when compared to TEDA-L33: molecular weight, steric hindrance, and incorporation into the polymer matrix. The molecular weight of hydroxymethyl-TEDA is approximately 27% higher than TEDA. Therefore, additional loading is needed to have an equivalent amount of nitrogen when compared to TEDA. In addition, the hydroxymethyl group also hinders the nearest nitrogen group. This hindrance is increased as the RZETA is incorporated into the polymer. Finally, this incorporation reduces the mobility of RZETA in the later stages of the reaction.

RZETA contains glycols as carrier. It is indicated that hydroxymethyl-TEDA has the strongest activity among

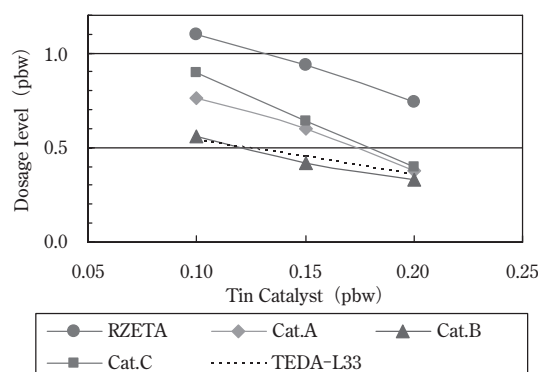


Fig. 4 Comparison of catalytic activity

non-fugitive amine catalysts, when comparing the required amine level to have similar foaming reactivity.

In addition, since RZETA provides a strong gelling ability, it can be used in combination with blowing catalyst at low SDO conditions. As shown in **Figure 6**, 20% addition of Catalyst-F for RZETA as ratio by weight can reduce the total catalyst dosage by 30% of the total dosage and is almost the same as Catalyst-B.

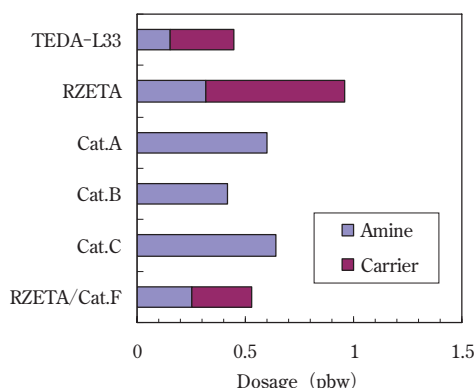


Fig. 5 Comparison of catalytic activity of non-fugitive catalysts (SDO=0.15pbw)

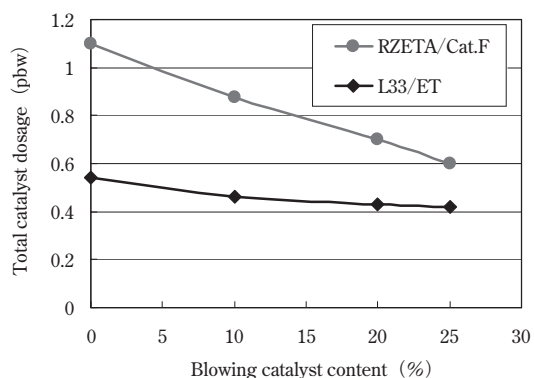


Fig. 6 Synergy effect with blowing catalyst (SDO=0.1pbw)

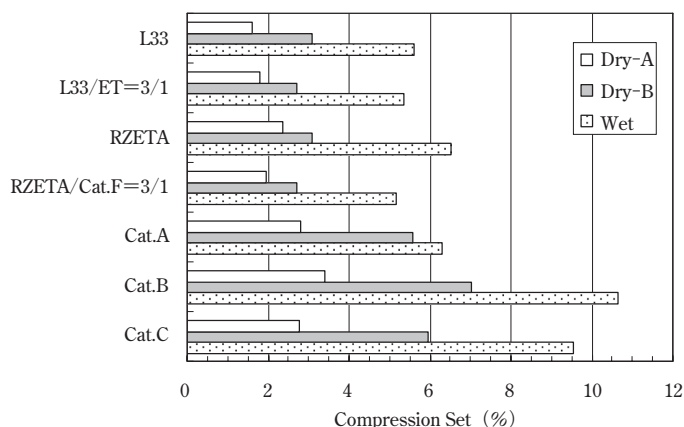


Fig. 7 Effect of Various Amine Catalysts on CS

(3) Foam Physical Properties

Table 7 shows the reaction profiles and foam properties of all water blown flexible slabstock foam with different amine catalysts. A combined use of RZETA with Catalyst-F provides relatively better physical foam properties compared to other reactive amine catalysts; particularly air flow and foam hardness.

As for durability performance, L33/ET exhibited the best result in all evaluated catalysts, and RZETA showed only slightly inferior performance compared with TEDA-L33. However, a combination use of RZETA and Catalyst-F gives better durability performance compared to other reactive amine catalysts.

Also, since this formulation is using a small quantity of SDO and a relatively high water dosage was applied to evaluate the catalytic performance of amine catalyst, this difference becomes smaller in accordance with the formulation change or optimization. However, this tendency is thought to be similar for RZETA and its combination with a blowing catalyst to provide a better durability performance at a wider process range.

(4) Amine Emissions

Table 8 shows the amine emission results by Emission Testing (B) after the CertiPUR® method. Test pieces were also collected at the center part of the foams. As for TEDA-L33, it indicates relatively higher levels of amine emission under ambient temperature condition (23°C for 72hours). Meanwhile, reactive type of amine catalysts such as RZETA, Catalyst-A and C were not detected.

Fig. 8 shows typical GC chromatogram pattern of this emission testing. Besides tertiary amines,

Table 7 Water Blown Flexible Slabstock, Reactivities and Foam Physical Properties

Catalyst		L33	L33/ ET (=3/ 1)	RZETA	RZETA / Cat.F (=4/ 1)	RZETA / Cat.F (=3/ 1)	Cat.A	Cat.B	Cat.C
		(pbw)	(mmol)						
		0.45	0.35	0.96	0.62	0.55	0.83	0.55	0.78
		1.3	1.2	2.3	1.8	1.7	9.3	3.8	3.6
Reaction Profile									
Cream time	(sec.)	24	21	22	20	20	21	19	20
blow off	(sec.)	100	99	99	98	98	100	98	100
Settling	(%)	0.7	0.6	0.5	0.9	0.7	0.3	1.0	2.4
Physical Properties									
Core Density	(kg/ m ³)	26.0	26.1	26.1	26.2	26.2	26.7	26.5	26.5
Airflow, Top	(cm ³ / (cm ² · s))	199	208	228	241	242	238	232	232
CLD, 40%	(kN/ m ²)	4.3	4.2	4.2	4.3	4.2	4.1	3.8	3.8
50% Dry-CS (A) ¹⁾	(%)	1.6	1.8	2.3	2.3	2.0	2.8	3.4	2.8
50% Dry-CS (B) ²⁾	(%)	3.1	2.7	3.1	2.7	2.7	5.6	7.0	5.9
Wet-CS	(%)	5.6	5.4	6.5	5.0	5.2	6.3	10.7	9.5

1) 50% compression under 70°C×22Hr, 2) 50% compression under 50°C×22Hr at 95% RH

emission of some other chemical compounds, e.g. BHT, cyclic organosiloxanes or chlorinated benzene were determined.

In the meantime, Catalyst-A shows a slightly higher

emission of formaldehyde. On the other hand: TEDA, RZETA and Catalyst-C exhibited almost no contribution to aldehyde emissions.

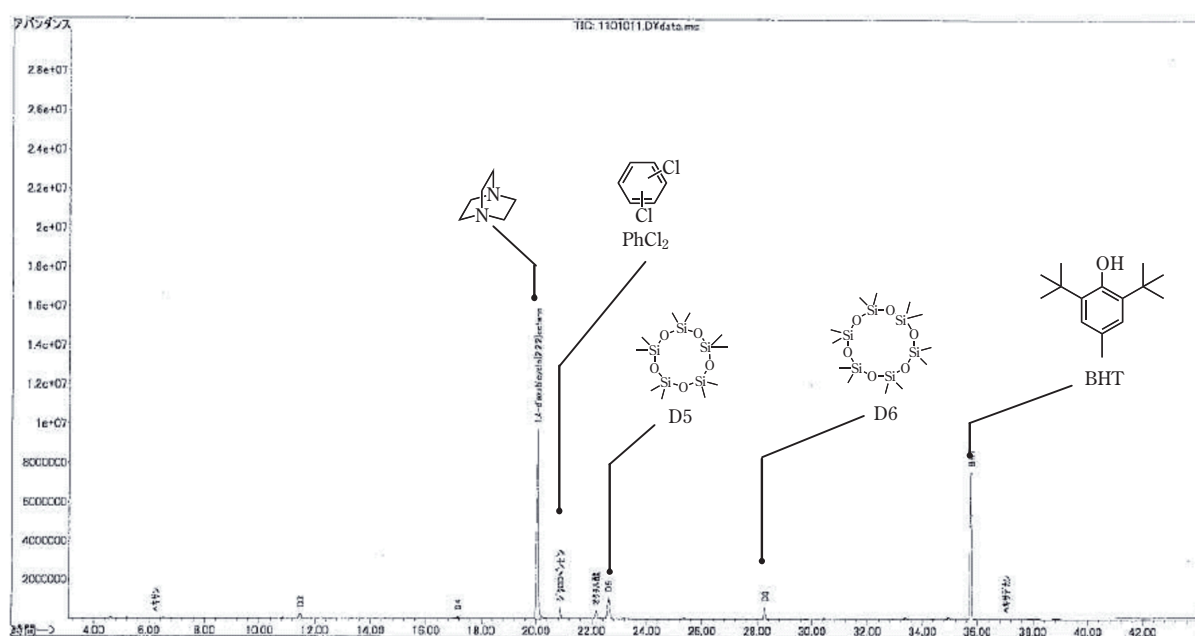
Table 8 Emission Analysis by CertiPUR® Method¹⁾

Catalyst	L33	RZETA	Cat.A	Cat.C
Total VOC ²⁾ (μg/ m ³)	342	199	200	166
Amine ³⁾ (μg/ m ³)	234	N.D.	N.D.	N.D.
HCHO (μg/ m ³)	N.D.	N.D.	3.8	1.3
CH ₃ CHO (μg/ m ³)	N.D.	1.1	N.D.	1.6

1) Values are corrected by using the background value

2) Total VOC : Values are cvtd as PhCH₃, Major chemicals found in the method are D5, D6, PhCl₂ and BHT.

3) Amine emission values are measured separately from the Total VOC
N.D. : Lower than detection limit

**Fig. 8** Typical GC Chromatogram Pattern of CertiPUR UR Analysis

3.2 Flexible HR-Molded Foam

The foam physical properties for All-MDI and TM80 formulations are summarized in **Table 9** and **10** respectively.

(1) Foam Durability Performance

The influence of various non-fugitive amine catalysts

on Wet Set was investigated. Non-fugitive amine catalysts tend to provide inferior durability performance compared to L33/ET. However, among evaluated non-fugitive amine catalysts, a combination of the use of RZETA and Catalyst-F provides relatively better durability performance.

Table 9 Reaction profiles and physical properties by Hand mixing (All-MDI)

Catalyst		RZETA / Cat.F (4 / 1)	L33 / ET (4 / 1)	RX24	Cat.A	Cat.B	Cat.D	Cat.E/ Cat.G
	(pbw)	1.69	0.62	1.46	1.64	1.33	1.05	1.54
Reactivity	(sec.)							
	Cream	12	10	13	9	13	14	11
	Gel	60	60	61	59	60	59	59
	Rise	80	85	82	84	79	75	78
Physical Properties								
Overall Density	(kg / m ³)	51.9	51.6	51.9	52.0	51.9	51.7	51.8
ILD, 25%	(kN / m ²)	6.6	7.0	6.3	6.3	6.0	6.1	6.1
ILD, 65%	(kN / m ²)	19.5	20.8	18.4	18.5	17.0	17.3	17.8
Core Density	(kg / m ³)	45.1	45.8	44.4	45.6	45.1	44.8	45.9
CLD, 40%	(kN / m ²)	6.5	6.9	6.2	6.1	5.9	6.1	6.0
Hysteresis Loss (65%)	(%)	33.1	33.0	33.6	33.1	26.6	31.8	33.7
Tensile strength	(kN / m ²)	136	126	126	106	119	120	126
Elongation	(%)	79	76	76	76	76	77	77
Tear strength	(kN / m)	0.5	0.5	0.5	0.5	0.4	0.5	0.5
50% Dry-CS (A)	(%)	7	6	7	9	7	7	7
50% Dry-CS (B)	(%)	9	7	10	12	11	10	13
Wet-CS	(%)	14	12	16	18	15	15	17
HACS	(%)	9	6	13	15	13	10	13
Amine Emission								
VOC	(μg / g)	N.D.	477 / 231	N.D.	N.D.	N.D.	N.D.	<20
FOG	(μg / g)	N.D.	N.D.	32	61	20	240	>400

Table10 Reaction profiles and physical properties by Hand mixing (TDI/MDI=8/2)

Catalyst		RZETA / Cat.F (10 / 1)	L33 / ET (7 / 1)	Cat.A	Cat.B	Cat.D
	(pbw)	1.58	0.60	1.40	0.86	0.65
Reactivity	(sec.)					
	Cream	11	10	7	11	10
	Gel	60	60	60	60	59
	Rise	69	75	71	78	76
Physical Properties						
Overall Density	(kg / m ³)	51.5	52.1	51.3	51.3	51.7
ILD, 25%	(kN / m ²)	7.6	7.5	6.6	6.9	7.4
ILD, 65%	(kN / m ²)	22.3	21.8	20.1	19.6	20.6
Core Density	(kg / m ³)	47.5	48.3	47.7	47.0	47.8
CLD, 40%	(kN / m ²)	7.3	7.6	6.6	6.8	7.2
Hysteresis Loss (65%)	(%)	22	21	23	20	20
Tensile strength	(kN / m ²)	197	180	176	188	196
Elongation	(%)	89	83	85	91	87
Tear strength	(kN / m)	0.7	0.7	0.6	0.6	0.6
50% Dry-CS (A)	(%)	5	4	8	6	6
50% Dry-CS (B)	(%)	9	6	32	13	12
Wet-CS	(%)	15	15	20	16	15

(2) Amine Emissions

The test pieces were sampled from the surface part of the foams. As for L33/ET, it indicates that higher level of free amine remains in the foam is emitted under VOC method condition (90°C for 30minutes). Meanwhile, RX24, Catalyst-A, B, D and E were not detected under VOC method, but under FOG method condition (120°C for 60minutes after VOC method). Secondary hydroxyl group like Catalyst-D forms strong linkage with isocyanate [9], but has low reactivity compared to primary hydroxyl group. Catalyst-D shows higher emission than Catalyst-A or B under fogging method.

In contrast, Catalyst-E exhibits a higher volatility under FOG method. This urea catalyst seems to be less reactive with isocyanate.

4. Conclusions

TOSOH has developed a novel reactive amine catalyst (RZETA), which contains a TEDA molecule with a reactive site toward isocyanate. Various kinds of non-fugitive amine catalysts were evaluated in flexible slabstock as well as HR-molded foam systems. In both systems, RZETA exhibited higher catalytic activity and better physical foam properties, including durability performance, while lowering the VOC emission of the system.

We believe that RZETA will contribute to the flexible polyurethane foam industry, being recognized as a reasonable choice for the environmentally friendly foam systems.

References

- 1) Reed D.(1999), "VW aims to cut amines", *Urethanes Technology*, 16/4, 3
- 2) Daimler-Chrysler, PB VWL 709
- 3) Y. Tamano, *TOSOH Research & Technical Review*, 44, 77 (2000)
- 4) Zimmerman R.L., Grigsby R.A., Felber G., Humbert H.H., "Comparison of Basic Physical Properties of Foams Prepared with Fugitive and Non Fugitive Amine Catalysts", UTECH(2000)
- 5) Wendel S.H. Mercado L.A., Tobias J.D., "Reduced Emanations Using Non-Fugitive Catalysts for Flexible Polyurethane Foams", UTECH (2000)
- 6) H.Kometani, Y.Tamano, T.Masuda, R.V.Maris and K.M.Gay., "The Investigation of Amine Emissions from Polyurethane Foam," *polyurethane 2000 Proceeding*.
- 7) Keimling S.U., Wehman C., Cordelair H., "New Additive Solutions for Low VOC in MDI-Based Moulded Foams", UTECH (2000)
- 8) T.Masuda, H.Nakamura, Y.Tamano, H.Yoshimura, R.V.Maris and K.M.Gay., "Advance in Amine Emission Free Catalyst Systems for Automotive Seating - A Fundamental Study on Durability Performance by Humid Aging Load Loss Test (HALL)" *polyurethane 2002 Proceeding*.
- 9) K.Tokumoto, T.Masuda, Y.Takahashi, H.Kometani, Y.Tamano, H.Yoshimura, K.M.Gay and R.V.Maris. "Non-fugitive Gelling & Blowing Catalysts to Improve Cure in Emission-Free HR Molded Systems", *Polyurethanes 2003, Proceedings*
- 10) El Ghobary H., Muller L., US Patent No 6,156,814
- 11) R. Herrington et al., "Moving Forward with New Low-Emissions Amine Catalyst Technology", *Polyurethanes 2008 Proceeding*.
- 12) A. Terheiden et al., "Novel Amine Catalyst for Low Emanation Flexible Polyurethane Foam", *Polyurethanes 2008 Proceedings*.
- 13) Burdeniuc J.J. et al., "New Additives to Improve the Performance of Low Emissions Flexible Polyurethane Foam", UTECH (2012)
- 14) H.Kiso, Y.Tamano. "Novel Strong Gelling Catalysts for Emission-Free Systems", *Polyurethanes 2006, Proceedings*.
- 15) T.Suzuki, Y.Takahashi, H.Kiso, J. Tucker. "Novel Gelling Catalyst for Non-Emission Flexible Polyurethane Foam" *Polyurethane 2010 Conference Papers*.
- 16) K. Tokumoto, Y. Takahashi, H. Kiso, R. V. Maris. "Advance in Reduced Amine Emission Catalyst Systems for Flexible Polyurethane Foams" *Polyurethanes 2011, Proceedings*.
- 17) T.Suzuki, K.Tokumoto, H.Kiso, R. V. Maris. "Novel Strong Gelling Catalyst for Emission-Free Polyurethane Foam", UTECH (2012)
- 18) European Association of Flexible polyurethane Foam Blocks Manufacturers, CertiPUR Label for Flexible Polyurethane Foams, III. Technical Requirements 2010
- 19) Daimler-Chrysler test Method PB VWT 278