Novel Gelling Catalyst for Non-Emission Flexible Polyurethane Foam

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ABSTRACT

Flexible and semi-rigid polyurethane foams have been widely used in automotive interior parts, residential upholstered furniture and bedding. In these, as well as other end use industries, a reduction of Volatile Organic Compounds (VOCs) emissions from polyurethane foams continues to be an important issue [1, 2].

To address this challenge, reactive amine catalysts, which have an active hydrogen group, have been developed, evaluated, and used for the purpose of reducing VOC emissions. Unfortunately, many of these reactive catalysts tend to lose their catalytic activity during the latter stages of the foaming process resulting in decreased performance during the curing function.

TOSOH Corporation has continued to research the next-generation of non-fugitive catalysts for polyurethane systems, and recently developed a novel gelling catalyst that provides improved performance in overall catalytic activity. This catalyst has a similar function as TEDA and exhibits better durability performance compare to other non-fugitive catalysts.

TOSOH Corporation will review this work and propose solutions for reduced VOC systems with low or non-emission catalyst.

INTRODUCTION

Polyurethane foam is made from polyols, isocyanates and additives such as catalysts, silicone surfactants, flame retardants, anti-oxidants, chain-extenders, crosslinkers, release agents, etc. In general, the automotive and furniture industries are sensitive to VOCs due to customer specifications and regulations.

Tertiary amine catalysts such as TEDA have been used for many years in the production of polyurethane foam. Their usage, however, is targeted for reduction due to emissions from the finished foam and associated unpleasant odor. In order to overcome the emission problems, a wide variety of non-fugitive amines containing hydroxyl, amino and urea groups have been proposed and evaluated[3-9], because such catalysts can react with isocyanate group during the foaming process and become part of polymer network. However, a fully adequate replacement catalyst system has not been found yet. The catalytic activity of these non-fugitive catalysts is lower than conventional catalysts and the foam properties, curing function and durability performance, tend to worsen due to the lack of gelling activity. For this reason, amine catalysts that have high gelling activity such as TEDA and exhibit low-emissions are a consistent demand from the market.

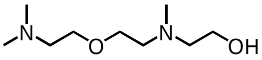
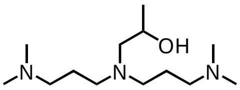
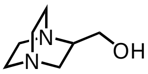
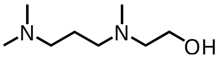
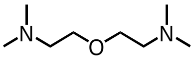
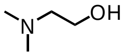
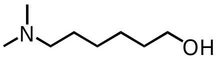
Previously, Tosoh has reported the gelling properties and potential of reactive TEDA (RTEDA) by using computational chemistry [10]. To establish this result, RTEDA was synthesized and evaluated by comparison of various kinds of reactive amines. In this paper, the characteristics of RTEDA are discussed. In addition, novel amine catalysts systems are proposed for Flexible and semi-rigid polyurethane foams.

EXPIRIMENTAL

Catalysts

The lists of amine catalysts evaluated in this paper and their abbreviation are shown in Table 1. TEDA (L33) and TOYOCAT®-ET are standard tertiary amine catalysts for flexible and semi-rigid polyurethane foams. L33 is a liquid type of TEDA and shows strong gelling catalytic activity. RTEDA, which has a hydroxylmethyl substituent in TEDA structure, is diluted by 33.3% with DPG like L33 to compare the reactivity. TOYOCAT-RX24 and catalysts A-E are conventional reactive amine catalysts used in PUR production.

Table 1. Amine Catalysts

Abbreviation	Chemical Structure	Abbreviation	Chemical Structure
TEDA		Catalyst-A	
TEDA-L33	 33.3% in DPG 66.7%	Catalyst-B	
RTEDA		Catalyst-C	
TOYOCAT-ET	 70% in DPG 30%	Catalyst-D	
TOYOCAT-RX24	Special Reactive Amine	Catalyst-E	

Formulation and Foam Preparation

Flexible slabstock and molded foam formulations were evaluated in this study, shown in Table 2 and 3. Forming conditions are given in Table 4.

The slabstock foams were prepared using an aluminum open mold (25x25x25 cm) at 23°C by hand mixing methods. The concentration of stannous dioctoate (SDO) was varied from 0.10 to 0.25 in order to investigate process latitude of the amine catalysts. The concentration of amine catalyst was adjusted to give similar rise times (100 seconds) in order to evaluate each catalyst system on the same criteria.

Molded foams were prepared using an aluminum mold (25 x 25 x 8 cm) which was preheated in an oven prior to molding (from 60 ± 1^{o}C). Over-all foam density was adjusted to 52 kg/m^3. All chemical components were conditioned at a temperature of 20 ± 1^{o}C. The concentration of each catalyst was adjusted to give an identical gelling time of 60 seconds. The demold time was fixed at 8 minutes.

Table 2. Formulations for Flexible slabstock foam

	OHv(mgKOH/g)	pbw
Tri-functional Polyether Polyol	57.5	92.6
Water		5
Silicon Surfactant		1
SDO		varied
Amine Catalysts		varied
	NCO content(wt%)	Index
Isocyanate(TDI、T-80)	48.2	110

Table 3. Formulations for HR molded foam

	OHv(mgKOH/g)	pbw
Tri-functional Polyether Polyol	33.6	92.6
Cell Openner	34.6	1.9
Water		3.2
Diethanolamine		0.65
Silicon Surfactant		1
Amine Catalysts		varied
	NCO content(wt%)	Index
Isocyanate(MDI)	31.7	100

Table 4. Forming Conditions

	Slabstock	HR molded
Liquid Temp.	20^{o}C	20^{o}C
Mixing speed	3,000rpm（10sec.)	6,000rpm (5sec)
Mold Temp.	23^{o}C	60^{o}C
Mold	25 x 25 x 25cm	25 x 25 x 8cm

Measurement of Rise Profiles

The evaluation of 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.

Measurement of Foam Physical Properties

After 7days at ambient conditions (23±0.3°C and 50±2%RH), physical foam properties such as foam density, CLD (compression load deflection), air flow, tensile strength, elongation and tear strength were measured according to the following test method (CLD: ISO 2439, Tensile strength and Elongation: ISO 1798, Tear strength: ISO 8067).

Durability Tests

Different static compression set and load loss tests were performed for durability testing. Dry compression sets were conducted with A method (70°C, 22hrs, 50% compression), B method (70°C, 72hrs, 50% compression) and C method (after 90°C /100% RH x 200hr aging, 70°C, 22hrs, 50% compression).

Wet compression set was conditioned at 50°C, 95% RH, 22hrs, at 50% compression.

Amine Emission Tests

Two different methods were used to trace the remaining free amine in the foam and determine the emission value of the individual catalyst compounds.

FOAM EXTRACTION

The total amount of free amine catalysts in the foam was measured via the solvent extraction method. 2.0grams of foam were placed into a 30 milliliter vial with 14.0 grams of methanol. The vial was sealed and placed into shaker with heated water at 50°C for 72 hours and allowed to cool. The methanol was compressed out of the foam completely, and then the extracts were identified by gas chromatographic determination.

EMISSION TESTING

Volatile emission from the foam was determined through a dynamic headspace test utilizing thermal desorption method (VDA278 method). VDA 278 is used as a standard emission test in the automotive industry to evaluate emissions from polyurethane foam under aggressive conditions [9]. Small section of material placed inside of a headspace vial. The vial was analyzed by the VOC GC–MS headspace method which was heated at 90^{o}C for 30 minutes. The vial was then re-analyzed by the FOGGING headspace method which was heated at 120^{o}C for 60minutes.

PVC Staining Measurements

Accelerated aging tests were carried out in closed containers in the presence of a PVC film according to VW PVC3937. A foam sample of 70 × 70 × 30 mm, cut from the top part of the foam, was placed at the bottom of a 2 liter glass separable flask. A piece of gray PVC soft sheet (VW sun visor sheet) was hung by the lid of the flask, which was then sealed. Aging was carried out at 100°C for 72 hours. After cooling, the PVC sheet discoloration was measured using a colorimeter. Smaller changes in color result in a lower ΔE measurement.

RESULTS AND DISCUSSION

To investigate characteristics of various reactive amine catalysts (RACs) including non-fugitive amine catalyst, hand-mixing was carried out. As a reference, TEDA-L33 and/or TEDA-L33/TOYOCAT-ET combination (=4/1(wt/wt)) were used. Catalyst-A (Cat.A) was used as blowing catalysts to improve closed cell foam. The formulations and properties of the foams are summarized in Table 6 and 7.

1. Slabstock Foam

1-1. Reactivity

In general, an amine catalyst is combined with a tin compound for flexible polyether slabstock foams. The amine catalyst used in producing flexible slabstock foams plays a very important role, from a technical and economical standpoint, because it accelerates both urethane and urea reactions and directly affects the foam physical properties. L33 is widely used as a standard amine catalyst for flexible polyether slabstock foams.

As shown in Figure 1, RTEDA exhibited an almost identical foam height to TEDA (L33), although RTEDA provided a faster initial reaction. In addition, the RTEDA-foams were observed health-bubble, which is an indication open/closed cell, and no-settling in all SDO ranges. In contrast, TEDA-foams were confirmed settling phenomena at low SDO amount. This suggests that RTEDA exhibits a wide process range of foam reaction owing to low catalytic activity and blowing ability compared with TEDA and supports our past computational study.

Regarding catalytic activity, RTEDA required about twice the dosage as TEDA. The introduction of hydroxymethyl group into the TEDA skeleton is thought to reduce the catalytic activity of adjacent nitrogen site by steric hindrance.

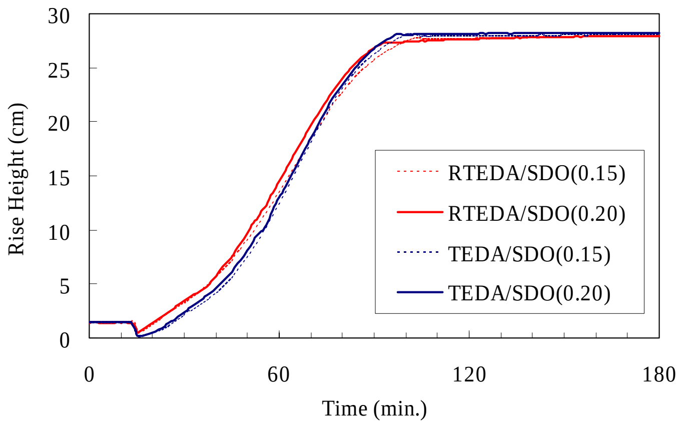


Figure1. Rise profiles

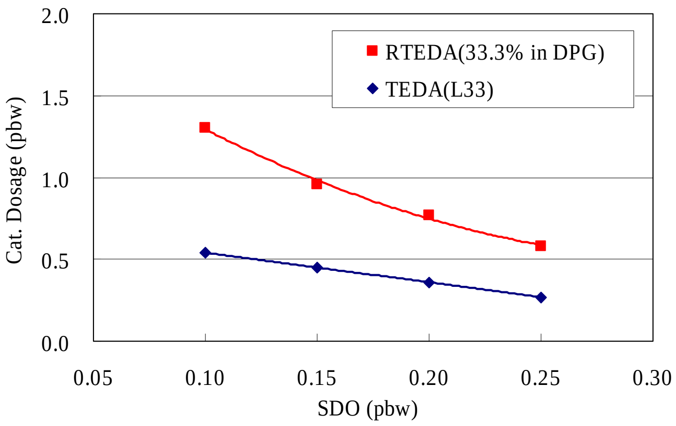
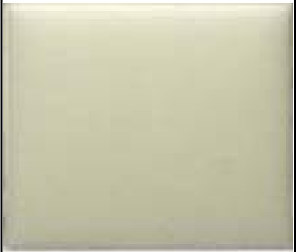
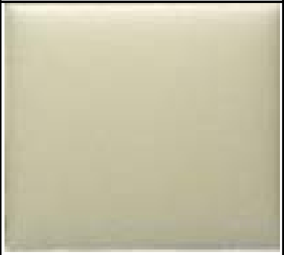
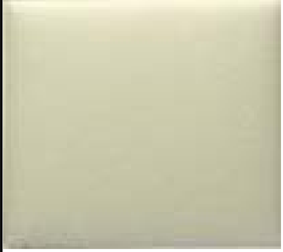
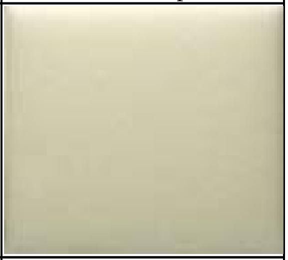
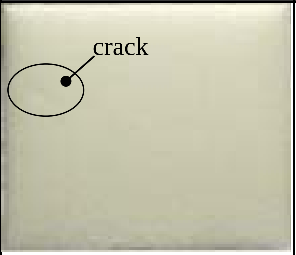
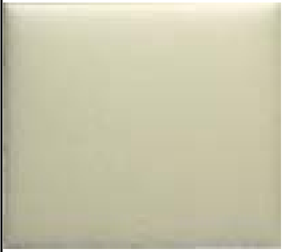
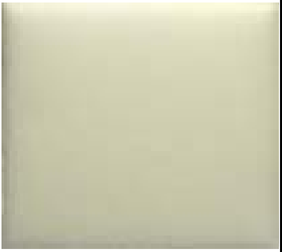
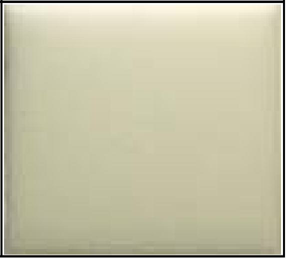


Figure2. Catalytic Activity

1-2. Foam Formability

Table 5 shows the result of foam formability compared with L33 under several different SDO dosages. RTEDA provided excellent formability regardless of SDO. In case of TEDA, cracks in the foam were observed at low amount of SDO usage.

Table5. Foam Formabilities under several different SDO dosages

	SDO=0.10pbw	SDO=0.15pbw	SDO=0.20pbw	SDO=0.25pbw
RTEDA				
TEDA				

1-3. Foam Physical Properties

Table 6 shows the reaction profiles and foam properties of RTEDA and TEDA. RTEDA exhibited better physical properties at reduced SDO level; particularly air flow, tensile strength and elongation properties.

As for durability performance, RTEDA showed slightly inferior performance compared with TEDA (L33), owing to reactive amine. However, we feel the values will be permissive.

Table6. Reaction profiles and physical properties by Hand mixing (H_2O=5pbw)

Catalyst	*RTEDA(33.3%,DPG)*				*L33(33.3%,DPG)*			
(pbw)	*1.30*	*0.96*	*0.77*	*0.58*	*0.54*	*0.45*	*0.36*	*0.27*
SnOct(SDO) (pbw)	*0.10*	*0.15*	*0.20*	*0.25*	*0.10*	*0.15*	*0.20*	*0.25*
*Mold Free Foam (Al mold:25*25*25(cm^3))*								
CT (sec.)	*20*	*20*	*20*	*20*	*26*	*25*	*24*	*22*
RT (sec.)	*104*	*102*	*93*	*89*	*105*	*100*	*97*	*95*
Core Density (kg/m^3)	*22.3*	*21.6*	*21.8*	*21.6*	*23.2*	*21.8*	*21.7*	*21.0*
CLD 25%compression (kN/m^2)	*3.1*	*3.2*	*3.7*	*4.3*	*3.3*	*3.4*	*3.6*	*3.8*
40%compression (kN/m^2)	*3.7*	*3.7*	*4.5*	*5.0*	*4.1*	*3.9*	*4.2*	*4.4*
65%compression (kN/m^2)	*6.4*	*7.0*	*8.4*	*9.2*	*7.2*	*6.6*	*7.2*	*7.4*
Air Flow (Upper) ($cm^3/(cm^2/s)$)	*273*	*247*	*156*	*102*	*135*	*203*	*186*	*178*
(Lower) ($cm^3/(cm^2/s)$)	*171*	*178*	*61*	*37*	*47*	*98*	*83*	*95*
Tensile strength (kN/m^2)	*100*	*90*	*87*	*97*	*86*	*91*	*92*	*95*
Elongation (%)	*139*	*127*	*112*	*113*	*101*	*115*	*112*	*118*
Tear strength (kN/m)	*0.59*	*0.57*	*0.55*	*0.52*	*0.41*	*0.46*	*0.48*	*0.55*
50% Dry-CS (A) (%)	*5.8*	*3.8*	*4.2*	*3.8*	*4.9*	*3.2*	*2.9*	*2.5*

2. HR Molded Foam

2-1. Foam Physical Properties

Foam Hardness

Considering core density and foam hardness in each catalyst, it can be said L33/ET (=4/1) and RTEDA/Cat.A provided the hardest foam in all evaluated catalysts (Shown in Figure 3). RTEDA showed high synergy effect with blowing catalysts like Cat.A as well as TEDA.

Tear Strength

Tear strength basically exhibited the same tendency as foam hardness. The results are shown in Figure 4. RTEDA/Cat-A and LE41 exhibited the highest tear strength in all evaluated catalysts.

Tensile Strength and Elongation

The relationship between tensile strength and elongation was investigated. The results are shown in Figure 5. RTEDA showed relatively high values among all catalysts. This result indicates that RTEDA may have crosslinking abilities compared with TEDA.

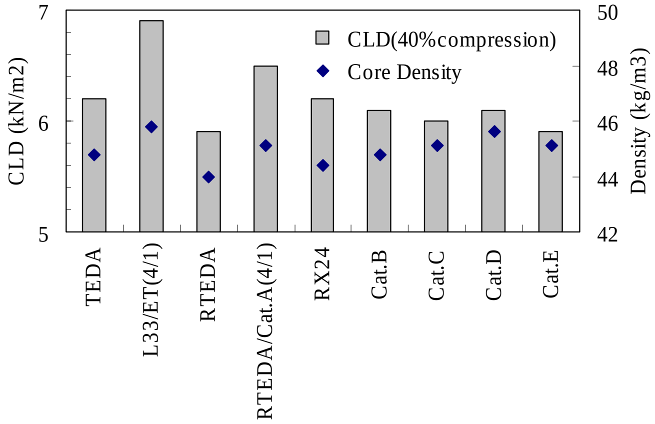


Figure3. Effect of Various Amine Catalysts on CLD Value

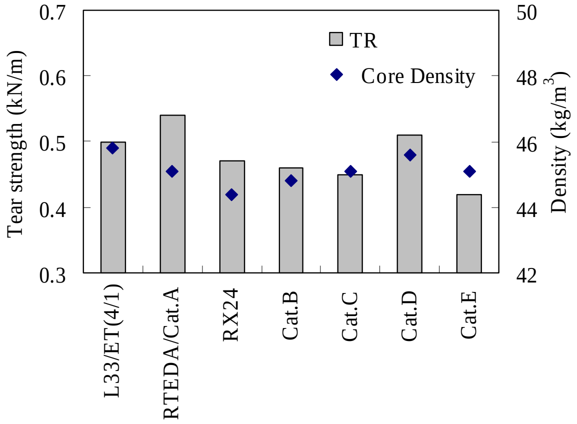


Figure4. Effect of Various Amine Catalysts on Tear strength

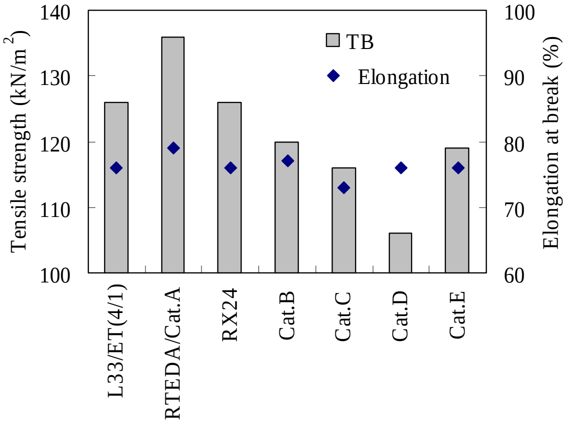


Figure5. Effect of Various Amine Catalysts on Tensile strength and Elongation

2-2. Foam Durability Performance

Dry Compression Set (DCS) A and B methods

The influence of various RACs on DCS was investigated. The results are shown in Figure 6. As for DCS-A, L33/ET exhibited the best result in all evaluated catalysts. Among RACs, RTEDA/Cat.A exhibited the best values.

As for DCS-B, there is significant difference between L33/ET and RACs. All DCS-B of RACs became worse results compared with L33/ET. However, RTEDA/Cat.A exhibited permissible values.

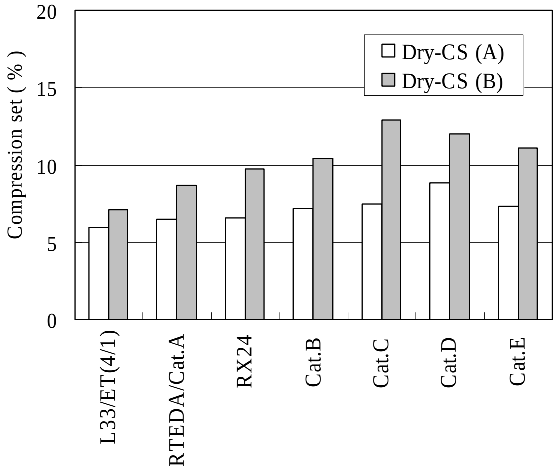


Figure 6. Effect of Various Amine Catalysts on DCS

Wet Compression Set (WCS)

The influence of various RACs on WCS was investigated. The result is shown in Figure 7. However, Wet Compression Set (WCS) testing did not show a significant difference among RACs except for Cat.D. There is a proportional relationship between catalyst dosage (mol equivalent) and Humid aging test such as WCS and HACS. The more catalyst loaded, the worse durability performances become. (Shown in Figure 8)

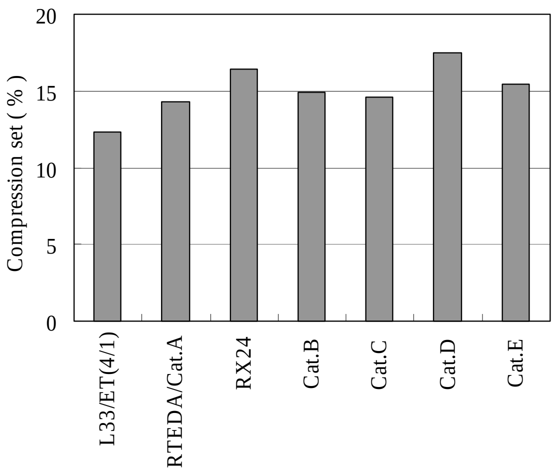


Figure7. Effect of Various Amine Catalysts on WCS

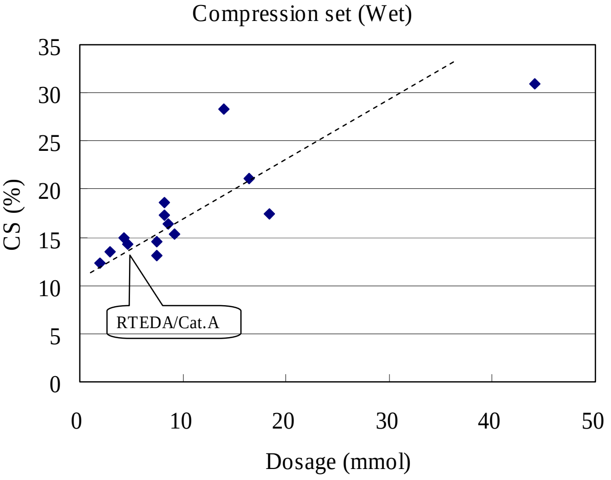


Figure8. The relationship between Catalyst dosage and WCS

Humid Aged Compression Set (HACS)

It is well known that HACS is most severe test for RACs to pass specification. This is because PUR polymer structure derived from RACs and NCO reaction is less stable when compared to those derived from standard non-reactive tertiary amine catalysts. To pass this specification by using RACs, modification of formulation itself also becomes an important factor.

The results of HACS are shown in Figure 9.

L33/ET exhibited the best results in all evaluated catalysts. Among RACs, RTEDA/Cat.A and Cat B exhibited permissible values.

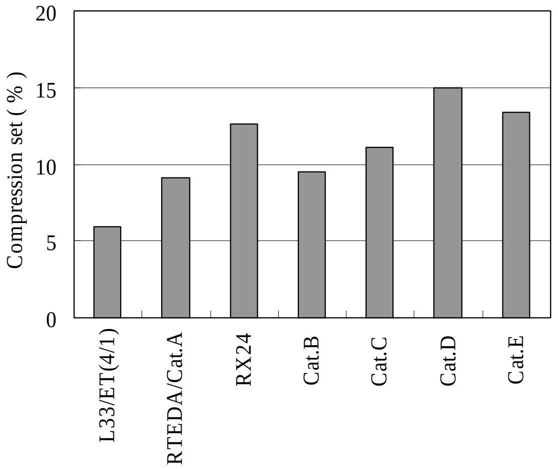


Figure9. Effect of Various Amine Catalysts on HACS

2-3. Amine Emissions

Figure 10 shows the extraction results as an eluted rate for the theoretical amount of catalyst in the foam. Test samples were taken at the surface part of foams (incl. skin layer). The conventional catalysts, TEDA and ETS, show extremely high values.

This result, which exceeds the theoretical value, is thought to be due to the shift of the amine catalyst from core to surface of the foam. Among RACs, significant differences were not been observed.

Figure 11 shows amine emission results by VDA278. Test pieces were also used the surface part of foams. As for L33/ET, it indicates that high levels of residual free amine remains in the foam and under VOC method condition (90°C for 30minutes). Meanwhile, RX24, Cat.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 Cat.B forms strong linkage with isocyanate [12], but has low reactivity compared to primary hydroxyl group. So unreacted catalysts remain in the foam, Cat.B shows higher emission than Cat.D or E under fogging method.

However, RTEDA/Cat.A was not detected under both conditions, RTEDA showed better performance.

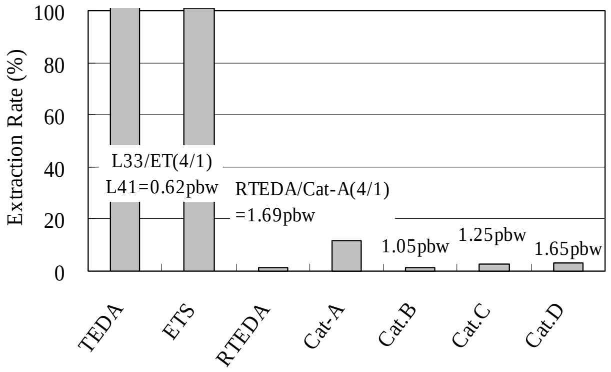


Figure 10. Eluted catalysts by methanol extraction

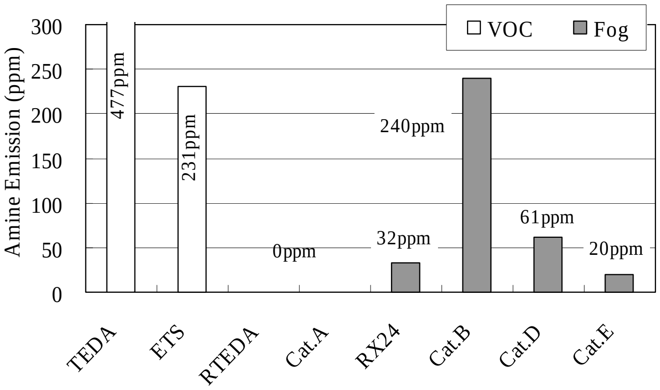


Figure 11. Amine Emissions by VDA278 method

2-4. PVC staining

The influence of various amine catalysts on PVC staining test was investigated as shown in Figure 12.

When a gray color of PVC sheet was used, there does not appear to be a significant difference among RACs. But in case of a white color of PVC sheet, PVC staining was observed in all of test samples. Among them, a combination of RTEDA and Cat.A exhibited relatively lower values.

These results (incl. Amine emissions) suggest RTEDA reacts with isocyanates and forms a strong linkage. Since unreacted RTEDA decreases without limit, amount of migration to PVC can be reduced. Regarding Cat.D, it volatilized out of foam immediately while or after foaming because of low molecular weight.

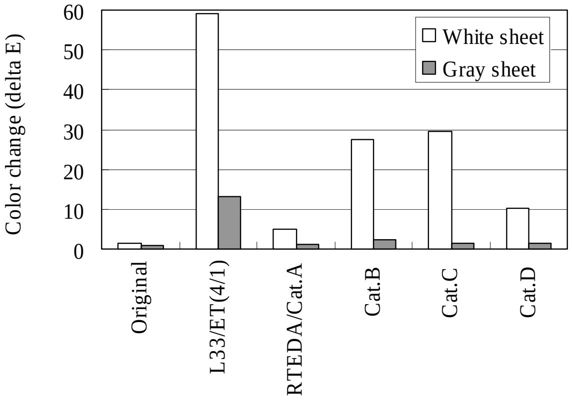


Figure 12. Effect of various amine catalysts on PVC staining

Table 7. Reaction profiles and physical properties by Hand mixing (All-MDI)

Catalyst	*LE41*	*RTEDA/ CatA*	*RX24*	*CatB*	*CatC*	*CatD*	*CatE*
(pbw)	*0.62*	*1.45/0.24*	*1.46*	*1.05*	*1.20*	*1.64*	*1.33*
(mmol)	*2.02*	*4.68*	*8.59*	*4.28*	*7.49*	*18.40*	*9.16*
Cup Free foam (Hand mixing)							
CT (sec.)	*10.2*	*12.2*	*13.3*	*13.8*	*13.1*	*9.2*	*13.0*
GT (sec.)	*60*	*60*	*61*	*59*	*62*	*59*	*60*
RT (sec.)	*85*	*80*	*82*	*75*	*83*	*84*	*79*
Core Density (kg/m^3)	*38.8*	*38.1*	*37.4*	*37.8*	*37.6*	*37.5*	*37.2*
*Mold pack foam (Al mold:25*25*8(cm^3))*							
Overall Foam weight (g)	*257.8*	*259.3*	*259.4*	*258.7*	*258.9*	*259.8*	*259.6*
Overall Density (kg/m^3)	*51.6*	*51.9*	*51.9*	*51.7*	*51.8*	*52.0*	*51.9*
ILD 25%compression (kN/m^2)	*7.0*	*6.6*	*6.3*	*6.1*	*5.9*	*6.3*	*6.0*
65%compression (kN/m^2)	*20.8*	*19.5*	*18.4*	*17.3*	*16.9*	*18.5*	*17.0*
Core Foam Density (kg/m^3)	*45.8*	*45.1*	*44.4*	*44.8*	*45.1*	*45.6*	*45.1*
CLD 40%compression (kN/m^2)	*6.9*	*6.5*	*6.2*	*6.1*	*6.0*	*6.1*	*5.9*
Hysteresis Loss (65%) (%)	*33.0*	*33.1*	*33.6*	*31.8*	*30.6*	*33.1*	*26.6*
Tensile strength (kN/m^2)	*126*	*136*	*126*	*120*	*116*	*106*	*119*
Elongation (%)	*76*	*79*	*76*	*77*	*73*	*76*	*76*
Tear strength (kN/m)	*0.50*	*0.54*	*0.47*	*0.46*	*0.45*	*0.51*	*0.42*
50% Dry-CS (A) (%)	*6.0*	*6.5*	*6.6*	*7.2*	*7.5*	*8.8*	*7.3*
50% Dry-CS (B) (%)	*7.1*	*8.7*	*9.7*	*10.4*	*12.9*	*12.0*	*11.1*
Wet-CS (%)	*12.3*	*14.3*	*16.4*	*14.9*	*14.6*	*17.5*	*15.4*
HACS (%)	*5.9*	*9.1*	*12.6*	*9.5*	*11.1*	*15.0*	*13.4*

CONCLUSIONS

TOSOH developed a novel gelling reactive catalyst we call RTEDA. Various kinds of amine catalysts were evaluated in flexible slabstock and HR molded systems. As a result, RTEDA exhibited better durability performance as well as better physical properties.

1. RTEDA, which has a hydroxylmethyl substituent in TEDA structure, can be used to reduce amine emissions.
2. In the slabstock test system, unlike TEDA, RTEDA provides improved physical properties at low SDO amount. RTEDA exhibits wide process range owing to low catalytic activity and blowing ability compared with TEDA.
3. In the HR molded test system, RTEDA exhibits high synergy effect with blowing catalysts. Combination use improves not only catalytic activity but also physical properties and durability performances.

We hope this catalyst and catalyst system will contribute to polyurethane industry.

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