

TEDA & TOYOCAT NEWS

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It is a great pleasure to present our fourth issue of the TEDA & TOYOCAT News. We hope it will serve to help you obtain maximum benefit from our products. We would be glad to supplement this information at some mutually convenient time. In the meantime, please do not hesitate to call upon us if there is some other way in which we can be of assistance.

TOPICS

TOSOH PRESENTES A NEW CATALYST "HX75" AT PU '95

At Polyurethanes '95 held on September 26-29 in Chicago, TOSOH introduced information on a new reactive amine catalyst. Our presentation title was "Evaluation of Tertiary Amine and Metal Catalyst in Automotive Polyurethane Foam".

TOSOH Corporation has examined the effectiveness of various metal and tertiary amine catalysts in several problems associated to the rapid cure instrument panel, as well as, seat application. We proposed developments for novel catalyst systems which used TOYOCAT-HX75 and Potassium octoate as shown in Table 1. This combination improves each of the technical problems normally associated to metal and amine catalysts separately. HX75 can improve flowability even when metal catalyst is used as co-catalyst. It is possible to clear the vinyl-staining as shown in Figure 1. and odor problem while maintaining fast cure speed, as well as, excellent moldability. This novel catalyst system can be applicable to fast cure system for instrument panel and to the solution of the fogging problem in automotive interior parts.

Table 1. Reaction Profiles and Physical Properties of Blend Catalyst Systems

Catalyst (pbw)					
DBTDL	0.15	0.15			
K-Oct			0.8	0.8	1.68
HX75	0.10		0.25		
HX35		0.11		0.32	
Reaction profiles					
C.T. (sec)	11	12	12	13	15
G.T. (sec)	50	50	50	50	50
R.T. (sec)	82	84	79	80	79
Physical properties					
Core density (kg/m ³)	45.8	44.8	42.9	44.6	63.9
Hardness (shore-C)	7	8	17	12	0
Flowability (g)	-9.8	-10.6	24.3	5.4	-15.3

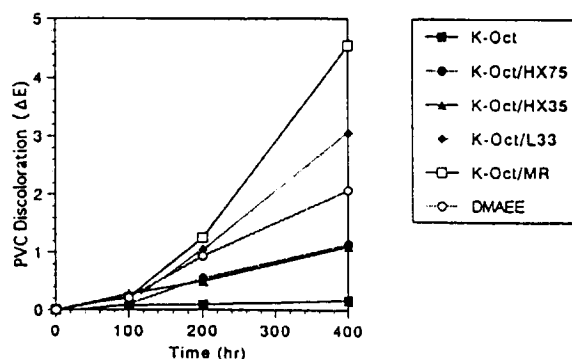


Figure 1. PVC Discoloration of Blend Catalyst Systems (K-Oct/Amine)

TOSOH's PRESENTATION AT PU CHINA '95

Followed from UTECH Asia '95 held May in Singapore, PU China '95 was held on November 8-10 in Beijing. This was the first international PU Exhibition held at the China, where remarkable growth in the PU industries is expected now and in near future. TOSOH Corp. presented, as last UTECH, to review tertiary amine catalysts in automotive application as well as appliance foam systems.

Flexible molded foams;

- long CT (cream time)
- Toyocat-TF & ETF
- long CT & improved moldability
- Toyocat-SPF2
- improved surface cure & moldability
- Toyocat-M50 & D60

Semi-rigid foams;

- Anti-vinyl staining
- Toyocat-HX63 & HX75

Appliance foams;

- improved flowability, dimensional stability, & thermal conductivity in HCFC-141b & cyclopentane blown
- Toyocat-TMF
- less expansion (fast cure)
- Toyocat-F40

REVIEW OF TEDA & TOYOCAT

BLOWING CATALYST

Toyocat-ET and DT are classified as the strongest blowing tertiary amine catalyst available today. The catalytic activities are shown in Table 2. Both compounds have similar molecular structure which contains an ethylene group chain between a nitrogen or oxygen atom. This structure makes the reaction of isocyanate and H₂O faster when one nitrogen atom coordinates the isocyanate group, the other nitrogen or oxygen atom forms hydrogen bond to adjacent H₂O molecule.

Toyocat-ET is commonly used in flexible and semi-rigid foam applications together with a gelling catalyst such as TEDA in order to improve cell-openness, as well as, flowability. In flexible slab-stock foams, ET is very common, but DT is also used in many cases. Therefore, the strong blowing catalyst DT has a possibility to replace ET in flexible and semi-rigid foams to provide almost similar performance with giving a cost merit. In some cases DT provides a better function.

At UTECH Asia 95, Dr. Wehman presented a unique difference between ET and DT (1). Using PMDETA(DT) as a blowing catalyst in hot cure moulding systems, it has been possible to provide 40% hard-

ness reduction, resulting in a CFC reduction of 10-12 php as shown in Table 3. This means DT provides stable foaming in all-water blown systems. This may be attributed to a little bit stronger gelling and crosslinking activities of DT (2).

When fogging or PVC staining is the problem, reactive catalyst having strong blowing activity such as RX3, RX5 and RX7 (RX7 is a new catalyst and not yet registered in TSCA & EINECS) are recommendable.

Toyocat-DT is primarily used in rigid foams. In rigid foams, blowing catalysts like DT can improve the dimensional stability, since the cell becomes more round while gelling catalyst has a tendency to provide an elliptical cell. However care should be taken when using DT as a sole catalyst because of poor k-factor. Blend of DT and other gelling catalysts produce lower k-factor and smaller cell size.

In order to improve dimensional stability with keeping better k-factor, cell nucleation catalyst Toyocat-TMF is recommendable as a blowing catalyst (3).

- (1) Cor Wehman and Jos Cenens., UTECH Asia 95, Conference paper 15
- (2) S.Okuzono et. al., Polyurethanes World Congress 1993, p.473.
- (3) H.Yoshimura, Polyurethanes 1994, p.300.

Table 2. Blowing Catalyst

Grade Name	Chemical Name	Gelling(1) TDI/DEG	Blowing(2) TDI/H ₂ O	Ratio (2)/(1)
Toyocat	ET Bis(dimethylaminoethyl)ether	29.9	117	39.0×10 ⁻¹
	DT Pentamethyldiethylenetriamine	42.6	159	37.3
	RX7 Reactive catalyst	32.6	60.7	18.6
	RX5 Reactive catalyst	28.9	43.3	15.0
	RX3 Reactive catalyst	18.4	25.5	13.9

Table 3. Effect of various amines on foam hardness in handmix moulding. (1)

Structure of screened amines	ILD 40% @ foam density of 30 kg/m ³ N
Reference	150
1) (CH ₃) ₂ -N-CH ₂ -CH ₂ -N-CH ₂ -CH ₂ -N-(CH ₃) ₂ <div style="text-align: center;"> $\begin{array}{c} \\ \text{CH}_3 \end{array}$ </div> PMDETA	119
2) (CH ₃) ₂ -N-CH ₂ -CH ₂ -CH ₂ -N-(CH ₃) ₂	146
3) (CH ₃) ₂ -N-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -N-(CH ₃) ₂	154
4) (CH ₃) ₂ -N-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -N-(CH ₃) ₂	163
5) (CH ₃) ₂ -N-CH ₂ -CH ₂ -CH ₂ -N-CH ₂ -CH ₂ -CH ₂ -N-(CH ₃) ₂ <div style="text-align: center;"> $\begin{array}{c} \\ \text{CH}^3 \end{array}$ </div>	150

TECHNICAL VIEW

REACTIVE AMINE CATALYSTS

TOSOH has supplied a variety of reactive tertiary amine catalysts as shown in Table 4, which covers blowing to gelling catalytic activity for many applications. Almost of listed reactive amine catalysts have OH group as terminal group.

Only Toyocat-RH2 and HX70 contain a terminal amino group, which quickly reacts with isocyanates compared to OH terminal group, thereby result in poor cure speed due to the decrease of catalytic activity after the reaction with isocyanate. The generated urea linkage, however, has a higher stability to thermal decomposition compared to urethane linkage produced by the reaction of OH group and isocyanate. Therefore RH2 and HX70 provide better improvement in fogging as well as vinyl-staining.

Toyocat-RX3, RX5, RX7 and HX75, which is classified as an OH group containing catalyst, provide relatively strong blowing catalytic activity, therefore these catalysts can improve flowability not only in semi-rigid foams but also in rigid foams. Especially Toyocat-RX7 and HX75 have the strongest blowing activity of the reactive amine catalysts.

Normally reactive amine has a weak catalytic activity compared to traditional non-reactive amine catalysts like TEDA, since the catalytic activity declines due to

the incorporation into the polymer structure by the reaction with isocyanate. Toyocat-RX5 and RX7, however, have a relatively strong catalytic activity.

Basically these reactive amine catalysts are applicable to semi-rigid foam systems in order to improve anti-vinyl staining as seen in Figure 2. Especially Toyocat HX4W, HX35W and HX63 are developed for the improvement of anti-vinyl staining as well as moldability.

In packaging foam, where the flowability and anti-fogging properties are strongly requested, RX3 and RX5 are utilized.

In rigid foams, especially in sprayed foam systems, where the odor and irritative property of amine catalyst is not favourable, the strong blowing catalytic activity, namely Toyocat-RX5 and RX7 are recommendable.

In the end, we must inform that Toyocat-RX7 is not registered in MITI, TSCA as well as in EINECS, and the registration is under preparation. Toyocat-HPW as well as HX4W and HX35W which contains HPW, are not registered in EINECS.

- (1) S.Arai et.al., SPI 30th Annual Technical/Marketing Conference, p.149 (1986)
- (2) Y.Tamano et.al., Conference Paper of UTECH92, p.57 (1992).
- (3) H.Yoshimura et.al., SPI 34th Annual Technical/Marketing Conference, p.364 (1992)
- (4) H.Kometani et.al., Polyurethane 1995, p.508

	Blowing/Gelling Activity Ratio
Reactive Amine	$\times 10^{-1}$
Toyocat-RH2	3.0
Toyocat-RX3	13.9
Toyocat-RX5	15.0
Toyocat-RX7	18.6
Toyocat-HPW	1.9
Toyocat-HX4W (1)	8.1
Toyocat-HX35W (1)	27.6
Toyocat-HX63 (2,3)	1.1
Toyocat-HX70 (2,3)	4.1
Toyocat-HX75 (4)	-
Non-reactive Amine	
TEDA-L33	1.3
Toyocat-DMCH	3.8
Toyocat-ET	39.0

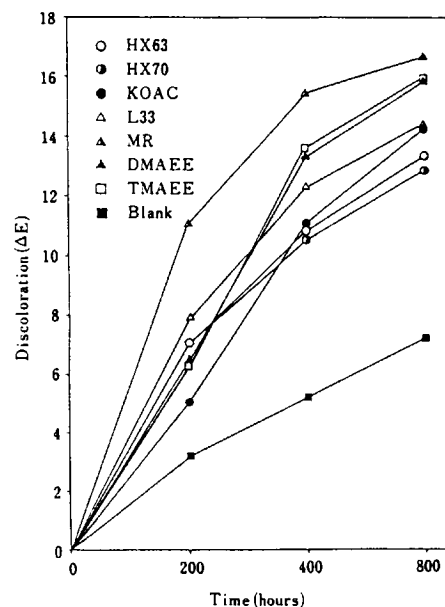


Figure 2. Discoloration of PVC covers on semi-rigid foams (at 120°C)

TOPICS IN JAPAN

JAPAN'S DEMAND OF POLYURETHANES IN 1994

PU foams demand in Japan in 1994 is a little bit increased compared to the year 1993 (Flexible = 166,400t, Rigid=100,800t), which is the worst year in these 7 years.

Compared to the best year 1990 (Flexible = 212,200t, Rigid = 109,000t), however, the production in flexible foams is only 77% while rigid foams is comparable. This is caused mainly by the reduction of automobiles production due to the economy recession and the decrease of exportation due to the strong yen rate. The automobiles production level in 1994 is also 78% of the year 1990. Since the flexible foams demand in Japan is strongly dependent on the automobiles industry (the ratio is 60%), this brought about unfortunate results of latest these years.

Table5. Japan's Demand of Polyurethane Material Applications in 1994.

	Volume (1000tonnes)	Ratio (%)	
Flexible Foams			
Automobiles	104.2	63.5	37.8
Beddings	12.0	7.3	4.4
Furnitures	12.7	7.7	4.6
Others	35.3	21.5	12.8
Total	164.2	(100)	-
Rigid Foams			
Appliances	39.5	35.4	14.3
Buildings	44.1	39.6	16.0
Transportations	4.5	4.0	1.6
Others	23.4	21.0	8.5
Total	111.5	(100)	(100)
Elastomers			
Castings	6.2		
TPUs	9.3		
Others	0.4		
Total	15.9		
Coatings			
Coatings	121.1		
Adhesives	37.8		
Coatings	49.8		
Sealings	29.8		
Leathers	18.5		
Fibers	11.8		
Total	560.4		

INFORMATION

TOYOCAT-TMF IN CYCLOPENTANE BLOWN APPLIANCE

Toyocat-TMF is successfully utilized in cyclopentane blown appliance foams, since TMF can improve flowability, dimensional stability as well as k-factor. As

clear in Figure 3, TMF provides not only lower density with narrower density distribution from the bottom to the top position, but also improved dimensional stability. The advantages of TMF will be introduced at UTECH'96.

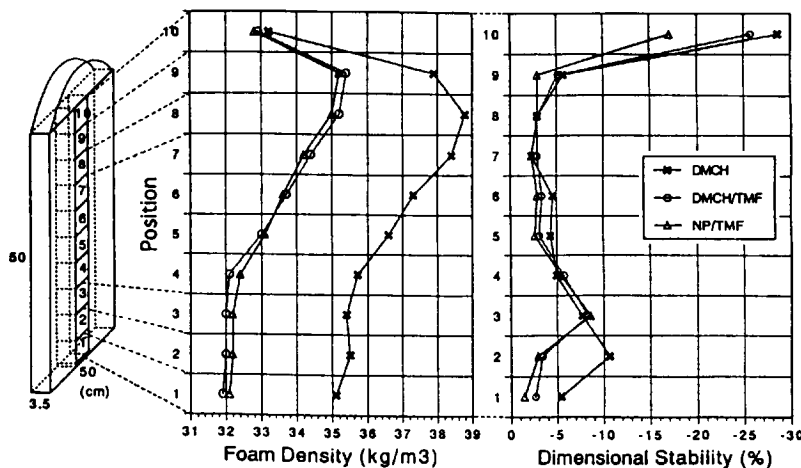


Figure 3. Flowability (Foam density distribution) and dimensional stability in cyclopentane blown appliance foam systems.

The blend with TMF provided low density and small density distribution, as well as improved dimensional stability in low density foams.

TOYOCAT-F94 APPLIES TO SYNTHETIC WOOD

Toyocat-F94 is now being applied to the production of synthetic wooden materials. The reason is that Toyocat-F94 can improve friability and surface hardness in all-water blown rigid foam systems.

The characteristics of F94 were previously introduced in TEDA & TOYOCAT NEWS Vol.3. Quicker demolding would be achieved with F94.