1995 January, Vol.2

TEDA & TOYOCAT NEWS

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A Happy New Year!! We hope you have continued great success in the new year.

It is a great pleasure for us to issue the second TEDA & TOYOCAT News. We hope it will serve to help you obtain maximum benefit of 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 PRESENTED A NEW CATALYST "TMF" AT PU '94

At Polyurethanes '94 held on October 10-12 in Boston, TOSOH presented an innovative amine catalyst TOYOCAT-TMF, which can be called a nucleation catalyst for cyclopentane(CP) and HCFC-141b blown rigid foam systems. TMF can improve flowability, dimensional stability as well as thermal conductivity. These improvement is due to its strong blowing activity, furthermore, improved thermal conductivity is contributed to a fine cell structure owing to a nucleation reaction during the initial foaming.

Moreover, TMF can reduce water level to obtain the identical foam density when using TMF as a co-catalyst.

The effect of a conventional blowing catalyst such as TOYOCAT-DT (PMDETA) on the reduction of foam density is relatively small. As seen in Table 1, however, TMF can dramatically reduce foam density with the same water level. For example, 2.4 parts of water can be reduced to 2.0 parts when using TMF as a co-catalyst, as compared with the case of using only base catalyst such as DMCHA and MR or together with DT. As a result, with less water formulated, improved dimensional stability as well as thermal conductivity is observed over water-rich systems.

Please try TMF in your CP or HCFC-141b blown systems in place of a conventional blowing catalyst!

Table-1. Reaction and phisical properties on 141b blown rigid foam system.

Catalyst (pbw)	MR 2.32	MR 2.20	DMCH 3.00	DMCH 2.80	NP 2.32	MR/DT 1.46/0.46	MR/TMF 1.57/1.0	DMCH/TMF 2.2/1.0	NP/TMF 2.75/1.0
H_2O (pbw)	2.0	2.4	2.0	2.4	2.0	2.0	2.0	2.0	2.0
Free rise foam 1)									
Cream time (sec)	14	12	12	13	12	9	10	9	8
Gel time	49	50	49	49	50	50	50	50	50
Rise time	73	74	77	70	75	77	77	78	77
Core density (kg/m3)	24.0	22.6	23.8	22.4	23.8	23.8	22.7	22.8	22.8
Panel mold foam (100% pack) 2)									
Min. fill density (kg/m3)	30.7	28.9	29.9	28.2	30.0	29.7	28.8	28.7	28.6
Core density (kg/m3)	26.7	25.4	25.9	24.6	26.3	26.0	25.3	24.9	24.9
Dimensional stability (%)	-20.7	-38.4	-13.1	-17.8	-11.7	-12.9	-11.3	-4.7	-4.0
K-Factor (mW/m.K)	17.1	17.4	17.3	17.6	17.3	17.4	17.1	17.1	16.9
Panel mold foam (112% pack) 2)									
Over all density (Kg/m3)	34.3	32.4	33.6	31.7	33.9	33.1	32.5	32.5	32.0
Compressive strength									
Parallel (kgf/cm2)	2.21	1.97	1.92	1.87	2.09	1.94	1.97	1.79	1.76
Perpendicular	1.13	1.06	1.08	1.01	1.23	1.04	1.05	1.02	1.09
Ratio (%)	1.96	1.86	1.78	1.85	1.70	1.87	1.88	1.75	1.61
Dimensional stability (%)	-1.8	-3.1	-0.8	-1.3	-0.2	-2.0	-0.2	-0.2	-0.2
K-Factor (mW/m.K)	17.6	17.8	17.6	17.8	17.6	17.7	17.3	17.4	17.3

1) Free rise foam, mold=2l polyethylene cup. 2) Panel = 50 x 50 x 4.5 cm. Details: : Proceedings of Polyuretahnes '94, p300.

REVIEW OF TEDA & TOYOCAT

CATALYTIC ACTIVITY OF ALL TOYOCATs

For many years TOSOH has supplied a wide variety of tertiary amine catalysts. For the convenience for customers in order to select a suitable catalyst, we previously presented the basic gelling and blowing catalytic activities for many conventional grades as shown in Figure 1. The determination of usage level of amine catalyst, however, bothers customers at the evaluation test.

Therefore we would like to show the general catalytic activity on the following table. Since the catalytic activity will be changed dependent on the application, the value is shown on each application. The value shows the usage level (pbw) of each catalysts when the level of TEDA-L33 or DMCH is 1.0 pbw. That is to say, the larger value means the weaker catalyst.

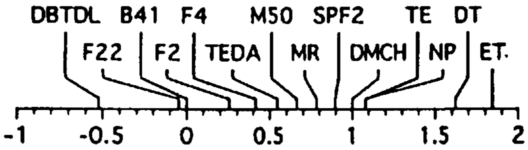

Figure 1. Blowing/Gelation activity ratio (log[k2c/k1c]. cf. Polyurethanes World Congress 1993, p.473)

Table 2. Catalytic Activity (pbw)

	Flexible Foam Slabstock Hot cure	Flexible Foam Cold cure	Semi-rigid Foam (ISF)	Rigid Foam Less water ca.2pbw	Rigid Foam Rich water ca.4pbw	Characteristics
L33	1.0	1.0	1.0	0.85	1.2	Reference (Flexible & Semi-rigid)
DMCH	-	-	-	1.0	1.0	Reference (Rigid)
ET	0.45	0.45	0.7	0.85	0.6	Blowing Catalyst
DT	0.45	0.5	-	0.6	0.5	Blowing Catalyst, Replaceable to ET
TE	-	-	-	0.8	0.8	Flowability
NP	0.6	0.95	-	1.2	1.25	Thermosensitive, Inside cure
MR	0.75	0.75	0.8	0.75	0.8	Non-thermosensitive, Surface cure & Moldability
TRC	-	0.8	-	-	1.1	Cure
TF	1.4	1.45	1.2	1.1	1.1	Delayed action catalyst of L33, Flowability, Cure
THN	-	-	-	1.2	1.2	Delayed action catalyst of L33, Flowability, Cure
ETF	-	1.0	1.2	1.2	-	Delayed catalyst of ET, Flowability
M50	0.9	0.9	0.85	-	-	Surface cure & Moldability
D60	1.4	2.0	-	2.0	2.0	Surface cure & Moldability
HX63	1.4	1.4	1.4	-	-	Reactive amine(Anti-vinyl stain, Fogging), Moldability
SPF2	0.85	0.85	0.85	-	-	Delayed action, Flowability, Moldability
B41	1.0	1.0	(1.1)	1.6	-	Delayed action (than TF), Cure
F22	-	0.9	(1.0)	-	-	Delayed action (than TF), Cure Skin formation (ISF)
F2	1.35	1.6	-	-	-	CFC-free, Low density & Moldability
F4	1.45	1.6	-	-	-	CFC-free, Low density & Moldability
TMF	-	1.4	-	1.25	-	Flowability, k-Factor, Dimensional stability
B20	-	-	-	0.75	-	Flowability, k-Factor
B54	-	-	-	0.6	-	Flowability, k-Factor
F83	-	-	-	1.2	1.5	Water-blown, Flow, Friability
F94	-	-	-	0.95	1.2	Water-blown, Friability
F40	-	-	-	0.6	-	Cure(Less expansion)

The value shows the usage level (pbw) of each catalysts when the level of L33 or DMCH is 1.0 pbw.

TECHNICAL VIEW

Tertiary Amine Catalysts F2, F4 & F94 for non-CFC Systems.

The establishment of CFC-free systems must be accomplished by the year 1995.

In flexible molded foams, all-water blown systems have been achieved, however, has led to an increase in the urea linkage in the polymer structure, and resulted in the increase of the foam hardness as well as the poor elongation and wet compression set. Furthermore, as the increase of water level, foaming stability becomes extremely poor, and the lowering of the foam density is limited. Moreover curing function as well as moldability becomes worse. For improving these problems, F2 & F4 is offered as a possible solutions.

In hot molded foams, as seen in Figure 2 and 3, F2 & F4 provided lower density as well as high air-flow, which could be applied to low density slabstock flexible foams. The combination of F2 and TEDA-L33(1/2-1/4) will be recommendable.

In all MDI and TDI/MDI based HR foams, F2 & F4 also provide lower density with high water level and improved cure and moldability as shown in Figure 4. The combination of F2/L33 (1/2-1/4) and ET is desirable for adjusting cell-openness.

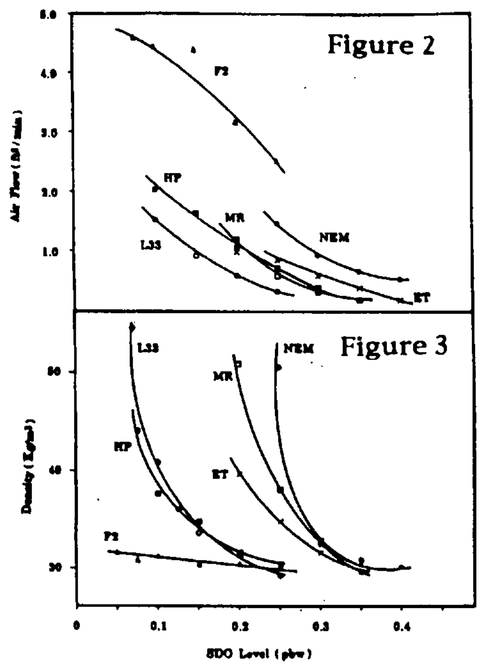

Figure 2 & 3. The influence of stannous diocotate level on foam density and air-flow for each amine catalyst in hot cure foam systems.

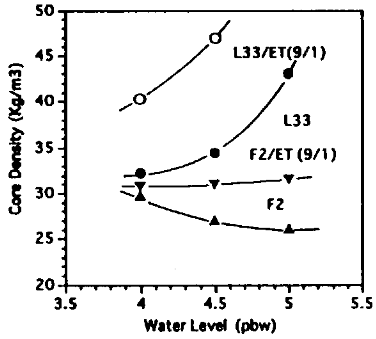

Figure 4. The effect of water level on foam density in all-MDI HR foam system.

On the other hand, in rigid foam systems, the attempts to utilize all-water blown systems or to apply an alternative blowing agents such as HCFC-141b or 22/142b, as well as n-/i- or cyclopentane are being examined. Even in the latter cases, water rich systems are required. When using high quantities of water, however, there exists a big problem in friability or adhesive strength as well as poor thermal conductivity and dimensional stability.

Among these problems, F94 can dramatically improve friability or adhesive strength as shown in Figure5. Since F94 has a stronger gelling activity than TEDA, however, dimensional stability is not improved. Therefore in order to achieve well-balanced properties for improving friability and dimensional stability, the combination of base catalysts such as DMCHA and MR with F94 is recommendable(DMCH or MR/F94=1/1-2/1). For improving dimensional stability, blowing catalyst such as DT and TMF is effective as a third component ([DMCHorMR+F94]/[DTorTMF] =7/3-8/2).

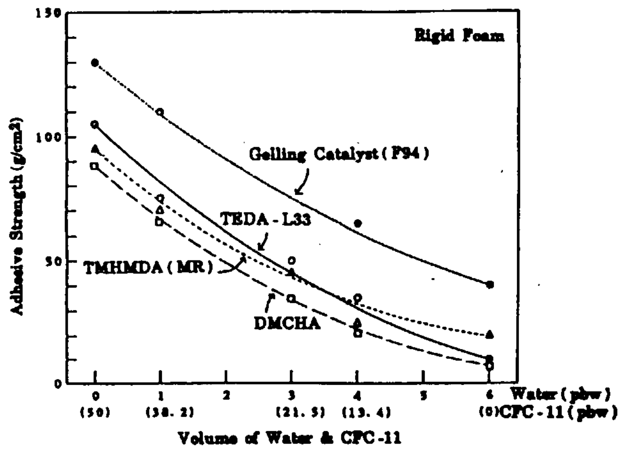

Figure 5. Effect of water & CFC-11 level on adhesive strength for each amine catalysts in rigid foam systems.

TOPICS IN JAPAN

CP BLOWN APPLIANCE FOAM SYSTEMS HAVE STARTED

In Japan, although one primary blowing agent is being changed to HCFC-141b, a few refrigerator manufacturers have just begun cyclopentane (CP) blown system. SHARP has adopted a CP-blown system combined with a vacuum insulation panels. They have changed their all-water blown systems to CP-blown in order to improve foam density as well as dimensional stability.

MATSUSITA, which is a biggest refrigerator manufacturer in Japan, also has just started. This decision may have a big impact on other Japanese manufacturers.

It is said that the thermal conductivity of CP blown systems is comparable to 50% CFC-11 reduction systems. Since HCFC-141b blown systems provide better thermal conductivity than CP blown ones, 141b systems are still major option.

However, there exists the trend that CP blown systems will spread not only in Japan but also throughout Asia.

INFORMATION

UTECH ASIA 95

The next UTECH meeting (UTECH Asia '95) will be held on May 23-25 in Singapore. TOSOH Corporation will have a stand and presentations which concerns tertiary amine catalysts for automobile parts (flexible and semi-rigid foams) as well as non-CFC rigid foam systems.

Please visit and contact us at TOSOH's stand.

TEST METHOD FOR MEASURING VISCOSITY PROFILE

The rise-gel profile is one of the most important factors on the evaluation and production of polyurethane foams. Especially gel profile is considered to have a concern with cure speed as well as moldability relating to the productivity.

Therefore evaluation method of gel profile is important for developing suitable catalyst systems.

TOSOH is using a dynamic vibrational viscometer for measuring viscosity profile which is one of gel profiles. The rod which is driven in a vibrational motion with a defined frequency is immersed in the foaming liquid as shown in Figure 6. Of course, the rod can be immersed from upperside with moving the rod as the foam rises. Moreover the rise and temperature profiles can be measured on the same foaming. Typical reaction profiles are shown in Figure 7.

The actual measured viscosity exhibited a decreasing curve in latter stage of foaming when the rod is fixed on the side of the cup. This temporary decrease in apparent viscosity profiles is caused by a decrease in foam density due to the initial expansion of the foam during foaming stage. Therefore the actual viscosity needs to be converted by the change of density, as shown in V-M in Figure 7..

cf. Proceedings of UTECH92, Page 57

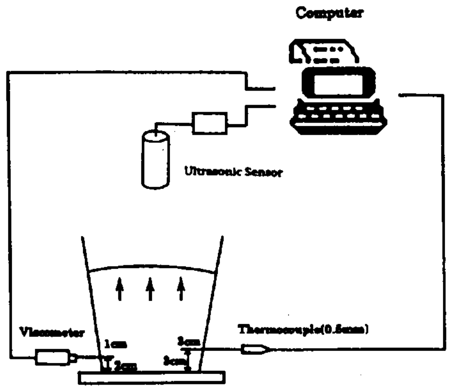

Figure 6. Measurement system for rise, viscosity and temperature profiles.

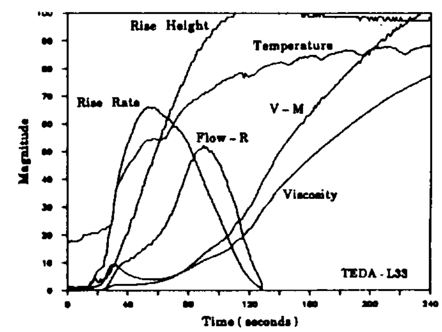

Figure 7. Typical reaction profiles of rise height, rise rate, temperature and viscosity.

Rise Height (%), Rise Rate (×10⁻¹, inches/s), Temperature (°C), Viscosity (×10⁻¹, Pa·s), V-M (Pa·s), Flow-R (Pa·inch).