TECHNICAL UPDATE

Resin Solutions

Mercury-Free Cure for Poly BD®-based Polyurethanes

Benefits

- Mercury-free catalyst system for Poly BD®-based polyurethane insulated glass sealants
- Long pot life
- Fast cure rate

Description

The goal of this study is to provide technical support for two upcoming changes within the Insulated Glass Sealants (IGS) application, namely the European REACH regulation regarding the use of mercury (Hg) and Hg-based compounds for industrial and professional applications, and the resulting current Hg-supply issue.

With regard to the IGS application, close attention will be given to two main parameters: pot life and cure rate. Pot life needs to be long enough to allow application (setting of the glass sheets) and cure rate fast enough to avoid any accident once the sheets are set up.

The components of the formulations used in this study are shown in Table 1.

Table 1: List of components used in the study.

Nature	Code	Base Metal(s)	Symbol	Description
Catalyst	REF	N/A	--	Reference = No catalyst
	A	Tin	Sn	Dibutyl tin dilaurate
	B	Bismuth	Bi	Bismuth neodecanoate (20% Bi) in polypropylene glycol
	C	Zinc	Zn	Zinc neodecanoate (19% Zn)
	D	Zirconium	Zr	Zirconium neodecanoate (12% Zr)
	E	Potassium	K	Potassium octoate (15% K)
	F	Bismuth/Zinc blend	Bi + Zn	Bismuth and zinc neodecanoate _ Bi:Zn=1:1
	G	Mercury[1]	Hg	Bis phenyl mercury dodecenylsuccinate
Isocyanate (MDI)	NCO_1	N/A		Isonate™ M 143[2]
	NCO_2			ONGRONAT® 3800[3]
Polyol	CTR			100% Poly BD® R45 HTLO
	Mix			Blend of Poly BD® R45 HTLO : LBH 3000 (95:5)

Screening of Different Metal-Based Catalysts: Cure at 80 °C

The PU elastomers tested are made with Poly BD® R45 HTLO and Isonate™ M 143 as diisocyanate (NCO/OH=1.03). Different catalysts are tested, which impacts the kinetics of the reaction. The extent of cure (S') versus time curves are shown in Figure 1.

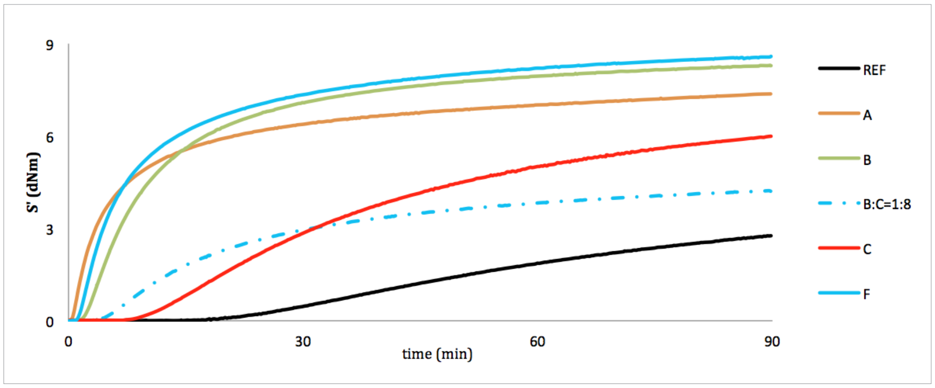

Figure 1: Curing profile at 80 °C and 2000 ppm catalyst.

Zn-based catalyst (C) offers the longest pot life (outside the non-catalyzed PU). Bi-based PU (B) is the quickest to react, as well as the blend of bismuth and zinc salts (F). Blending metals such as Bi and Zn seems to allow compromises of the wanted properties for each metal; it might increase the pot life compared to Bi-catalyzed PU and improve reactivity of the Zn-catalyzed PU.

Screening of Different Metal-Based Catalysts: Cure at Room Temperature

The raw PUs are made with Poly BD® R45 HTLO, 2000 parts per million (ppm) of different catalysts and ONGRONAT 3800 as diisocyanate (NCO/OH=1.08). Formulations are made at room temperature (RT), and the cure takes place in a room at constant temperature (23 °C) and humidity level (50%) for several days (about one week). Shore hardness development versus time curves are shown in Figure 2.

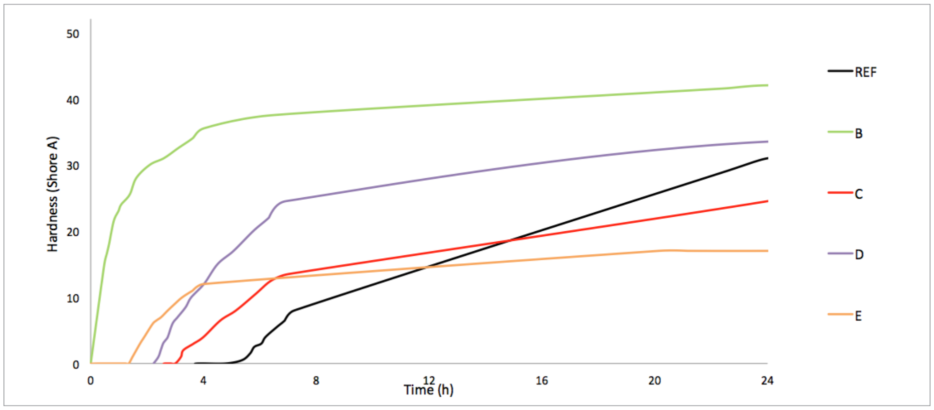

Figure 2: RT maturation curves for PU catalyzed with metallic salts (Ref vs. Bi, Zn, Zr and K).

Zirconium (D) and potassium (E) salts do not present any interest for this application due to very low final hardness value and slower cure. Even blended, Zr (D) does not bring any remarkable improvements (not presented here).

Focus on Bismuth and Zinc

The raw PUs are made with Poly BD® R45 HTLO, 2000 ppm of different Bi:Zn blends and ONGRONAT® 3800 as diisocyanate (NCO/OH=1.08).

Bi:Zn ratios are varied from 1:1 to 1:8, as shown in Table 2, to determine the influence of each metal. PUs are formulated and cured at RT.

Table 2: Bismuth:zinc catalyst ratios and metal content.

Composition (2000 ppm catalyst)	Metals content (approximation)
F = Bi:Zn =1:1	16.0%
B:C = 1:2	19.5%
B:C = 1:4	19.2%
B:C = 1:6	19.2%
B:C = 1:8	19.1%

Increasing the Zn portion of the catalyst system tends to slow down the cure rate, especially during the first hours of the cure, but also increase the pot life. Figure 3 shows cure profiles as hardness development after 4 and 24 hours, and pot life versus catalyst composition. Overall, catalyst composition does not significantly impact the hardness development. Table 3 gives detailed data in comparison with the Hg-cured system. The fastest curing and shortest pot life are observed for Hg-cured PU.

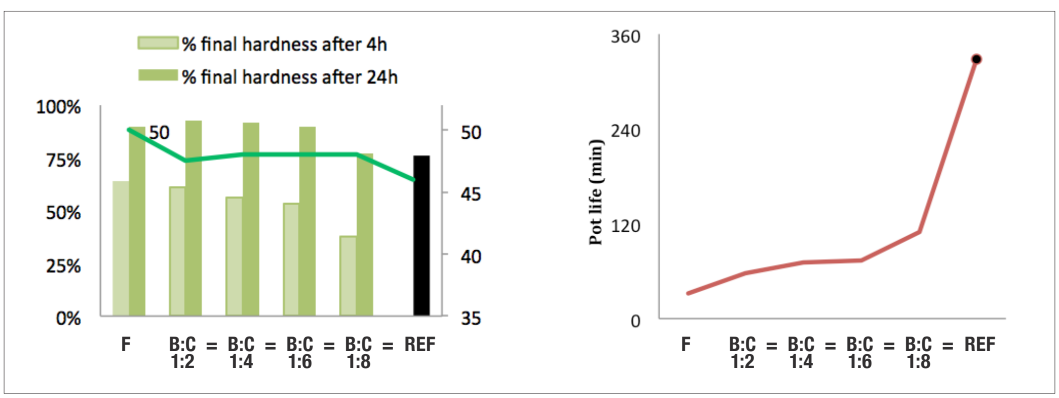

Figure 3: Effects of Zn increase on the cure profile of Poly bd-based PU (RT cure; 2000 ppm catalyst).

Table 3: Hardness development and pot life comparison between the bismuth:zinc-catalyzed PUs and the Hg-cured system[4].

Code	Pot Life (min)	Hardness (Shore A)					Delta (%) versus Hg ref (2000)			
		4h	24h	Final Hardness (Shore A)	% Final Hardness after 4h	% Final Hardness after 24h	Pot Life (min)	Final Hardness (Shore A)	% Final Hardness after 4h	% Final Hardness after 24h
F	32	32	45	50	64%	90%	28%	-20%	-8%	-2%
REF	328	0	35	46	0%	76%	1212%	-100%	-29%	-10%
B:C = 1:2	57	29	44	47, 5	61%	93%	128%	-28%	-10%	-7%
B:C = 1:4	71	27	44	48	56%	92%	184%	-33%	-10%	-6%
B:C = 1:6	74	25, 5	43	48	53%	90%	196%	-36%	-12%	-6%
B:C = 1:8	110	18	37	48	38%	77%	340%	-55%	-24%	-6%

A small amount (5%) of a secondary hydroxy terminated polybutadienediol can be added to the Poly BD® R45 HTLO in order to delay the beginning of the cure, and so extend pot life without decreasing the cure rate. Open time and hardness development values are shown in Table 4.

Table 4: Effect on open time and hardness of mixing a secondary diol and Poly BD® R45 HTLO (RT cure)[5].

	Open Time (min)		Final Hardness (shore A)		% Final Hardness after 4h		% Final Hardness after 24h	
	CTR	Mix	CTR	Mix	CTR	Mix	CTR	Mix
B	32	29	37	33	81%	79%	100%	94%
F	30	37	39	40	72%	68%	92%	93%
C	255	261	36	35	0%	0%	86%	77%
REF	464	524	39	39	0%	0%	59%	62%

Pot life tends to increase when using the mix of polyols (Mix), regardless of the type of catalyst, and even without catalyst. In addition, final hardness[6] and cure rate are not affected.

Conclusion

In order to find a suitable alternative to Hg catalysts for PU IGS application, two critical factors must be preserved: pot life long enough to allow application and quick curing after application. Several formulating alternatives have been identified:

- A catalyst based on bismuth and zinc seems to be a good compromise: it offers quick cure (thanks to Bi) and pot life can be adjusted (thanks to Zn).
- Another way to increase pot life is by adjusting the catalyst quantity, but this approach does affect the cure rate.

To summarize, these alternative solutions can get close to the efficiency of typical Hg catalysts while avoiding the environmental issues associated with tin and mercury. The above results need to be used with caution, as they concern non-formulated PU only. The addition of fillers during the formulation step requires more developmental work to fine-tune a suitable Hg-free solution.

Notes

[1] Due to Resin Solutions safety rules, Hg catalyst is not allowed in our R&D sites; values used in this report were collected and given by a partner (same test methods).

[2] Isonate M 143 modified MDI is a trademark of The Dow Chemical Company ("Dow") or an affiliated company of Dow.

[3] ONGRONAT 3800 is a carbodiimide-modified MDI manufactured by BorsodChem.

[4] Due to Resin Solutions safety rules, Hg catalyst is not allowed in our R&D sites; values used in this report were collected and given by a partner (same test methods).

[5] The raw PU is obtained by reaction of "Mix" (see Table 1), 2000 ppm of catalyst (various catalysts) and Isonate M 143 as diisocyanate (NCO/OH=1.08).

[6] Especially with a +/-5 precision for Shore A Hardness measurements.

About Resin Solutions

Resin Solutions is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemical, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings and other materials. Resin Solutions has pioneered the development of these advanced technologies, introducing products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics, and other demanding applications.

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Resin Solutions
665 Stockton Drive, Suite 100
Exton, PA 19341
1-484-284-8998