

EMERGING HYCAT™ CATALYST SYSTEMS

In curing studies examining the reaction of epoxides with carboxylic acids, anhydrides or phenols, three emerging Hycat™ catalyst products have demonstrated unique catalytic activity. These catalysts are called **Hycat™ UC**, **Hycat™ ZC** and **Hycat™ ZEP** and are prepared using a DTCS proprietary process. Tests have shown that these new catalysts perform similarly to Hycat™ 2000S and Hycat™ 3000S but because they are *colorless or nearly colorless*, they have the added advantage of not imparting color to the final product. Because Hycat™ UC, ZC and ZEP are not registered, they are available in *research quantities only*.

Hycat™ UC also behaves like Hycat™ AO-1 with some cure advantages in certain formulations. Hycat™ UC is an extremely good acceleration catalyst for the reaction of anhydrides with either bisphenol A (or F) epoxides or cycloaliphatic epoxides. It appears to be only moderately effective in reacting aliphatic carboxylic acids with epoxides. Hycat™ UC is not corrosive in nature and, therefore, suitable for use in the electronic industry. Hycat™ UC is light yellow in color and imparts little color to the final cured formulation.

The **Hycat™ ZEP** and **Hycat™ ZC** catalysts were developed to provide an efficient, *non-basic, essentially colorless* catalyst to promote the reaction of aliphatic carboxylic acids (e.g., Empol 1016 Dimer acid) with cycloaliphatic epoxides (e.g., UVACure 1500 series, ERL 4221). Hycat™ ZC (and probably Hycat™ ZEP) was found to be a more active catalyst than Hycat™ UC in this reaction. Neither Hycat™ ZC nor Hycat™ ZEP accelerated the reaction of epoxide/anhydride systems nor, in preliminary studies not yet complete, epoxide/hydroxy-phenol systems. Based on the results of reactions of epoxides with saturated carboxylic acids, Hycat™ ZC (and probably Hycat™ ZEP) is a more effective catalyst than Hycat™ UC. By comparison, it would be reasonable to assume that Hycat™ ZC (and probably Hycat™ ZEP) would greatly accelerate the reaction of unsaturated carboxylic acids, such as acrylic acid, with epoxides like the UVACure series 1500 provided that double bond polymerization inhibitors are used. Like Hycat™ ZC and Hycat™ ZEP, Hycat™ UC does not impart high color to the final product.

Hycat™ ZC, **Hycat™ ZEP** and **Hycat™ UC** are temperature dependent for its catalytic activity. In typical epoxy-carboxylic acid systems at room temperature, the pot life is greater than 24 hours while at 100^o C the cure takes but a few minutes. The attached data tables demonstrate this point more clearly.

CURE STUDIES – VARIOUS HYCAT™ CATALYSTS

The catalysts were evaluated in four different epoxy-resin/hardener compositions, namely (weight ratio given respectively):

Composition A: DGEBA/MHHPA (100/80)

Composition B: ERL 4221/MHHPA (42/48)

Composition C: ERL 4221/Empol 1016 Dimer Acid (50/50)

Composition D: ERL 4221/Bisphenol A (70/30)

Cure studies were conducted at 130^o and 100^o C. Into small aluminum dishes (diameter 1.5 inch) were placed 5 grams of the liquid epoxy/hardener mixture containing the catalyst to be evaluated. The dish was then quickly placed into a preheated oven onto a massive steel plate to effect rapid heat up to the desired temperature. The time required (measured in minutes) to transform the liquid test sample into a hard, non-flowing mass was noted as the “cure time”. For comparison, data obtained using 1-methylimidazole as the catalyst is included.

Table 10

CATALYST	Temp, °C	Catalyst Loading, Wt. %	Comp A Cure Time, Min.	Comp B Cure Time, Min.	Comp C Cure Time, Min.	Comp D Cure Time, Min.
Hycat™ AO-1	130 ^o	0.25	16	--	--	--
Hycat™ AO-1	130 ^o	0.5	9	--	--	--
Hycat™ UC	130 ^o	2	5	3	15	36
Hycat™ UC	130 ^o	1	9 ^a	6	--	--
Hycat™ UC	130 ^o	0.5	14	9	--	--
Hycat™ UC	100 ^o	2	9	6	--	--
Hycat™ UC	100 ^o	1	12	9.5	--	--
Hycat™ UC	100 ^o	0.5	19	16	--	--
Hycat™ ZC	130 ^o	2	--	--	< 3	--
Hycat™ ZC	100 ^o	3	~ 40 ^b	25	6	--
Hycat™ 2000S	130 ^o	4	4	4	--	30
Hycat™ 3000S	130 ^o	4	4	4	--	30
1-Methylimidazole	130 ^o	2	6	5	40	--

(a) Pot life about 2 days at room temperature

(b) Catalyst not completely miscible in composition A

Note: Composition A will give a hard cure in 8 minutes when 0.25% Hycat™ AO-1 is used at 150^o C, but remains mobile for 3.5 hrs at 80^o C and 100 hours at 22^o C.

COMPARATIVE REACTION RATE STUDIES

The **Hycat™ Catalysts** were evaluated using a stoichiometric mixture of UVACure 1502 and 2-ethylhexanoic acid (EHA). This acid was selected because of its good handling characteristics. Studies were conducted at **75°** and **100° C** and aliquots of the test samples were analyzed for unreacted EHA after a short reaction time. The data shows the amount of EHA that reacted after 23 minutes at 75° C in one series of experiments and after 10 minutes at 100° C in another series of experiments. The reaction time intervals were considered long enough to allow for equilibration of the reaction temperature. It was found that in practically all the tests that used an equivalent amount of reactants, unreacted acid was still present although the epoxide had been consumed, presumably due to homopolymerization of the epoxide moiety. Depending on the reaction conditions and the type of acid used, the degree of acid conversion using Hycat™ ZC ranges from 85 to 95%. A slight excess of the epoxide is required to completely react the carboxylic-acid.

CATALYSIS OF STOICHIOMETRIC MIXTURES OF UVACURE 1502 AND 2-ETHYLHEXANOIC ACID (EHA)

Table 11

CATALYST	Temp, °C	Catalyst Loading Wt. %	Reaction Time, Min.	% EHA Reacted	% EHA After Epoxy Depleted
Hycat™ ZC ^{a,b}	75°	2	23	78	87
Hycat™ UC	75°	2	23	26	90
Hycat™ 2000S	75°	2	23	97	98
Hycat™ 3000S	75°	2	23	97	98
1-Methylimidazole	75°	2	23	30	82
Control (none)	75°	--	960	37	--
Hycat™ ZC	100°	2	10	86	89
Hycat™ UC	100°	2	10	51	89
Hycat™ 2000S	100°	2	10	98	99
Hycat™ 3000S	100°	2	10	98	99

- (a) At room temperature (22° C) and with 2% catalyst, only 6% of the EHA reacted after a 24 hr. period.
- (b) Substituting proponic acid for EHA, 90% of the acid reacted in 10 minutes. On depletion of the epoxide, 95% of the acid reacted.

HOMOPOLYMERIZATION – HYCAT™ ZEP & HYCAT™ ZC

Both **Hycat™ ZEP** and **Hycat™ ZC** were found to be very strong *homopolymerization* catalysts for DGEBA(F) epoxides, hydroxy terminated polybutadiene epoxides and cycloaliphatic epoxides (temperature ranging from 20 to 130^o C). In this regard, Hycat™ ZEP is a much more efficient homopolymerization catalyst than Hycat™ ZC. Work is continuing to observe how these catalysts behave in the homopolymerization of lower molecular weight epoxides.

Using **Hycat™ ZEP** at a 2 to 4% concentration and at a temperature range of about **20^o to 130^o C** different types of epoxy resins were effectively *homopolymerized*. The epoxides studied included bisphenol A type diglycidyl ether (EPON 828, Shell), internally epoxidized hydroxy terminated polybutadiene (Poly BD® 605, Elf Atochem) and Cycloaliphatic diepoxide resins (UVACure 1502, UCB Chemicals; ERL 4221, Union Carbide). Working with these materials, the order of reactivity was found to be:

(UVACure 1502 or ERL 4221) >>> Poly BD® 605 > EPON 828

Table 12 shows the typical performance of **3% Hycat™ ZEP** as a homopolymerization catalyst at **100^o C** is shown below:

Table 12

Epoxy Compound	Temp, °C	Cure Time, Min.	Hardness, Type D Durometer	Pot Life, Hours
Poly BD® 605	100^o	9 – 10	10 – 15	> 20 @ 32 ^o C
EPON 828	100^o	10 – 11	75 – 85	> 20 @ 25 ^o C
UVA Cure 1502	100^o	3 – 5	85 – 90	3 @ 25 ^o C
ERL 4221	100^o	3 – 5	85 – 90	3 @ 25 ^o C

By changing the cure conditions, i.e., temperature, catalyst loading, the rate of homopolymerization and properties of the resulting plastic can be easily changed. For example, at **80^o C** the cure time for Poly BD® 605 with 3 % **Hycat™ ZEP** was about **3 hours** and the polymer had a hardness of about 5 (Type D, Durometer).

Other resinous epoxides are expected to work as well.

HYCAT™ ZEP & HYCAT™ ZC – CURE TESTS

DONE IN 2.25 in. DIAMETER ALUMINUM PANS (10 gram loading).

Table 13

Polymer Composition	Hycat™ Catalyst	Catalyst Loading (pph)	Oven Temp, °C	Gel/Cure Time, Min.	Appearance	Hardness Type A	Hardness Type D
<i>Homopolymerization</i>							
UVA Cure 1501 (UCB Chem)	ZC	3.3	125°	< 7	Hard, slight yellow	---	87
UVA Cure 1501 (UCB Chem)	ZEP	2.9	125°	< 7	Hard, Lt. Yellow	---	90
DER 332 (Dow)	ZEP	3.3	125°	11	Clear, soft, yellow	32	7
Poly BD 605 (Atofina/Elf Atochem)	ZC	2.8	125°	47		soft	---
Poly BD 605 (Atofina/Elf Atochem)	ZEP	3.6	125°	30	Clear, soft, yellow	14	---
UVA Cure 1501/Poly BD 605 (10:6.4)	ZEP	3.2	125°	17		43	10
Epithio-ERL 4221 (DTCS)	ZEP	3	125°	< 10	Clear, yellow	---	85
<i>Acid/Anhydride Curing Agents</i>							
UVA Cure 1502 / MHHPA (42:48)	ZC	3	125°	> 8 < 12	Hard, slight yellow	---	68
UVA Cure 1502 / MHHPA (42:48)	ZEP	3.4	125°	< 5	Hard, Lt. Yellow	---	78
UVA Cure 1502 / Empol 1016 dimer acid (40:50)	ZC	3	140°	> 5 < 10	Clear, soft, yellow	21	6
UVA Cure 1502 / Empol 1016 dimer acid (40:50)	ZEP	3	140°	> 5 < 10	Clear, soft, yellow	39	12
UVA Cure 1502 / MHHPA / Empol 1016 (30:19:51)	ZC	3	145°	> 2 < 5.5	Clear, yellow	80	38
UVA Cure 1502 / MHHPA / Empol 1016 (30:19:51)	ZEP	3.4	145°	> 2 < 5.5	Clear, yellow	95	49
Epon 828/MHHPA (100:85.4)	ZC	3	105°	> 120	tacky	---	---
Epon 828/MHHPA (100:85.4)	ZEP	3	105°	> 120	soft	---	---