CHROMIUM (III) HYCAT™ CATALYSTS

The active ingredient in **Hycat™ 2000S, Hycat™ 3000S,** and **Hycat™ OA** is based on an activated (DTCS Proprietary Process) oxo-centered-trinuclear [chromium III] complex. Chromium III compounds are generally considered to be non-toxic by the EPA. Depending on catalyst concentration and formulation, cured products range in color from light to dark green. Typical catalyst loadings range from **1 to 5 %** however higher or lower concentrations can be used depending on the formulation and desired end result. Cures and gels are typically realized at low to moderate temperatures **(15-50^{O} C.)** Fast cures, from seconds to a couple of minutes are realized with temperatures higher than 50^{O} C.

It is important to note that non-toxic **Chromium (III) derivatives should not to be confused with the hazardous chromium (VI) valency compounds.** Large quantities of chromium (III) compounds are used by the general public and various industries. **For example, chromium (III) picolinate, a vitamin supplement, is sold in drug stores and health food stores**. Chromium (III) compounds are also used by the petroleum industry in a number of applications and are considered to be environmentally friendly. A recently published EPA report [Toxicological Review of Trivalent Chromium] addresses this issue. This report can be acquired from: www.epa.gov/iris/toxreviews/0028-tr.pdf. Clearly, chromium (III) compounds, found in the Hycat™ 2000S, Hycat™ 3000S and Hycat™ OA should not be confused with the hazardous chromium (VI) compounds.

Hycat™ OA, Hycat™ 2000S and **Hycat™ 3000S** are commonly used to accelerate the reaction of epoxy compounds with carboxylic acids, anhydrides and imides. These catalysts are especially effective in polymer cure systems at **room temperature** or slightly elevated temperatures. Studies show that when epoxide systems are catalyzed with these Hycat™ Catalysts, very little homopolymerization occurs. By using compounds with monomeric, dimeric or trimeric functional groups, the degree of cross-linking and therefore the mechanical properties of the resulting product can be advantageously modified.

Both the **Hycat™ 2000S** and **Hycat™ 3000S** are designed to have ***non-corrosive properties*** in their final composition. This attribute makes Hycat™ Catalysts useful in coatings, electronic circuit boards and other systems that require low-corrosion properties.

Hycat™ 3000S acts similarly to Hycat™ 2000S except that it has additional ***cure-system modifiers*** that enhance its performance in a variety of epoxy-anhydride formulas. Hycat™ 3000S ***improves the solubility characteristics*** in difficult epoxy-anhydride formulas resulting in uniform cures.

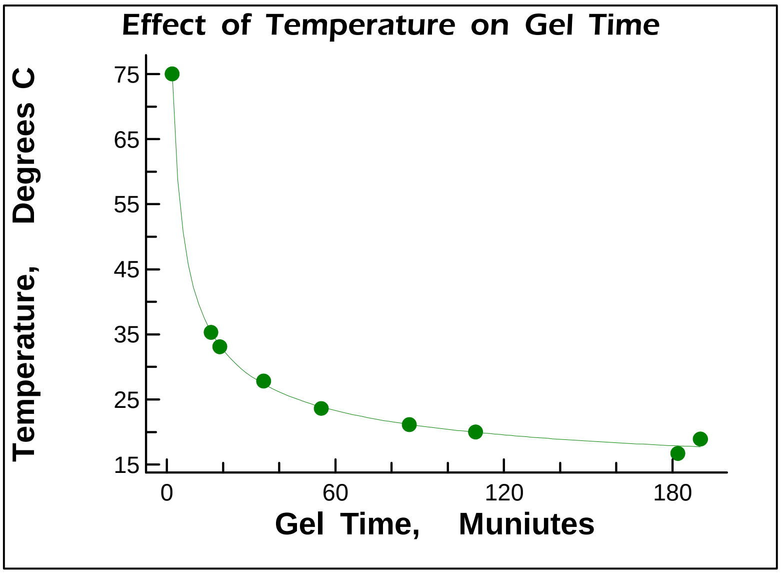
Hycat™ OA shows similar performance (e.g., gel time vs. temperature) as Hycat™ 2000S and Hycat™ 3000S but was developed to ***meet certain European regulatory requirements***; especially products that may come in contact with humans, e.g., toys, packaging, laminates, etc.

Hycat™ OA, Hycat™ 2000S and **Hycat™ 3000S** are all pre-registered and **REACH** compliant.

HYCAT™ TEMPERATURE & CONCENTRATION EFFECTS

When using any of the Hycat™ Catalysts in systems that have adequate stoichiometry, the cure or reaction time can be significantly altered by controlling the reaction temperature or the Hycat™ Catalyst concentration. ***Figure 1*** shows the temperature effect in a simple epoxy-acid system with **Hycat™ 2000S.**

Figure 1

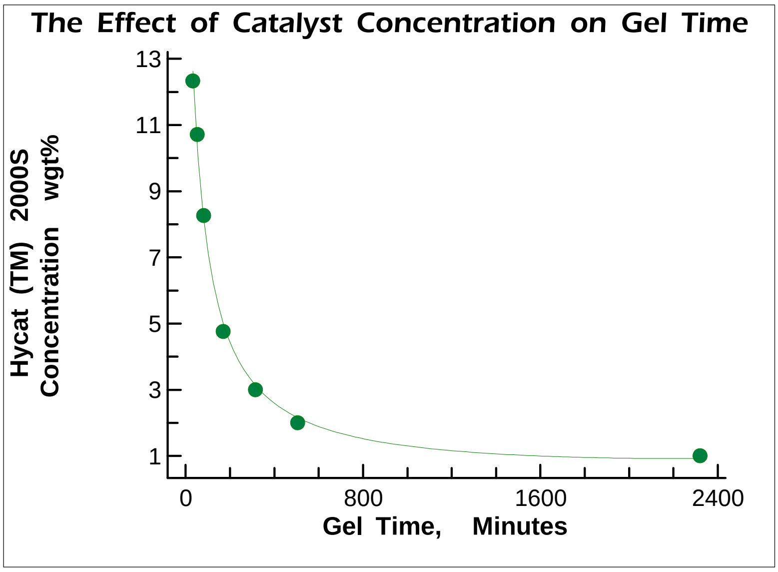


Composition (weight ratio) ***Figure 1***:

EMPOL 1016 Dimer Acid (Henkel):	61.6
ERL 4221 Epoxy Resin (Union Carbide)	28.4
Hycat™ 2000S:	10.0
COOH/Epoxy Equivalent Ratio:	1.1 / 1.0

Hycat™ Catalyst concentration has a dramatic effect on gel/cure or reaction time, even at room temperature. The effect **Hycat™ 2000S** has on the reaction of a diepoxide with a dicarboxylic acid is shown in ***Figure 2.*** By changing the catalyst concentration from **12%** to approximately **1%**, the pot life was extended from **1** hour to **40** hours. This versatility can be advantageously used in production when pot life is a critical factor.

Figure 2



Composition (weight ratio) ***Figure 2***:

EMPOL 1016 Dimer Acid (Henkel):	61.6
ERL 4221 Epoxy Resin (Union Carbide):	28.4
Hycat™ 2000S:	1.0%-12.3%
COOH/Epoxy Equivalent Ratio:	1.1 / 1.0

Test Temperature, ^{O}C **20 to 22**

HYCAT™ CATALYST GEL TEMPERATURE PROFILE & PHYSICAL PROPERTIES

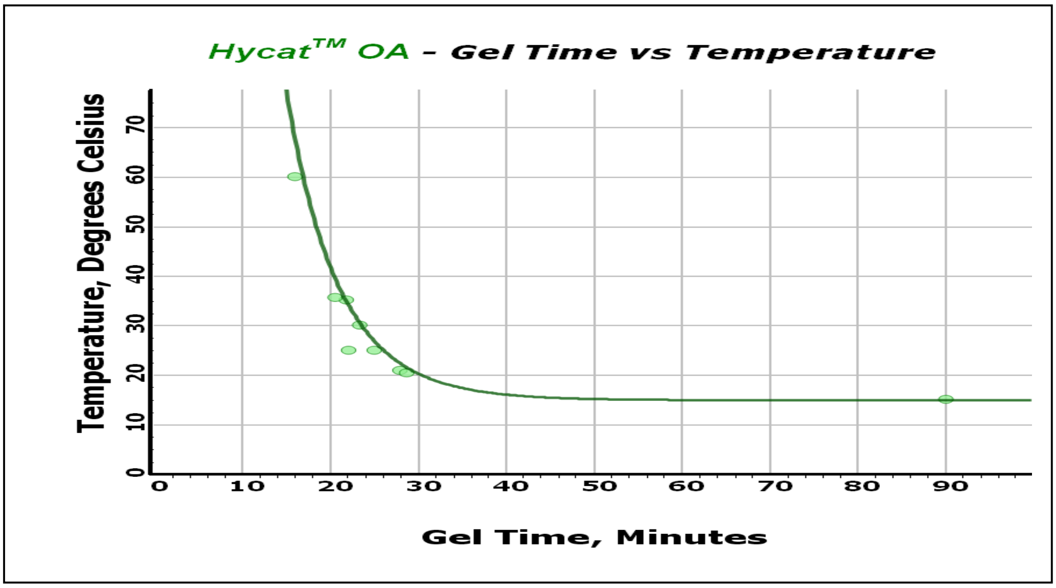
Hycat™ OA, Hycat™ 3000S and Hycat™ 2000S have similar performance in low to moderate temperature reactions. **Hycat™ OA** has the added benefit of a special formulation that addresses emerging regulatory requirements that makes it ideal for formulations where human contact is a consideration. While **Hycat™ 3000S** has special cure system modifiers that make it particularly ideal for epoxy/anhydride formulations where solubility characteristics are a factor. ***Figure 3*** below shows gel time versus temperature (15° – 80°C) for various lots of Hycat™ OA, Hycat™ 3000S and Hycat™ 2000S along with the respective physical properties of each catalyst.

Composition (weight ratio) ***Figures 3a, 3b, 3c***:

EMPOL 1016 Dimer Acid (Henkel):	61.6
ERL 4221 Diepoxide Resin (Union Carbide):	28.4
Hycat™ Catalysts:	**10.0**
COOH/Epoxy Equivalent Ratio:	1.1 / 1.0

Test Temperature Range ~ **15 to 80 °C**

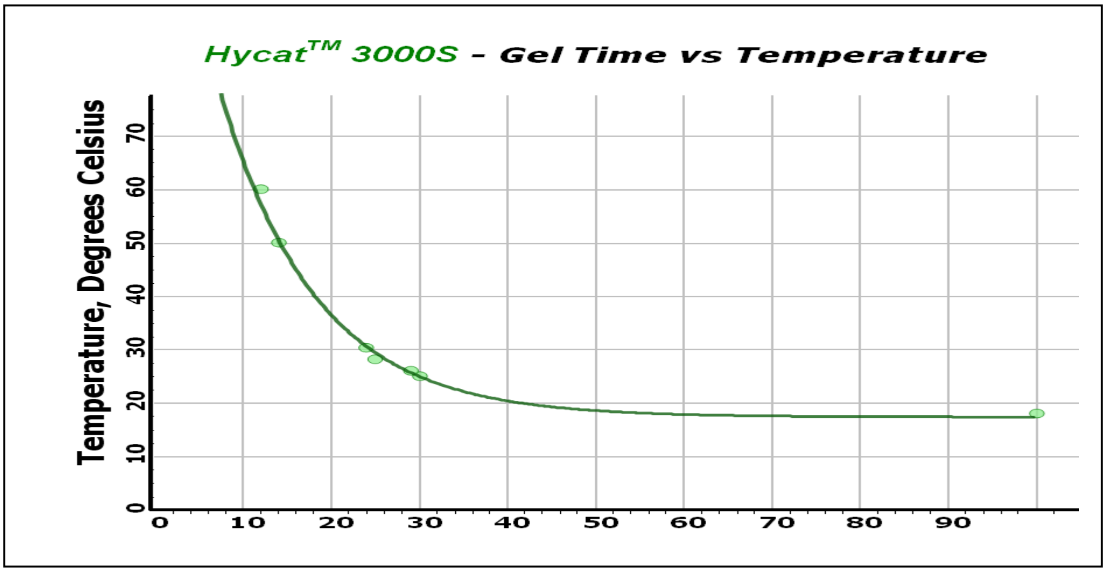
Figure 3a



Hycat™ OA – Physical Properties

Physical State	Liquid
Appearance (color)	Emerald Green
Viscosity (cps)	100 – 500 @ 25°C
Density	0.99 @ 25°C
Boiling Point	> 232°C
Flash Point	> 135°C

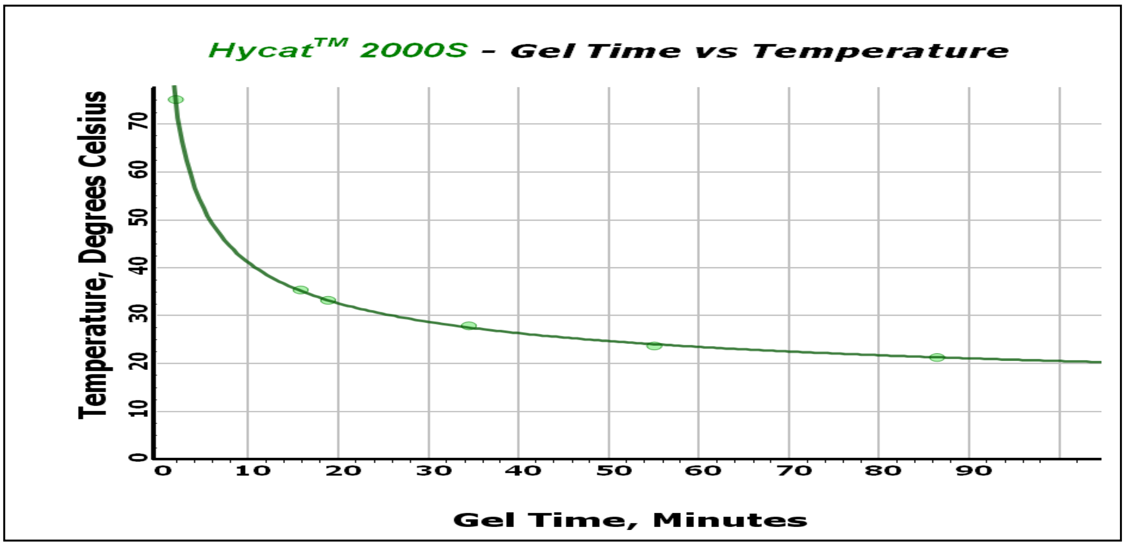
Figure 3b



Hycat™ 3000S – Physical Properties

Physical State	Liquid
Appearance (color)	Emerald Green
Viscosity (cps)	200 – 800 @ 25°C
Density	0.99 @ 25°C
Boiling Point	> 232°C
Flash Point	> 135°C

Figure 3c



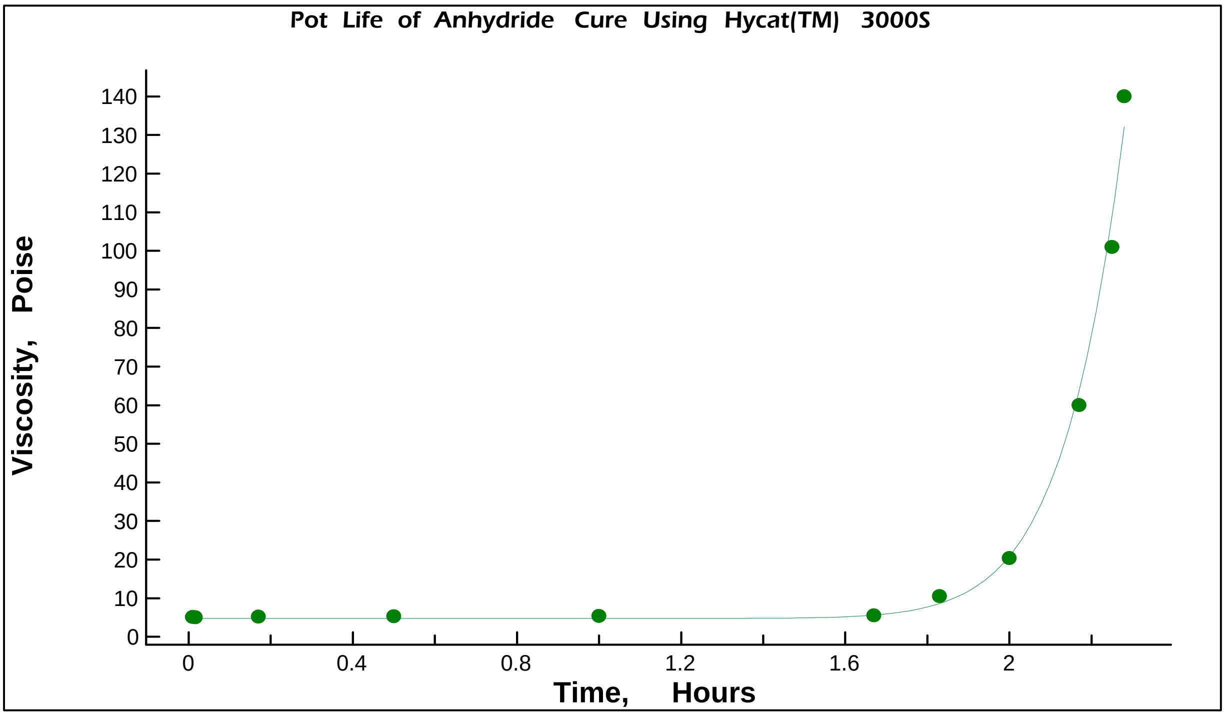
Hycat™ 2000S – Physical Properties

Physical State	Liquid
Appearance (color)	Emerald Green
Viscosity (cps)	200 – 800 @ 25°C
Density	0.99 @ 25°C
Boiling Point	> 230°C
Flash Point	> 200°C

HYCAT™ POT LIFE PROFILE

Hycat™ Catalysts greatly enhance the reaction of **epoxides** with **anhydrides**. In a typical reaction the viscosity of the formulation remains constant for a reasonable period of time before curing occurs. By adjusting reaction temperature or catalyst concentration, the overall curing process is significantly changed. Using **Hycat™ 3000S** as the catalyst, a profile showing the viscosity increase as a function of time at high catalyst concentration (10 pph) is shown below in ***Figure 4***. In cycloaliphatic epoxide/anhydride formulations at room temperature, a significantly **longer pot life (20 – 24 hours)** is realized at a lower catalyst loading (e.g., 1 pph).

Figure 4



Composition (weight ratio) ***Figure 4***:

EPON 828 (Shell):	258
MTHPA[1] (Lonza, Inc.)	232
Hycat™ 3000S:	**49**

Temperature Profile: Start: 21°C End: 33°C

[1] MTHPA (Methyltetrahydrophalic anhydride)

Testing performed on **Hycat™ 2000S** and **Hycat™ OA** produced comparable results to those shown above.

HYCAT™ PERFORMANCE WITH DIMERIC AND TRIMERIC ACIDS

Hycat™ Catalysts are extremely versatile. ***All*** epoxide reactions with carboxylic acids, anhydrides or imides are accelerated using a Hycat™ Catalyst provided the catalyst has some solubility in the formulation. Also, because the degree of homopolymerization of the epoxide is low (in comparison to other catalysts such as tertiary amines), the mechanical properties or quality of the resulting cure or prepolymer is greatly improved. Typical cure systems that incorporate the use of Hycat™ Catalysts are listed below in ***Table 1*** featuring **Hycat™ 2000S** as the accelerator.

Table 1

EPOXIDE	DIMER ACID	Hycat™ 2000S LOADING, WT. %	ACID TO EPOXIDE EQU., RATIO	INITIAL CURE TEMP, °C	GEL TIME, HOURS
EPON 828	EMPOL 1016	1%	1.05	**21°**	**38**
EPON 828	EMPOL 1016	3%	1.05	**21°**	**5**
EPON 828	EMPOL 1016	1%	1.05	**50°**	**3**
EPON 828	EMPOL 1016	3%	1.05	**50°**	**0.4**
ERL 4221	EMPOL 1016	10%	1.10	**22°**	**1.2**
ERL 4221	EMPOL 1016	10%	1.10	**30°**	**0.9**

EPOXIDE	TRIMERIC ACID	Hycat™ 2000S LOADING, WT. %	ACID TO EPOXIDE EQU., RATIO	INITIAL CURE TEMP, °C	GEL TIME, HOURS
EPON 828	EMPOL 1040	3%	1.0	**25°**	**2.8**
EPON 828	EMPOL 1040	3%	1.0	**50°**	**0.3**
ERL 4221	EMPOL 1056	12%	1.0	**25°**	**0.3**

EPON 828: Diglycidyl ether of bisphenol A (wt./epoxide, 185-192); Shell Chemical Company
ERL 4221: Cycloaliphatic epoxy resin (equivalent wt., 131-143); Union Carbide Chemicals and Plastics Company, Inc.
EMPOL 1016: C-18 to C-54 mixed dimeric acid (average FW-600, equivalent wt., 273), Henkel-Emery Group
EMPOL 1040: Trimeric acid (equivalent wt., 290); Henkel-Emery Group
EMPOL 1056: Polyfunctional carboxylic acid (equivalent wt., 290); Henkel-Emery Group

Physical Properties of Trimeric Acid Cures Featuring Hycat™ 2000S

Table 2 reports test data demonstrating that a complete cure can be obtained at ambient temperature since the cure occurs above the glass transition temperature (T_g).

Table 2

Formulation	ERL 4221 Epoxide	EMPOL 1056A Trimer Acid	Hycat™ 2000S	Gel Time, Min. @ 25° C	Post Gel Time	Hardness Shore A	T_g (°C)
Sample I	**28**	**60**	**12**	**20**	**24 hrs @ 25° C**	**48**	**< 20**
Sample II	**28**	**60**	**12**	**20**	**1 hr @ 100° C**	**46**	**< 20**

HYCAT™ PERFORMANCE WITH ANHYDRIDES

Hycat™ catalysts are excellent accelerators for all types of anhydride formulations. ***Table 3*** includes gel time information for various anhydrides at different catalyst loading and temperatures of **25°** and **50° C.** **Hycat™ 3000S** with its cure-system modifiers that improve solubility in epoxy/anhydride formulations is featured.

Table 3

Epoxide	Anhydride	Hycat™ 3000s Loading Wt. %	Anhydride To Epoxide Equ., Ratio	Initial Cure Temp, °C	Gel Time, Hours
EPON 828	MTHPA	4%	0.9	**25°**	**11.7**
EPON 828	MTHPA	10%	0.9	**25°**	**1.1**
EPON 828	MTHPA	6%	0.9	**50°**	**0.4**
DER 332	MTHPA	6%	0.9	**25°**	**10.1**
DER 332	MTHPA	10%	0.9	**25°**	**2.8**
DER 332	MTHPA	6%	0.9	**50°**	**1.1**
EPON 828	NADIC-MA	6%	0.9	**50°**	**0.5**
EPON 828	HHPA	10%	0.9	**25°**	**1.0**
EPON 828	HHPA	4%	0.9	**50°**	**1.4**

EPON 828: Diglycidyl ether of bisphenol A (wt./epoxide, 185-192); Shell Chemical Company (or suitable substitute)
ERL 4221: Cycloaliphatic epoxy resin (equivalent wt., 131-143); Union Carbide Chemicals and Plastics Company, Inc. (or suitable substitute)
HHPA: Hexahydrophthalic anhydride; Lonza, Inc.
MTHPA: Methyltetrahydrophthalic anhydride; Lonza, Inc.
NADIC-MA: Nadic methyl anhydride; Buffalo Color Corporation

HYCAT™ PERFORMANCE WITH POLYFUNCTIONAL AZIRIDINES

A unique attribute of the activated chromium (III) based Hycat™ catalysts (**2000S, 3000S & OA)** is their ability to effect uniform cures of **aziridines**. For example, when Xama 7 (polyfunctional aziridine) was combined with EMPOL 1016 (difunctional carboxylic acid) and left to cure at room temperature, a very tacky mass was formed over a 48 hour period. However, when **Hycat™ 2000S** was included in the same formulation, again at room temperature (~ 25° C), a very nice cure was achieved in 10 – 15 minutes. Furthermore, when trimethylolethane (TMP) *or* dimethylolproprionic acid (DMPA) were added to an aziridine, cures were achieved in less than 4 minutes at elevated temperatures (100° C and 150° C). Data from these experiments is shown in ***Table 4*** on the next page.

FORMULATION OF TME AND DMPA CURES WITH POLYAZIRIDINES

Table 4

Cure Temp.,^{O}C	PFAZ 322 Aziridine	Xama-7 Aziridine	Lindride 52D Anhydride	EMPOL 1016 Dimer Acid	EPON 828 Epoxy	ERL4221 Epoxy	TME[1]	DMPA[2]	Hycat™ 2000S Catalyst	Hycat™ 3000S Catalyst	Cure Time, Min.	Durometer (Type A) Hardness	Durometer (Type D) Hardness
150^{O}	4.0	---	9.4	---	3.8	---	---	---	---	**1.8**	1.5	---	87
150^{O}	4.0	---	9.4	---	3.8	---	---	1.5	---	---	2	---	76
150^{O}	4.0	---	9.4	---	3.8	---	---	1.5	---	**1.8**	1	---	86
150^{O}	4.0	---	---	14.0	---	4.0	---	---	---	**1.8**	3	41	---
150^{O}	4.0	---	---	14.0	---	4.0	2.0	---	---	---	60	no cure	---
150^{O}	4.0	---	---	14.0	---	4.0	2.0	---	**2.3**	---	3	16	---
150^{O}	4.0	---	---	14.0	---	4.0	---	2.0		---	8	very soft	---
150^{O}	4.0	---	---	14.0	---	4.0	---	2.0	**2.3**	---	3	25	---
100^{O}	4.0	---	---	14.0	---	4.0	---	---	**0.5**	---	3	29	---
100^{O}	---	4.0	---	14.0	---	4.0	---	1.5	---	---	4	tacky	---
100^{O}	---	4.0	---	14.0	---	4.0	---	1.5	**0.5**	---	3	48	---

Formulation given in grams. Cured at 100^{O} or 150^{O}C in 57mm Aluminum Pans.

[1] – Trimethylolethane

[2] – Dimethylolpropionic Acid

HYCAT™ 2000S GEL TIME COMPARISON TO BDMA

Hycat™ catalysts are far superior to BDMA for low temperature cures. ***Table 5*** reports data from the comparison of **Hycat™ 2000S** and **BDMA** in epoxide/carboxylic acid reactions at various concentrations cured at 25^{o} C and 50^{o} C. A simple rearrangement of the data for ***Table 6*** allows for a quick evaluation of how dramatic the effect of raising temperature conditions from **25^{o} C to 50^{o} C** has on cure times for Hycat™ 2000S at identical catalyst loading. **Hycat™ OA** and **Hycat™ 3000S** perform similarly.

1 – EQUIVALENT OF EPOXIDE IS REACTED WITH

1 – EQUIVALENT OF CARBOXYLIC ACID

Table 5

Epoxide	COOH	Temp	Loading	Hycat™ 2000S Cure Time, Hours	BDMA Cure Time, Hours
EPON 828	EMPOL 1016	25^{o}	1 %	38.7	No cure
EPON 828	EMPOL 1016	25^{o}	2 %	8.5	No cure
EPON 828	EMPOL 1016	25^{o}	3 %	5.3	> 67
EPON 828	EMPOL 1016	50^{o}	1 %	2.7	66.0
EPON 828	EMPOL 1016	50^{o}	2 %	0.8	18.5
EPON 828	EMPOL 1016	50^{o}	3 %	0.5	12.0
EPON 828	EMPOL 1040	25^{o}	1 %	13.5	No cure
EPON 828	EMPOL 1040	25^{o}	2 %	5.3	No cure
EPON 828	EMPOL 1040	25^{o}	3 %	3.0	> 67
EPON 828	EMPOL 1040	50^{o}	1 %	1.7	17.0
EPON 828	EMPOL 1040	50^{o}	2 %	0.8	7.8
EPON 828	EMPOL 1040	50^{o}	3 %	0.5	5.2

Table 6

Epoxide	COOH	Temp	Loading	Hycat™ 2000S Cure Time, Hours	BDMA Cure Time, Hours
EPON 828	EMPOL 1016	25^{o}	1 %	38.7	No cure
EPON 828	EMPOL 1016	**50^{o}**	1 %	2.7	66.0
EPON 828	EMPOL 1016	25^{o}	2 %	8.5	No cure
EPON 828	EMPOL 1016	**50^{o}**	2 %	0.8	18.5
EPON 828	EMPOL 1016	25^{o}	3 %	5.3	> 67
EPON 828	EMPOL 1016	**50^{o}**	3 %	0.5	12.0
EPON 828	EMPOL 1040	25^{o}	1 %	13.5	No cure
EPON 828	EMPOL 1040	**50^{o}**	1 %	1.7	17.0
EPON 828	EMPOL 1040	25^{o}	2 %	5.3	No cure
EPON 828	EMPOL 1040	**50^{o}**	2 %	0.8	7.8
EPON 828	EMPOL 1040	25^{o}	3 %	3.0	> 67
EPON 828	EMPOL 1040	**50^{o}**	3 %	0.5	5.2

MECHANICAL PROPERTIES – FEATURING HYCAT™ 3000S

Table 7 reports mechanical property data comparing **Hycat™ 3000S** and **BDMA**. Cure conditions and references are listed below the table.

Table 7

Components	I	II	III	IV	V	BDMA[a]	BDMA[b]	BDMA[b]
Epoxide								
EPON 828	100	100	100			100		
EPON 828/EPON 1031				100				
DER 332					100			
DER 218								
ARALDITE 6020							100	100
Anhydride								
MTHPA (phr)	78			90	91			
MNA (phr)		84						82
HHPA (phr)			72				71	
MSA (phr)						62		
Catalyst								
Hycat™ 3000S	**4**	**4**	**4**	**4**	**4**			
BDMA						**1**	**1**	**1**
Mechanical Properties @ 25° C								
Flexural Strength, psi x 10^{-3}	24.9	20.8	20.5	24.1	23.0	15.5	15.0	11.2
Flexural Modulus, psi x 10^{-5}	5.6	5.2	4.7	5.3	5.1	4.1	3.2	3.6
Tensile Strength, psi x 10^{-3}	11.5	12.1	11.6	9.6	12.1	---	11.9	12.5
Tensile Modulus, psi x 10^{-5}	4.7	4.7	4.0	6.2	5.1	---	3.6	3.9
Elongation, %	3.1	3.0	3.8	1.7	3.2	---	---	---
Heat Deflection Temperature, °C	128	120	123	118	102	90	117	122
Hardness, Barcol	47	46	45	46	46	---	---	---

Cure Conditions – Hycat™ 3000S

Gel Time: 45 min @ 80° C

Cure Time: 140 min @ 150° C

Cure Conditions – BDMA

120 min @ 85° C

Then 24 hours @ 150° C

Reference a: J. Chem. Eng. Data, 1959, 4(1), 79-82

Reference b: Ind. &. Eng. Chem., 1957, 49(7), 1089-1090

DIMENSION TECHNOLOGY CHEMICAL SYSTEMS, INC.