Coatings Trends & Technologies

Lower-Temperature Cure Catalysts for Epoxy Carboxy Coatings

Dr. Ravi Ravichandran – Vice President, R&D
King Industries, Inc.
Norwalk, Connecticut

Epoxy Resins

- Commercially important in several key end use applications.
  - Coatings
  - Adhesives
  - Laminates
  - Castings
  - Encapsulations and moldings.

- Most relevant in the automotive clear coats and powder coating market segments.

- Versatile crosslinking chemistries
  - Acids
  - Anhydrides
  - Phenolics
  - DICY
- Provide superior end use properties
  - Acid etch resistance in automotive clear coats
  - Adhesion

Environmental Etch of Automotive Clearcoats

- Environmental etch induced field damages in automotive import storage areas.

- Environmental etch of Acrylic melamine based automotive Clearcoats

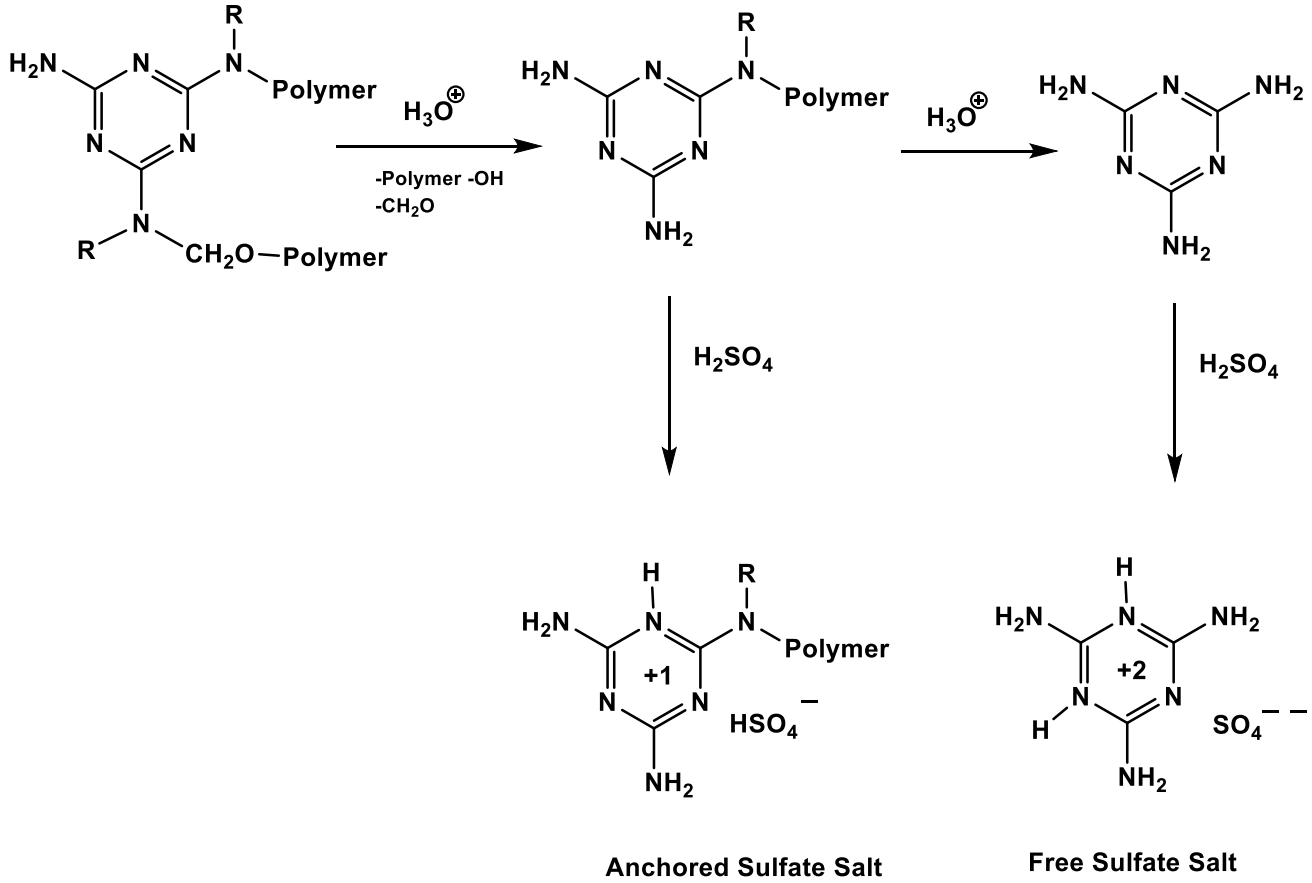
  - Clear coat appearance issue caused by acid rain from airborne pollutants in heavy industrial areas. Typical pH of acid rain at Jacksonville, Florida is about 3.5-4.5

  - Primarily the result of crosslink acid hydrolysis of acrylic melamine clearcoats and network fragmentation.

  - Primary mode of melamine crosslink degradation is due to hydrolysis of acetal linkages and subsequent formation of melamine sulfates

  - Results in localized loss of material and visible pitting of clear coat surface.

Mechanistic Pathway for Environmental etch of Acrylic Melamine Clearcoats



Schmitz, P.J.,Holubka, J.W., and Xu Li-Feng,(2000) Mechanism for Environmental etch of Acrylic Melamine –based Automotive Clearcoats: Identification of Degradation Products. Journal Of Coatings Technology,72, 904, 39-45.

Development of Etch Resistant Clearcoats

- Several approaches were attempted to address this issue including
  - Modifications of acrylic melamine with additional crosslinking with blocked NCO or silanes.
  - Carbamate functional acrylics crosslinked with melamine resins result in a hydrolysis resistant urethane crosslink.

- Technology using epoxy/acid, the most robust producing very powerful acid etch and scratch resistant coatings.

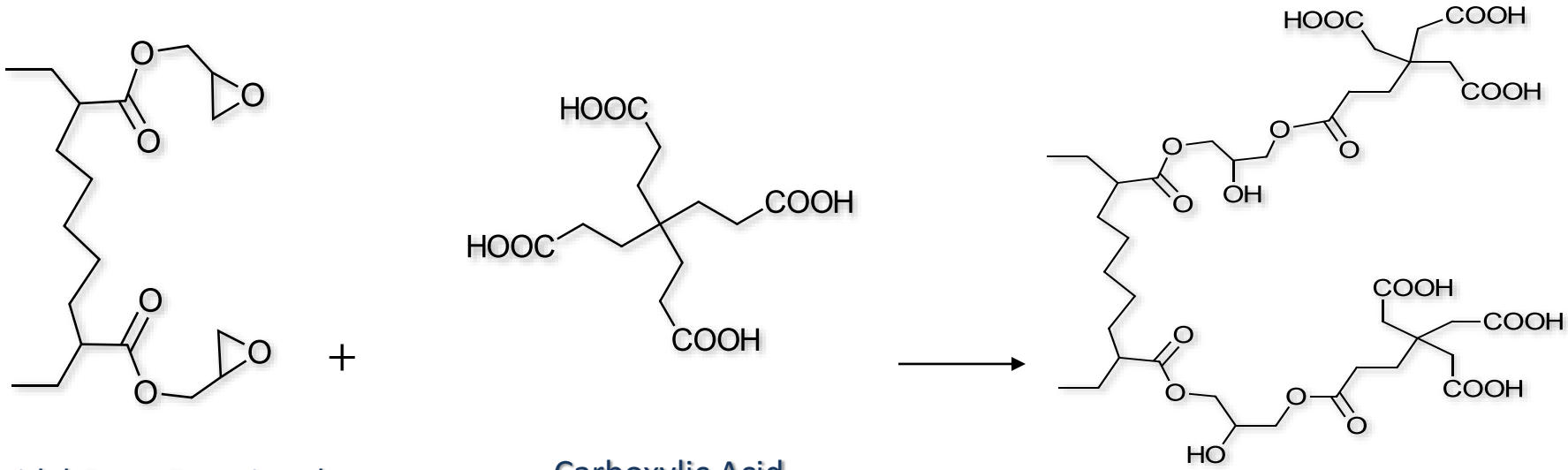
- Can be formulated as either 1K or 2K Coatings

- One component epoxy acid is the leading etch resistant clear coat technology used in Japan, and Korea with more than 80% of clear coat markets.

Epoxy Acid Powder Coatings

- Powder Coatings are an attractive alternate to conventional coatings.
  - High efficiency
  - Low environmental impact
  - Durability of finishes
- Major Crosslinking Chemistries
  - Esterification reaction-cure profile of 150^0C-220^0C (hydroxyalkylamide-Primid®**)**
  - Hydroxyl/blocked isocyanate reaction-cure profile of 140^0C-160^0C
  - Epoxy/acid or epoxy/anhydride-cure in the range of 120^0C-140^0C
  - Epoxy/phenolic or epoxy/DICY-cure profile of 110^0C
- Higher curing temperatures not useful with heat sensitive substrates(plastics, wood etc.)
- Epoxy/phenolic systems and epoxy homo polymerizations provide lower temperature cure options but lack the desired UV resistance for outdoor applications.
- Polyester/epoxy hybrids more versatile
  - Lower cure temperature potential
  - Better external weatherability at lower cost
  - Industrial uses including furniture, appliance, information technology and telecom.
  - Fastest growth at a CAGR of 8.1% from 2016 to 2024 and will account for > 50% of powder coating markets by 2024.

Reaction Scheme
GMA Epoxy/COOH Functional Resin



Glycidyl Ester Functional Acrylic Resin

Carboxylic Acid Functional Resin

Chemical Reaction of Resins Containing an Epoxy and a Carboxyl Group:

- Ring Opening Condensation Reaction
- Resulting in Stable Ester Linkages
- High Crosslink Density Capabilities
- Excellent Chemical Resistance Properties

Available Catalyst Technologies

- Basic amine catalysts are effective at lower temperatures but suffer from
  - Severe yellowing
  - Limited stability in 1K systems

- Quaternary Ammonium and phosphonium salts are effective 1K catalysts but suffer from
  - Problems with water permeability
  - Humidity resistance
  - Inadequate mar resistance

- Metal salts and Chelates are stable at higher temperatures and impart little yellowing, but suffer from
  - Inefficient cure at 120^0C, though effective at 140^0C
  - Divalent Zn can contribute to ionic crosslinking leading to storage instability, and gelation.

Non-Metal Catalysts for Epoxy Resins

High Active Catalyst for Epoxy/Acid Coatings

Catalyst XC-2007

Properties

Property	Description/Value
Appearance	Clear Liquid
Active	80%
Volatile	Water
Specific Gravity (25°C)	1.068

Non-Metal Catalysts for Epoxy Resins

High Active Catalyst for Epoxy/Acid

Performance Attributes

- High Active Catalyst
- Capable of Significant Reductions in Bake Temperature
- Excellent MEK Resistance and Gloss
- Low Color & Viscosity of Neat Catalyst
- Great Color of Catalyzed Films
- Good Overbake Resistance

Non-Metal Catalysts for Epoxy Resins

High Active Catalyst for Epoxy/Acid

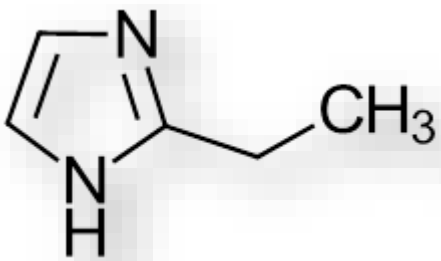
Recommendations

Application/Formulation	Incorporation/Storage
▪ **2K SB or WB Epoxy/Acid Clearcoats**	• Fully Disperse and Store in Acid Component
▪ **Epoxy/Acid Hybrid Powder Coatings**	• Capable of Being Added to Fully Formulated Powder Coatings System • Add Catalyst Before or at the End of Extrusion Process, Depending on Catalyst Dosage and Extrusion Temperatures

Relevant Control Catalysts

Octyldimethylamine

- ADMA-8
- Tertiary Amine
- 2K Epoxy
- 100% Solids
- Liquid



2-Ethylimidazole

- 2-EI
- Selective Catalyst
- 2K Epoxy
- 100% Solids
- Solid

Catalyst XC-2007 in 2K SB Epoxy/Acid Clearcoat Film Evaluation and Rheology Cure Study

Objective

Demonstrate Efficacy of Catalyst XC-2007 in a 2K SB Epoxy/Acid Formulation using GMA/Acrylic Hybrid Resin System

Solid Resins

Physical Properties

- **Carboxyl Functional Acrylic Resin:** White Powder/Flakes

Resin	Acid EW (g/eq)	Softening Point (°C)	Tg (°C)
Acrylic Resin 819	148	115	57

- **Glycidyl Methacrylate (GMA) Epoxy Resin:** White Powder/Flakes

Resin	Epoxy EW (g/eq)	Melt Index (g/10min, 125°C)	Tg (°C)
GMA Epoxy AC 2710	300-350	100-120	~45

Formulation
2K SB Epoxy/Acid Clearcoat

Material	Description	%
Component 1- *Acid Component*		
Acrylic Resin 819	**Carboxyl Functional Acrylic**	31.1
Xylene	Solvent	15.1
PM Acetate	Solvent	15.1
n-Butyl Acetate	Solvent	7.5
BYK 310	Surface Additive	0.2
Component 2- *Epoxy Component*		
GMA Epoxy AC 2710	**Glycidyl Methacrylate (GMA)**	14.0
Xylene	Solvent	6.8
PM Acetate	Solvent	6.8
n-Butyl Acetate	Solvent	3.4
TOTAL		**100.0**
% TRS	45	
Acrylic / GMA Solids	~ 70 / 30	
Acid / Epoxide (molar ratio)	~ 1 / 1	

Catalyst XC-2007

Dosage = 1% Solids on TRS

Dispersed and Stored in Acid Component

Epoxy Component Post-Added to Pre-Catalyzed Acid

KING INDUSTRIES SPECIALTY CHEMICALS

Pot Observations

Dispersing Catalyst 2007 in a SB Epoxy/Acid System

System	Observation	
	Incorporating Catalyst into Acid Component	Incorporating Epoxy Component into Pre-Catalyzed Acid Component
Catalyst XC-2007	Clear Pot, Fully Dispersed	Clear Pot, Fully Dispersed

Implications
Aqueous Catalyst Fully Dispersible in SB System

Rheology Studies
Oscillation Tests: Cure Profile

Terminology and Definitions for Rheology Studies Shown in Exp. I and Exp. III

Rheological Property	Typical Notation	Definition
Normal Force	*Normal Force* -or- *N*	Perpendicular Force Applied to Sample By Rheometer ***Note:*** *Studies Shown were Conducted with Fixed Gap*
Storage (Elastic) Modulus	*G'*	Measures Elasticity or Ability to Store Energy (i.e. properties of solids)
Loss (Viscous) Modulus	*G''*	Represents Viscous Region or Ability to Dissipate Energy (i.e. properties of liquids)
Tan(delta)	*Tan(Delta)* -or- *Tan(δ)*	Ratio of G''/G' – Measurement of "Viscous" to "Elastic" Portion of a Substance*

* **Tan(*δ*) > 1** → G'' > G' → More Viscous → **Behaving more-like Liquid**
Tan(*δ*) = 1 → G'' = G' → Viscoelastic → **Gel Point**
Tan(*δ*) < 1 → G'' < G' → More Elastic → **Behaving more-like Solid**

KING INDUSTRIES SPECIALTY CHEMICALS

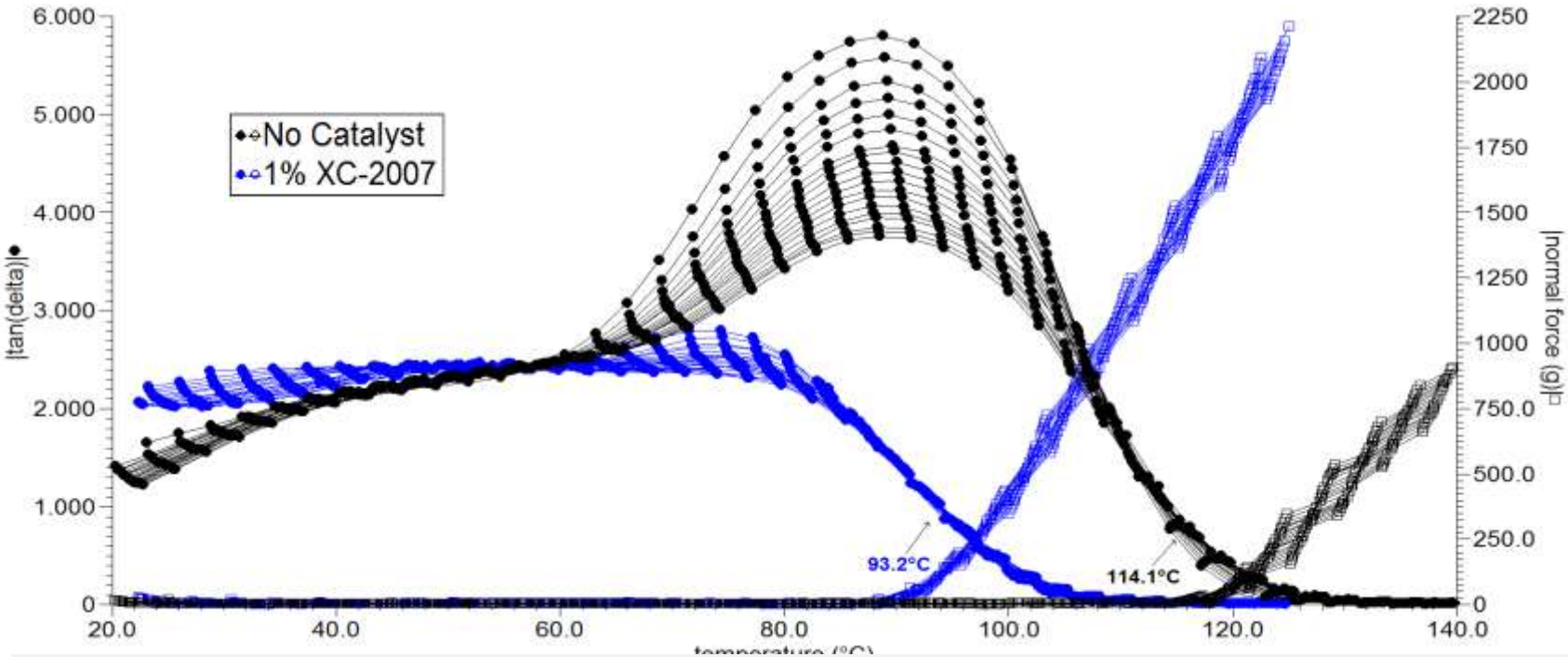
Rheology Studies
Oscillation Tests: Cure Profile

Pre-Exp. Step #	Description
Step 1	Place Sample on Peltier Plate at 25ºC
1a	Immediately Bring Geometry to Zero-Gap (400 micron)
1b	Shear at $100s^{-1}$ / 1 min
1c	Raise Geometry and Allow Sample to rest at 25ºC / 5 min
Step 2	Bring Geometry back to Zero-Gap (400 micron)
2a	Increase Temperature to 80ºC
2b	Shear at $200s^{-1}$ Until Temperature Reaches 80ºC
2c	Raise Geometry and Allow Sample to rest at 80ºC / 5 min
2d	Equilibrate at 20ºC / 1 min

Exp. Step #	Description
Step 1	Temperature Ramp of 1ºC/min from 20-140ºC

KING INDUSTRIES SPECIALTY CHEMICALS

Rheology Studies
Oscillation Tests: Cure Profile

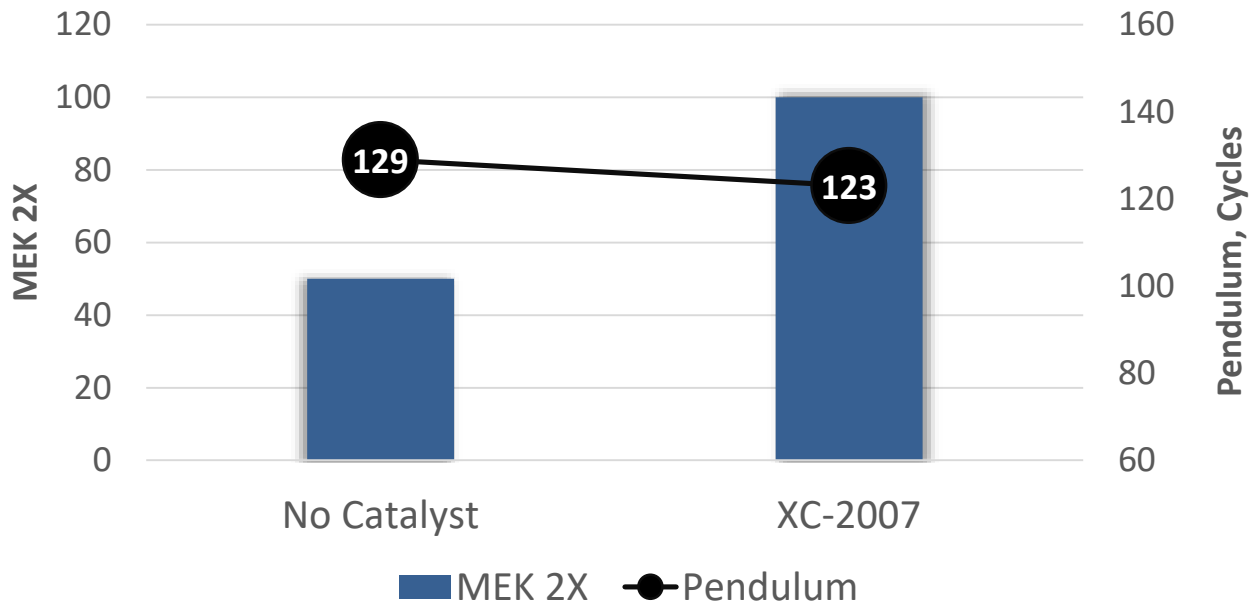


- **Oscillation Curve of Tan(δ) & Normal Force as a Function of Temperature**
- Heat Ramp: 1°C/min, 20-140°C
- 0.5% Strain, Frequency = 2.0, 3.0, 4.0 …. 19, 20 Hz
- 0% Catalyst vs. 1% Catalyst Solids on TRS
- Catalyst XC-2007 Reduced Gel Time by ~20°C

Film Properties
Gloss, Hardness, and Cure
SB Clearcoats DTM over Bare CRS

- **Substrate:** Bare CRS
- **DFT:** 2.0-2.2 mil
- **Bake Schedule:** 100°C/30min

System	Gloss 20°	Gloss 60°
No Catalyst	108	128
Catalyst XC-2007	106	125



Good Cure at 100°C:
1% Catalyst Solids on TRS

Film Properties
Overbake Resistance
Color Study—Yellowing and Total Color Change

- **Substrate:** Bare CRS • **DFT:** 1.0-1.2 mil • **Bake Schedule:** 100°C/30min • **Overbake:** +100°C/30min

Yellowing Resistance

System	b^*_o	b^*_f	Δb^*
No Catalyst	0.24	0.25	0.01
Catalyst XC-2007	0.29	0.31	0.03

Total Color Change

System	ΔL^*	Δa^*	Δb^*	ΔE^*
No Catalyst	-0.07	-0.01	0.01	0.07
Catalyst XC-2007	-0.11	-0.03	0.03	0.12

- **Clearcoat Color Tested over White WB BC**
- Good Overbake Resistance with 1% Catalyst XC-2007 solids on TRS
- No Significant Increase in Color Versus Uncatalyzed Film

KING INDUSTRIES SPECIALTY CHEMICALS

Catalyst XC-2007 in 2K SB Epoxy/Acid Clearcoat Comparison against Imidazole and Amine Catalyst

Objective

Compare Catalyst XC-2007 to 2-ethylimidazole and octydimethylamine in a 2K SB Epoxy/Acid Formulation using GMA Epoxy/Acrylic Hybrid

Solid Resins
Physical Properties

- **Carboxyl Functional Acrylic Resin:** White Powder/Flakes

Resin	Acid EW (g/eq)	Softening Point (°C)	Tg (°C)
Acrylic Resin 819	148	115	57

- **Glycidyl Methacrylate (GMA) Epoxy Resin:** White Powder/Flakes

Resin	Epoxy EW (g/eq)	Melt Index (g/10min, 125°C)	Tg (°C)
GMA Epoxy AC 2570	460-500	35-45	~55

Formulation
2K SB Epoxy/Acid Clearcoat

Material	Description	%
Component 1- *Acid Component*		
Acrylic Resin 819	**Carboxyl Functional Acrylic**	27.0
Xylene	Solvent	13.2
PM Acetate	Solvent	13.2
n-Butyl Acetate	Solvent	6.5
BYK 310	Surface Additive	0.2
Component 2- *Epoxy Component*		
GMA Epoxy AC 2570	**Glycidyl Methacrylate (GMA)**	18.0
Xylene	Solvent	8.8
PM Acetate	Solvent	8.8
n-Butyl Acetate	Solvent	4.3
TOTAL		**100.0**
% TRS	45	
Acrylic / GMA Solids	~ 60 / 40	
Acid / Epoxide (molar ratio)	~ 1 / 1	

Catalysts Tested

Catalyst XC-2007
Octydimethylamine (ADMA-8)
2-Ethylimidazole (2-EI)

Dosage = 1% Solids on TRS

Dispersed and Stored in Acid Component

Epoxy Component Post-Added to Pre-Catalyzed Acid

KING INDUSTRIES SPECIALTY CHEMICALS

Gloss and Hardness

100°C/30min

Bare Cold Roll Steel (Polished)

System	20°	60°	Pendulum
ADMA-8	96.4	109	138
2-EI	95.8	109	143
Catalyst XC-2007	94.8	109	145

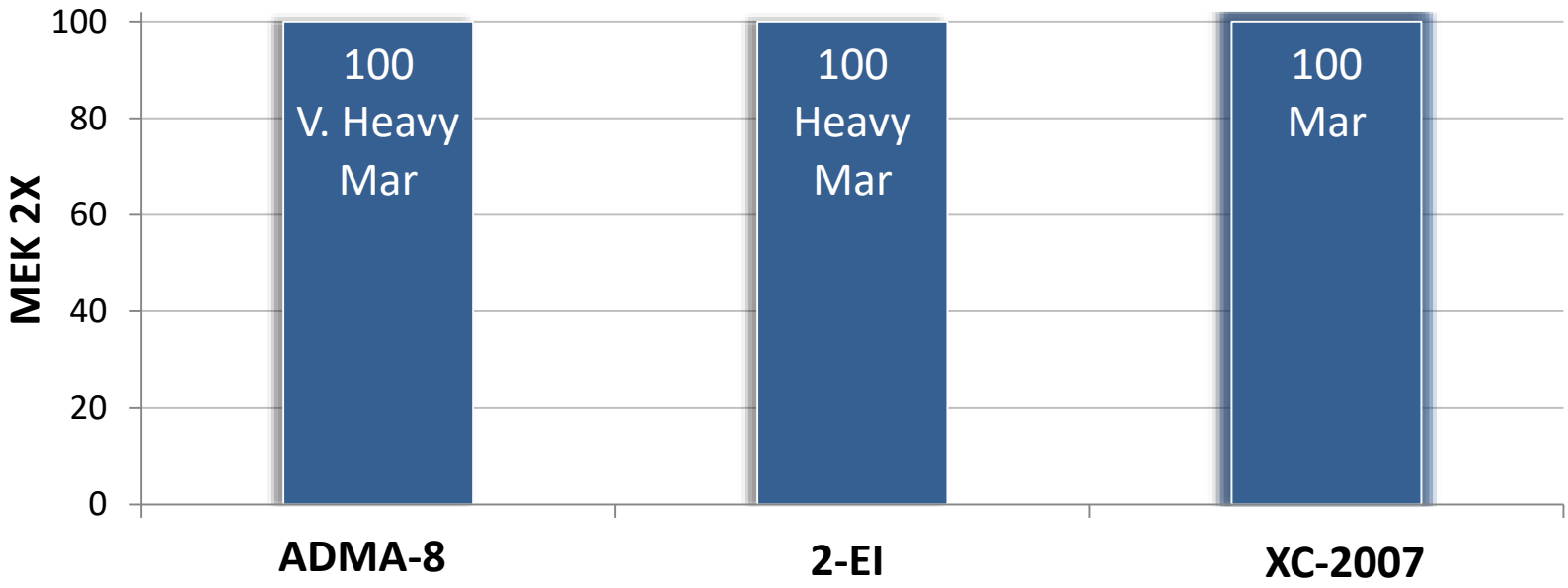
All Films Show Good Gloss and Hardness

(Not Necessarily Indicative of Cure Response)

MEK Resistance

100°C/30 min

Bare Cold Roll Steel (Polished), ~1 mil DFT



Catalyst XC-2007 Provided Superior Cure Response

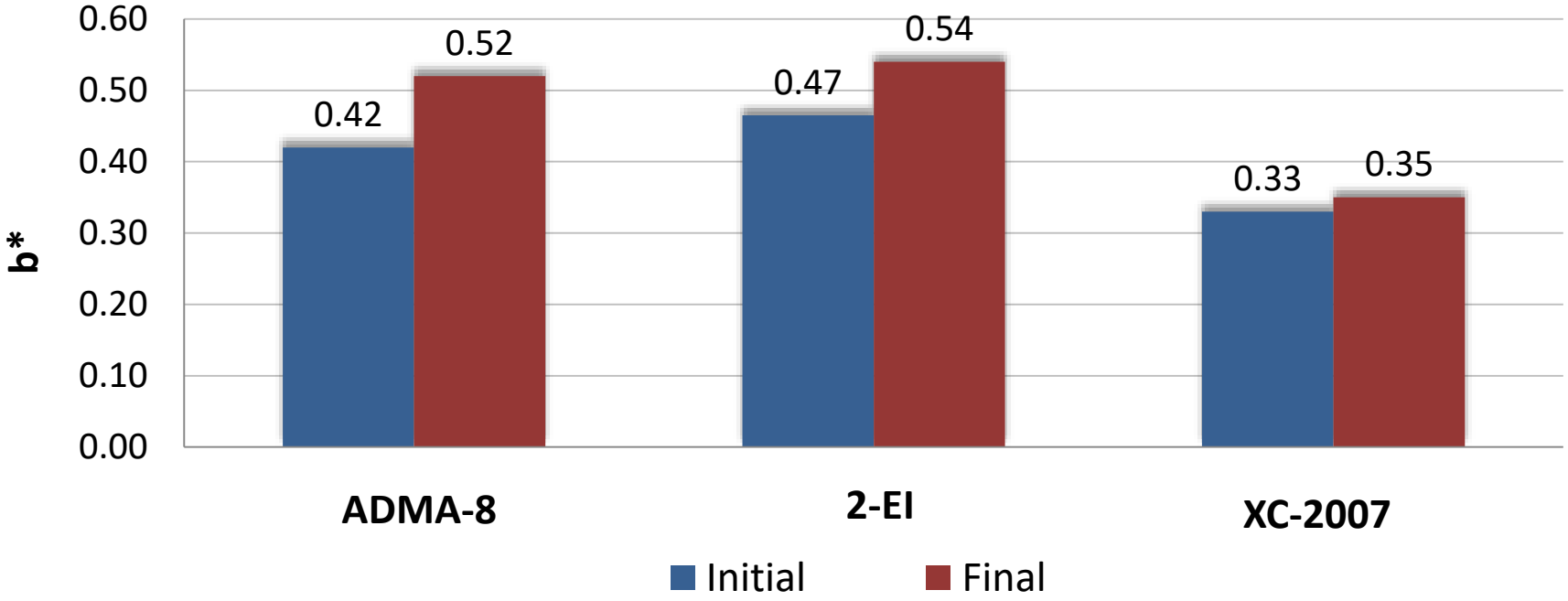
Better Mar Resistance after 100 MEK 2X

QUV Resistance: b*- 250 Hrs

SB Epoxy/Acid Clear over White WB Melamine Base Coat

100°C/30 min

Bare Cold Roll Steel (Polished), ~1 mil DFT



Catalyst XC-2007 Shows Lower Initial Color and Least Color Change

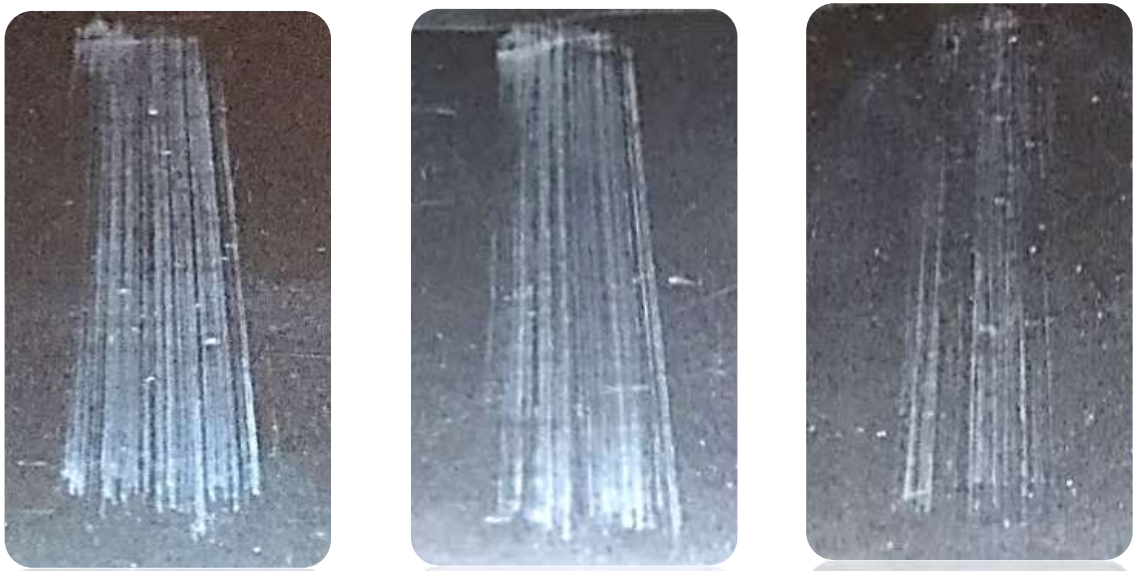
KING INDUSTRIES SPECIALTY CHEMICALS

Crockmeter Testing

Borax Dry Method—10 Cycles—TIC Crockmeter Square (2x2)

100°C/30 min

Bare Cold Roll Steel (Polished), ~1 mil DFT



ADMA-8 | 2-EI | XC-2007

Catalyst XC-2007 Improved Resistance to Crockmeter Abrasion

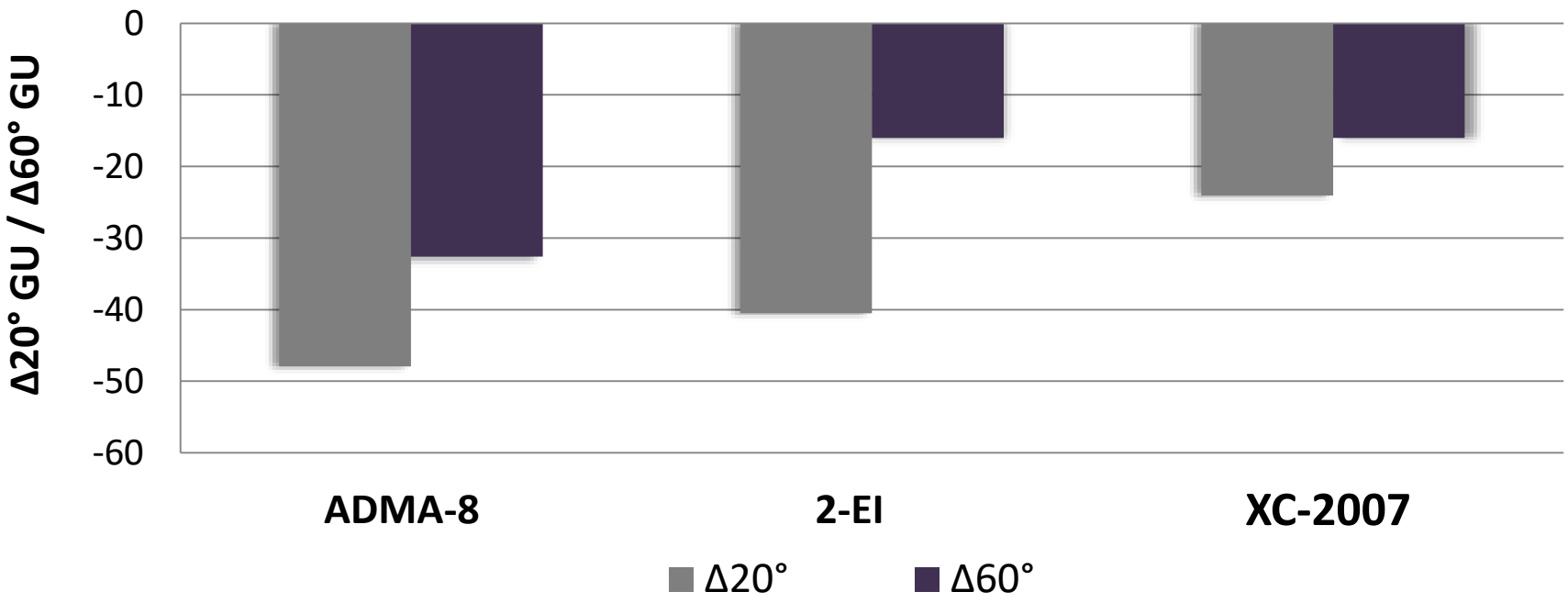
Better Crosslink Density → Less Scratch and Mar → Less Change in Gloss

Crockmeter Testing

Borax Dry Method—10 Cycles—Crockmeter Square (2x2)

100°C/30 min

Bare Cold Roll Steel (Polished), ~1 mil DFT



Catalyst XC-2007 Improved Resistance to Crockmeter Abrasion

Better Crosslink Density → Less Scratch and Mar → Less Change in Gloss

KING INDUSTRIES SPECIALTY CHEMICALS

Overbake: Total Color Change

100°C/30 min

Bare Cold Roll Steel (Polished), ~1 mil DFT

OVERBAKE: Additional 100°C/30min

System	ΔL*	Δa*	Δb*	ΔE
ADMA-8	-0.13	-0.01	0.12	0.18
2-EI	-0.14	-0.01	0.17	0.22
Catalyst XC-2007	-0.11	-0.01	0.15	0.19

All Catalysts Show Low Change in Color with Overbake

Experiment III:
Catalyst XC-2007 in Powder Epoxy/Acid Hybrid
Rheology Cure Studies

<u>Objective</u>

Demonstrate Catalyst Cure Capabilities of Catalyst XC-2007 in a Powder Epoxy/Acid Formulation Based on GMA Epoxy/Acrylic Hybrid

Solid Resins:
Physical Properties

- **Carboxyl Functional Acrylic Resin:** White Powder/Flakes

Resin	Acid EW (g/eq)	Softening Point (°C)	Tg (°C)
Acrylic Resin 819	148	115	57

- **Glycidyl Methacrylate (GMA) Epoxy Resin:** White Powder/Flakes

Resin	Epoxy EW (g/eq)	Melt Index (g/10min, 125°C)	Tg (°C)
GMA Epoxy AC 2710	300-350	100-120	~45

Formulation:

Powder (No Solvent) Epoxy/Acid Clearcoat

Material	Description
Acrylic Resin 819	**Carboxyl Functional Acrylic**
GMA Epoxy AC 2710	**Glycidyl Methacrylate (GMA)**
% TRS	100
Acrylic / GMA Solids	~ 70 / 30
Acid / Epoxide (molar ratio)	~ 1 / 1

Catalyst XC-2007

Dosage = 1% Solids on TRS

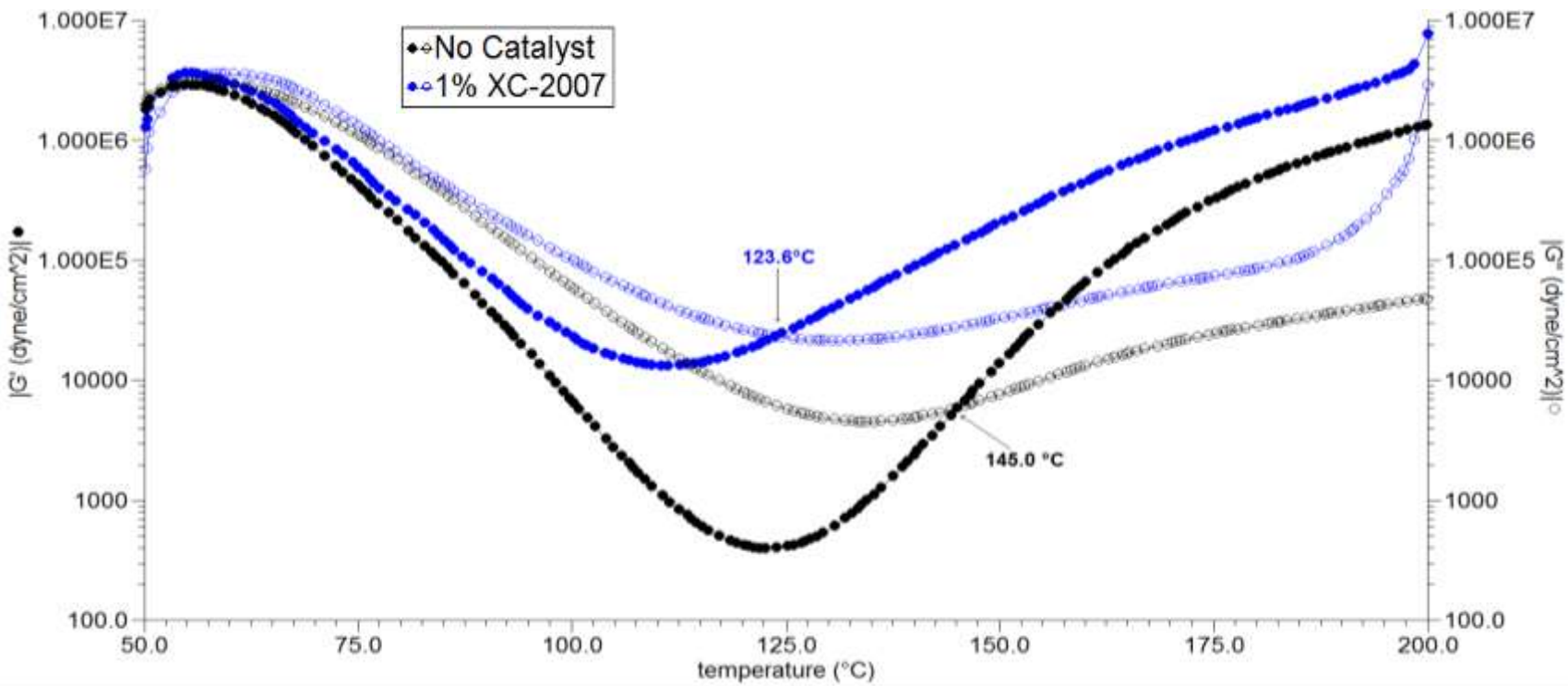
Preparing Test Specimen For Rheology Study

GMA/Acrylic Hybrid Powder

1) Solid Grade GMA and Acrylic Resins Pulverized using Mortar and Pestle
2) Catalyst Post-Added to Fine Powder Mixture
3) Catalyzed Formulation Mixed Slowly in FlackTek Speed Mixer
4) Formulation Re-Pulverized using Mortar and Pestle

GMA/Acrylic Hybrid Formulation Pressed into Powder Disc to Test via Rheometer

Rheology Studies—Oscillation Tests: *Cure Profile*



- **Oscillation Curve of G' & G'' as a Function of Temperature**
- Heat Ramp: 1°C/min, 50-200°C
- 0.25% Strain, Frequency = 1.0 Hz
- 0% Catalyst vs. 1% Catalyst Solids on TRS
- Catalyst XC-2007 Reduced Gel Time by ~20°C

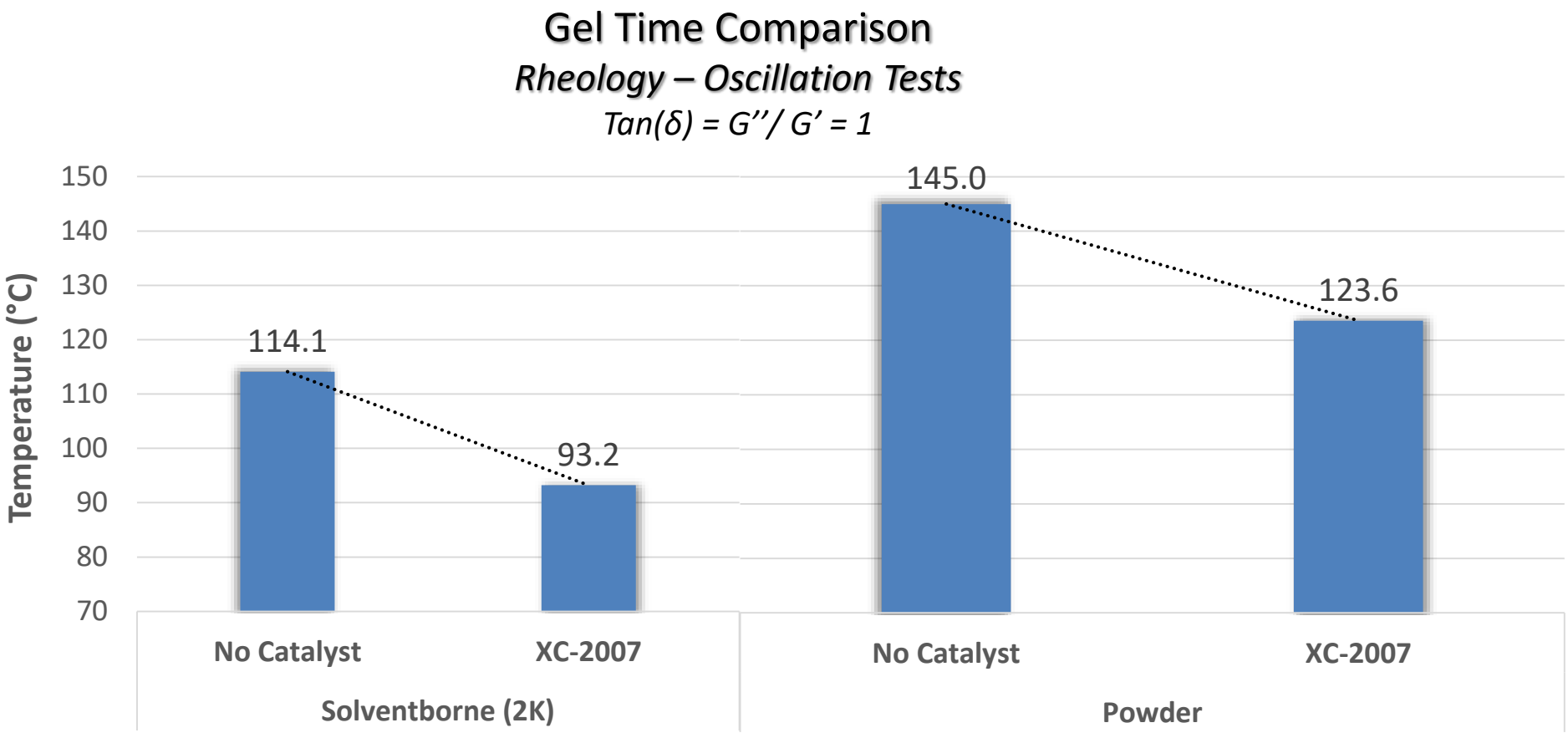
Discussion:

Cure Capabilities of SB vs. Powder Epoxy/Acid

Final Conclusions

Discussion— Cure Capabilities: 2K SB vs. Powder

GMA / Acrylic Hybrid

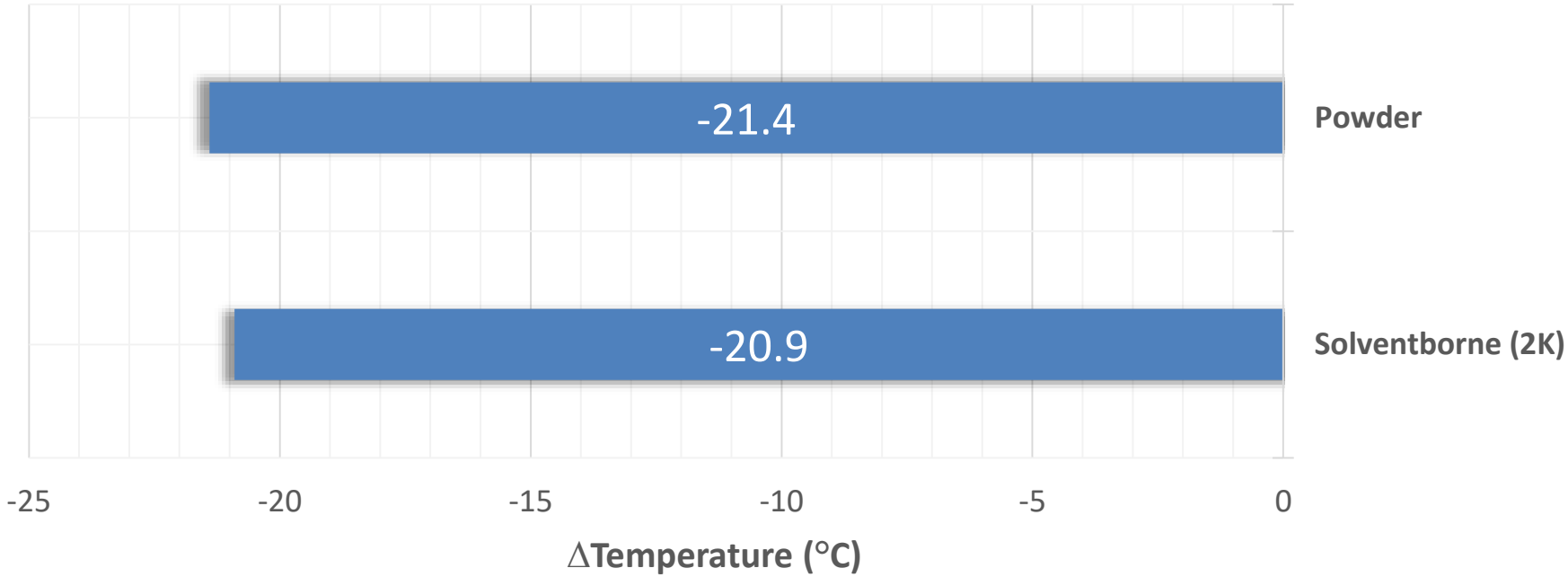


~ 70/30 Acrylic Resin 819/GMA Epoxy AC 2710 + 1% Catalyst XC-2007 Solids on TRS

Discussion— Cure Capabilities: 2K SB vs. Powder
GMA / Acrylic Hybrid

Gel Time Comparison
Rheology – Oscillation Tests

Tan(δ) = G''/ G' = 1



Temperature Reduction Compared to Uncatalyzed System

~ 70/30 Acrylic Resin 819/GMA Epoxy AC 2710 + 1% Catalyst XC-2007 Solids on TRS

Conclusions

Based on Studies in **Epoxy/Acid Hybrid** using **GMA/Acrylic** Resin System
+1% Catalyst XC-2007 Solids on TRS

Catalyst Technology Validated as High Active Catalyst Capable of Promoting Epoxy/Acid Reaction at Lower Temperatures

- Significant Reduction in Bake Temperature of Epoxy/Acid Hybrid Systems
- Capable of Lowering Cure Temperature by 20°C
- Potential for Achieving Good Cure at 100°C
- Minimal Change in Gloss with Good Lower Temperature Cure
- Low Color of Neat Catalyst
- Low Film Color with Good Overbake Resistance

Conclusions

Based on Studies in **Epoxy/Acid Hybrid** using **GMA/Acrylic** Resin System
+1% Catalyst XC-2007 Solids on TRS

Catalyst Technology Validated as High Active Catalyst Capable of Promoting Epoxy/Acid Reaction at Lower Temperatures

- Significant Reduction in Bake Temperature of Epoxy/Acid Hybrid Systems
- Capable of Lowering Cure Temperature by 20°C
- Potential for Achieving Good Cure at 100°C
- Minimal Change in Gloss with Good Lower Temperature Cure
- Low Color of Neat Catalyst
- Low Film Color with Good Overbake Resistance

Strong Candidate for Replacing Imidazole or Amine Type Catalysts

- Significantly Less Heath and Physical Safety Hazards
- Superior Cure Response with Improved Mar Resistance (MEK 2X)
- Better UV Resistance (QUV)
- Enhanced Crockmeter Abrasion Resistance

Coatings Trends & Technologies

Lower-Temperature Cure Catalysts for Epoxy Carboxy Coatings

Acknowledgements

Matthew Gadman
Steven Woltornist
John Florio
Mike Emmett

See you at King Industries Booth # 75

KING INDUSTRIES SPECIALTY CHEMICALS