CVC Thermoset Specialties
An Emerald Performance Materials Company

# Specialty Epoxy building blocks for demanding coating, adhesive applications.

Presenter:
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Product Manager- Epoxies.
CVC Thermoset Specialties, Inc.,

Latin America Coating show.
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Mexico

## Epoxy Resins:

First commercially developed in 1936

- Dr. Pierre Castan - Switzerland
- Dr. S.O Greenlee - USA

First Commercial producer:

- Ciba Giegy - Switzerland
- Devoe-Reynolds – USA

First Epoxy resin synthesis:

- Reaction product of Bisphenol- A and Epichlorohydrin

## Current Scenario:

- Epoxy resin produce in multi 100K lbs world wide
- More than 20 large commercial producers worldwide.
- Epoxy resin produce by using different starting material other than Bisphenol-A

**Bisphenol-A epoxy resin is still workhorse of the industry.**

## Bisphenol-A epoxy resin offers:

( When cured with appropriate curing agents)

- Adhesion
- Chemical resistance
- Mechanical properties
- Thermal properties.

## Applications:

Currently epoxy resin used in many diverse applications:

- Civil engineering
- Pultrution and composites
- Adhesives
- Coatings

**With technological advancement:**

Various application demands higher performance from epoxy resins

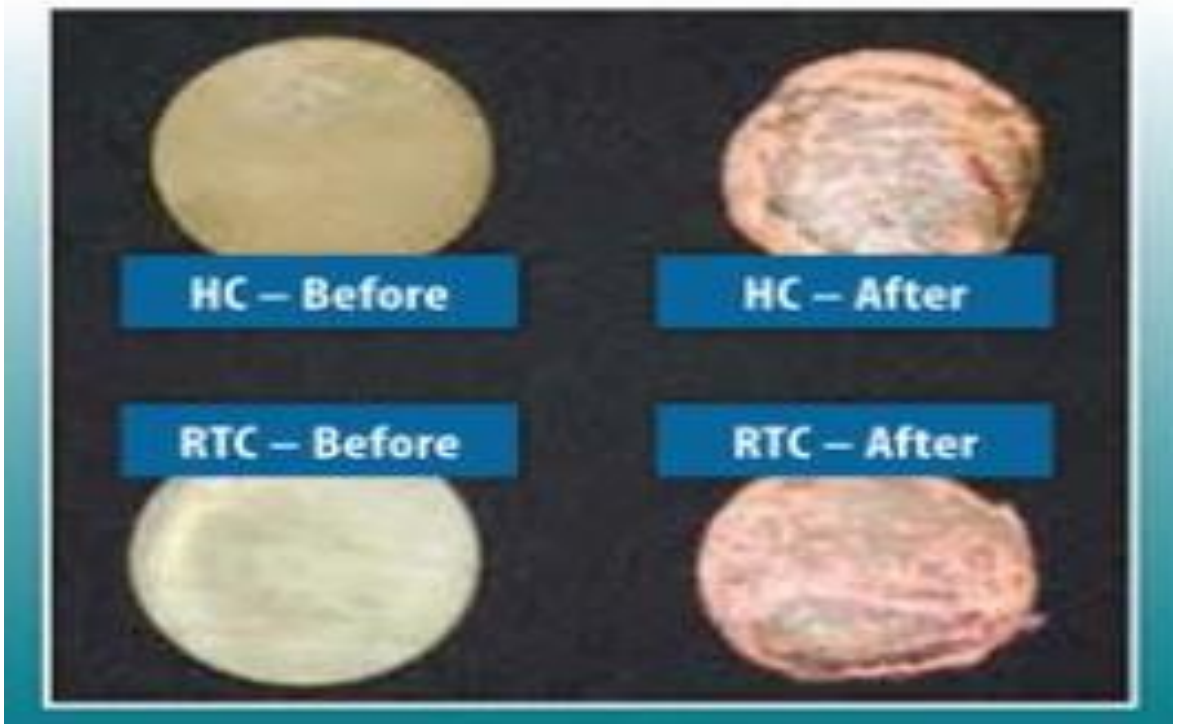
- Better Chemical resistance
- Better UV resistance
- Faster cure at wide range of temperature
  ( especially at low temperature)
- Better toughness
  ( especially at lower temperature)

CVC has unique products that helps to meet these high performance requirements.

- **Better Chemical resistance**

# Example: 98 % Sulfuric acid immersion

Samples after 24 hrs immersion in 98 % sulfuric acid.




HC = Standard LER with heat cured curing agent
RTC = Standard LER with room temperature curing agent

# Structure comparison

| Epoxy resin | Chemical resistance | Functionality | Viscosity | Comment |
|---|---|---|---|---|
| Bisphenol-A | Good | 2 | 11000-14000 cP at 25C | Good crosslink density |
| Bisphenol-F | Better | 2.05 | 3000 – 6000 cP at 25C | Small molecule, better crosslink density |
| Novolacs | Best | 2.3 – 3.8 | up to 40000 cP at 52C | Much higher crosslink density. Higher viscosity |

Ideal solution:

- Very high chemical resistance
- Low in viscosity at 25C
- Can be used as diluent for EPN's for better handling

# Acid resistance

## Starting formulation: 7 days at 25C

| Resin system | Composition., % | Viscosity @ 25C, cP |
|---|---|---|
| Epalloy 8230 | 100 | 3800 |
| Epally 8250 | 100 | 18000 |
| Epalloy 8230/Erisys GE 30 | 80/20 | 1400 |
| Epalloy 8230/RDGE | 70/30 | 1500 |
| Epalloy 8250 / RDGE | 75/25 | 5500 |

Epalloy 8230, 8230
(Epoxy Phenol Novolacs, F = 2.3 & 2.5)
Erisys GE 30
(Trimethyolpropane triglycidyl ether
Erisys RDGE
( Resorcinol Diglycidyl ether)

| Curing agent | Supplier | Composition |
|---|---|---|
| 624CE | Henkel | Aliphatic amine adduct |
| 670CE | Henkel | IPD/BA blend |
| 676CE | Henkel | DCH/NP blend |
| PAC 1693 | Air Products | DCH/BA blend |
| PAC 2280 | Air Products | Polycyclic aliphatic amine / BA blend |
| HY 265 | Ciba | Cycloaliphatic amine/ BA blend |

IPD = Isophorone Diamine
BA = Benzyl Alcohol
NP = Nonyl Phenol

# 28 Days immersion in 98% Sulphuric acid

## (Curing : 7 days at RTC)

| Resin system | Composition, % | Curing agent | | | | | |
|---|---|---|---|---|---|---|---|
| | | 624CE | 670CE | 676CE | PAC 1693 | PAC 2280 | HY 265 |
| Epalloy 8230 | 100 | -0.9 | -0.9 | -24.0 | 0.5 | 0.4 | -11.9 |
| Epalloy 8250 | 100 | 0.4 | -0.7 | -15.8 | -0.1 | -0.1 | -3.0 |
| Epalloy 8230/Erisys GE 30 | 80/20 | -1.0 | -7.1 | -50.7 | -0.4 | 0.6 | -22.8 |
| Epalloy 8230/RDGE | 70/30 | -0.3 | 0.5 | -9.5 | 0.5 | 0.4 | 1.0 |
| Epalloy 8250 / RDGE | 75/25 | 0.3 | -0.2 | -7.4 | 0.3 | 0.3 | -0.0 |


After 24 hrs in 98 % sulfuric acid


After 28 days in 98 % sulfuric acid

# 28 Days immersion in Glacial Acetic Acid

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## (Curing : 7 days at RTC)

| Resin system | Composition, % | Curing agent | | | | | |
|---|---|---|---|---|---|---|---|
| | | 624CE | 670CE | 676CE | PAC 1693 | PAC 2280 | HY 265 |
| Epalloy 8230 | 100 | D | D | D | -12.7 | 9.2 | D |
| Epalloy 8250 | 100 | D | D | D | -7.7 | 15.2 | D |
| Epalloy 8230/Erisys GE 30 | 80/20 | 6.0 | D | D | D | 3.3 | D |
| Epalloy 8230/RDGE | 70/30 | -2.6 | -3.9 | D | -3.8 | 17.7 | D |
| Epalloy 8250 / RDGE | 75/25 | 4.9 | -7.6 | D | -1.5 | 10.5 | D |

*D= Destroy

# Acid resistance- Heat cured

## Curing: Gel at RT + 2hrs at 80C + 3 hrs at 150C

| Resin system | Composition., % | Viscosity @ 25C, cP |
|---|---|---|
| Epalloy 8230 | 100 | 3800 |
| Epally 8250 | 100 | 18000 |
| Epalloy 8230/Erisys GE 30 | 80/20 | 1400 |
| Epalloy 8230/RDGE | 70/30 | 1500 |
| Epalloy 8250 / RDGE | 75/25 | 5500 |

Epalloy 8230, 8230
(Epoxy Phenol Novolacs, F = 2.3 & 2.5)
Erisys GE 30
(Trimethyolpropane triglycidyl ether
Erisys RDGE
( Resorcinol Diglycidyl ether)

| Curing agent | Composition |
|---|---|
| PACM | Polycyclic aliphatic amine |
| IPD | Isophorone Diamine |
| DCH | 1,2-Diamino cyclohexane |

# 28 Days immersion in 98% Sulphuric acid

Curing: Gel at RT + 2hrs at 80C + 3 hrs at 150C

| Resin system | Composition, % | Curing agent | | |
|---|---|---|---|---|
| | | PACM | IPD | DCH |
| Bis- A | 100 | D | D | D |
| Epalloy 8230 | 100 | 1.0 | 1.0 | 1.0 |
| Epalloy 8230/RDGE | 70/30 | 1.0 | 1.0 | 1.3 |

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# 28 Days immersion in Glacial Acetic Acid

Curing: Gel at RT + 2hrs at 80C + 3 hrs at 150C

| Resin system | Composition, % | Curing agent | | |
|---|---|---|---|---|
| | | PACM | IPD | DCH |
| Bis- A | 100 | 5.0 | 6.1 | 7.3 |
| Epalloy 8230 | 100 | 7.5 | 9.5 | 6.2 |
| Epalloy 8230/RDGE | 70/30 | 5.5 | 6.2 | 4.3 |

# Remarks:

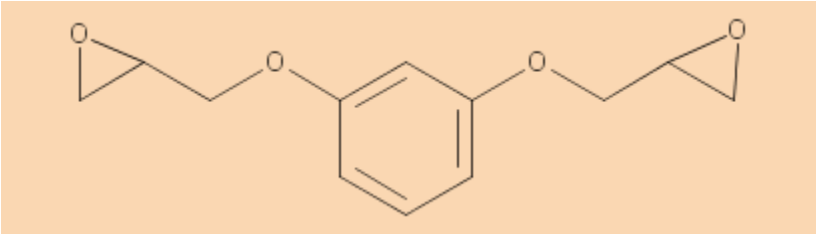
- Epoxy Phenol Novolacs are giving better acid resistance than Bisphenol-A epoxy

- Resorcinol Diglycidyl ether and Epoxy Phenol Novolacs blend give improved acid resistance than Epoxy Phenol Novolacs alone.

# Erisys RDGE

## Resorcinol Diglycidyl ether

Structure



| Property | EEW g/eq | Viscosity @ 25C cP | Functionality |
|---|---|---|---|
| LER- BPA based | 180-190 | 10000 – 14000 | 2 |
| BPF resin | 165 – 180 | 3000 – 6000 | 2.05 |
| EPN's | 170 – 190 | 18000 - semisolid | 2.3 -3.9 |
| RDGE | 118 – 125 | 300 – 500 | 2 |
| RDGE modified EPN's | 152 -160 | 5000 - 9000 | 2.4 -2.8 |

- **Better UV Stability**

# Structure comparison

| Structure | Chemical nature | UV stability | Viscosity | Comment |
|---|---|---|---|---|
| Bisphenol-A | Aromatic | Poor | 11000-14000 cP at 25C | Improve by using cycloaliphatic hardener |
| Bisphenol-F | Aromatic | Poor | 3000 – 6000 cP at 25C | Improve by using cycloaliphatic hardener |
| Novolacs | Aromatic | Poor | up to 40000 cP at 52C | Need solvent to reduce viscosity. |

Ideal solution:

- 100 % cycloaliphatic resin
- Very low in viscosity at 25C

# Formulation components

## Resin component

| Sample | Composition | Description |
|---|---|---|
| R1 | Epon 828/TMPTA/TPGDA ( 80/10/10) | Bis-A epoxy+fast acrylate+flexible acrylate |
| R2 | Epalloy 5001/TMPTA (90/10) | Hydorgenated epoxy + fast acrylate |
| R3 | R1/R2 ( 50/50) | |
| R4 | Epon 828/Ancarez 2364/Epodil 748 (24/50/16) | Urethane modified Bis A epoxy |
| R5 | R2/R4 (50/50) | |

## Hardener component

| Sample | Composition | Description |
|---|---|---|
| A1 | PACM | Good gloss and color retention |
| A2 | Cycloaliphatic amine + polyether amine | High reactivity and flexibility than A1 |
| A3 | Isolated Aliphatic amine adduct | Fast reactivity, good gloss retention |
| A4 | Aliphatic amine + cycloaliphatic amine + high MW polyether amine | Slow cure, high flexibility |

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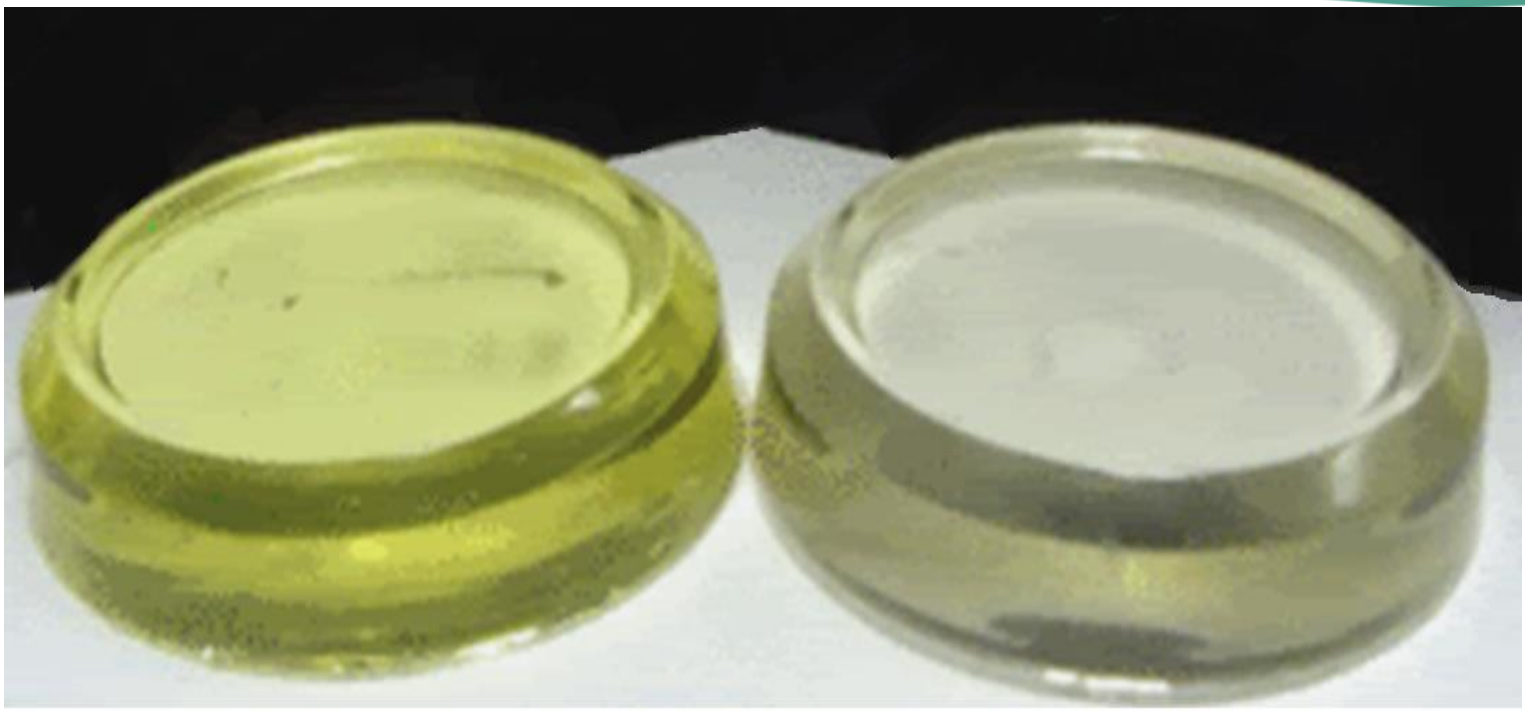
# Gloss Retention and Yellowing Resistance

| Sample | Gloss 0 time 20o/60o | Gloss 7 days UV 20o/60o/85o | Yellowness 0 time | Yellowness 3 day UV | Yellowness 7 Day UV |
|---|---|---|---|---|---|
| R1A1 | 90/96 | 55/78/86 | 1.0 | 27.0 | 49.7 |
| R1A2 | 39/67 | 4/20/48 | 3.2 | 57.0 | 62.7 |
| R1A3 | 75/97 | 28/60/62 | 2.8 | 56.7 | 66.0 |
| R2A1 | 91/97 | 76/89/91 | 2.5 | 12.8 | 22.5 |
| R2A2 | 28/76 | 13/60/78 | 8.1 | 26.0 | 46.5 |
| R2A3 | 85/95 | 12/28/28 | 4.7 | 49.2 | 61.9 |
| R3A1 | 5/22 | 1/6/21 | 13.8 | 26.4 | 29.1 |
| R3A2 | 73/100 | 2/11/57 | 7.8 | 51.1 | 61.5 |
| R3A3 | 97/95 | 13/22/13 | 3.5 | 48.9 | 59.3 |
| R4A2 | 22/38 | 1/3/13 | 20.8 | 37.5 | 60.8 |
| R5A2 | 57/76 | 7/20/62 | 11.9 | 56.7 | 68.9 |

- System R2A1 is clearly the most promising candidate for a durable weatherable coating.
- It exhibited good reactivity, hardness, toughness and weathering

# UV resistance



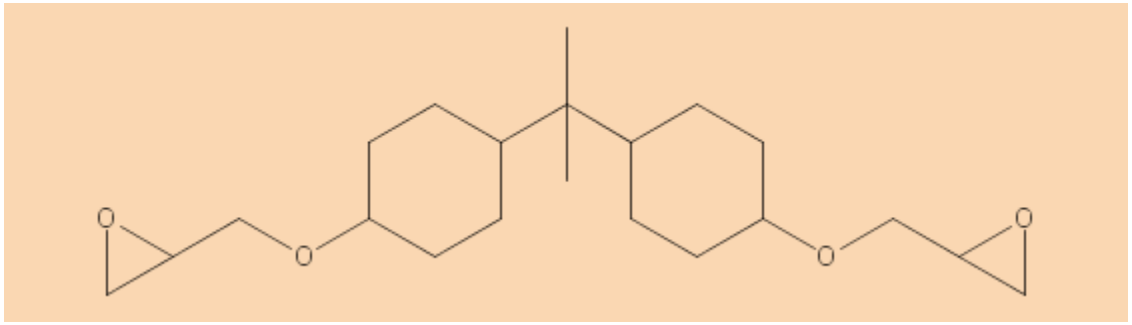
Bisphenol-A epoxy resin
exposed to
Sunlight for 10 days

Epalloy 5001 epoxy resin
exposed to
Sunlight for 10 days

# Epalloy 5000/5001

## Hydrogenated Bisphenol-A Diglycidyl ether

Structure



| Property | EEW g/eq | Viscosity @ 25C, cP | Functionality |
|---|---|---|---|
| Epalloy 5000 | 210-230 | 1500-2500 | 2 |
| Epalloy 5001 | 190-210 | 2000 – 4500 | 2.4 |

- **Faster cure at wide temperature**
  **Especially at low or subzero temperature**

# Structure comparison

| Structure of resin | Curing agent | Comment |
|---|---|---|
| Bisphenol-A | Polyamide | Good reactivity at RT<br>Very long gel time at 5C or below |
| | Aliphatic amine | Faster reactivity, brittle, amine blush |
| | Cycloaliphatic amine | Slower reactivity at RT. |
| | Mercaptan | faster reactivity at 5C or below. Smell and handling problem. |
| | Phenalkamine | Good reactivity at 5C<br>Color issue |
| Bisphenol-A + acrylates | Amine | Faster reactivity at 5C or below<br>Smell, handling issue . Loss in property. |
| Bisphenol-A + Benzyl alcohol | Amine | Faster reactivity at 5C or below<br>Smell, handling issue . High VOC. Loss in property. |
| Bisphenol-A + Nonyl phenol | Amine | Faster reactivity at 5C or below<br>Smell, handling issue . Loss in property. |

Ideal solution:

- Resin with higher reactivity ability with any curing agent.

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# Mercaptan replacement

| Formulation | A | B |
|---|---|---|
| DER 331 ( Standard Bisphenol-A epoxy resin) | 100 | 0 |
| Epalloy 7200 (Modified Bisphenol-A epoxy resin) | 0 | 85 |
| Erisys GE 20 ( Neopentyl diglycidyl ether) | 0 | 15 |
| Capcure 3-800 (polymercaptan) | 90 | 0 |
| Versamine EH-50 | 10 | 0 |
| Versamine F-11 | 0 | 49 |

| Property | A | B |
|---|---|---|
| Gel time ( 20 gm), min | 3.10 | 4.20 |
| D Hardness @ 15 min | 55/42 | 79 |
| D Hardness @ 30 min | 73 | 82 |
| D Hardness @ 40 min | 74 | 84 |
| D Hardness @ 16 hrs | 78 | 82 |
| Water absorption ( 24 hrs boil), % | 10 | 7.97 |

## Advantage:

- No odor
- Longer working time
- Faster property development
- Improved water absorption

# Acrylate replacement

| Formulation | A | B |
|---|---|---|
| DER 331<br>( Standard Bisphenol-A epoxy resin) | 75 | 0 |
| Epalloy 7200<br>(Modified Bisphenol-A epoxy resin) | 0 | 80 |
| Epon 8111<br>( Acrylated resin) | 25 | 0 |
| Erisys GE 20<br>( Neopentyl diglycidyl ether) | 0 | 20 |
| TETA<br>(Tri ethylene tetra amine) | 14 | 13.4 |

# Acrylate replacement

| Property | A | B* |
|---|---|---|
| Viscosity @ 25C, cP | 5300 | 5200 |
| Gel time ( 20 gm), min | 12 | 11 |
| Hardness ( hours to D=80+) | 7 | 1 |
| Tg ( 48 hrs RTC), oC | 51 | 70 |
| Tg ( 10 days RTC), oC | 53 | 80 |
| MEK Rub/Heat cure1 | >300 | >300 |
| MEK Rub/16 Hrs. RTC | < 50(2) | >300 |
| MEK Rubs/4 days RTC | >300(2) | >300 |
| Xylene Resistance/Heat cure (1) | -0.004%(3) | +0.056%(3) |
| Xylene resistance/4 days RTC | +1.05%(3) | +0.17%(3) |

(1)= 16 Hrs at RTC + 2 Hrs at 100C

(2) = Stained film appearance

(3) = 3 days immersion

B*= Formulation with Epalloy 7200

**Advantage:**

- No odor
- Similar working time
- Faster property development
- Higher chemical resistance

# Low temperature faster cure

## With polyamide and Phenalkamine K 541 as Hardener

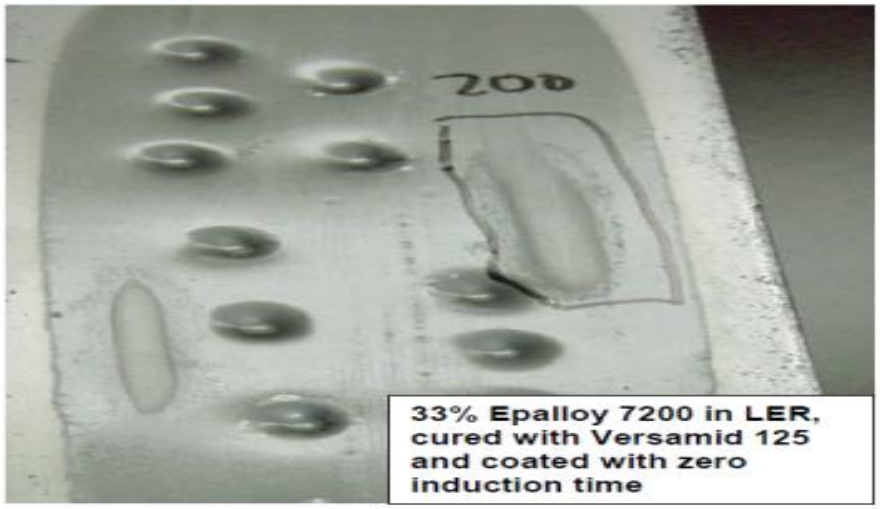
| Formulation | DER 331x90 | Epalloy 7200x90 | DER 331x90 | Epalloy 7200x90 |
|---|---|---|---|---|
| Hardener | Versamide 125 | | Phenalkamine K-541 | |
| Resin Viscosity @ 25C, cP | 725 | 4170 | 725 | 4170 |
| Resin solid | 90 | 90 | 90 | 90 |
| VOC ( gm/liter) | 72 | 74 | 68 | 68 |
| Dry time ( Hrs), RTC | 19 | 4 | 16 | 15 |
| Dry time ( Hrs) , 4oC | 88 | 42 | 48 | 19 |
| MEK Double Rubs, RTC | Very poor | 300 slight dull | Fail | 300 dull |
| MEK Double Rubs, 4oC | Very poor | 300 dull | Fail | 300 dull |
| Gardner impact ( inch-lbs), RTC | 12 | 10 | 13.5 | 6 |
| Gardner impact ( inch-lbs), 4oC | X | 7 | X | 6 |

# Low temperature faster cure

With polyamide and Phenalkamine K 541 as Hardener

Epalloy 7200 containing formulation is showing …

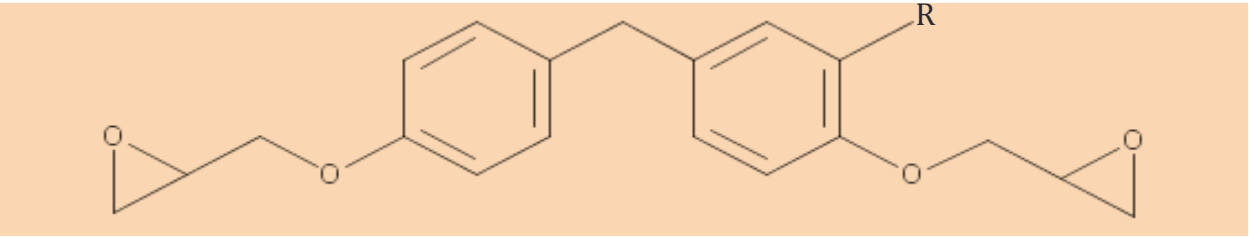
- faster property development
- better chemical resistance
- better impact resistance




# Epalloy 7200

## Modified Bisphenol-A diglycidyl ether

Structure

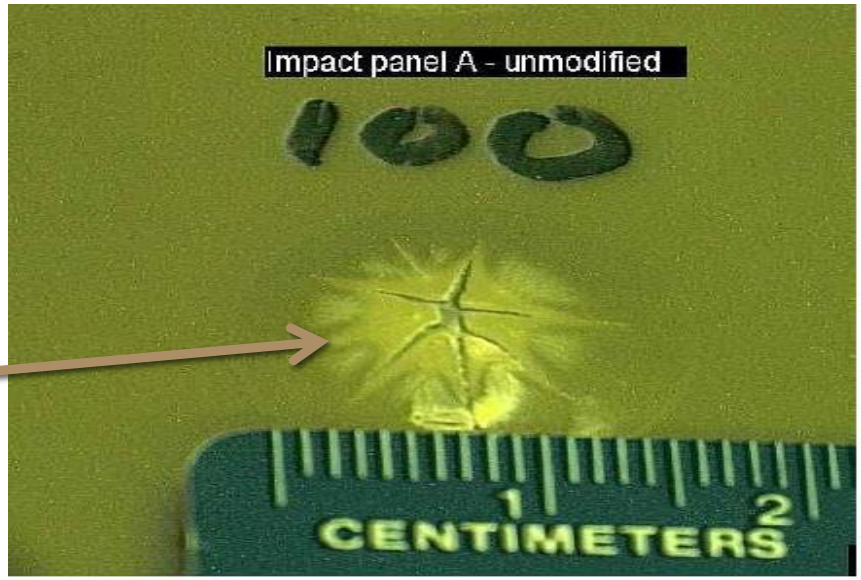



| Resin | EEW g/eq | Viscosity @ 25C, cP | Functionality |
|---|---|---|---|
| Standard Bisphenol A epoxy resin | 180-190 | 11000 – 14000 | 2 |
| Epalloy 7200 | 195-215 | 2000 – 4000 @ 72C | 2 |

- **Better Toughness at Wide temperature**
  **Especially at low or subzero temperature**

- Epoxy in general are brittle when cured.
- Brittleness is increasing when temperature is low.

Impact – Brittle-Crack




Ideal solution:

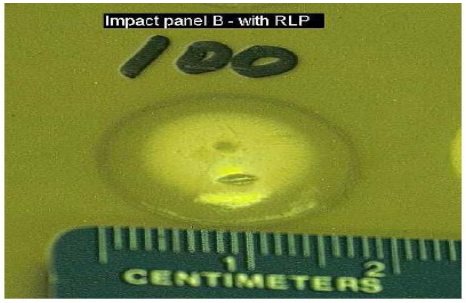
- Resin with modifier which improves impact strength or toughness.

# Toughened powder coating

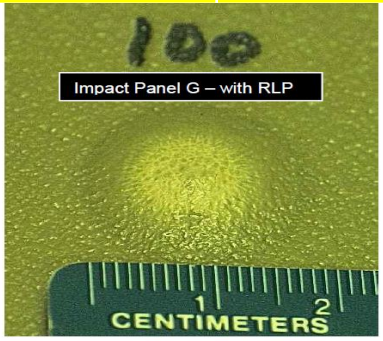
## Model formulation

| Formulation | A | B | C |
|---|---|---|---|
| Epon 2004 (Solid epoxy resin) | 100 | 0 | 0 |
| Hypox RA 840 | 0 | 100 | 0 |
| Hypox RA 1340 | 0 | 0 | 100 |
| Epikure P-104 (Phenolic curing agent) | 4 | 3.5 | 3.5 |
| Barium sulfate | 35 | 35 | 35 |
| Modaflow | 1.4 | 1.4 | 1.4 |
| Coating property | | | |
| Impact , in-lbs (Direct/ reverse) | 40/40 | 160/160 | 160/160 |


Formula A – Unmodified Epon 2004




Formula B – 1300X8 CTBN Modified Epon 2004




Formula G – 1300X13 CTBN Modified Epon 2004

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# Toughened Epoxy Adhesives

## High peel strength 2 part adhesive ( Heat Cured)

| Formulation | 1 | 2 | 3 |
|---|---|---|---|
| Standard Bisphenol-A epoxy | 100 | 62.5 | 62.5 |
| Hypox RA 840 | 0 | 62.5 | 0 |
| Hypox RA 1340 | 0 | 0 | 62.5 |
| Aliphatic amine adduct | 28.2 | 27.4 | 27.4 |
| Polyamide | 26.3 | 25.6 | 25.6 |
| Filler ( Tabular Alumina) | 40 | 40 | 40 |
| Rubber concentration, phr | 0 | 25 | 25 |
| Property( cured 1hr at 125C) Subtract -Cold roll steel | | | |
| Lap Shear , Mpa (Psi) | 4.8 (700) | 11.3 (1640) | 13.1 (1900) |
| T-peel, Kg/cm(Pli) | 0.9 (4.9) | 2.9 (16.4) | 6.0 ( 33.3) |
| Subtract – Electrogalvanized steel | | | |
| Lap Shear , Mpa (Psi) | 3.5 (505) | 11.4 (1660) | 8.1 ( 1180) |
| T-peel, Kg/cm(Pli) | 0.8 ( 4.3) | 3.3 (18.2) | 4.3 (24.3) |

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# Toughened epoxy adhesives

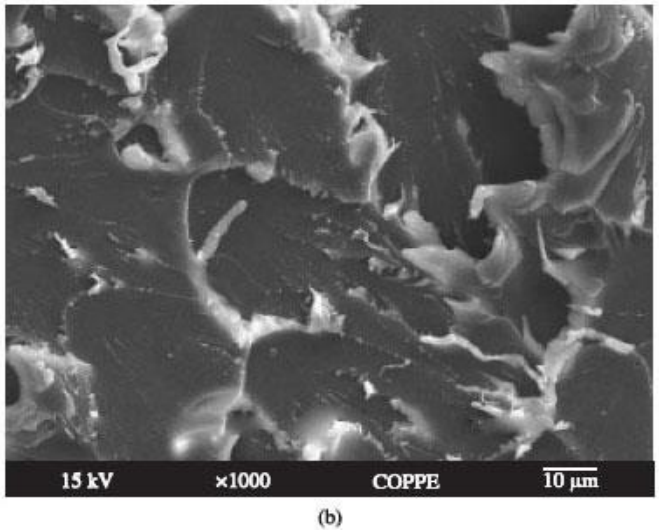
## High peel strength 2 part adhesive ( RT Cured)

| Formulation | 1 | 2 | 3 |
|---|---|---|---|
| Standard Bisphenol-A epoxy | 100 | 77.5 | 77.5 |
| Hypox RA 840 | 0 | 37.5 | 0 |
| Hypox RA 1340 | 0 | 0 | 37.5 |
| Aliphatic amine adduct | 60 | 59.3 | 59.3 |
| Atomite Whiting | 30 | 30 | 30 |
| Rubber concentration, phr | 0 | 25 | 25 |
| Property( cured 2 weeks at RT) Subtract –sand blasted Cold roll steel | | | |
| Lap Shear , Psi at -40C | 1000 | 3500 | 1500 |
| Lap Shear , Psi at RT | 1200 | 2700 | 2500 |
| Lap Shear , Psi at 83C | < 100 | < 100 | < 100 |
| T-peel, Pli at RT | < 5 | 28 | 12 |

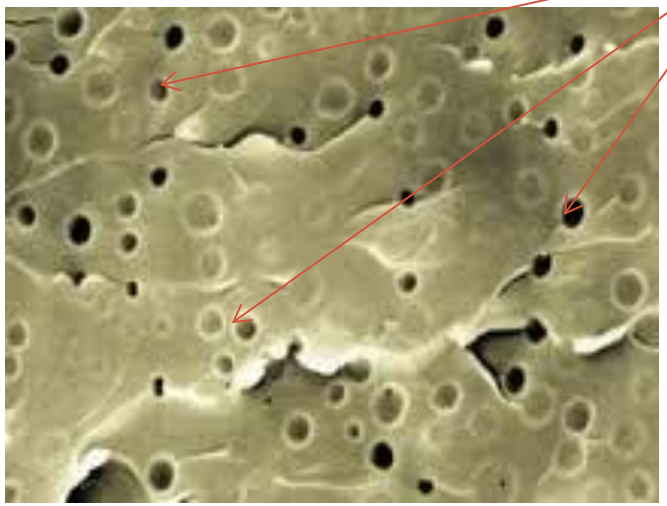
# Toughening:

CTBN/ATBN modified epoxy formulations are better .

- in fracture toughness
- in T-peel strength – especially at RT and low temperature
- in Lap shear strength ( adhesiveness).



(b)



Micro phase separated
Polymer.
Energy diffuser.
Stop crack propagation

Epoxy without toughened- brittle

Epoxy with Hypox- Toughened

# Conclusion:

Utilizing these specialty building blocks, formulator can…

- Increase chemical resistance of coating
- Increase UV stability of coating
- Increase work output even at lower temperature coating, adhesives, composite
- Find better alternate to Mercaptan and / or acrylates in coating , adhesives
- Improve fracture toughness of brittle epoxy coating , adhesive, composite even at -40C