BENZOXAZINES

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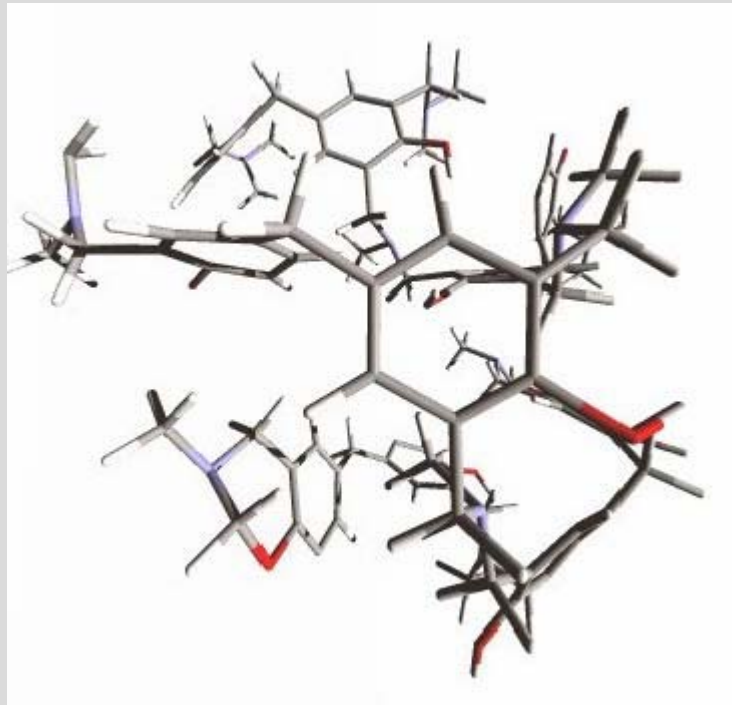
Benzoxazine Chemistry: A New Material to meet Fire Retardant Challenges Aerospace Interior Applications



Roger Tietze

Huntsman Corporation

The Fith Triennial International Aircraft Fire and Cabin Safety Research
October/November 2007

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Agenda

- History of Chemistry
- Characteristics of Chemistry & Material
- Chemistry Description
- Benzoxazine Types
- Benzoxazines & other Chemistries
- Curing of Benzoxazines
- Flammability of Benzoxazines
- Benzoxazines & Aircraft Interiors
- Summary and Conclusions

Benzoxazines: Since 1944

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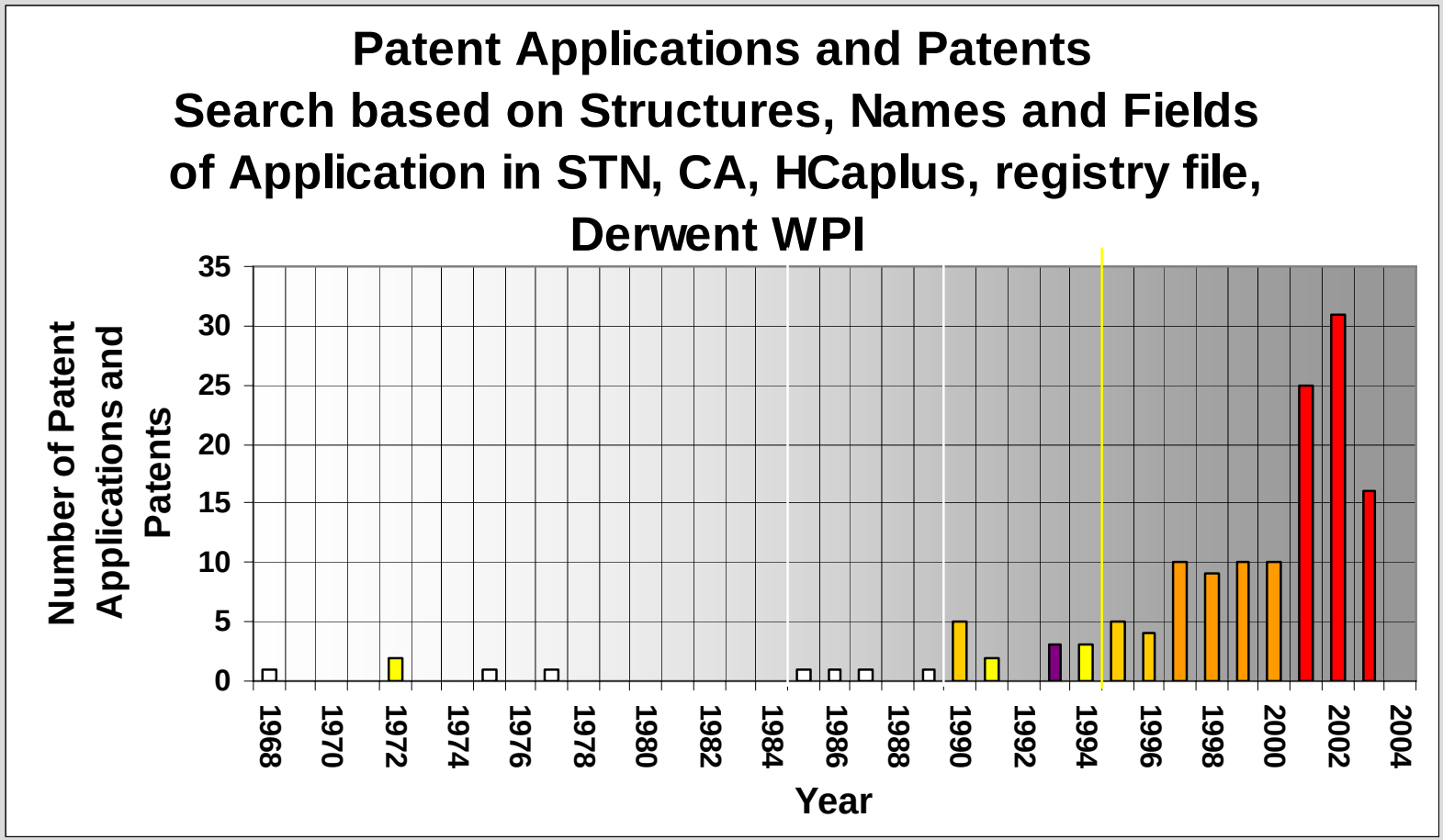
- F. W. Holly, A.C. Cope J. Am. Chem. Soc. (1944), 66, 1875
- Burke et al. J. Am. Chem. Soc. 72, 4691 (1950)
- Burke et al. J. Org. Chem. 26, 4403 (1961)
- Kuehne, J. Med. Pharm. Chem. 5, 257 (1962)
- Bishop, Dissertation Summary, 63-1372, University Microfilms Inc.
- Ann Arbor, Michigan (1962)

Benzoxazines : IP/Patents



Benzoxazines at Huntsman

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HISTORY

1995: **Acquisition of Gurrit Essex Patents**

H. Schreiber, Gurrit Essex, Betamide patents, DE 2,255,504,(1973)
DE 2,323,936 (1973)

1997: **Benzoxazine Technology Licensed to Hitachi**

Why an interest from Huntsman in Benzoxazines technology ?

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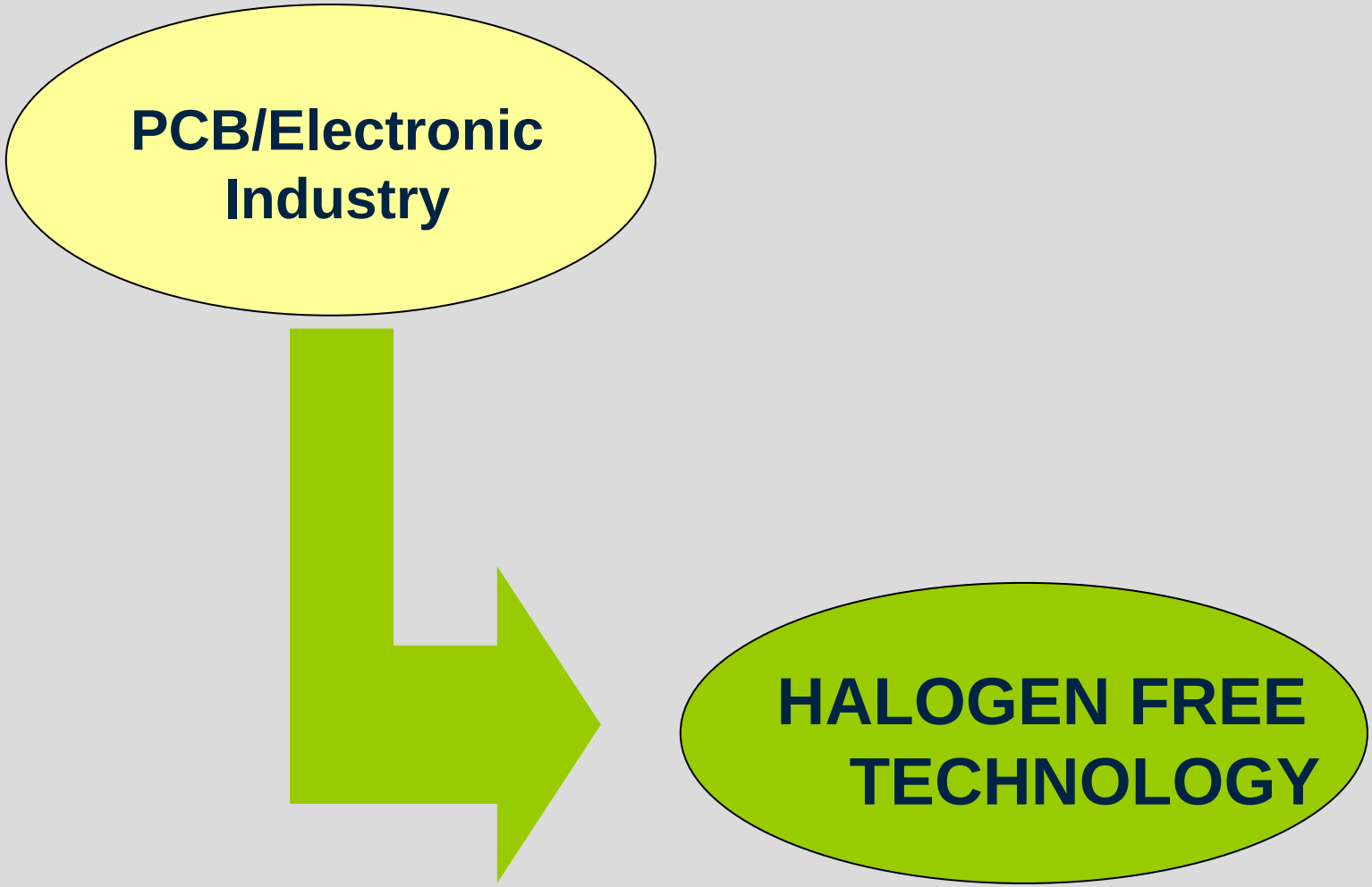

Benzoxazines Properties

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ADVANTAGES

- **Low cost materials**
- **No volatile release during cure**
- **High Tg**
- **Excellent thermal properties**
- **Good flame retardant properties**
- **Low water absorption / moisture pickup**
- **Excellent mechanical properties (modulus)**
- **Good electrical properties**
- **Near zero shrinkage of resin**
- **Storage stable at Room Temperature**
- **Compatible with various thermosetting resins**

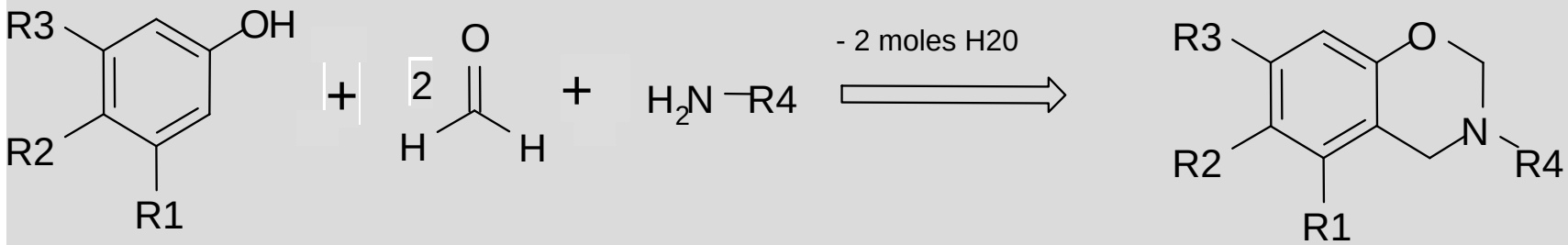
Today …

sales in PCB/Electronic Industry (1000 T/year)

What are Benzoxazines ?

- **Benzoxazines are the reaction products of an amine, a phenol and formaldehyde**
- **Water is lost during reaction process**

Example of reaction scheme :



Phenol

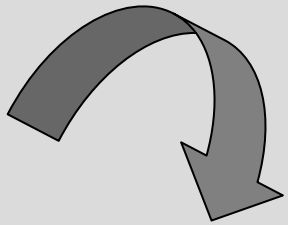
Formaldehyde

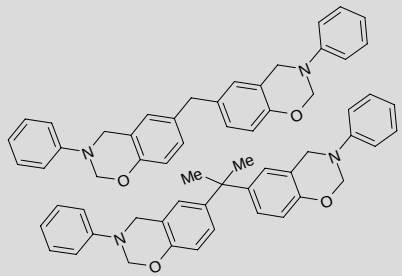
Amine

Benzoxazine

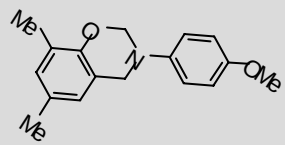
Benzoxazine Technology

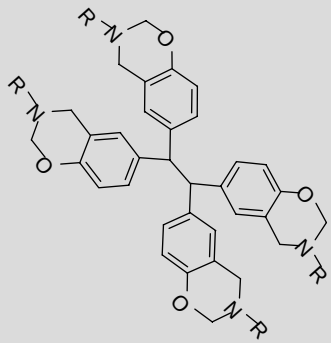
Various PHENOLS

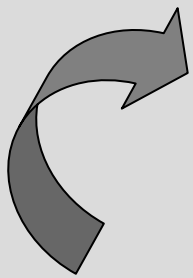




Various BENZOXAZINES

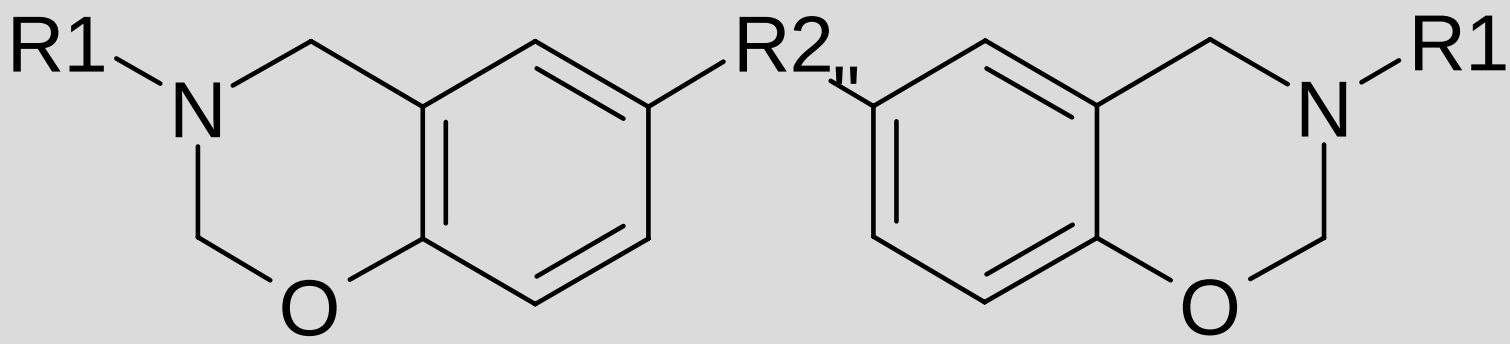






Various AMINES

Di-functional benzoxazines
for cross linked network



R1 = alkyl, phenyl, alkenyl, alkoxy, OH, halogen …etc

R2 = single bond, alkyl (CH_2, $C(CH_3)_2$ …) , O, S, SO_2, …etc

Bi-functional benzoxazines Homopolymerization

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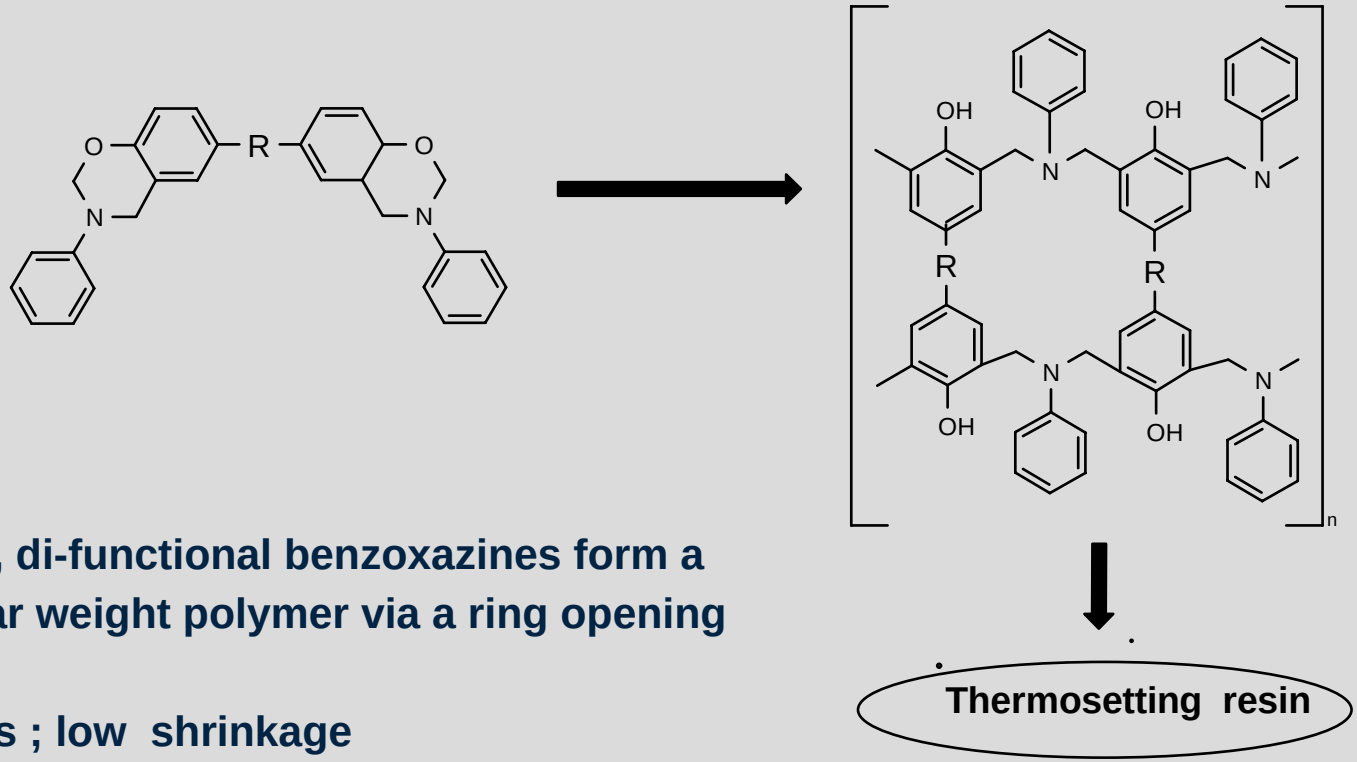

- **Upon heating, di-functional benzoxazines form a high molecular weight polymer via a ring opening mechanism**
- **No weight loss ; low shrinkage**

Curing of benzoxazines according to:

V. M. Russell, J. L. Koenig, H. Y. Low, H. Ishida, **J. Appl. Polym. Science** , Vol. 70, 1413-1425 (1998)

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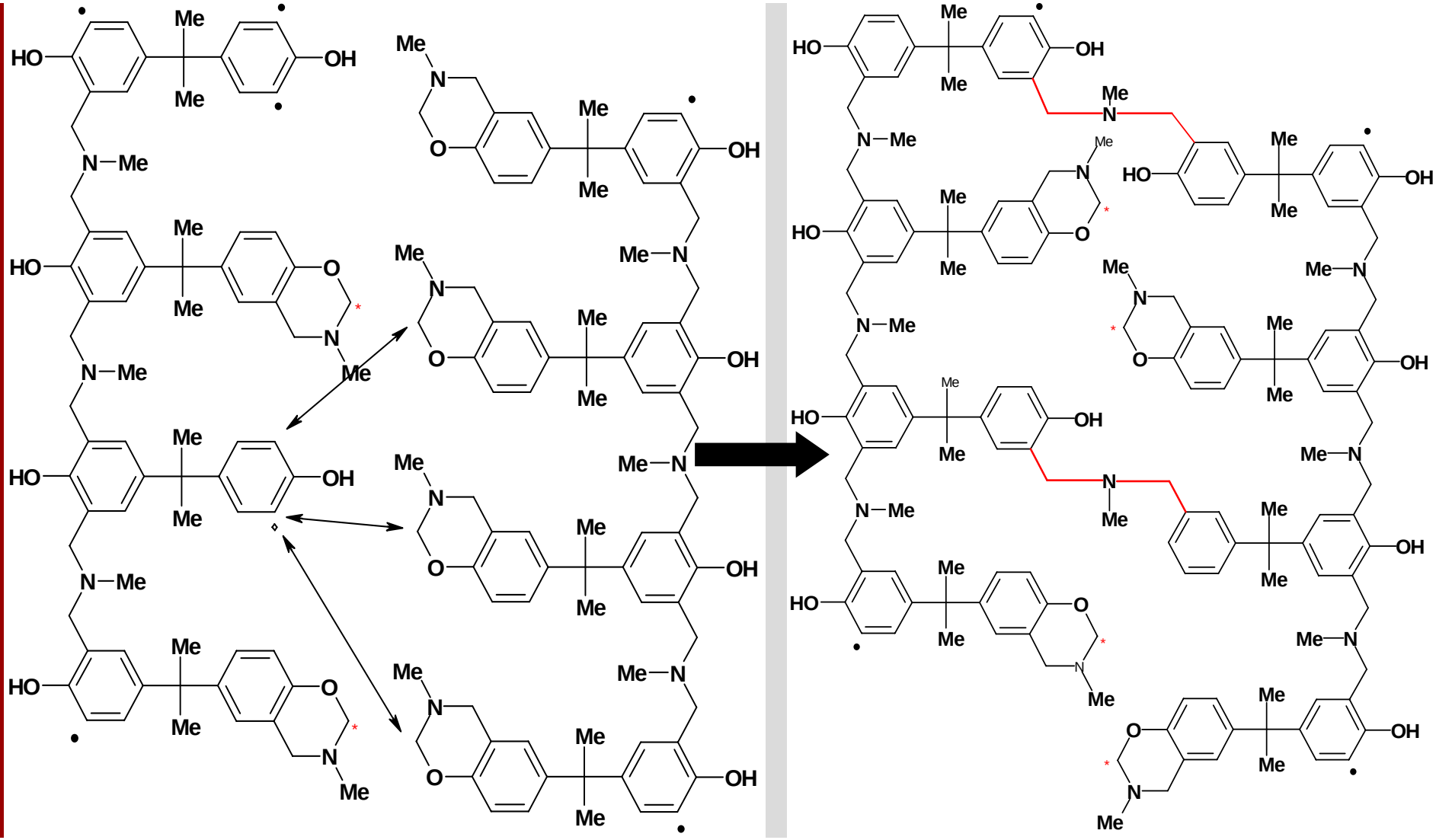

Benzoxazines and blends

Polymeric materials based on the reaction of Benzoxazines with the following chemistries have been realized :

- Epoxy resins
- Cyanate Esters
- Maleimides / Bismaleimides
- Isocyanates
- Polyamides
- Phosphazenes
- Thermoplastics (PPO)
- Acrylates / Vinylmonomers
- Triazine compounds
- Anhydrides

Remark : Not exhaustive list …

Bisphenol A Benzoxazine

(N-Phenyl Bisphenol A benzoxazine)

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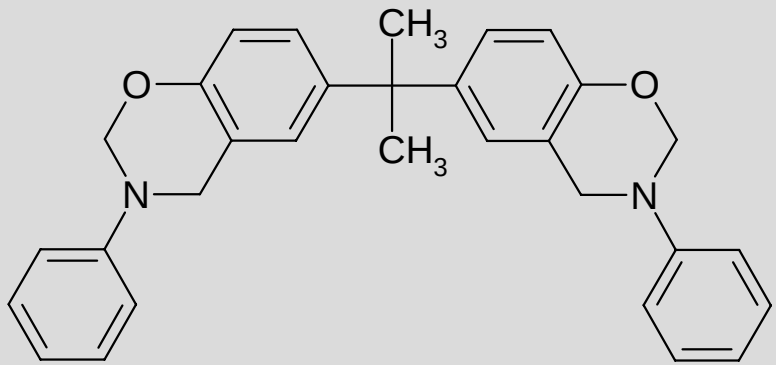

XU3560

- **Visual appearance** — **Yellow chunks**
- **Softening point, °C** — **30-40 (DSC – 10°C/min)**
- **Melting Point, °C** — **55-65 (Glass tube – Totoli – 0.5°C/min)**
- **Viscosity @ 125°C, cps** — **80-180**
- **Volatile, %** — **<1**
- **TSCA listed**

Bisphenol F Benzoxazine

(N-Phenyl Bisphenol F Benzoxazine)

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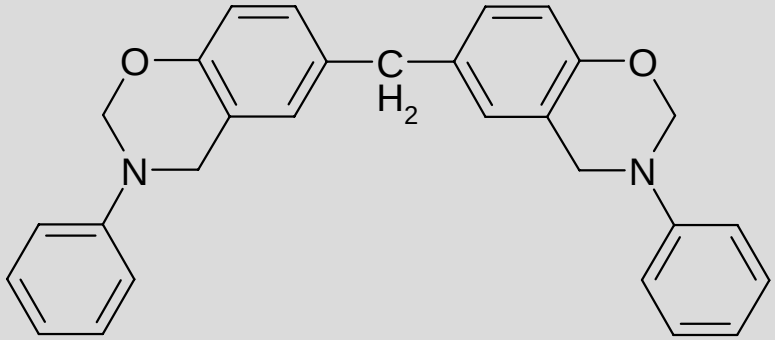

LMB6493

- **Visual appearance** — **Yellow chunks**
- **Softening point, °C** — **20-30 (DSC – 10°C/min)**
- **Melting Point, °C** — **50-60 (Glass tube – Totoli – 0.5°C/min)**
- **Viscosity @ 125°C, cps** — **50-150**
- **Volatile, %** — **<1**
- **TSCA listed**

Phenolphthalein Benzoxazine
(N-Phenyl Phenolphtaleine Benzoxazine)

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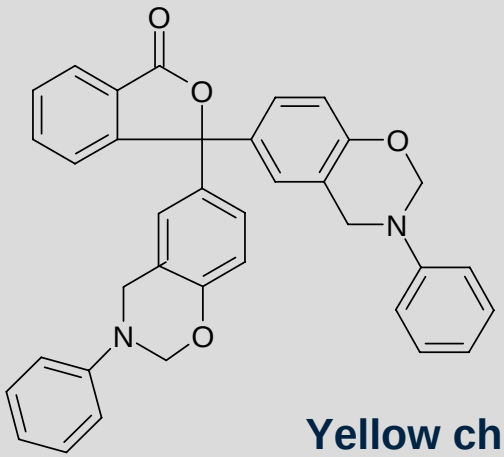
Patented



LMB6490

- **Visual appearance** — **Yellow chunks**
- **Softening point, °C** — **55-60 (DSC – 10°C/min)**
- **Melting Point, °C** — **98-103 (Glass tube – Totoli – 0.5°C/min)**
- **Viscosity @ 150°C, mPa.s** — **1400-1600**
- **Volatile, %** — **<1**
- **TSCA listed**

Solvented version only

Properties of Cured Benzoxazines

Bis-A (LMB 6452) and Bis-F (LMB 6493) based

- Tg in the range of 170-180°C (dry) and 150-165 °C (wet)
- Both exhibited high modulus and low water absorption
- Bis-A based resin has slightly higher Tg
- Bis-F based resin shows better mechanical strength

Phenolphtaleine (LMB6490) Based

- High Tg and Modulus Even better thermal performances than Bis-A and Bis-F
- Highly flame resistant UL94 V0

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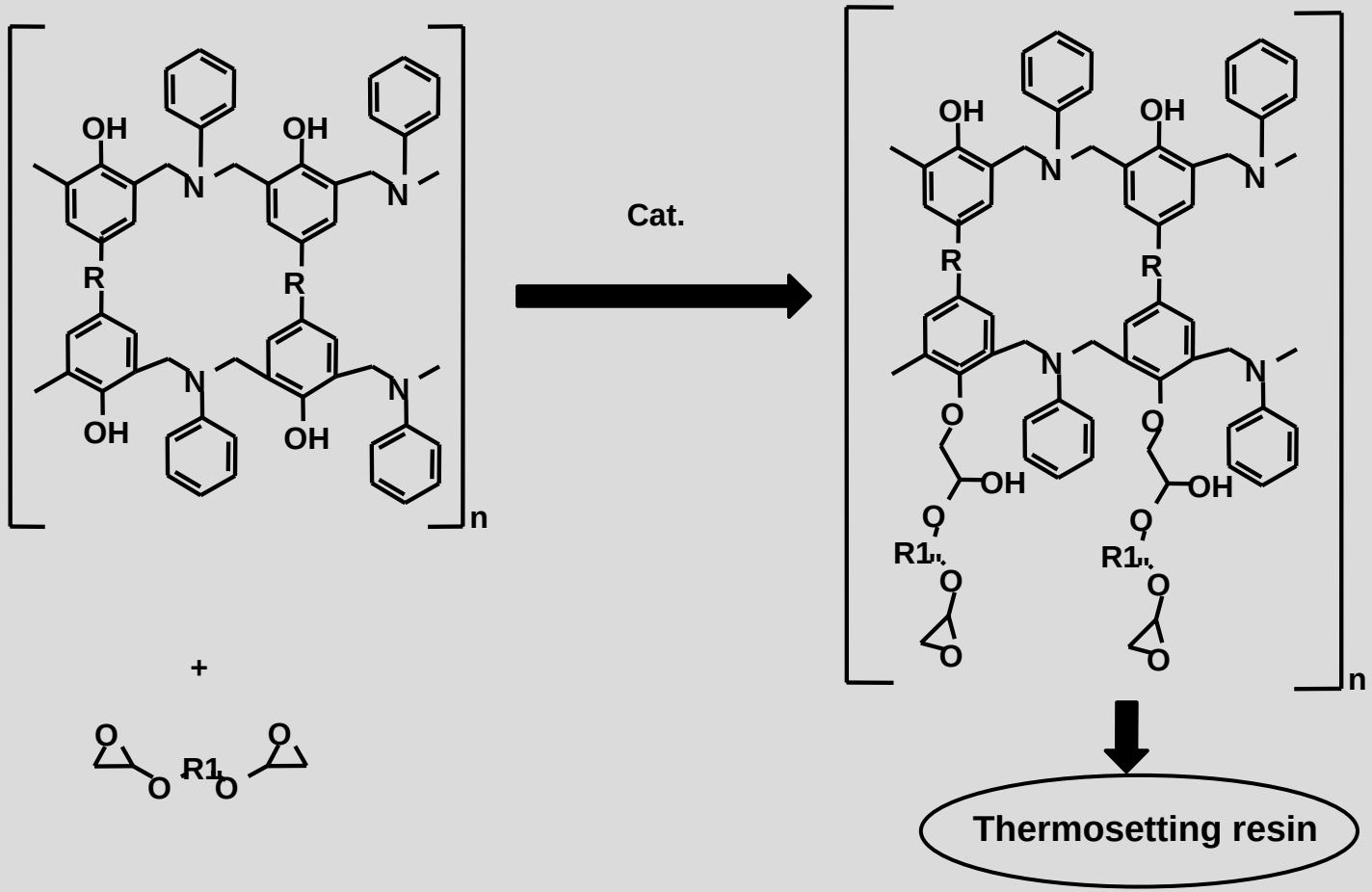
Mechanical Properties of Bis-A Benzoxazine

Curing Cycle	2hr/180°C + 2hr/200° C
Tg(°C) DSC	171
Tg(°C)DMA (E' SRM 18R-94)	184
Tg(°C)DMA (E" ASTM D-4065)	190
Tg(°C)DMA Wet* (E' SRM 18R-94)	173
Tg(°C)DMA Wet* (E" ASTM D-4065)	180
Flex Properties Dry @ RT	
Modulus, (MPa)	4602
Strength, (MPa)	132
Tensile Properties Dry @ RT	
Modulus, (Mpa)	5334
Strength, (MPa)	31
Elongation, %	1.2
Compression Properties Dry @ RT	
Modulus, (MPa)	3505
Strength, (MPa)	228
Elongation, %	8.3
Toughness Properties Dry @ RT	
K_{Ic} (MPa$\sqrt{m}$)	0.94
G_{Ic} (J/m^2)	168

*48hrs boiling water

Benzoxazines and Epoxies



Benzoxazines and Epoxy Resin Blends

	MY 720 / 4,4'DDS		Bis A Benzox. / CY179 (75/25)	
Curing Cycle	2hr / 100° C, 6hr / 177 C, 5hr / 200° C		2hr / 180 C, 2hr / 200° C	
	Dry	**Wet**	**Dry**	**Wet**
Tg [°C], DMA	250	190	227	181
Water pick-up,%, 48hr b.w.	4.3		1.7	
Flex Dry, Modulus, MPa	3740	3455	4609	4430
Strength, MPa	143	61	115	84
Elongation, %	5	1.9	2.7	1.8
Tensile, Modulus, MPa	3995	3491	4512	4319
Strength, MPa	52	30	52	45
Elongation, %	1.4	1.0	1.6	1.1
Compression Modulus, MPa	1939		3243	
Strength, MPa	40.5		33.6	
Elongation,%	32.6		10.2	
G1c J/m^2	72		82	

Box-EP system exhibits …

Low water pick up / High Modulus dry and wet / High Tg dry and wet

CY179 = Cycloaliphatic epoxy resin

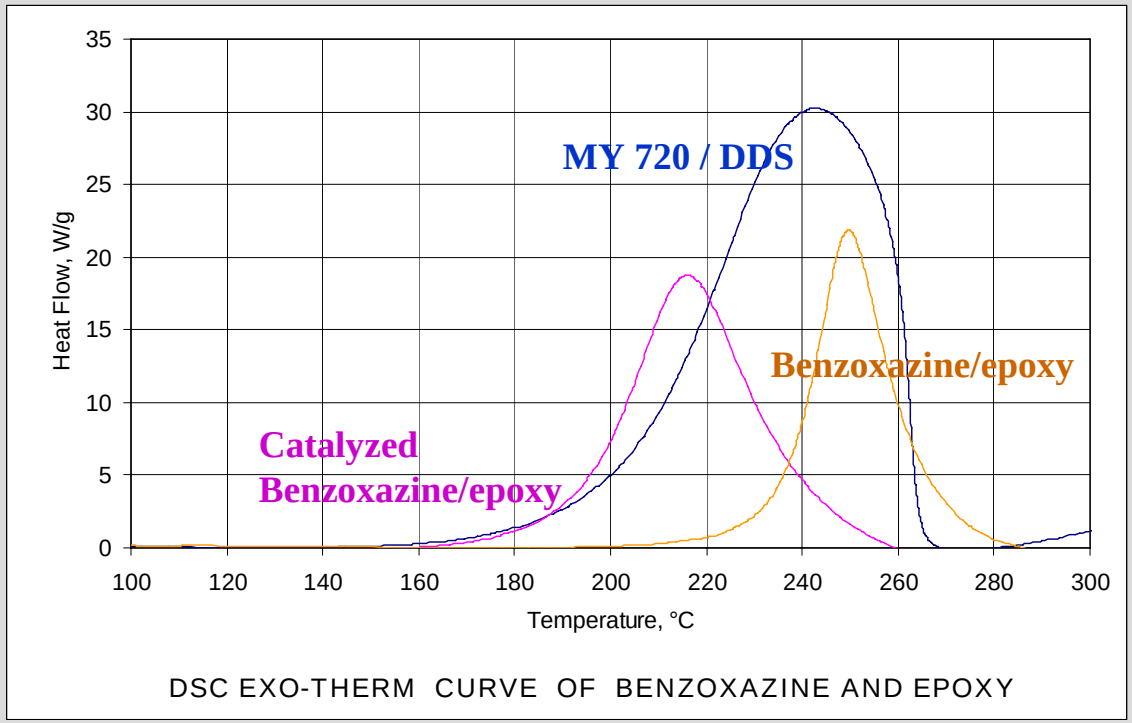
Toughening of Benzoxazines

- Rubber technology proved to be efficient
- Flexibilizer DY965 giving promising results
- Nano technologies under investigation

- State of the art Box/Epoxy formulated systems reach …
  - K_{1C} 1.6 – 1.7 MPa
  - G_{1C} 600-800 J/m2
  - ✓ Dry Compression Modulus 4.7 Gpa
  - ✓ Dry Tg 190°C
  - ✓ Wet Tg 165°C

Acceleration of Benzoxazine cure

- Various acids, anhydrides, phenols, and sulfonic esters have been studied and **work in this field is still ongoing ….**



DSC EXO-THERM CURVE OF BENZOXAZINE AND EPOXY

Acceleration of Benzoxazine Cure

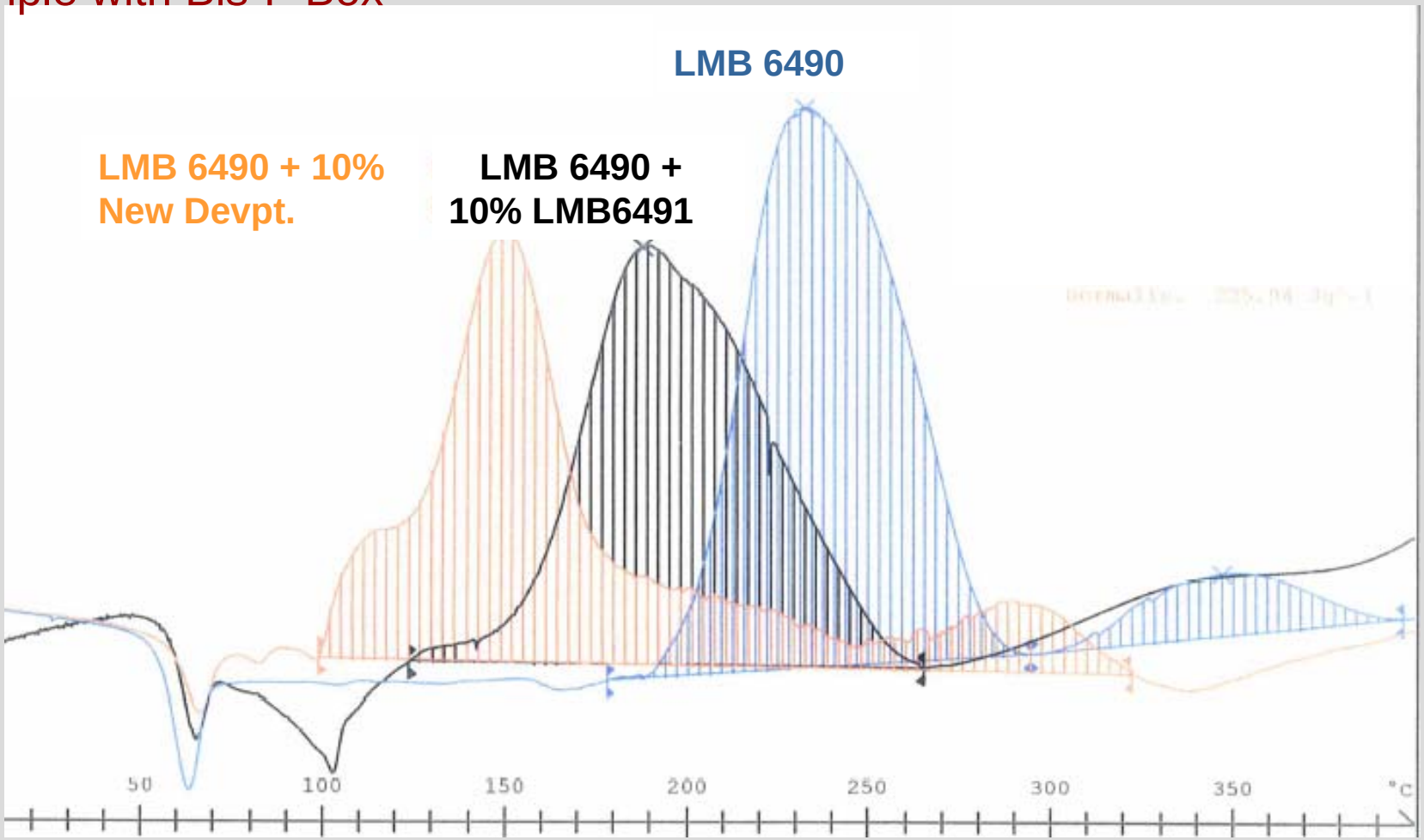
Example with Bis-F Box

Formulation	Curing Cycle	Tg, °C
Bis F Box	2 hrs / 200 °C	169
Bis F Box 100 CAT 1 7.5	2 hrs / 177 °C	168
Bis F Box 100 CAT 1 7.5 CAT 2 5	0.5 hr / 177 °C	164
Bis F Box 100 CAT 1 7.5 CAT 2 5	2 hrs / 150 °C 4 hrs / 150 °C	154 162
Bis F Box 75 CY 179 25 CAT 1 7.5	2 hrs / 177 °C	207

Bis F Box = Bisphenol F N-Phenyl Benzoxazine --- **CAT 1 and CAT 2 = Huntsman's propietary catalysts**

Acceleration of Benzoxazine Cure

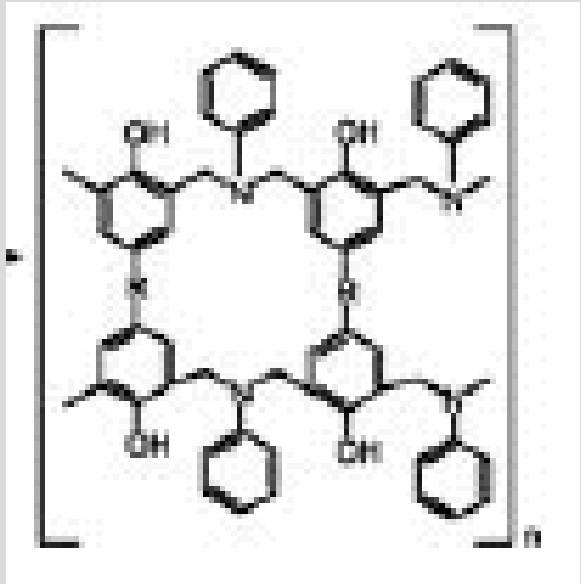
Example with Bis-F Box



Flammability of Benzoxazines

On curing, Benzoxazine resins create a Phenolic like structure with inherent Flame retardant properties …

… strongly influenced by the backbone



Flammability of Benzoxazines

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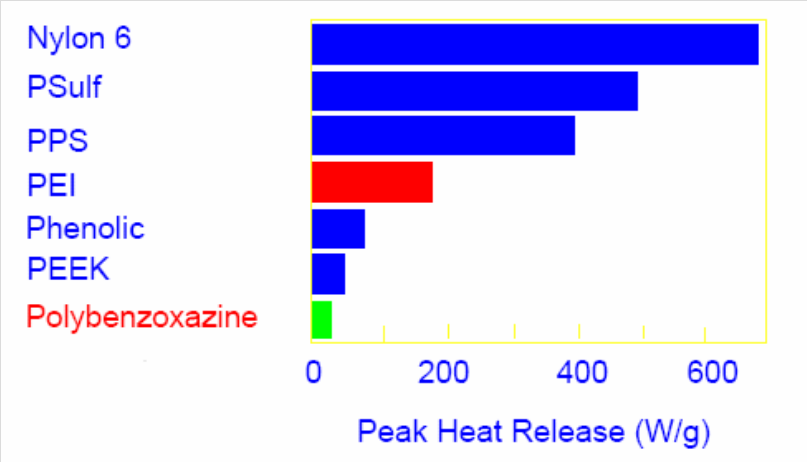
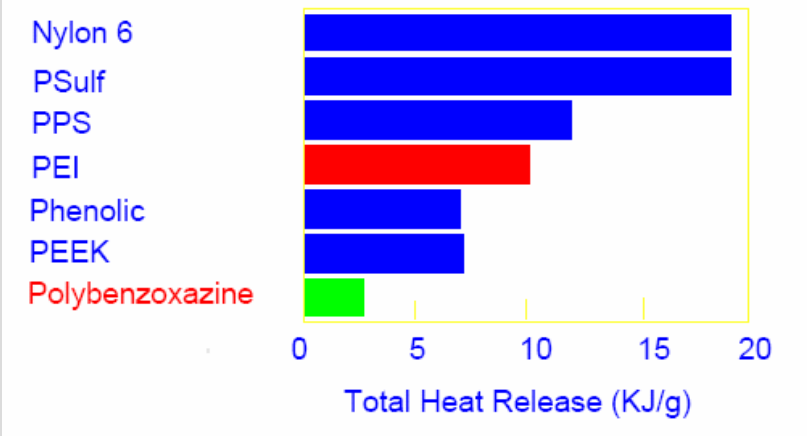
- Amount of Bromine needed to reach UL94-V0 requirements

Resin System	UL 94	% Bromine
Bisphenol A Epoxy / Dicy	Burns	16
MY 720 ($_{\text{TGMDA epoxy}}$) / DDS	Burns	14
Bisphenol A Benzoxazine	Burns	9
Bisphenol F Benzoxazine	V1	7
Polyphenol A Benzoxazine	V1	3
Phenolphthalein Benzoxazine	V0	0

Flammability of Benzoxazines

- Heat realease properties compared to Thermoplastics





(From litterature : H.Ishida)

Comparison to Phenolic system for Aircraft Interiors

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Burning behaviour	Test methods	Units	Phenolic Prepreg, 296 g/m² E-glass, 40% resin, specification Laminate 1 layer	Benzoxazine LMB6498 Laminate 1 layer	Benzoxazine LMB6531 Laminate 1 layer
Flammability (12s):	AITM 2.0002 B	mm/s/s	-	128/0/0	142/2/0
Flammability (60s)	AITM 2.0002 A	mm/s/s	60/0/0	144/0/0	167/0/0
Smoke Density (Flaming mode)	AITM 2.0007	Ds	5	6	6
Toxicity (Flaming mode)	AITM 3.0005	ppm HCN	0	2	1
		ppm CO	50	113	74
		ppm NO_x	10	5	3
		ppm SO_2	0	1	6
		ppm HF	0	0	0
		ppm HCl	0	0	0
Heat Release & Rate (HRR / HR):	AITM 2.0006	kw/m² kw*min/m²	65/40	58/34	63/33
Resin content (cured)		%	40	38.3	40
Curing conditions				180°C, 120min, 1.0bar	**150°C, 120min, 1.0bar**

Very promising results : Smoke Density, Heat Release and toxic gases concentrations

Airbus Bremen Evaluation

Preliminary data regarding flamability of monolayer glass laminate 40% resin b.w.

Benzoxazines Properties

ADVANTAGES

- **Low cost materials**
- **No volatile release during cure**
- **High Tg**
- **Excellent thermal properties**
- **Good flame retardant properties**
- **Low water absorption / moisture pickup**
- **Excellent mechanical properties (modulus)**
- **Good electrical properties**
- **Near zero shrinkage of resin**
- **Storage stable at Room Temperature**
- **Compatible with various thermosetting resins**

Today …

sales in PCB/Electronic Industry (1000 T/year)

Tomorrow

… in

Structural Composites !

Benzoxazines Properties

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DRAWBACKS

- Require high temperature (min 180°C) for self curing
- Catalysts/Hardeners still not existing for low temperature (120°C) cure
- Mainly solid resins
- Not inherently tough

Axis of Research for Huntsman

- Catalysts for Box Resins
- Liquid Box resins
- Toughening of Box resins

Benzoxazines Technology

Summary and Conclusion

- **Benzoxazines with different backbones are available.**
- **Benzoxazine accelerating systems have been identified and work is still ongoing.**
- **Several products have been developed for Laminating and Structural Composite applications.**
- **Sales are growing in Electronic applications**

- **Unique benzoxazine based formulations proved to be key materials in the PCB / Electronic Industry, particularly in halogen-free applications.**

- **Benzoxazine resins are also promising candidates for Aerospace Composites due to their performance profiles:**
  - **High Tg,**
  - **Excellent mechanical properties,**
  - **Low moisture absorption**
  - **Flame retardancy.**