Roy Tess Award Cliff Schoff

Delayed (Latent) Catalysis in Coatings

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Why Delay

Latent catalyst
Delayed catalyst
Stabilized

Before Application

Improved Pot life
Improved Stability
Lower Losses

After Application

Controlled cure speed
Improved flow leveling

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Crosslinking Mechanism

CROSSLINKER	Catalyst
MELAMINE	Acid
ISOCYANATE	Base, Metal
EPOXY	Base, Acid (cationic)
SILOXANE	Base, Acid, Metal
UNSATURATION	Free Radical
MICHAEL ADDITION	Base

Applications

Aerospace 2K
Automotive Topcoats,
    OEM (Amino), Refinishing 2K
Coil Coating Amino Resin
Maintenance Epoxy-amine
Powder Coating
Waterborne 2K

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ACTIVATION OF CATALYST

↓

TRIGGER

↓

POTLIFE STABILITY → EQUILIBRIUM / MIXING / HEAT / MOISTURE / OXIDATION / RADIATION UV → X-LINKING REACTION

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Catalyst Delay

Blocking Catalysts

In-situ Catalyst Formation

Physical-Mechanical

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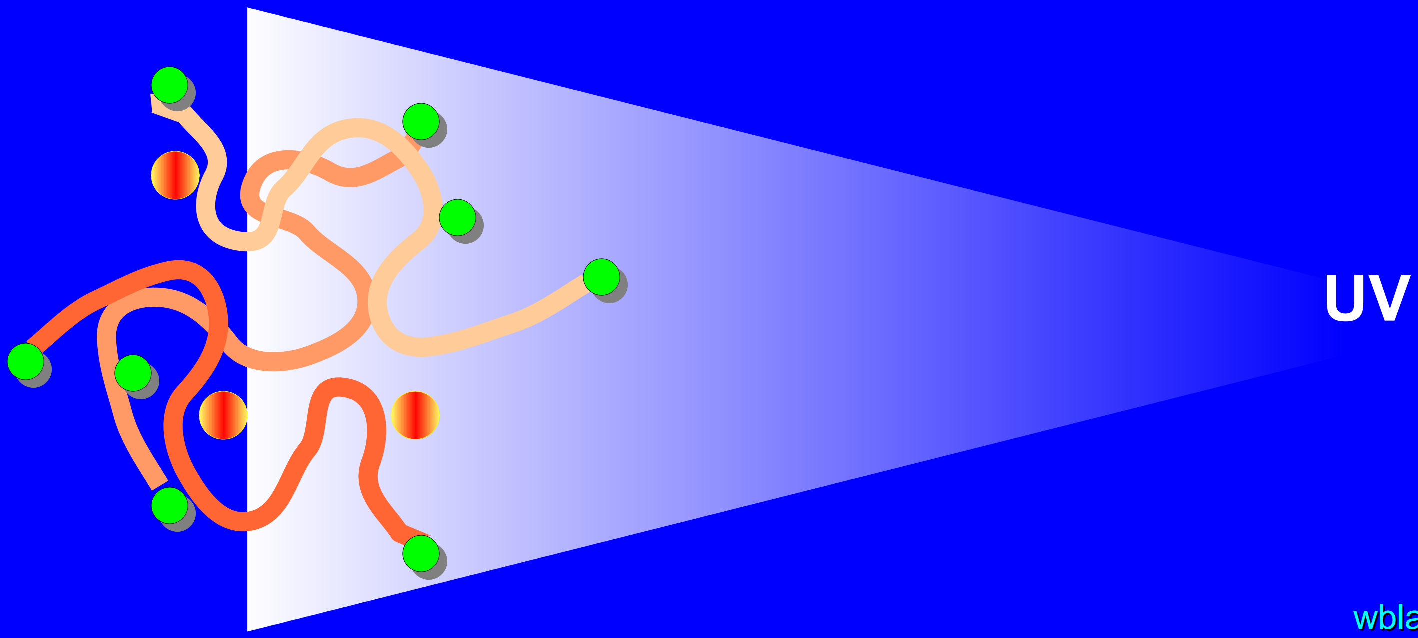
Photoinduced Catalyst: Principals

No Arrhenius rate control
Thermally stable catalyst
Photocleavage: very fast

Blocking Catalysts
- Photoactive blocker
  - Sulfonium
  - Iodonium

In-situ Catalyst Formation
- Acid catalyst
- Base catalyst
- Free radical



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Catalyst Delay

- Blocking Catalysts
  - Evaporation
  - Reaction
  - Thermal decomposition

- In-situ Catalyst Formation
  - Thermal decomposition of precursor
  - Hydrolysis
  - Reaction Oxide-salt
    - Thermal
    - Reaction
  - Oxidation
  - Rearrangement

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Catalyst Delay

Blocking Catalysts

- Acid-Base
- Base-Acid
- Metal Chelate
- Metal (Acid-salt)
- Superacid-Quaternary Amine
- Superacid-Iodonium, Sulfonium (Photo)

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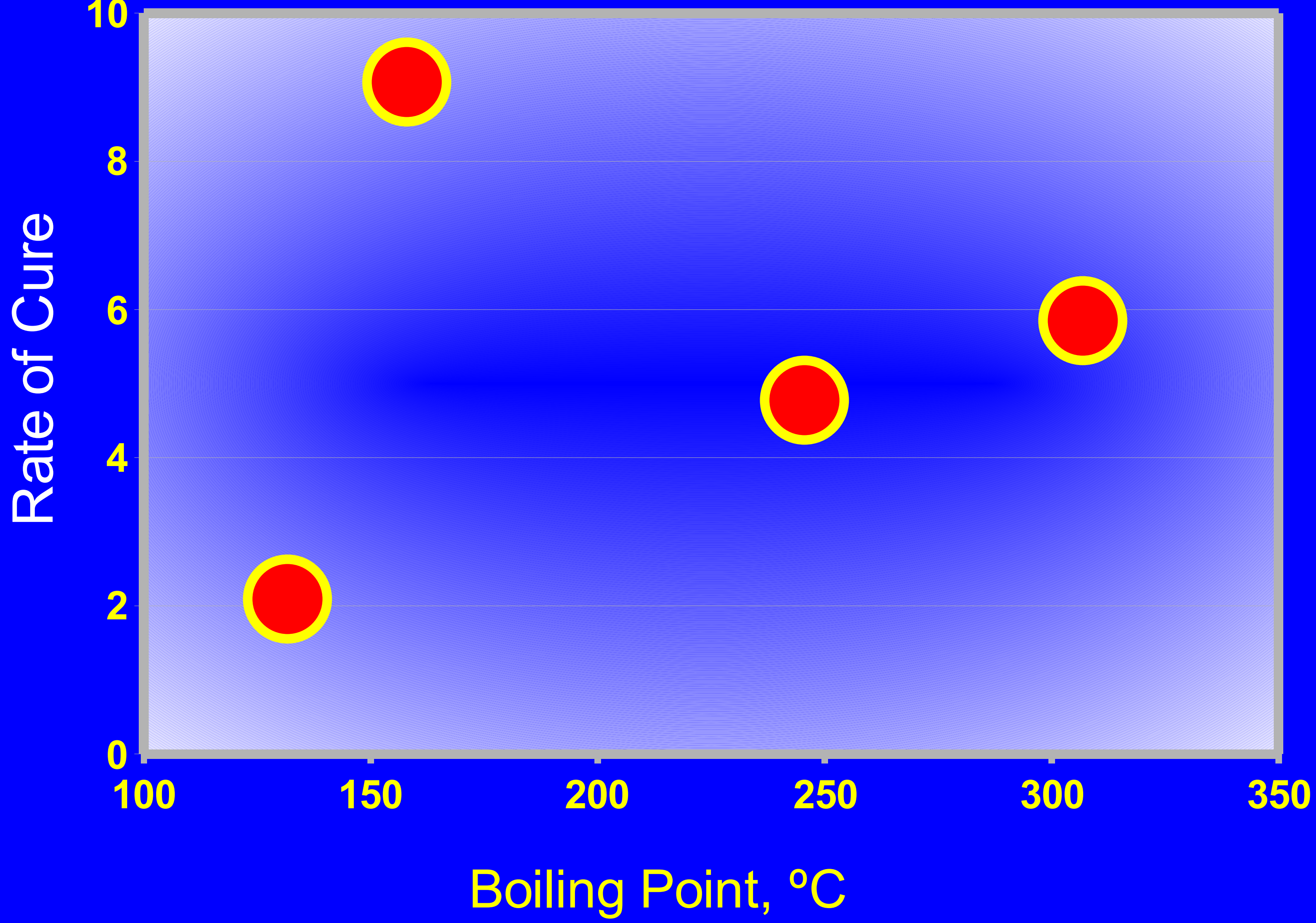
Amine Blocking of Acid Catalyst, pTSA

HMMM crosslinked polyol



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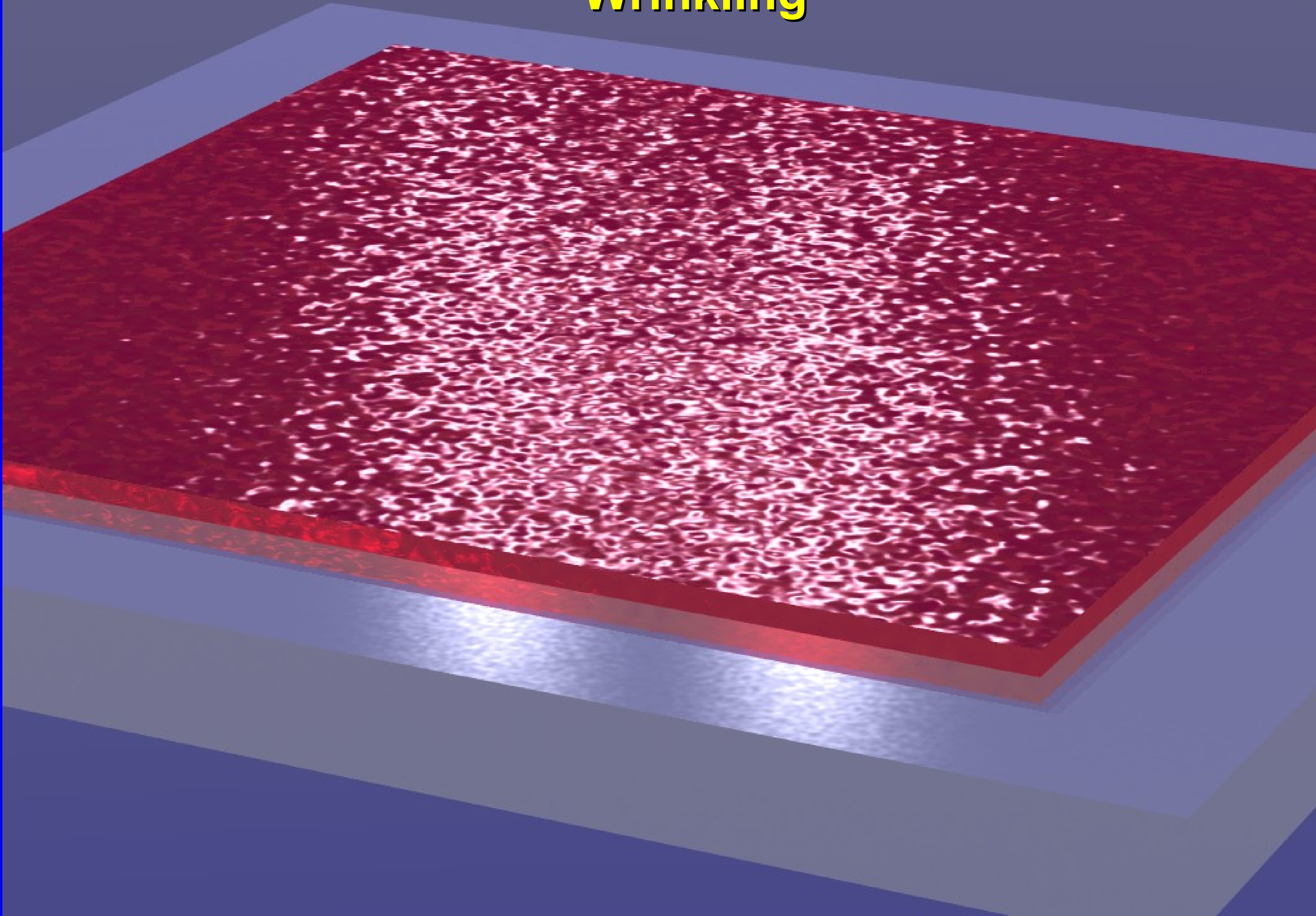
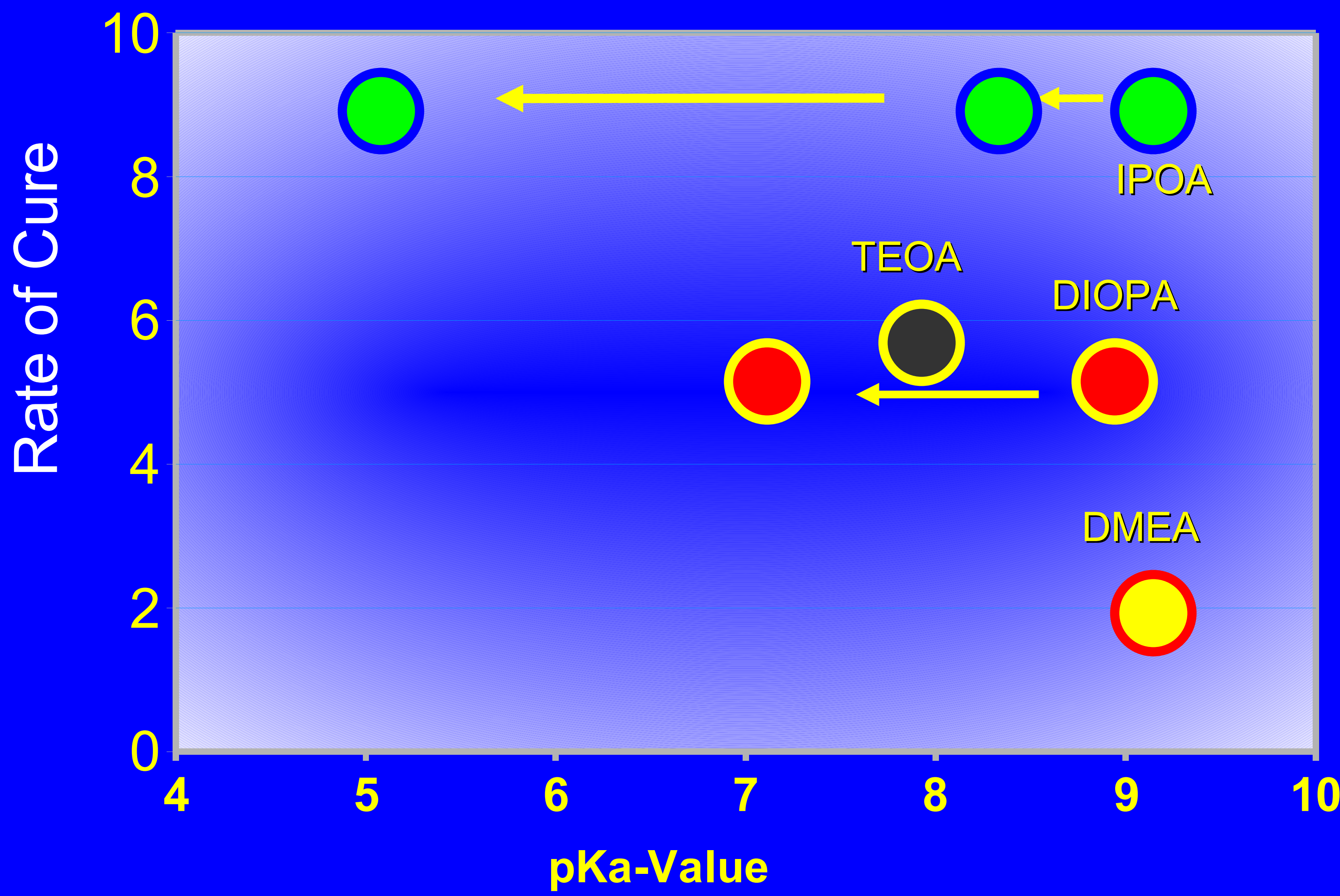
Wrinkling



Amine Blocking of Acid Catalyst, pTSA

pKa Amine, Formaldehyde Reaction



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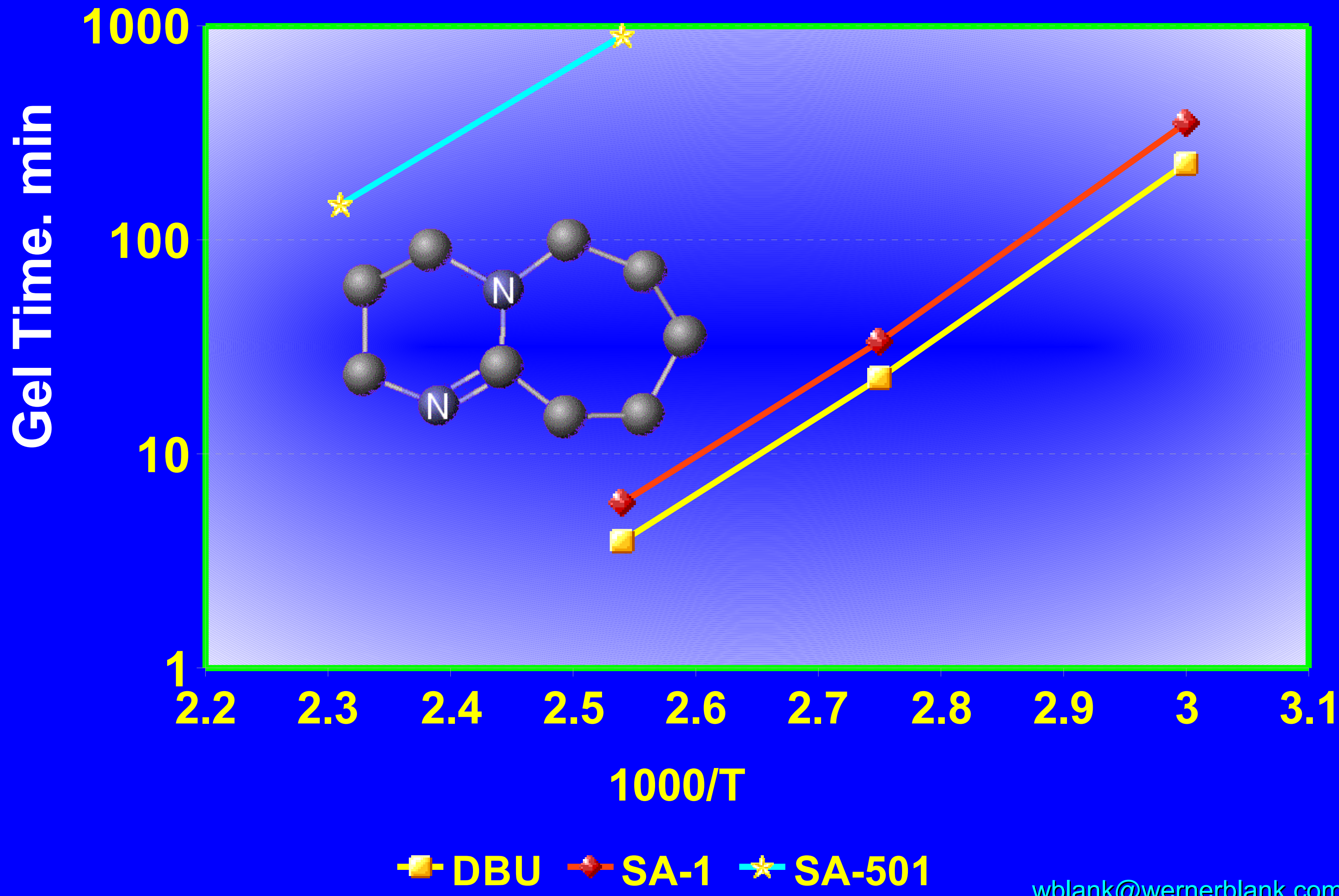
REACTIVITY vs. TEMPERATURE

Bis A epoxy Amine catalyzed



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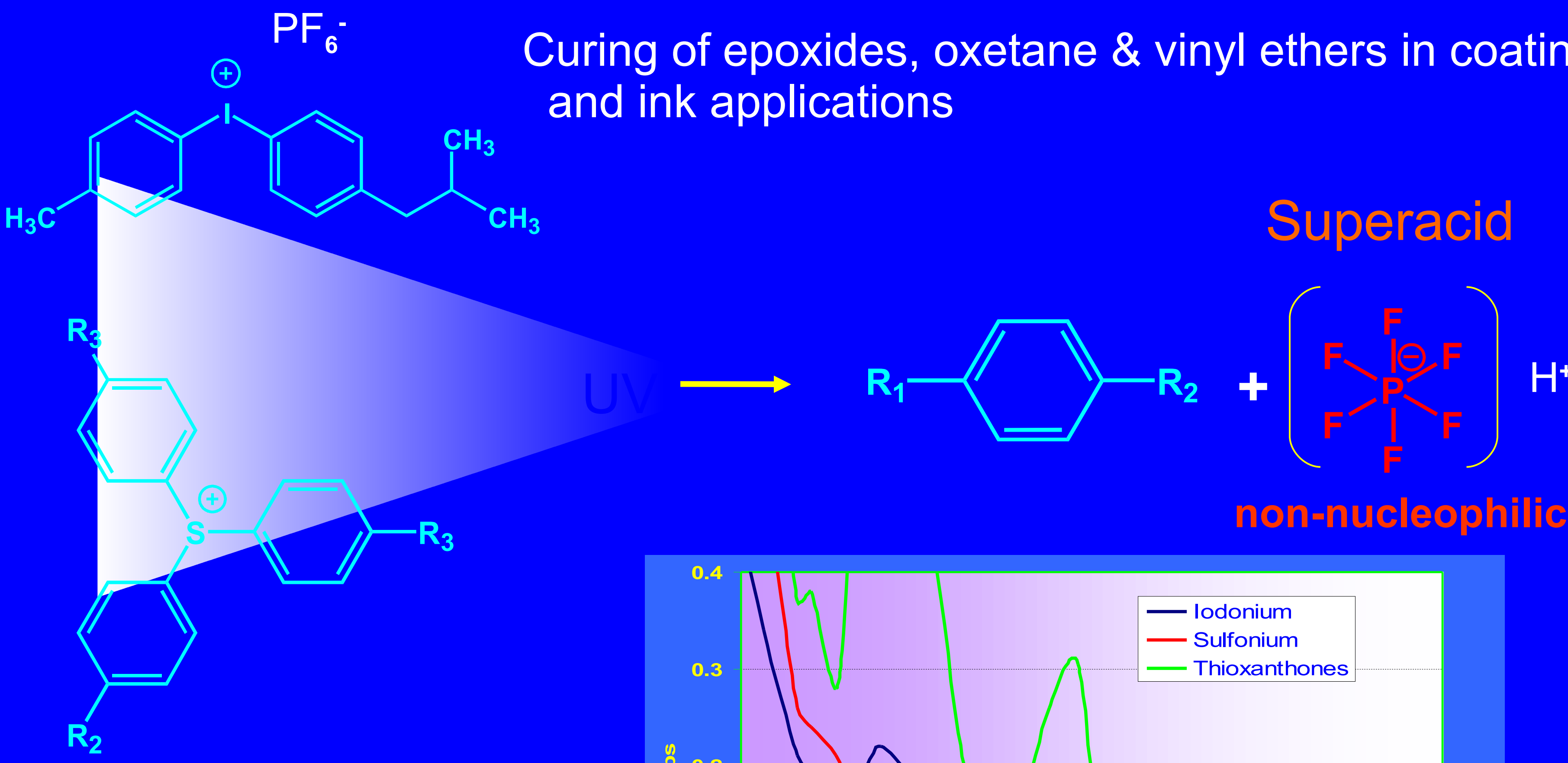
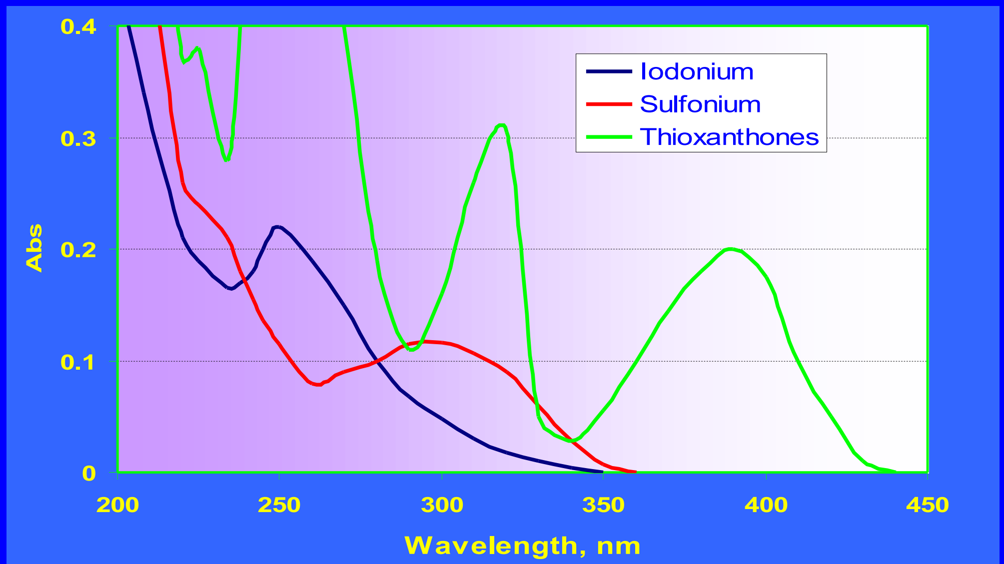
Onium Salt Photoinitiators: Latent Superacids

Curing of epoxides, oxetane & vinyl ethers in coating and ink applications



R_1, R_2 = H, $R_1C_6H_4$-S-, $R_2C_6H_4$-S-, $R_3C_6H_4$-S-



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Catalyst Delay

In-situ Catalyst Formation

- Sulfonic acid ester
  - Thermal, Hydrolysis, Photo
- Amines
  - Thermal
  - Photo Generation
- Metal catalysts
  - Hydrolysis
  - Oxides reaction
  - Thermal
  - Oxidation
  - Rearrangement

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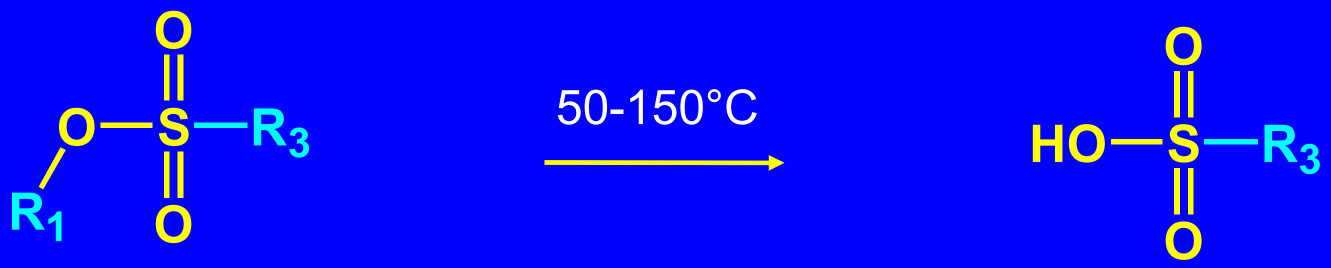
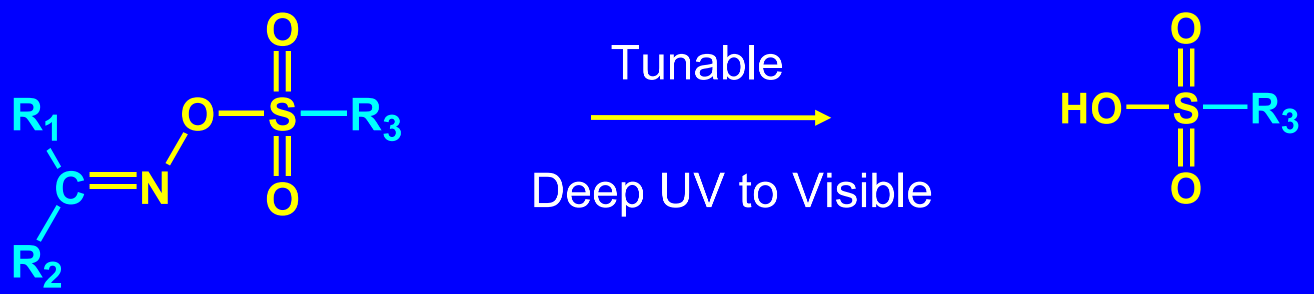
In-situ Catalyst Formation: Sulfonic Acid Ester

Thermal - Hydrolysis



R_1 = Alkyl, ß-hydroxyalkyl R_3 = Phenyl

Photoacid Generation



R_1, R_2: tunig of the chromophore,
thermal stability and solubility

R_3: tuning of acid strength/diffusion properties
thermal stability

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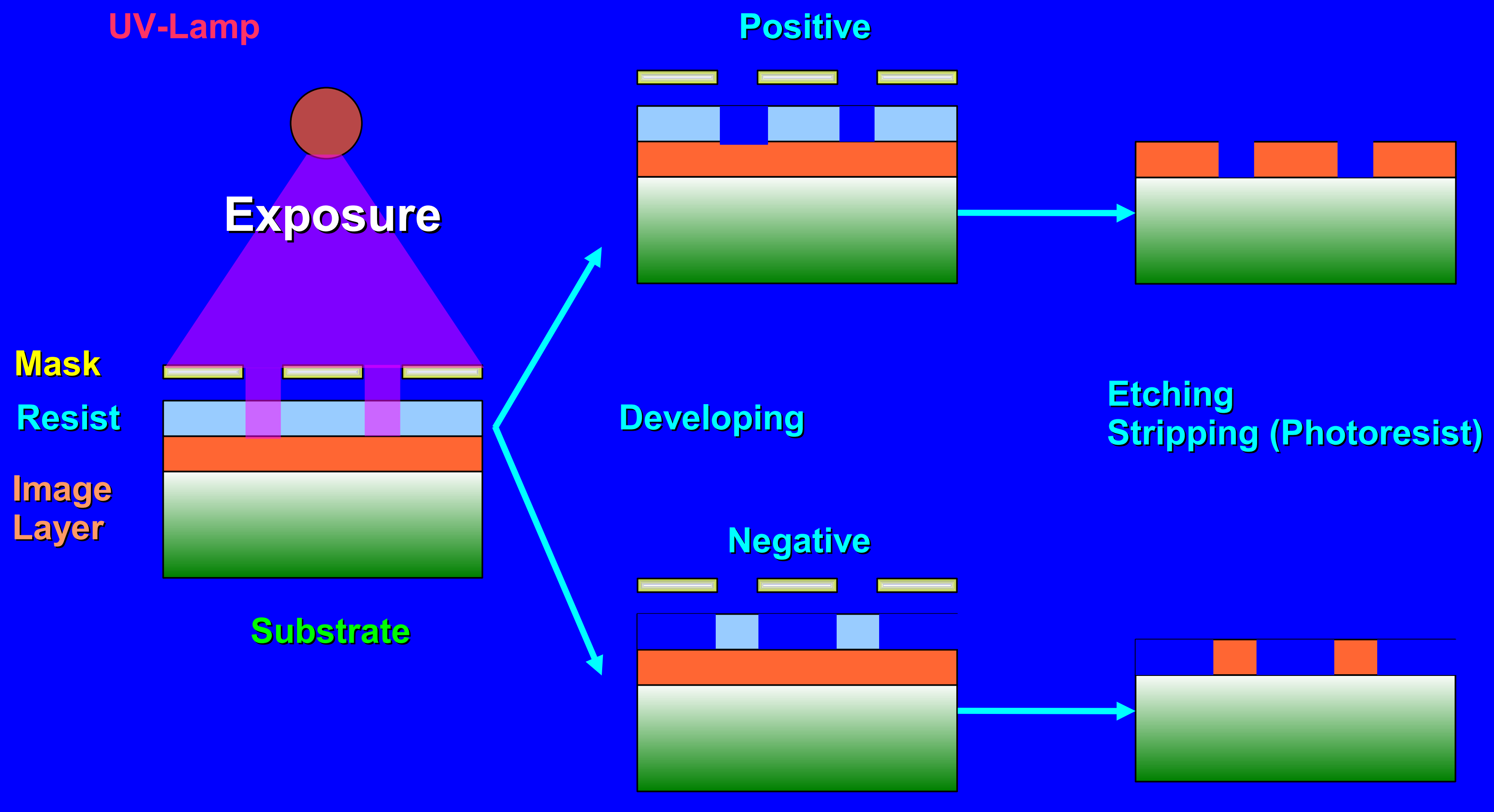
Photoresist Technology



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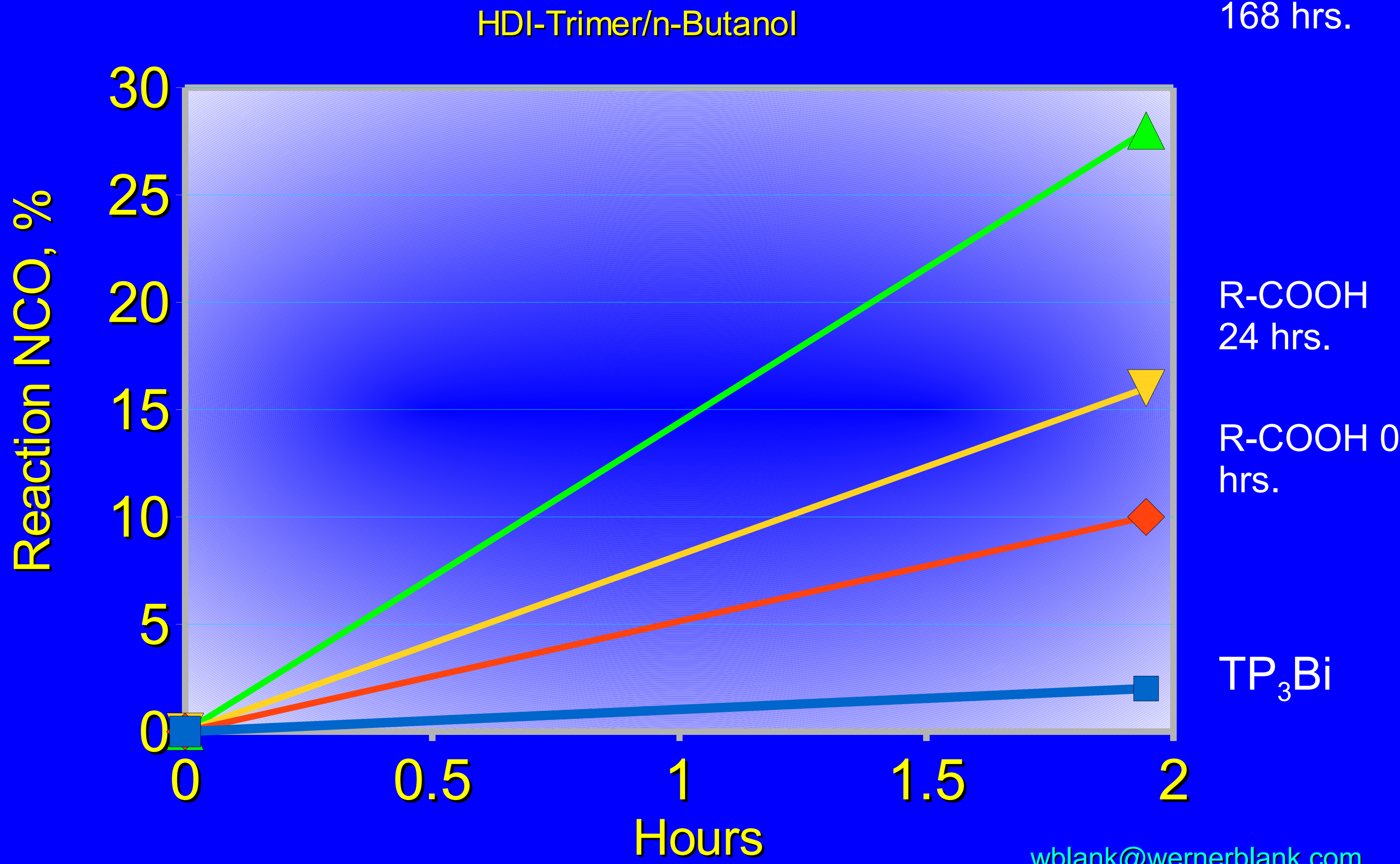
In-situ Catalyst Metal Catalysts Formation Hydrolysis

Triphenylbismuth Catalyst (0.09%)



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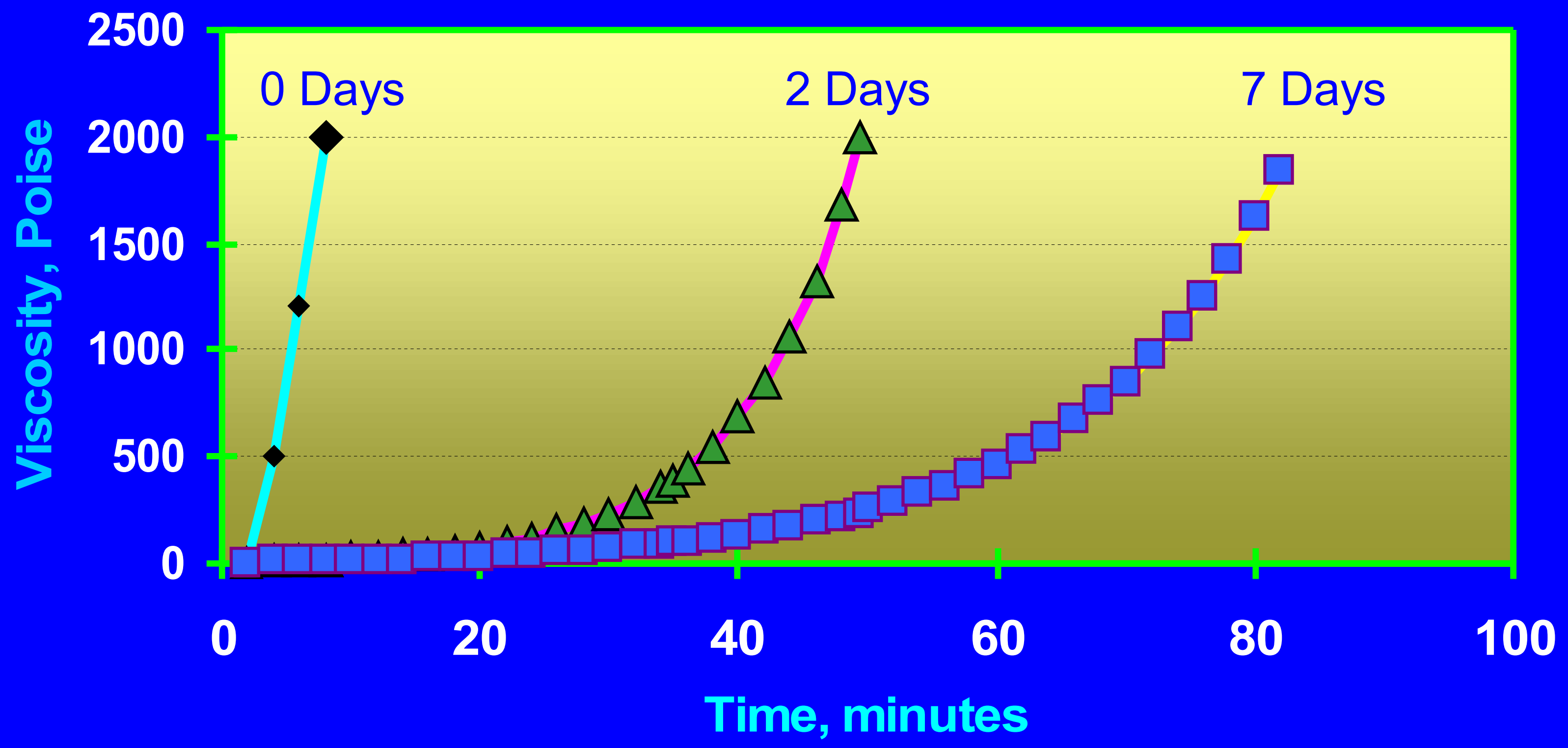
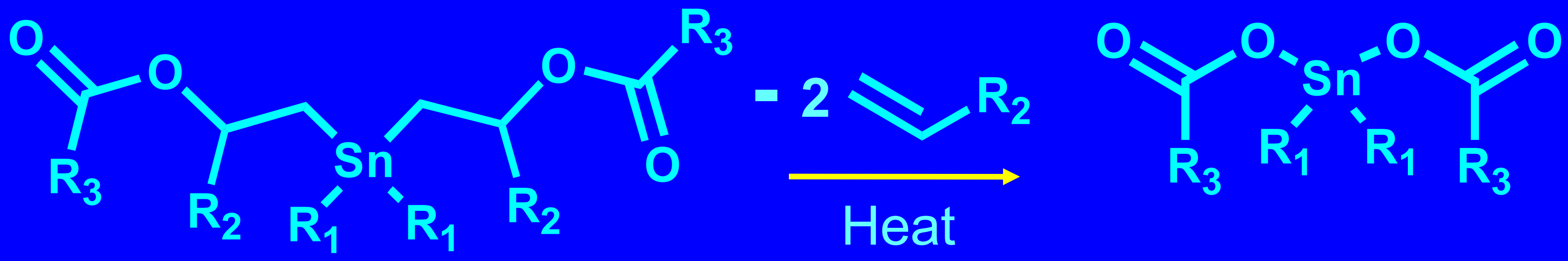
In-situ Metal Catalyst Formation Reaction

$$Bi(RCOO)_3 \xrightarrow{+\ H_2O} Bi(OH)_3 + RCOOH \xrightarrow{-\ H_2O} Bi(RCOO)_3$$

Polyether MDI Elastomer
Bi Oct. 1/5 mol WATER



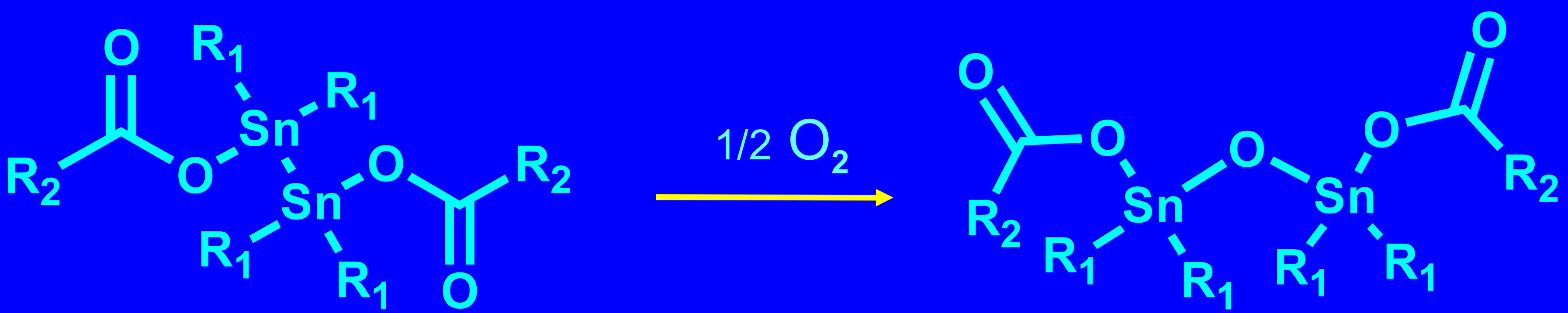
In-situ Metal Catalyst Formation Reaction



Tetraorganostannanes

anti β-elimination

bis(acyloxy)dialkylstannanes



tetraalkyldistannanes

distannoxanes

B. Jousseaume, N. Noiret, M. Pereyre and A. Saux, Organometallics, 13, 1034-1038 (1994).

B. Jousseaume, N. Noiret, M. Pereyre, M. Franc and M. Petraud, Organometallics, 11, 3910 (1992).

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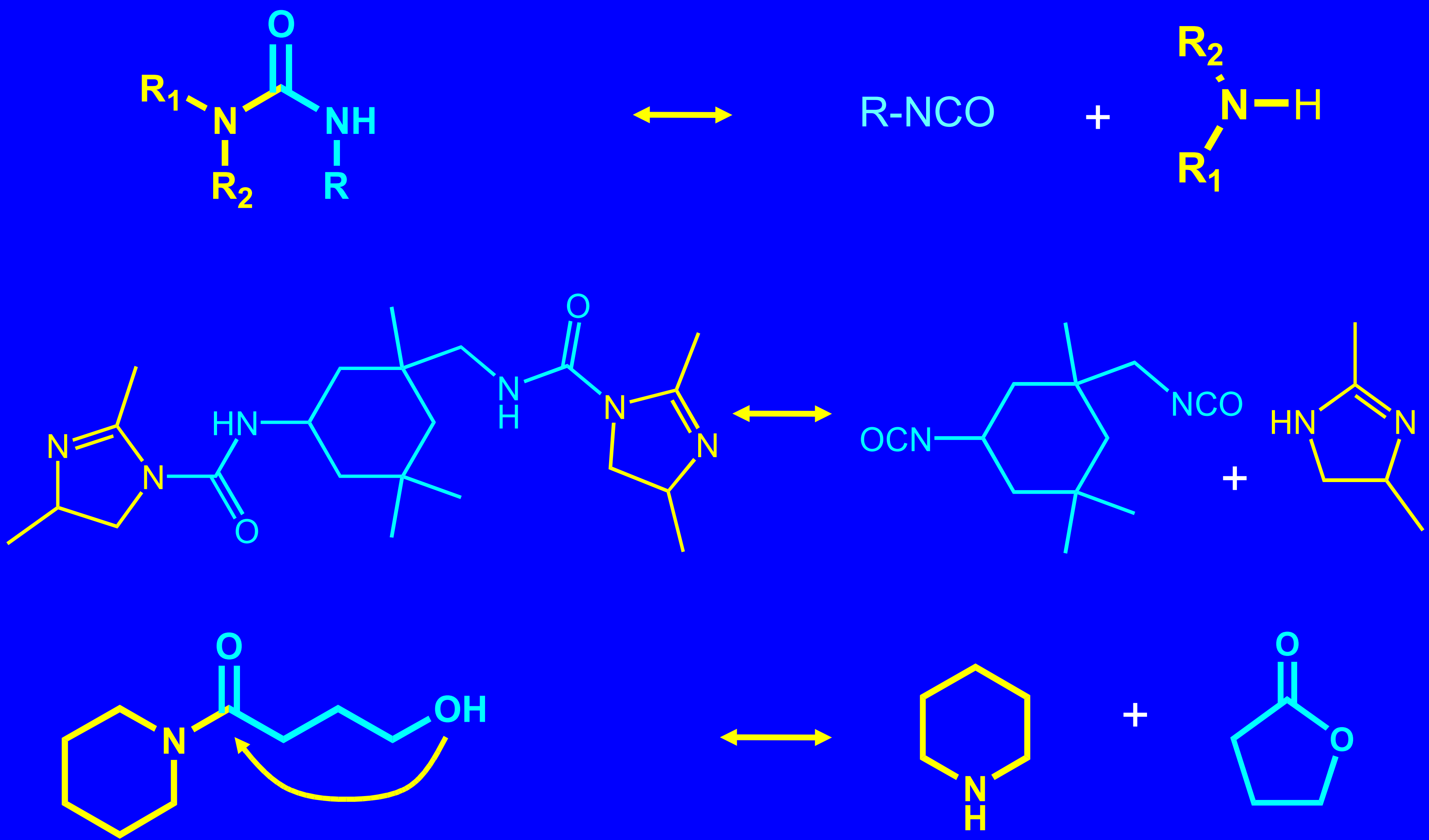
In-situ Base Catalyst Formation Reaction



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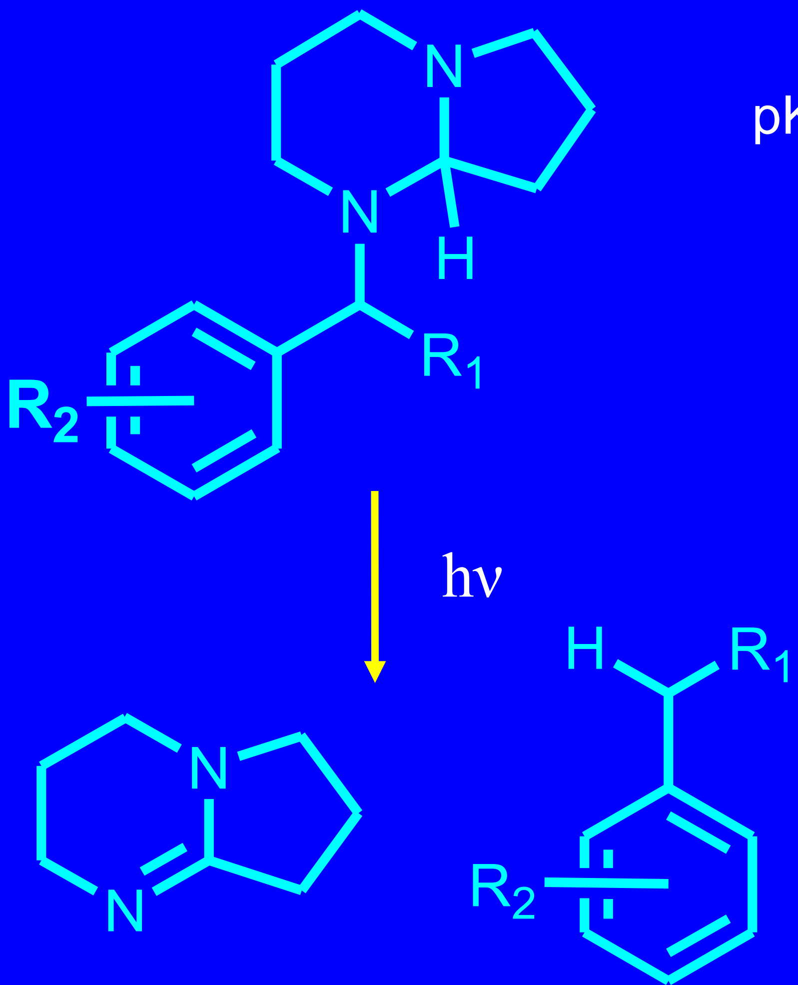
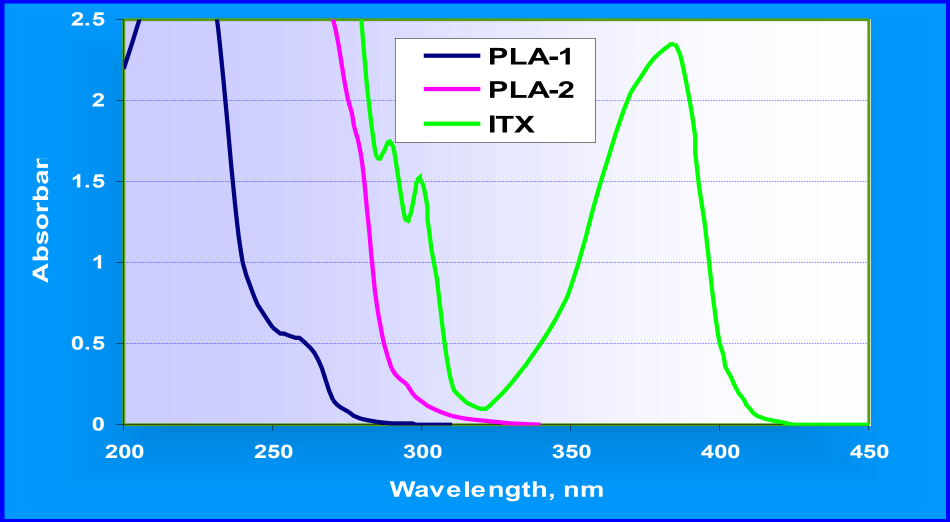
In-situ Photoinduced Base Generation
of Amidine Double Bond

pKa= 8.96 ± 0.20





pK_a = 12.7

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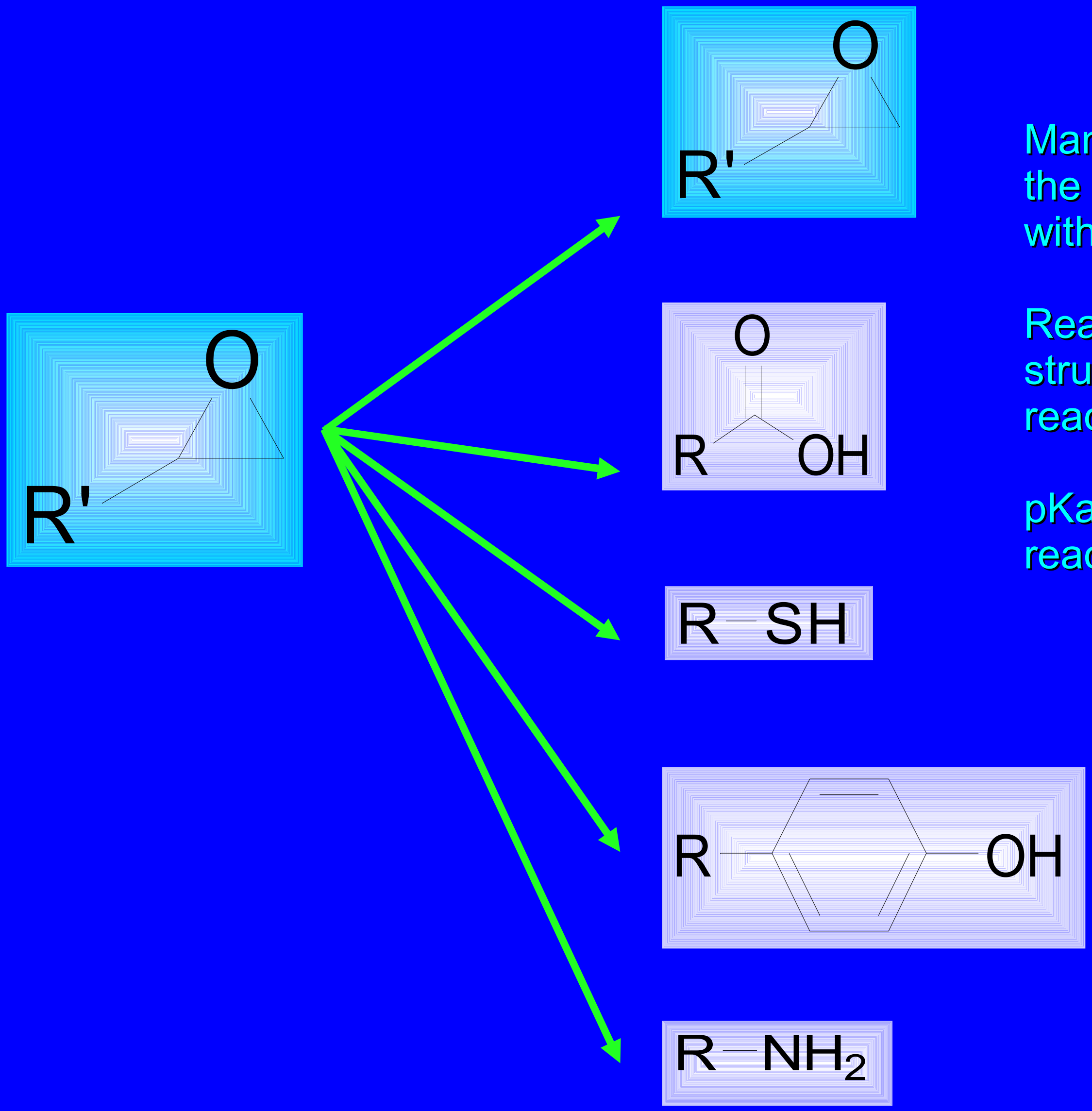
Base Catalyzed Epoxy Reactions



Many bases can catalyze the reaction of an epoxy group with a functional group

Reaction rate depends on the structure of the epoxy, the reactant and the amine catalyst.

pKa value does not determine reaction rate.

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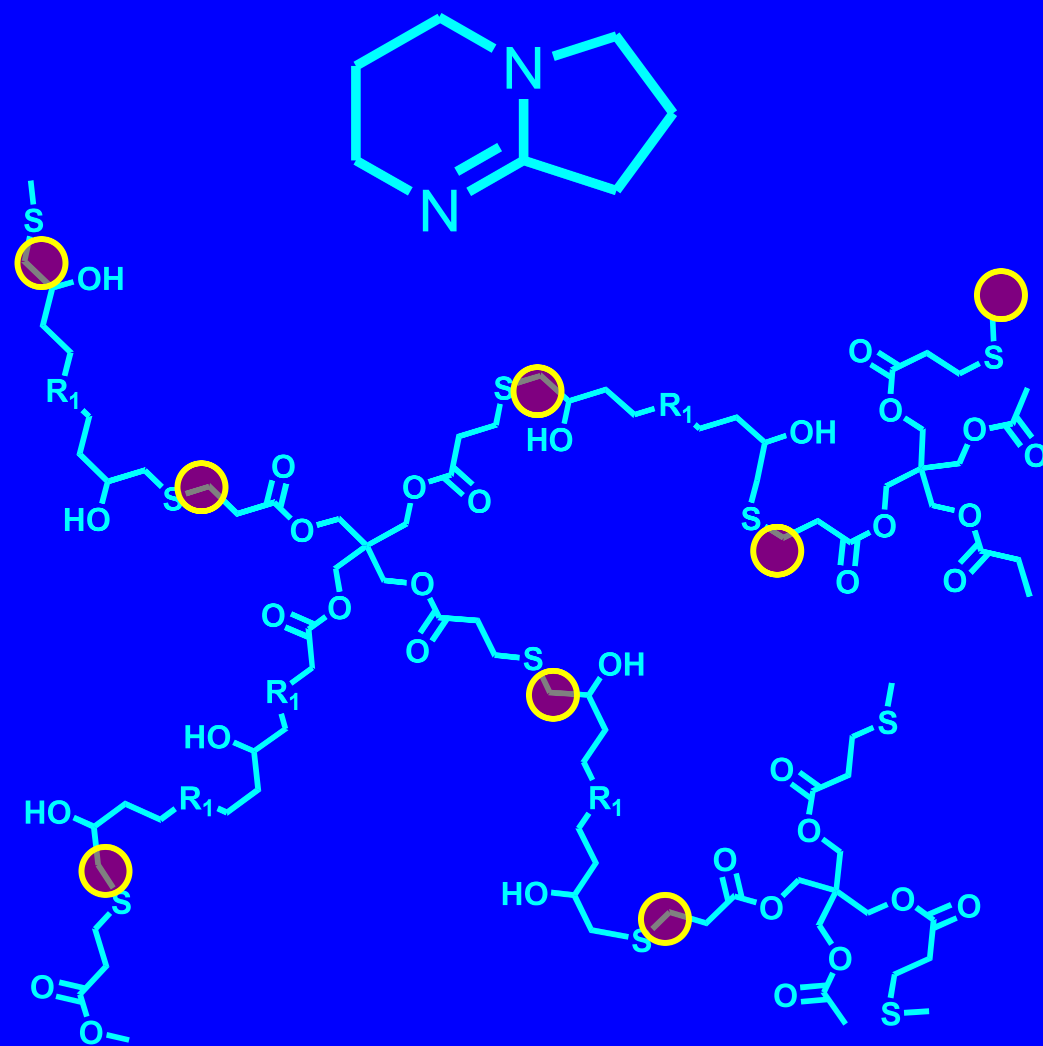
Thiol/Epoxy System: PL-DBN catalysis



Room Temperature Curing

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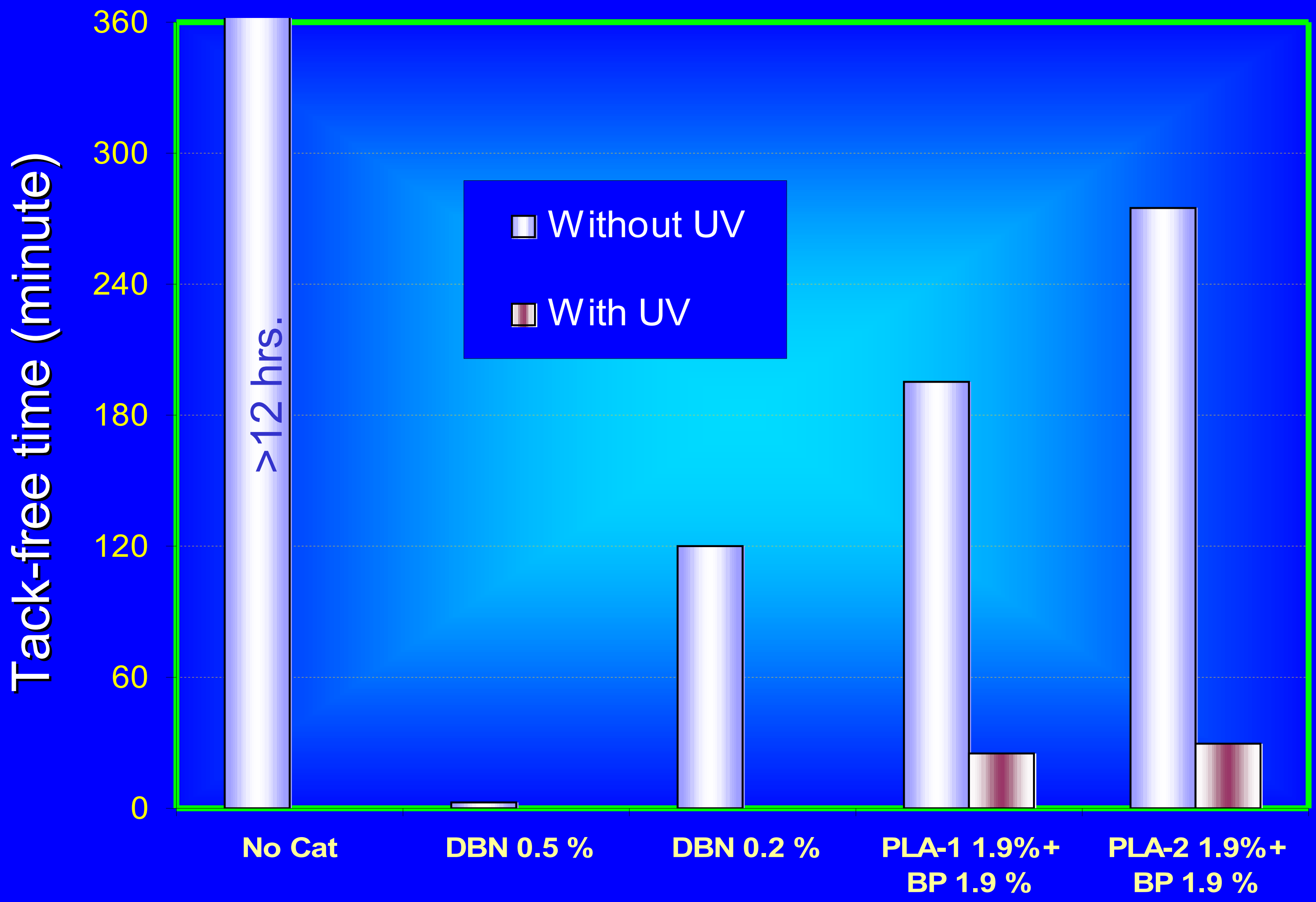
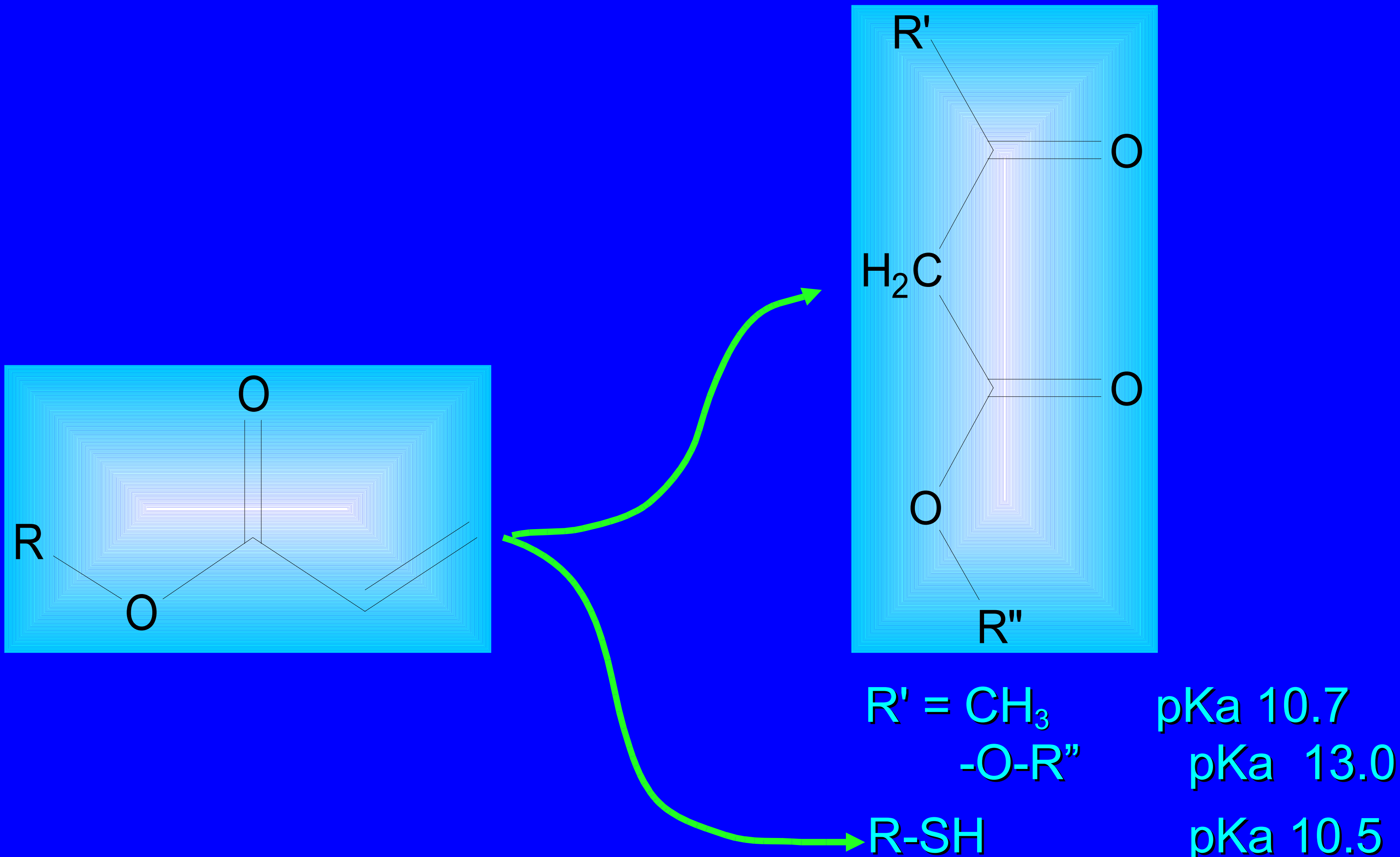
Thiol/Epoxy System: Reactivity

Coating applied onto glass plate at 70 µm thickness

Byk recorder (12hrs. cycle) after UV exposure (5 m/min. under 2 Hg lamps 100W/cm)



Base Catalyzed Michael Addition Reactions



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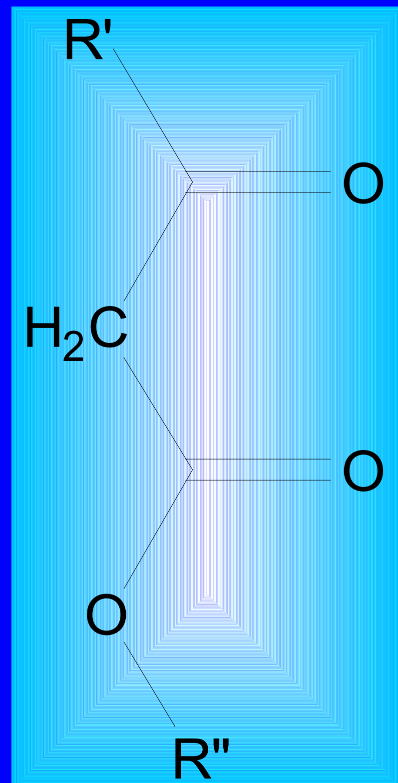
Base Catalyzed Isocyanate Reactions

R-NCO



R' = CH_3 pKa 10.7

-O-R” pKa 13.0

R-OH	pKa	17.0
R-SH	pKa	10.7
H-OH	pKa	15.7

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Delayed Catalysis in Coatings

Essential for
- Potlife
- Application Characteristics
- Film Appearance

Photo Catalysis New Technology Platforms
Wide Variety of Crosslinking Mechanisms
accessible for radiation curing

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Acknowledgment

Slide 13
Trends in Controlling Reactivity in Epoxy Formulation
SPI publications Peter Lucas ERDI Conference Publications 1986 Air Products
Slide 19 Private communication with J. Florio, Ram Subrayan King Industries
Slide 20
Air Activated Organotin Catalysts for Silicone Curing and Polyurethane Preparation
B. Jousseaume, N. Noiret, M. Pereyre and A. Saux, Organometallics, 13, 1034-1038 (1994).
B. Jousseaume, N. Noiret, M. Pereyre, M. Francès and M. Petraud, Organometallics, 11, 3910 (1992).