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Catalysis of Isocyanates

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SL2195

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CATALYSIS OF ISOCYANATES

**HYDROXYL-ISOCYANATE REACTION
DIFFERENT CATALYSTS DBTDL, Al, Bi, Zr
HOW TO SELECT A CATALYST
REACTION RATES WITH HYDROXYL
SELECTIVITY OF OH vs WATER
FORMULATION GUIDE LINES**

BLOCKED ISOCYANATES

POLYURETHANES IN COATINGS

-Reactive two components

Two package

Polyisocyanate + Polyol

One package

Blocked isocyanate +
Polyol

-Reactive one component

NCO prepolymer +
moisture; Oxidative

-Nonreactive one component

Solution

Thermoplastic PU

Aqueous solution

High and low MW PU

Thermoplastic and XL

ISOCYANATE REACTIONS

R-NCO

R-OH

HOH

R-COOH

R-NHCONH-R

R-NHCOO-R

R-CH₂ act.

R-NH₂

EPOXY

TRIMER

DIMER

CARBODIIMIDE

CATALYSIS PROBLEMS

HIGH SOLIDS COATINGS

**POTLIFE/REACTIVITY
MOISTURE REACTION
SOLUBILITY
NETWORK STABILITY**

WATERBORNE

**WATER REACTION
POTLIFE
GASSING
STABILITY
GLOSS**

Objectives of this Study

ENVIRONMENTALLY ACCEPTABLE CATALYSTS

REACTION RATE OF CATALYSTS WITH OH

SELECTIVE CATALYSTS FOR OH

IMPROVED POTLIFE/REACTIVITY

REDUCED WATER REACTION

CATALYSTS USED

DIBUTYLTIN DILAURATE / DIACETATE

DIBUTYLTIN OXIDE

MERCURY COMPOUNDS

LEAD COMPOUNDS

AMINES

ZINC SALTS

MANGANESE SALTS

CATALYST PROPERTIES

POTLIFE / REACTIVITY

SELECTIVITY

DELAYED ACTION

LOW TEMPERATURE

HIGH TEMPERATURE

WATER

HIGH RATE (RIM)

EXTERIOR DURABILITY

RESISTANCE PROPERTIES

ENVIRONMENT - TOXICITY

Isocyanate-Hydroxyl Reactions



ADDITIONAL REACTIONS



SCREENING OF CATALYSTS

APPLICATION TESTS FORMULATION

POTLIFE (2X VISC.)

GEL TIME

TACK FREE

DRY-THROUGH

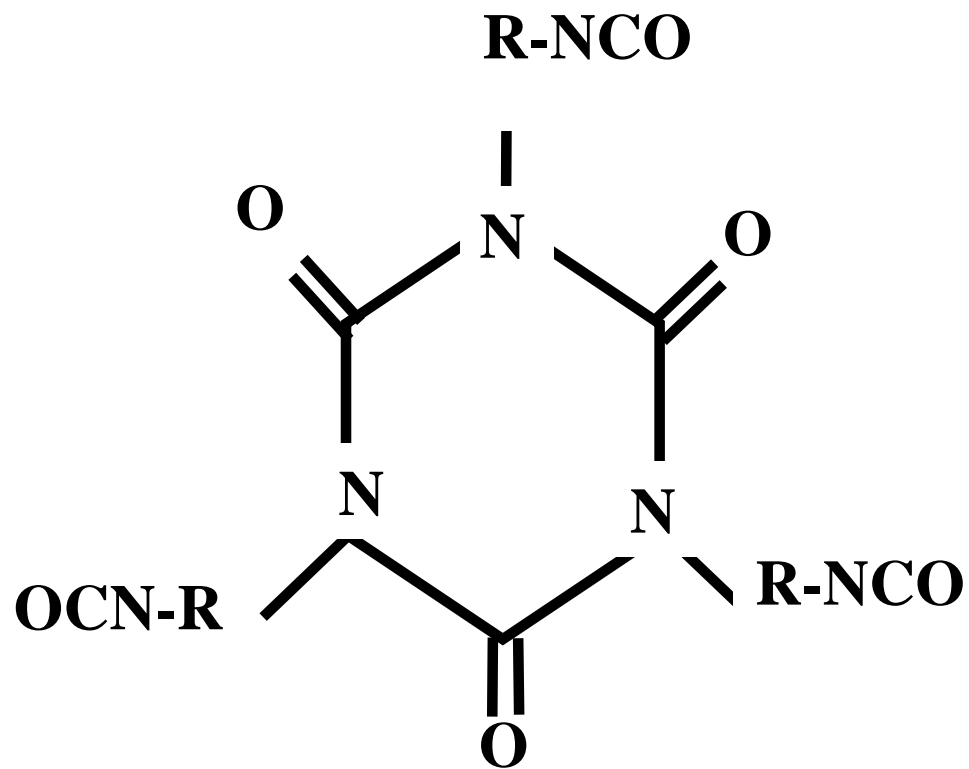
MODEL SYSTEMS (ANALYTICAL)

DISAPPEARANCE OF NCO

FORMATION OF URETHANE / UREA

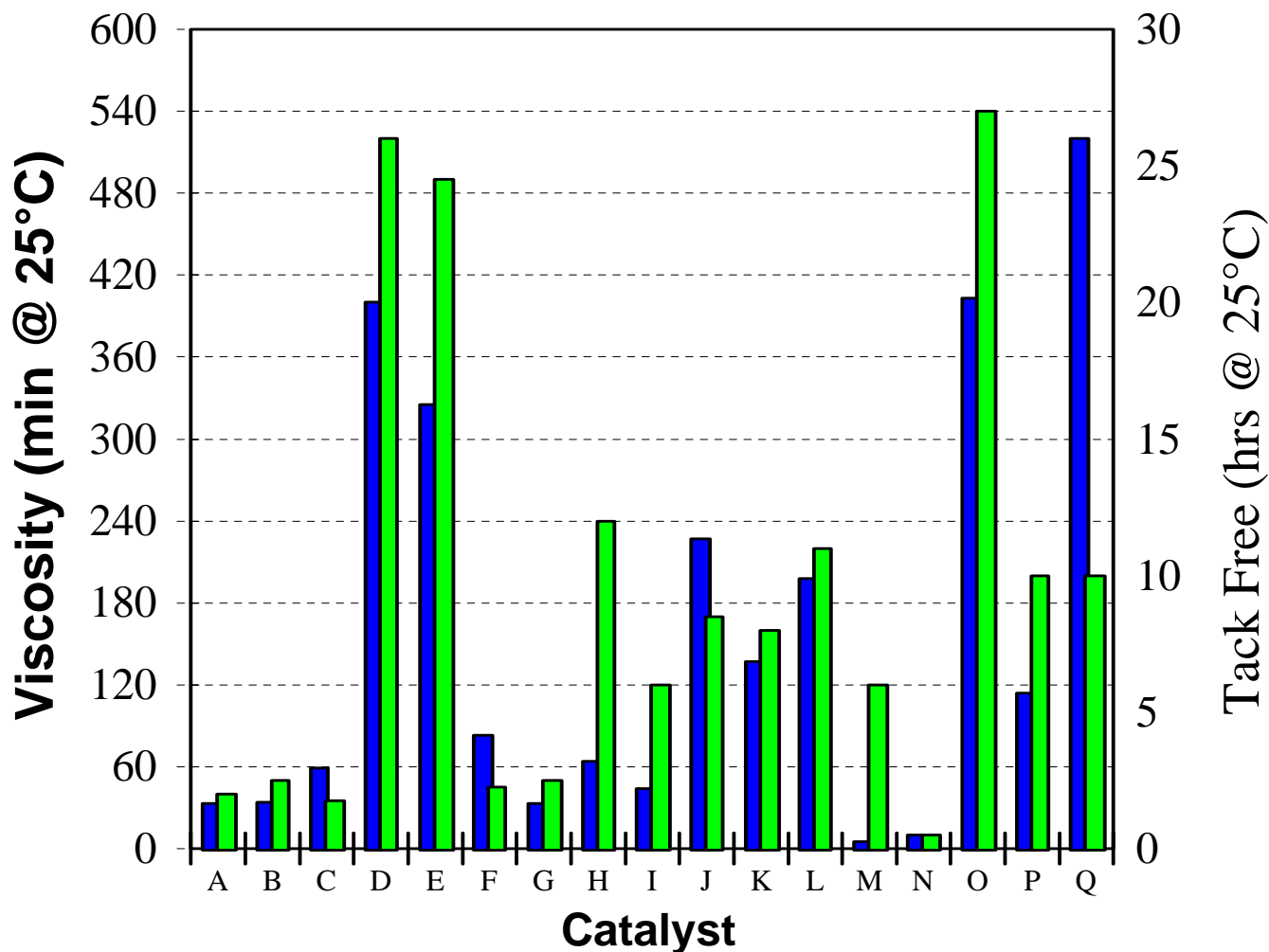
MW

HDI-TRIMER



Catalyst Study (HDI TRIMER)

Metal (0.0065% on Solids)



- A: DBTDL
- B: DBTDA
- C: Mn Naph/PD
- D: Mn Oct
- E: Sn Oct/PD
- F: Vn acac/PD
- G: Vn acac
- H: Bi Oct
- I: Bi Naph
- J: Zn acac/PD
- K: Zn Oct
- L: Co Oct
- M: Zr acac
- N: Zr acac/PD
- O: Zr Oct
- P: Al acac
- Q: Al chelate/PD



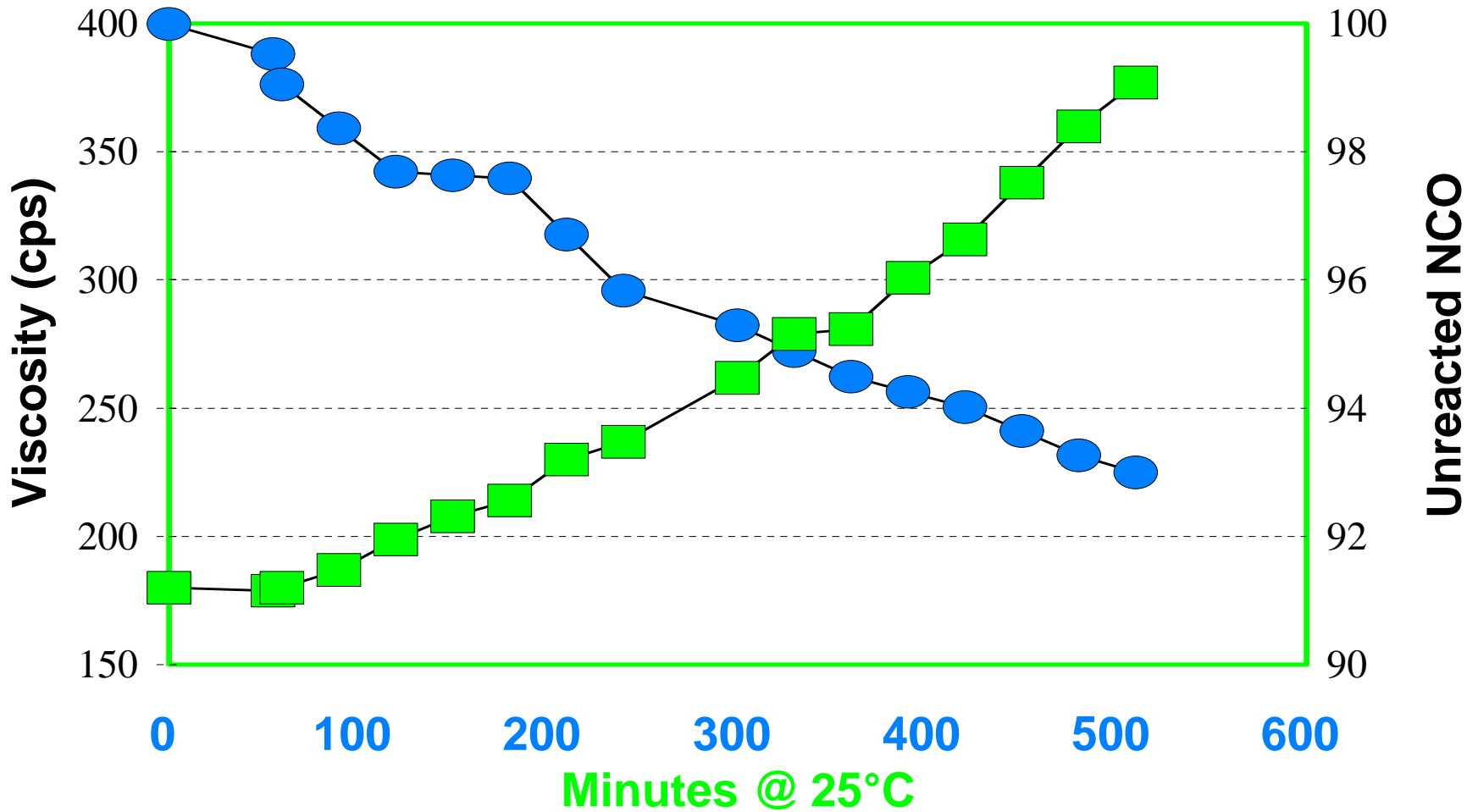
VISC. 2X



Tack Free (hrs)

PE/HDI-TRIMER

No Catalyst



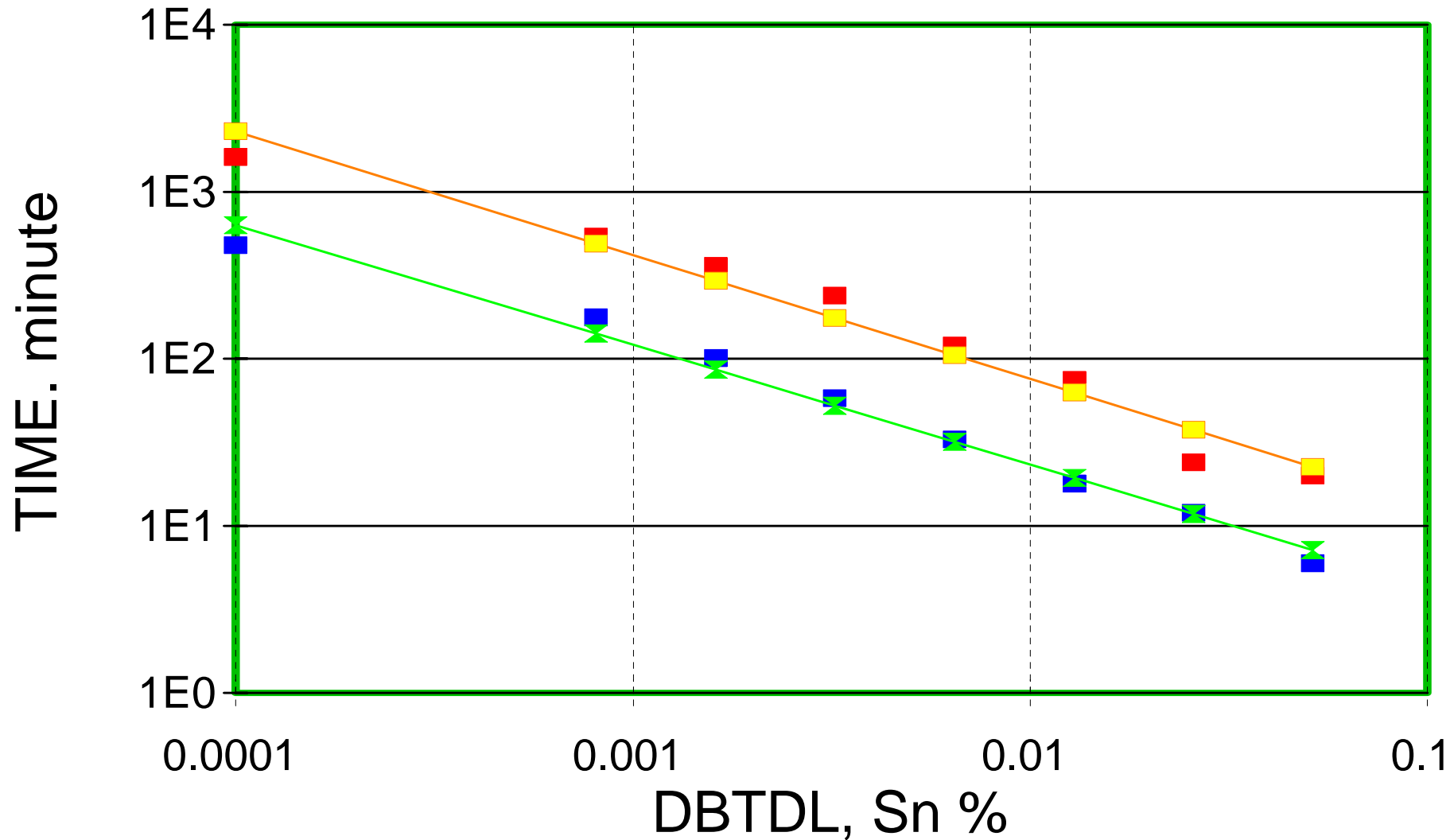
● % NCO

■ VISCOSITY

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PE/HDI-TRIMER

CATALYST REACTION RATE



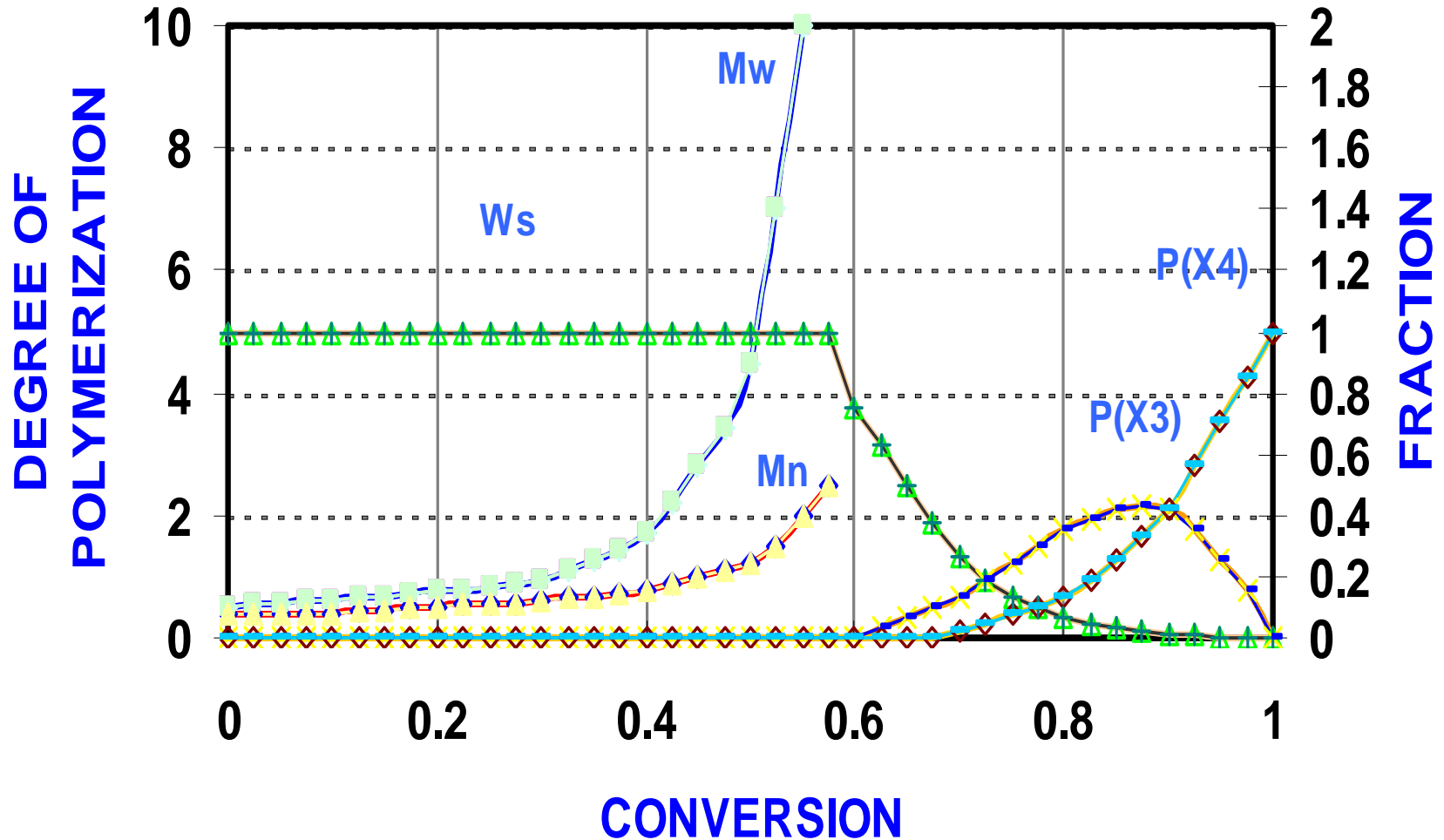
—x— Potlife

—□— TACK FREE

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NETWORK FORMATION

A4 + B2



CATALYSTS

Zr ChA.....XC-4205.....ZrAcAc

Zr ChB.....XC-6212.....Zr Dionate

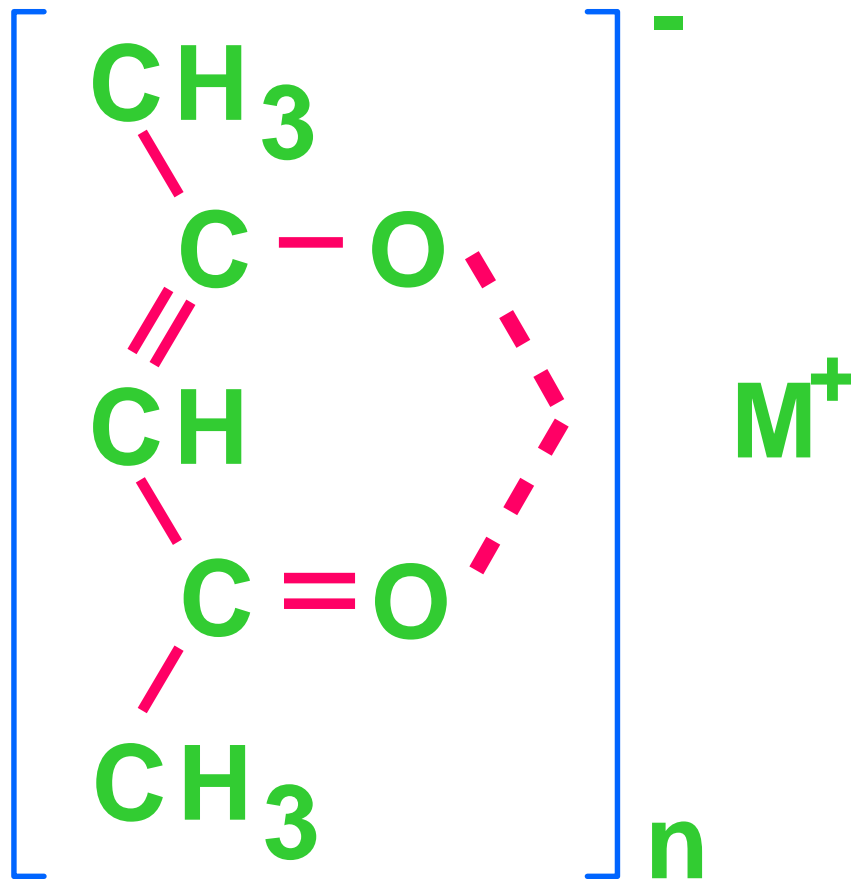
Al Ch1.....XC-5218.....Al Dionate

Bi carb.....K-348.....Bi Oct.

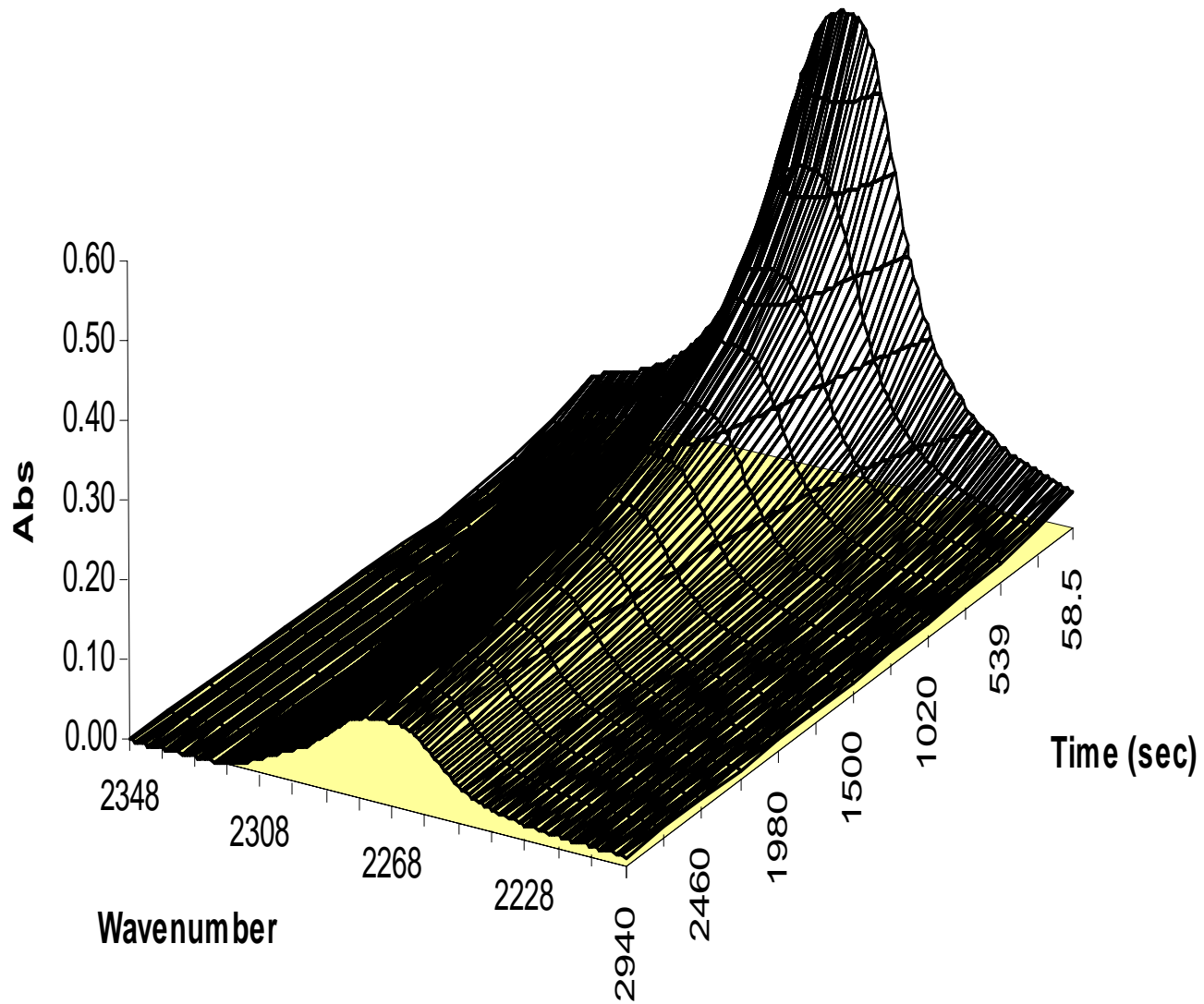
DBTDL.....Dibutyltin C₁₂

DBTDA.....Dibutyltin Ac

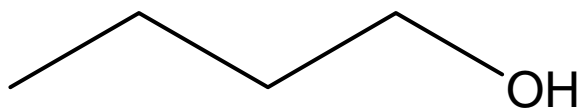
Metal Chelate with 2,4-PD



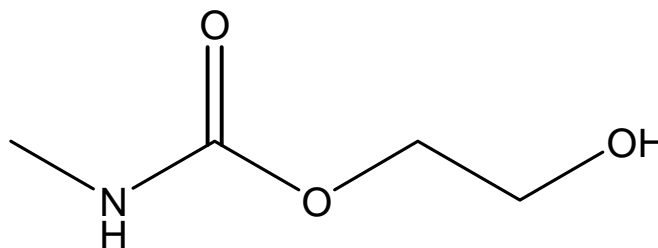
Isocyanate Peak Decay



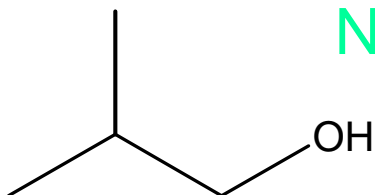
REACTIVITY WITH DIFFERENT HYDROXYL GROUPS



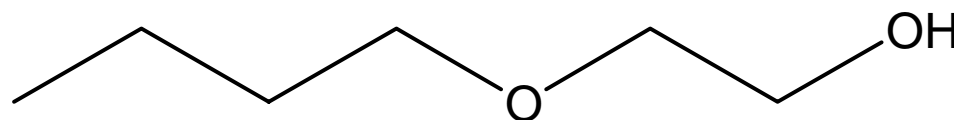
N-BUTANOL



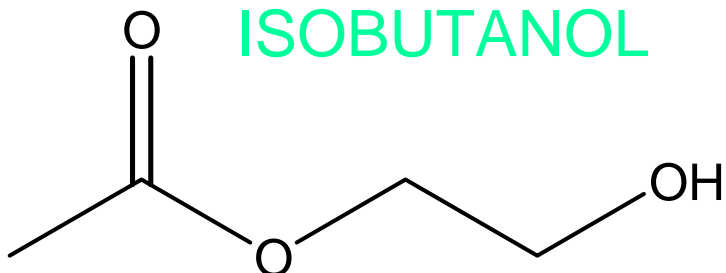
HEC



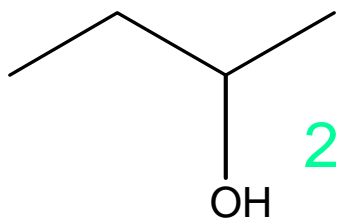
ISOBUTANOL



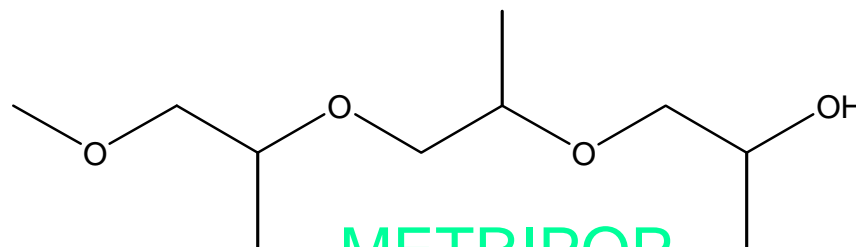
BUCCELL



HEE

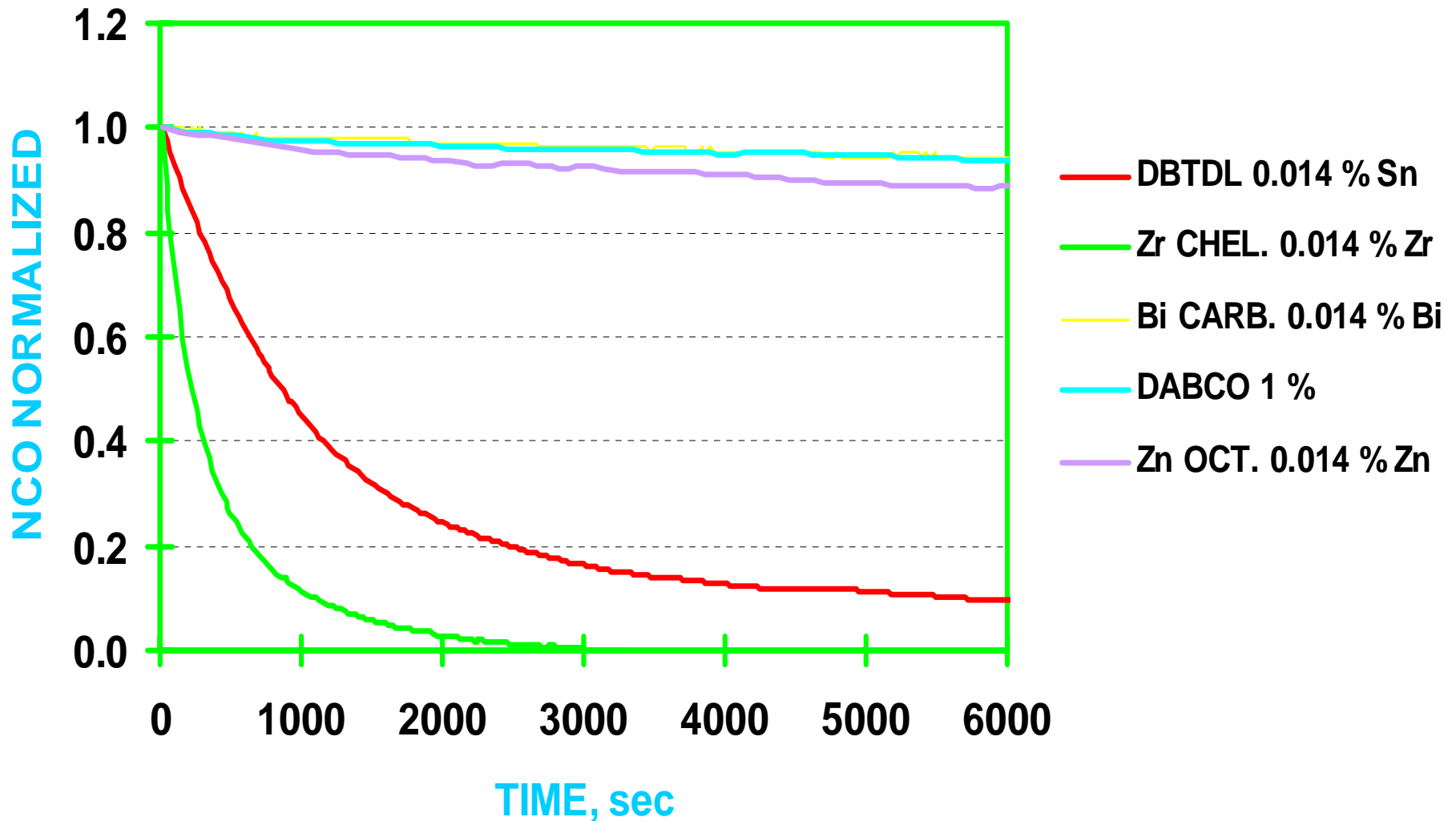


2-BUTANOL

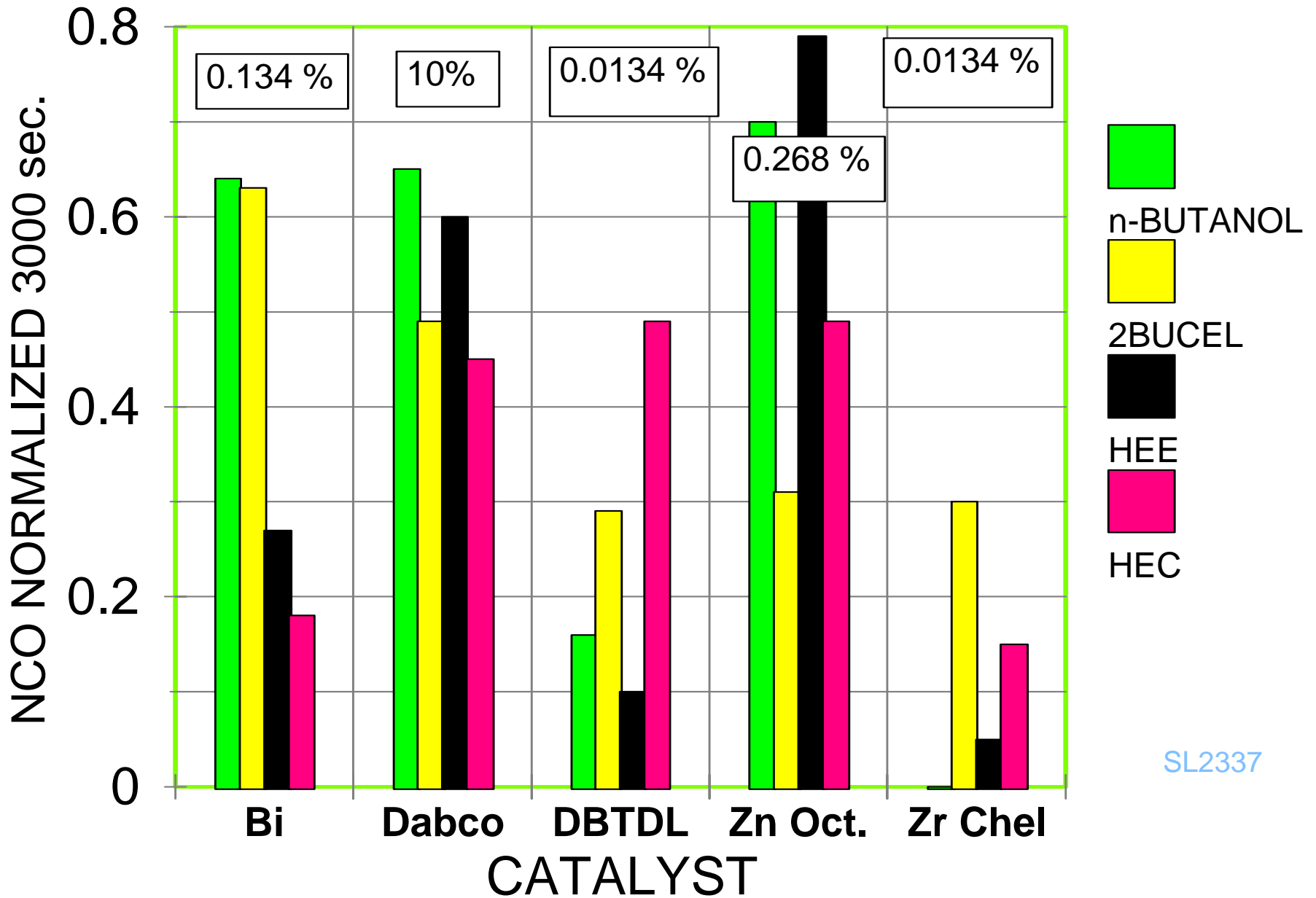


METRIPOP

HDI TRIMER / HYDROXYL
DBTDL 0.0140% Sn
n-BUTANOL

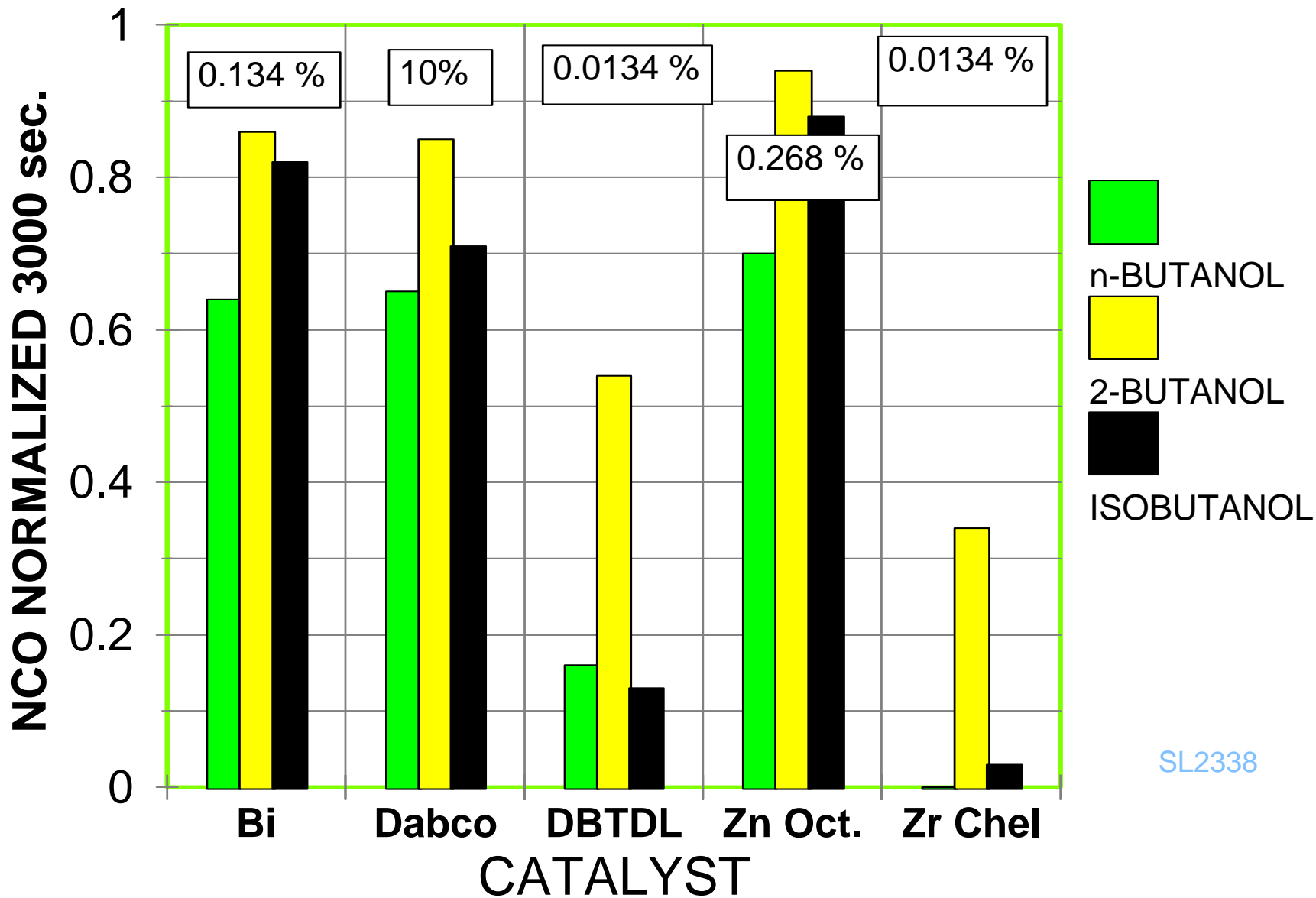


HDI-TRIMER/HYROXYL PRIMARY HYDROXYL



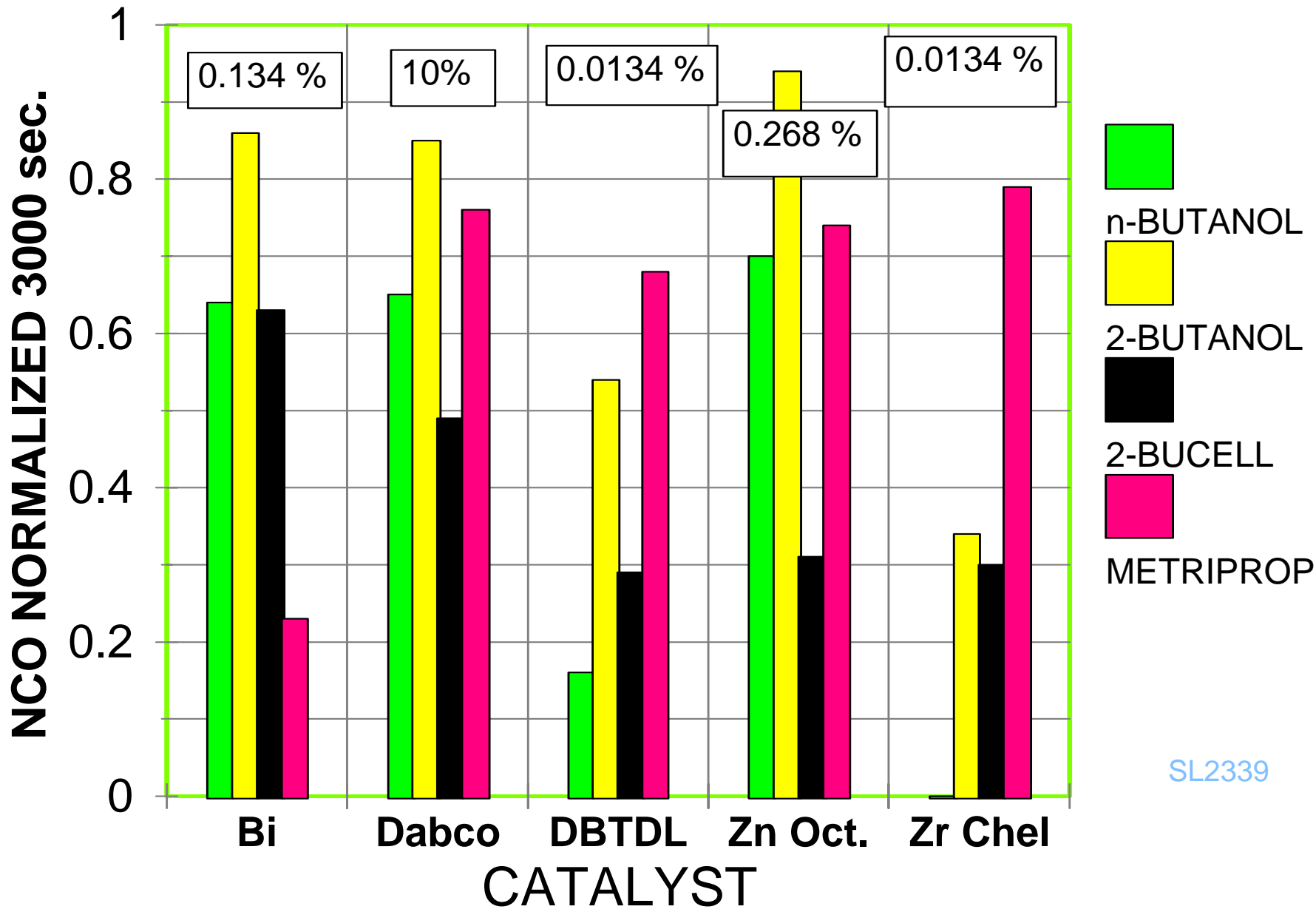
HDI-TRIMER/HYROXYL

pri, sec BUTANOL

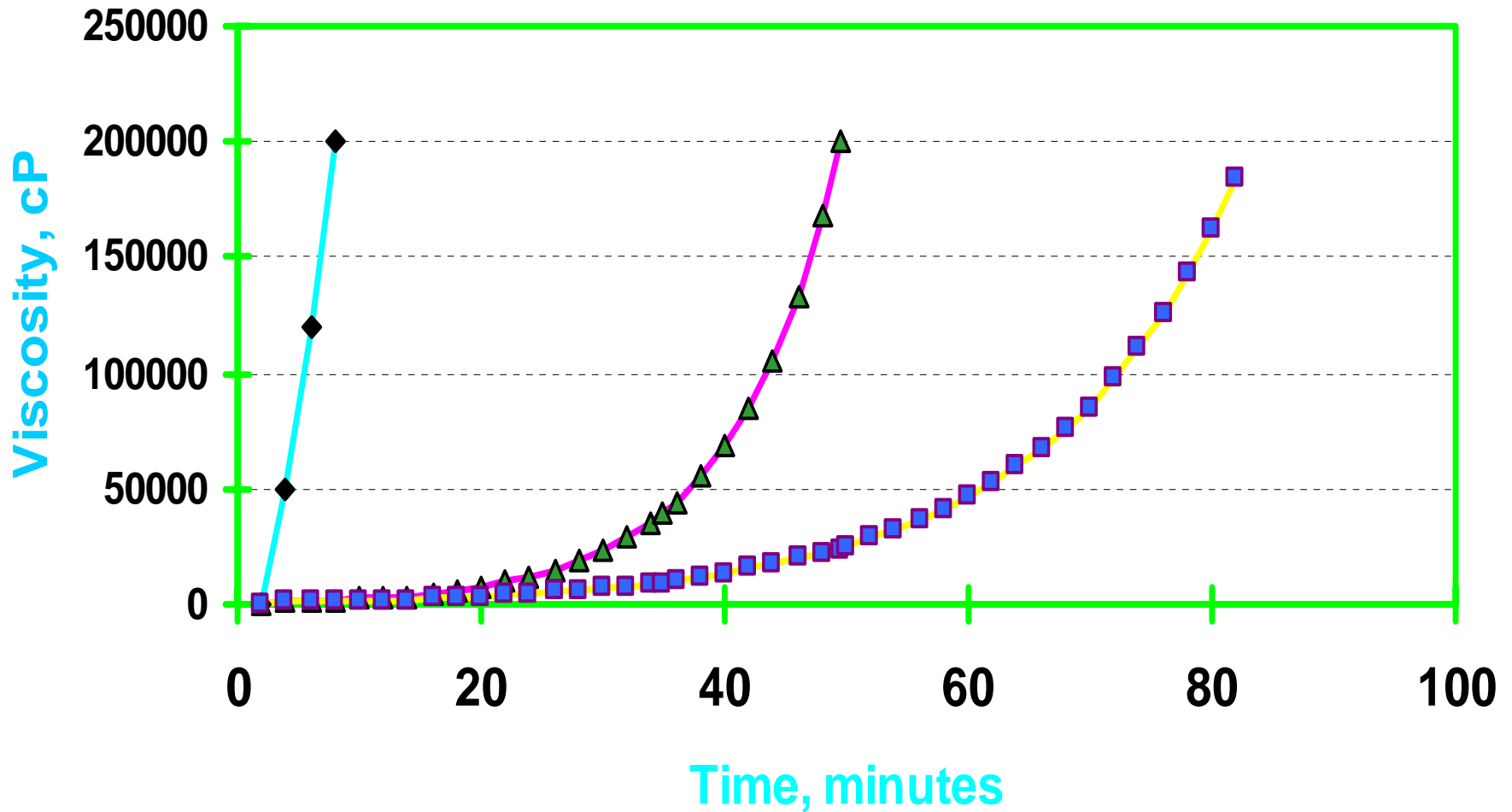


HDI-TRIMER/HYROXYL

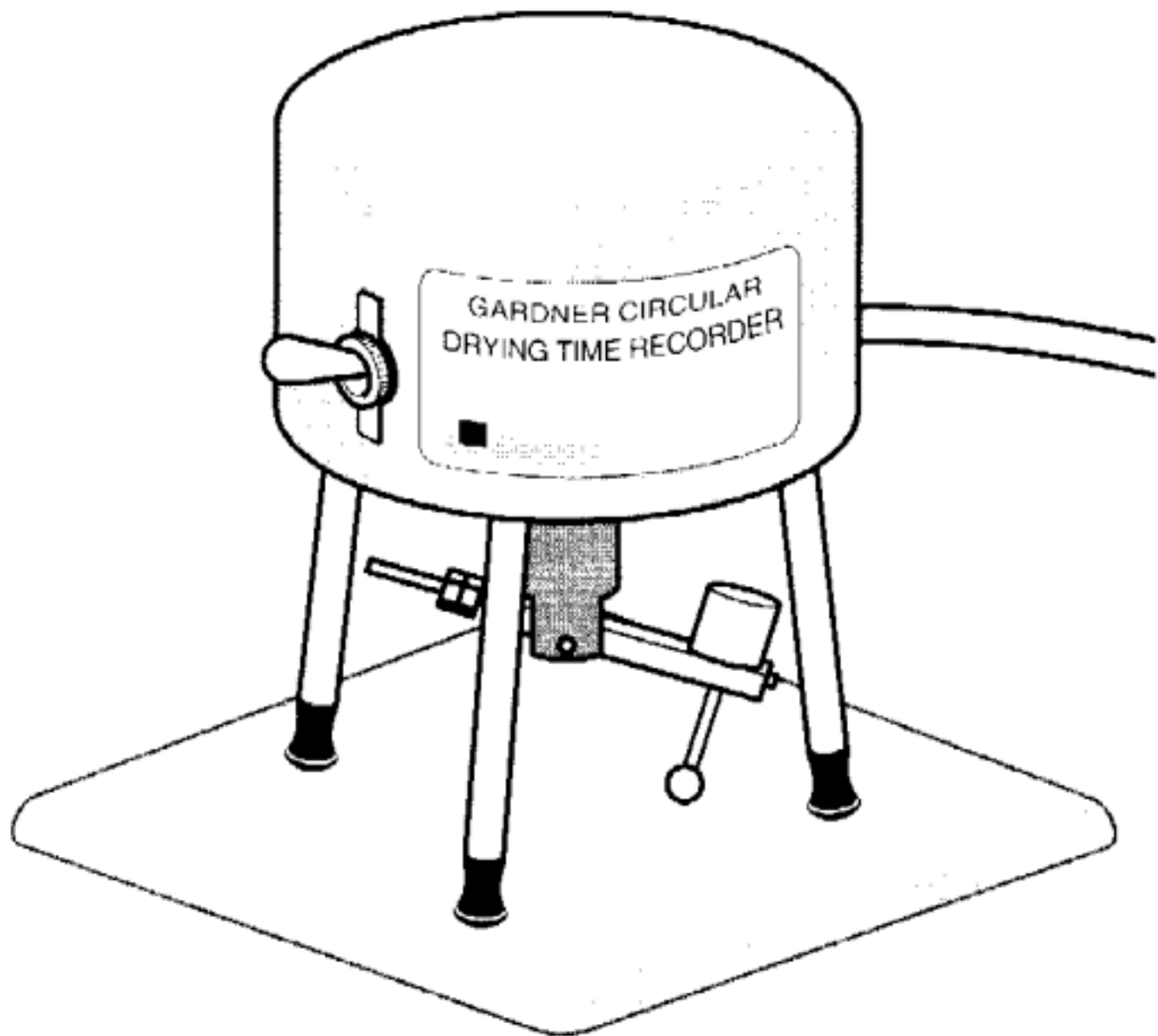
pri, sec BUTANOL, ETHER



Polyether MDI Elastomer Bi Oct. 1/5 mol WATER



◆ Bi Oct. Initial ▲ Bi Oct. 2 days ■ Bi Oct. 7 days



CATALYSTS

Zr ChA.....XC-4205.....ZrAcAc

Zr ChB.....XC-6212.....Zr Dionate

XC-9213.....Zr Dionate

Al Ch1.....XC-5218.....Al Dionate

Bi carb.....K-348.....Bi Oct.

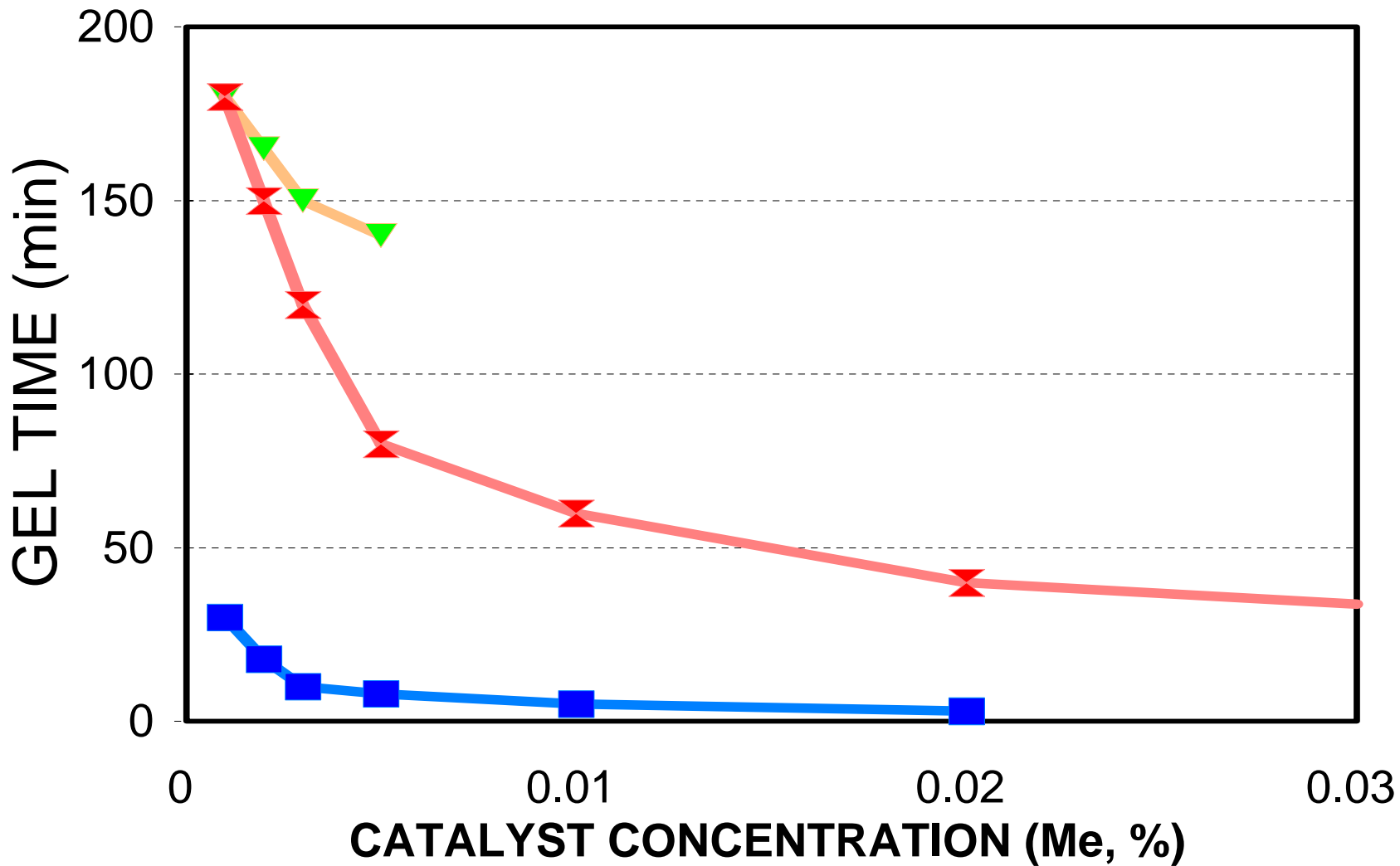
Bi carb.....XC-8203.....Bi Carb.

DBTDL.....Dibutyltin C₁₂

DBTDA.....Dibutyltin Ac

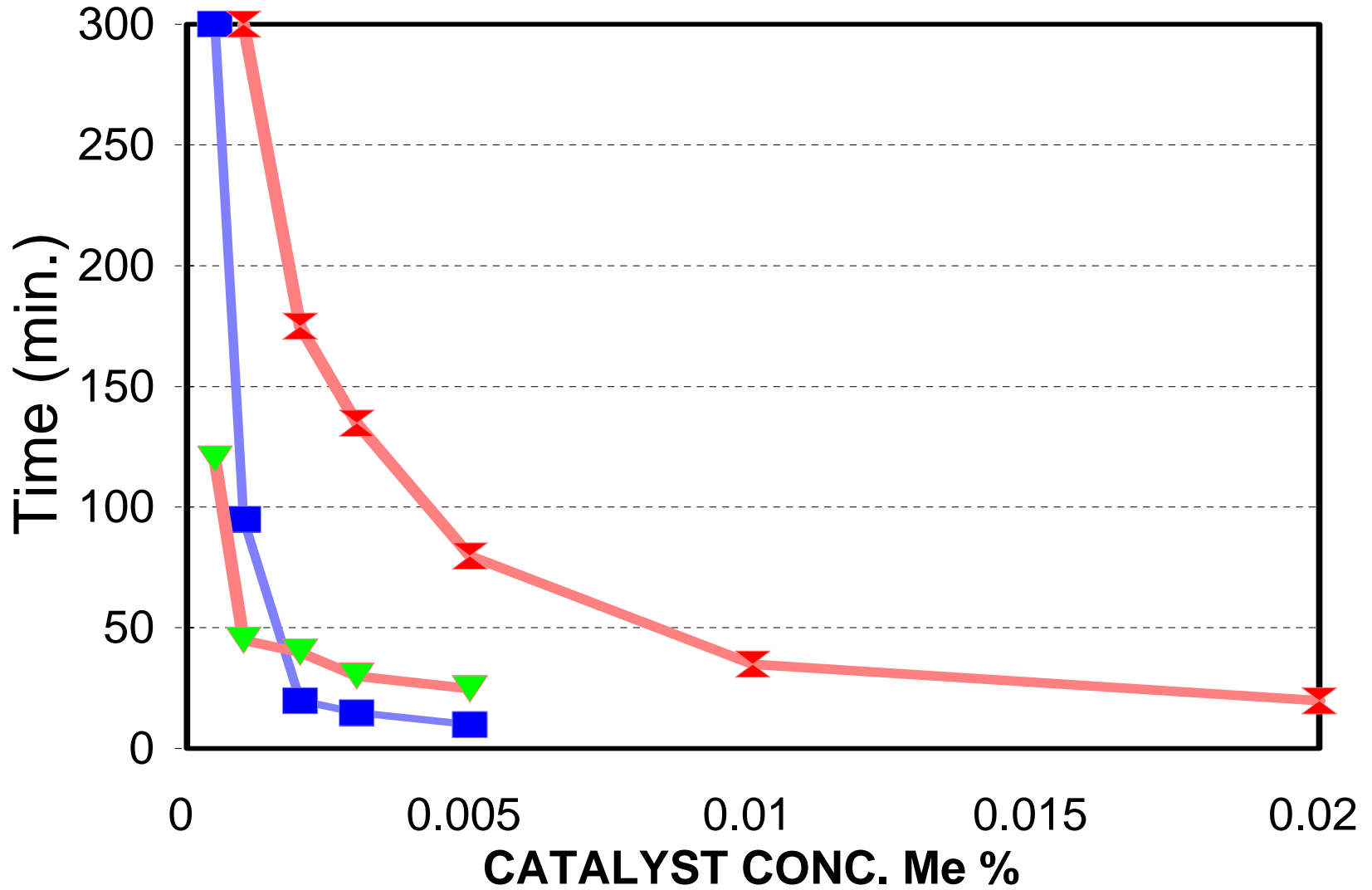
GEL TIME

ACRYLIC/HDI-TIMER



■ Zr B ▼ Zr A × DBTDL

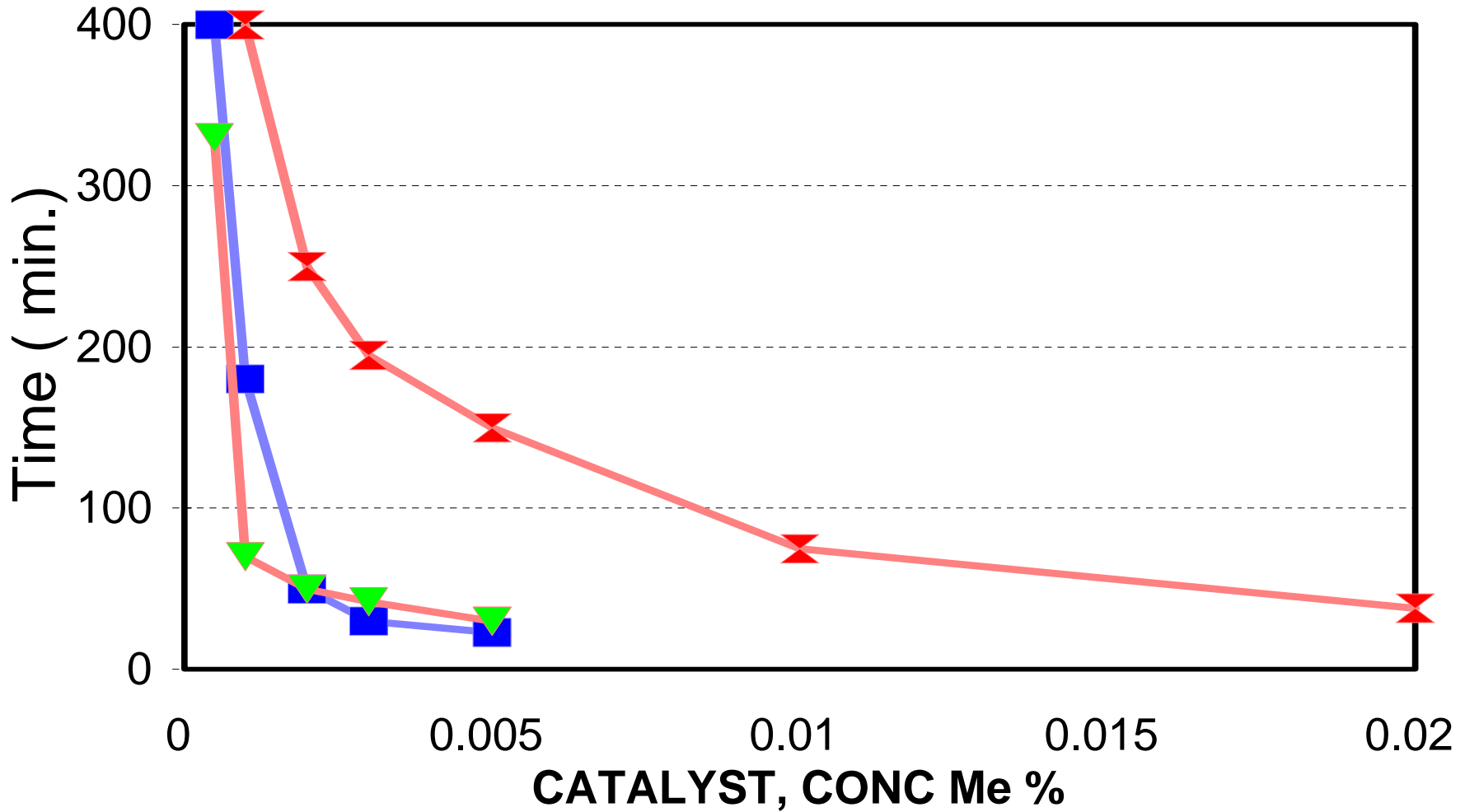
Tack Free time Acrylic HDI-Trimer



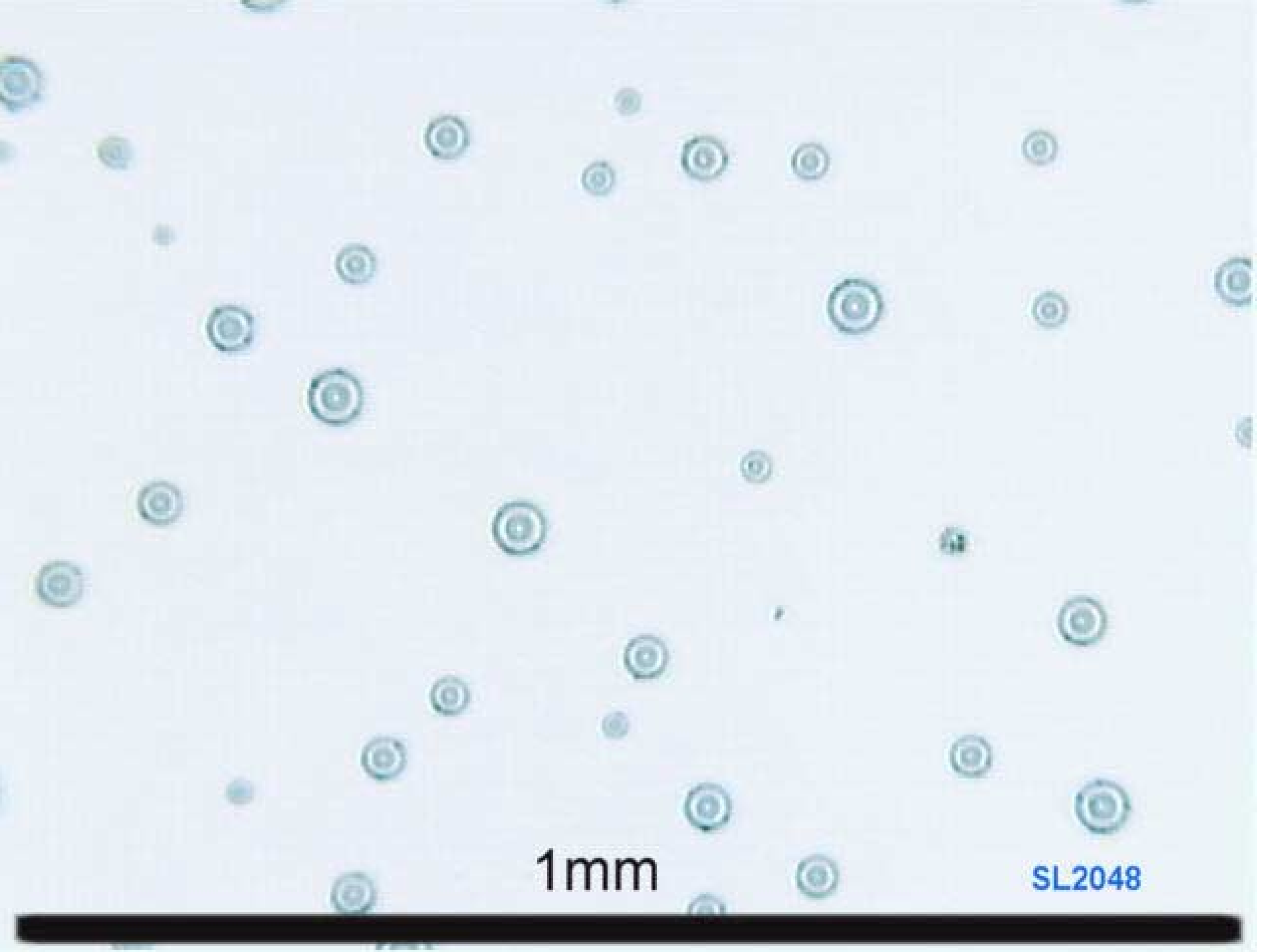
■ Zr B ▼ Zr A × DBTDL

DRY THROUGH TIME

ACRYLIC/HDI-TRIMER, 30 μ , RT, 66 % RH



■ Zr B ▼ Zr A × DBTDL



1mm

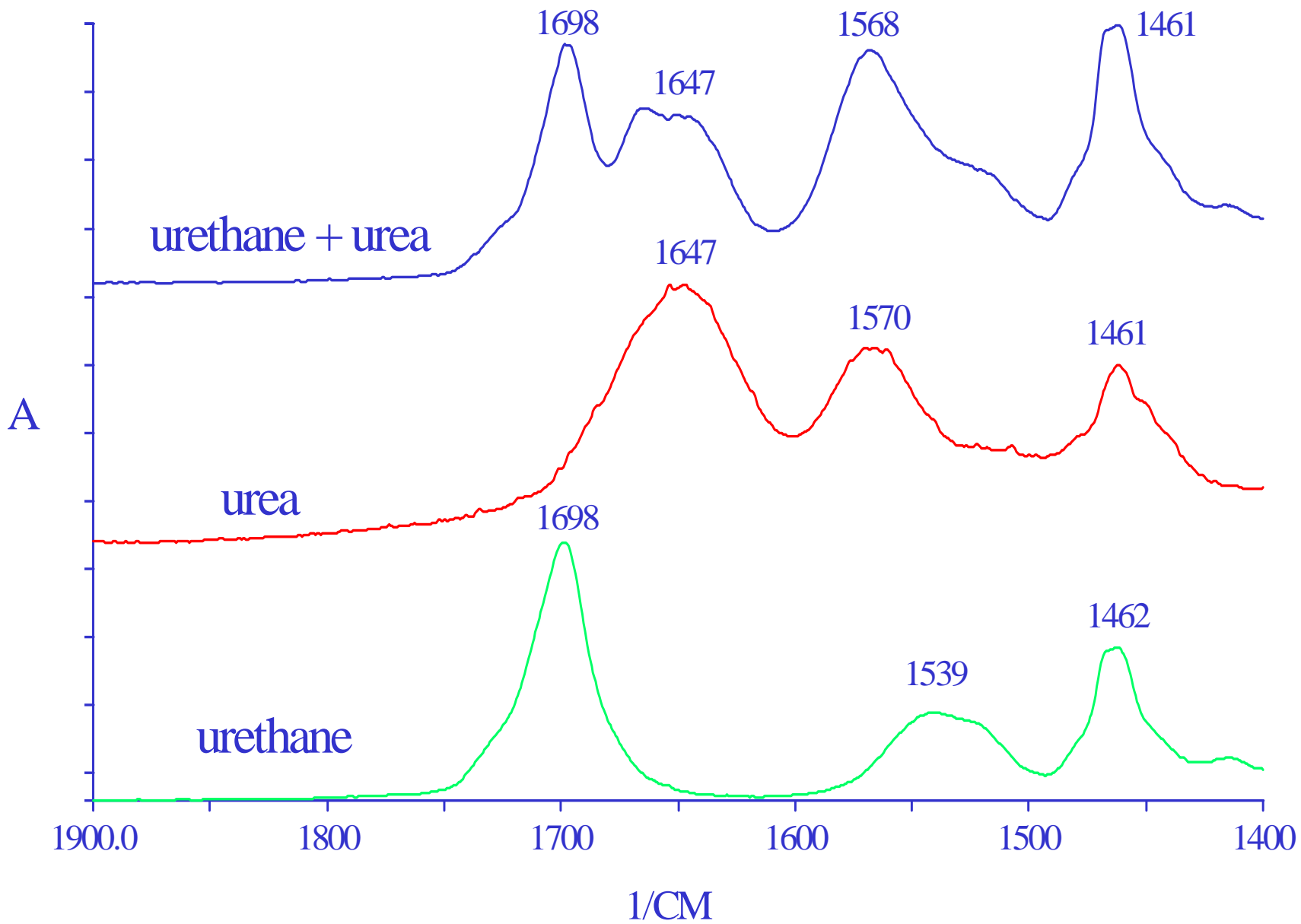
SL2048

**HDT-LV ISOCYANATE
WATER (2%) 0.0045 % Me**



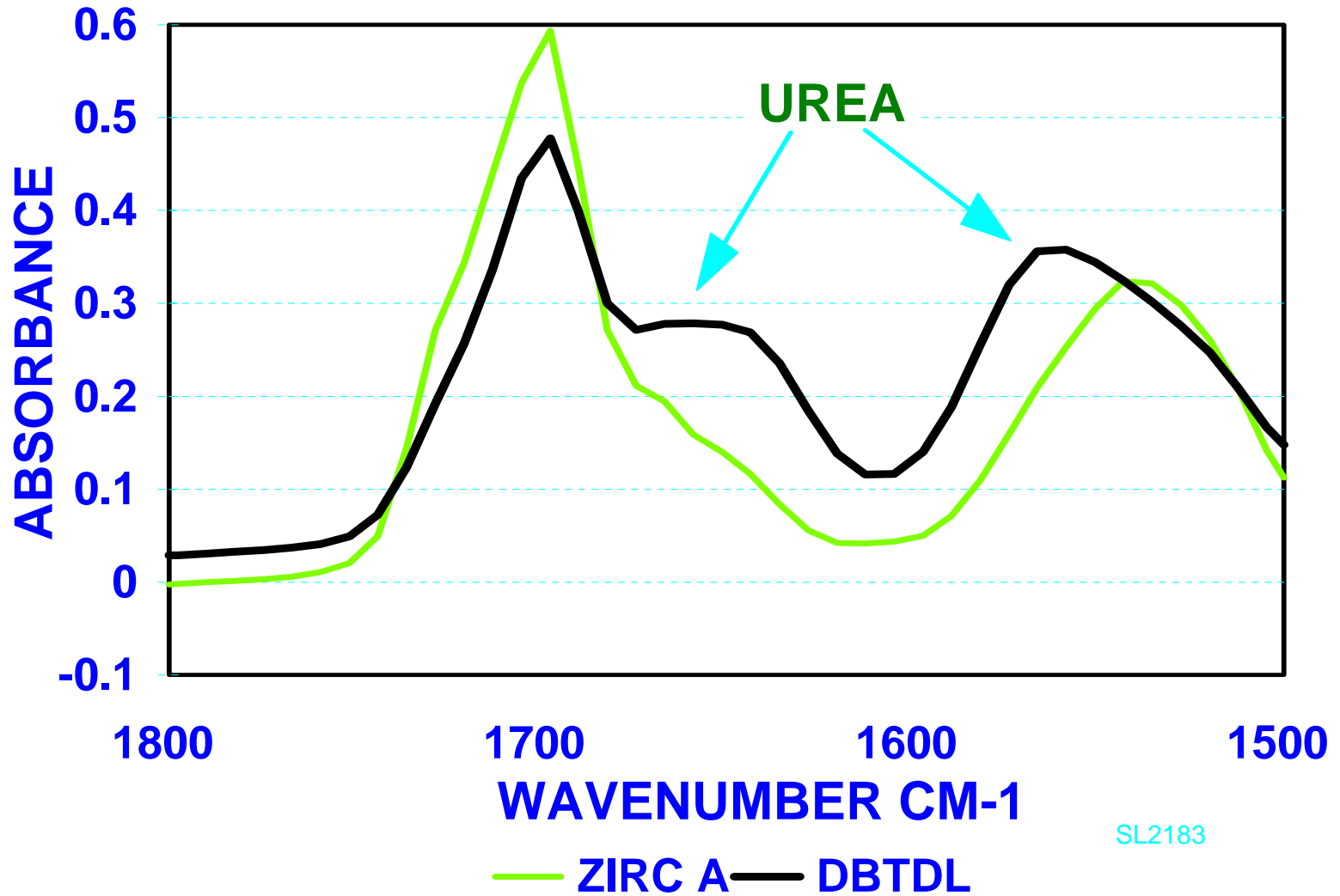
K-KAT XC-4205

DBTDL

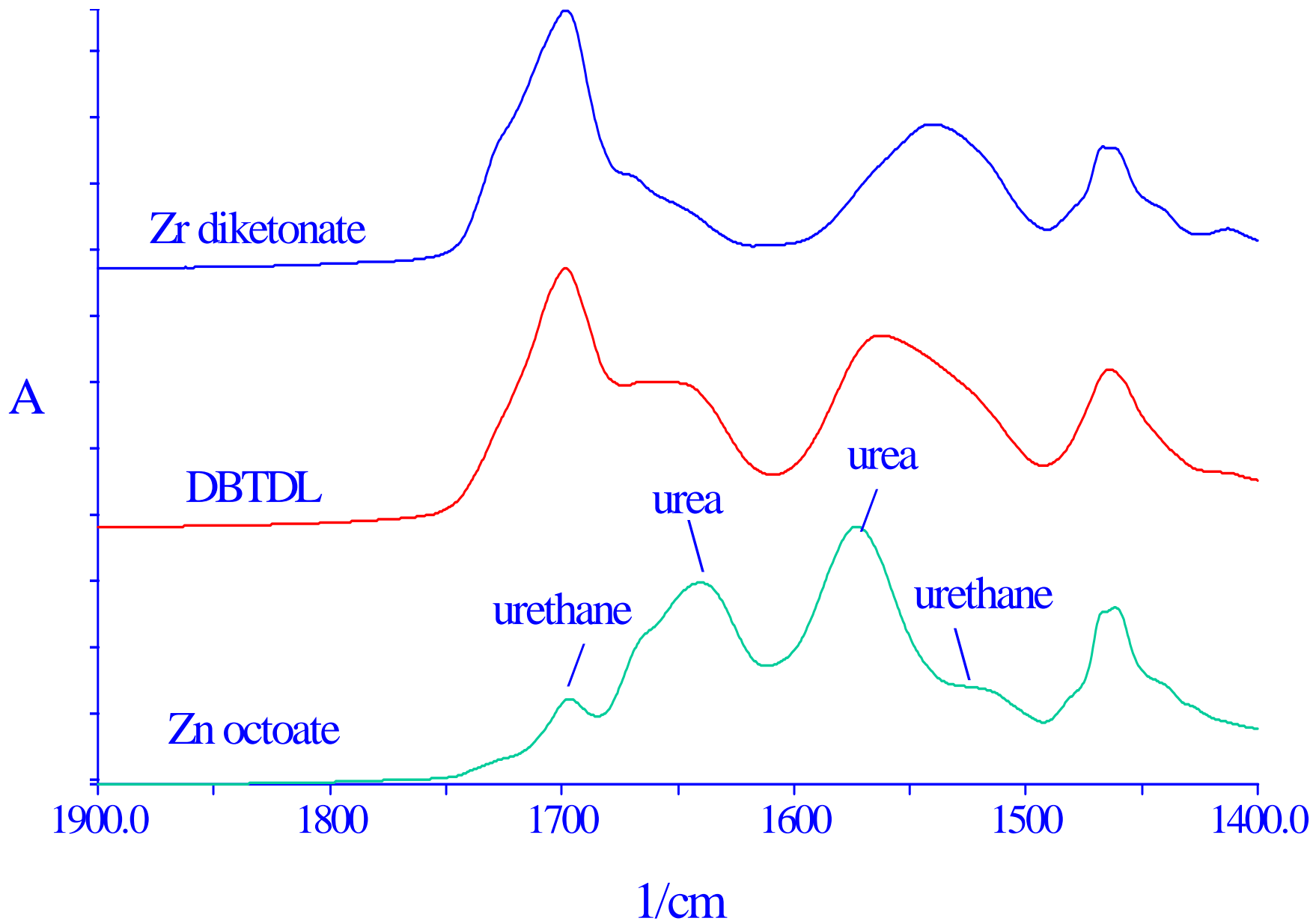


SELECTIVITY OF CATALYSIS

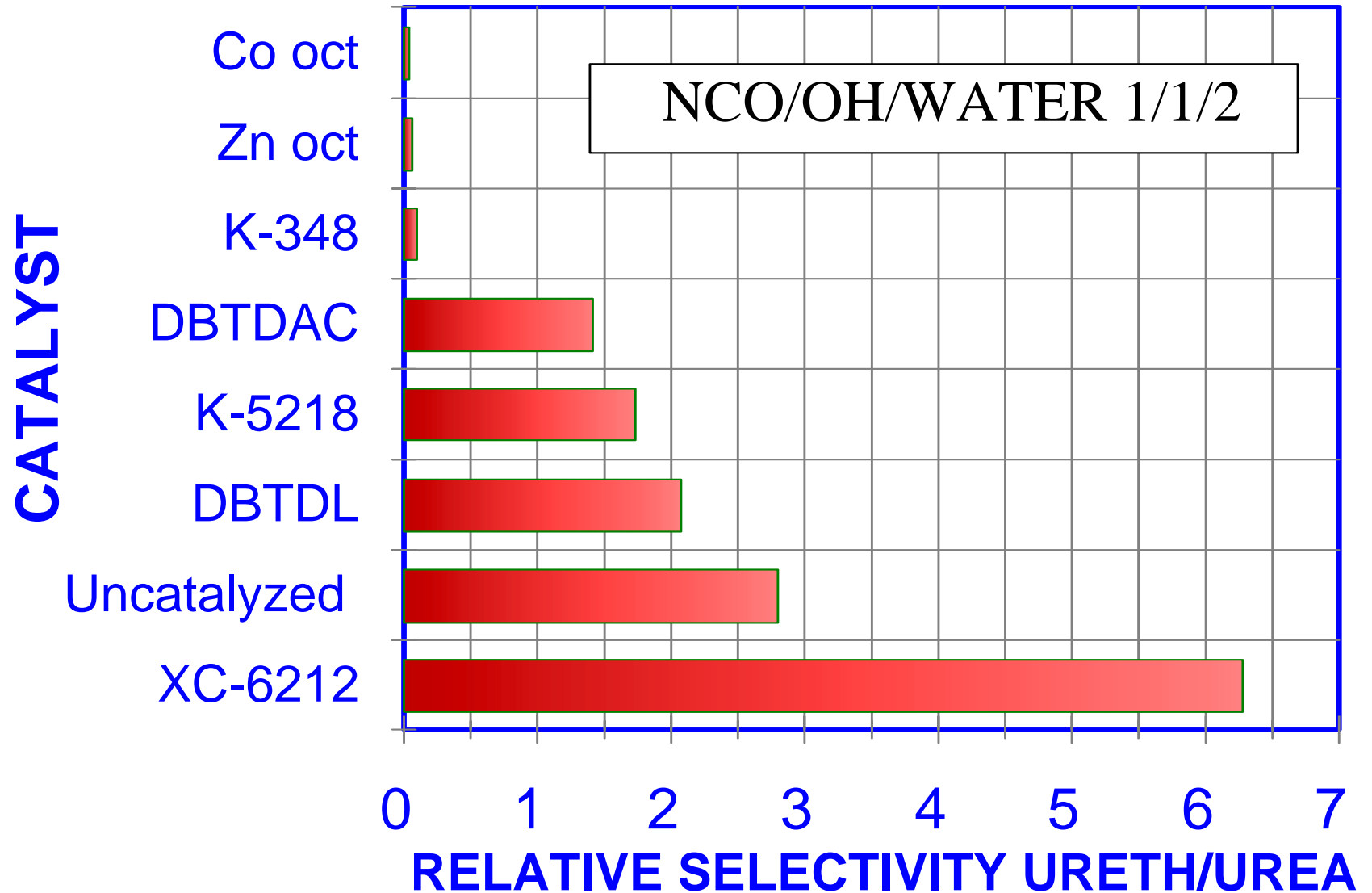
DBTDL & Zr CHELATE



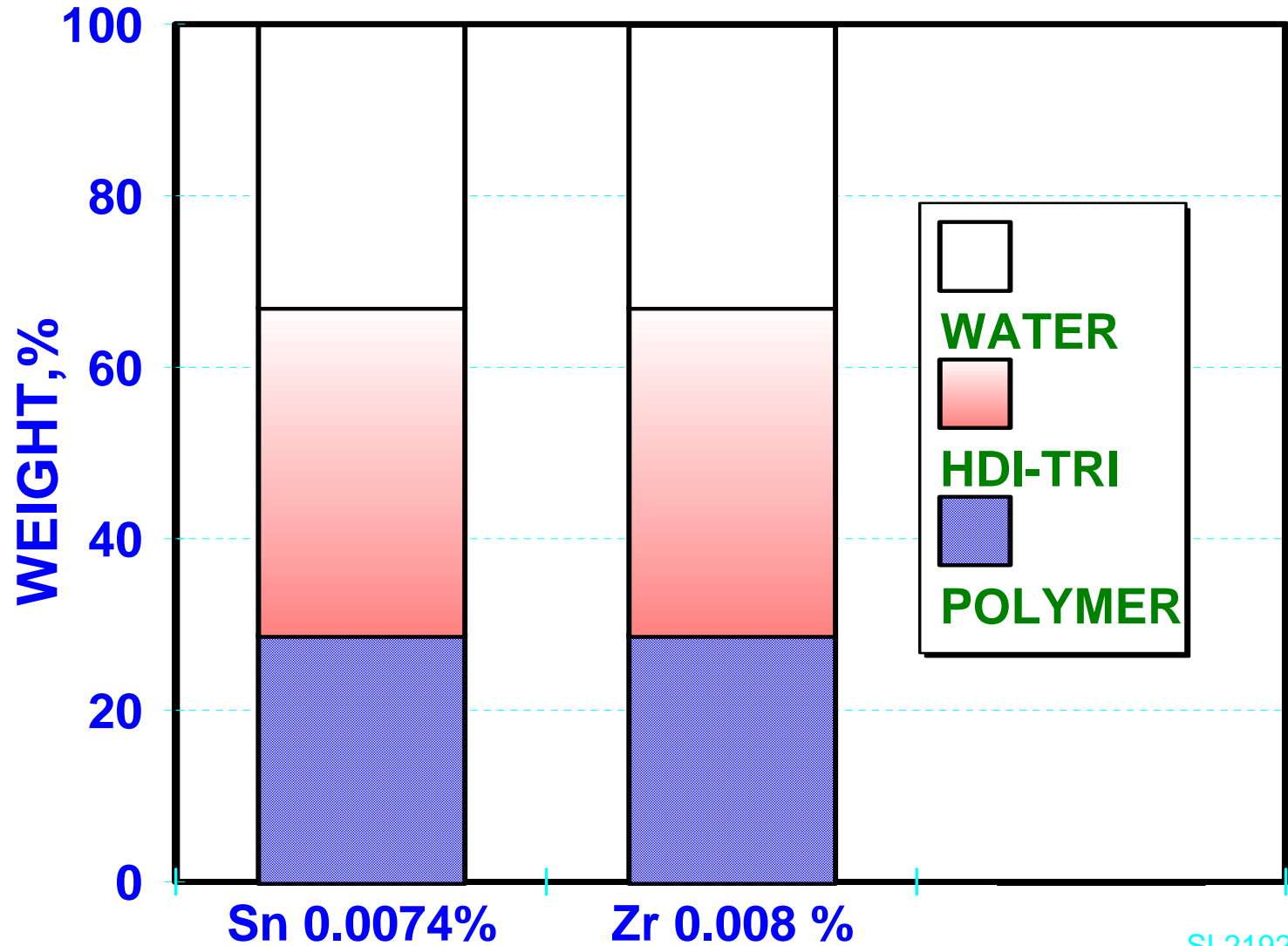
SL2183



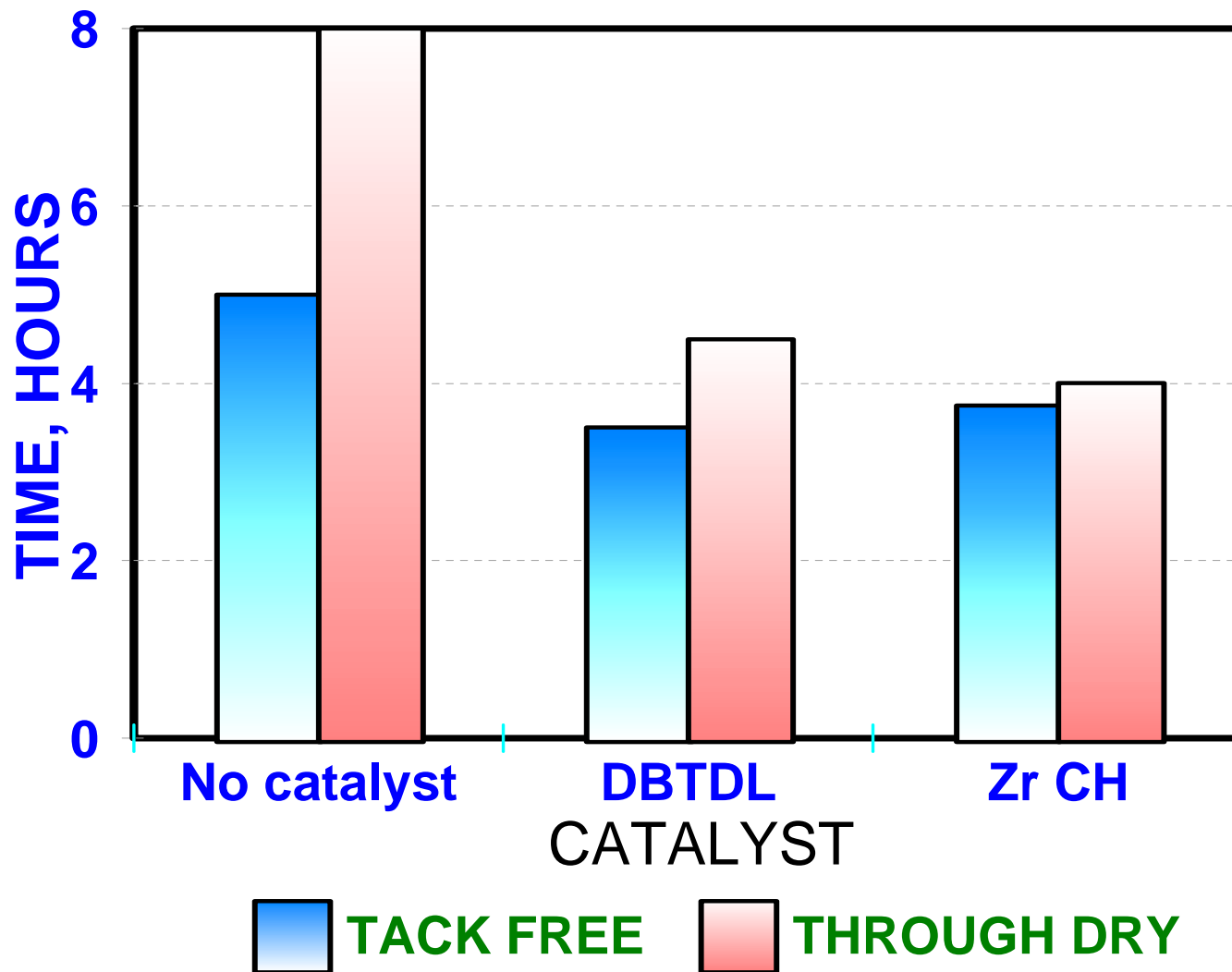
SELECTIVITY HYDROXYL / WATER



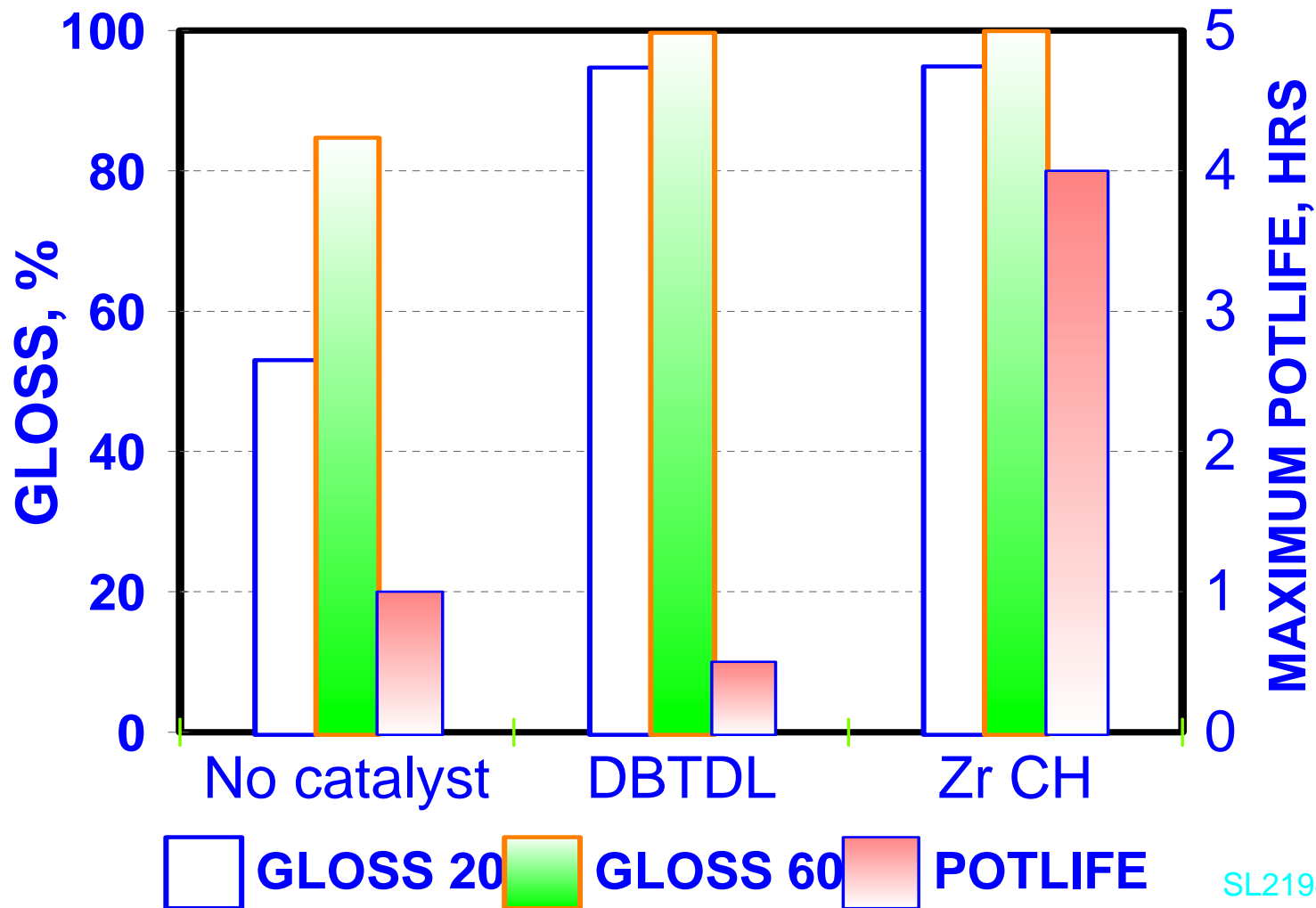
WATERBORNE TWO COMPONENT



WATERBORNE TWO COMPONENT



WATERBORNE TWO COMPONENT CATALYST SELECTION



WATERBORNE TWO COMPONENT

XC-6212

XC-6212

DBTDL



A100 XC6212 0H RT 496-10

0 HOUR



A107 XC6212 RT 496-10

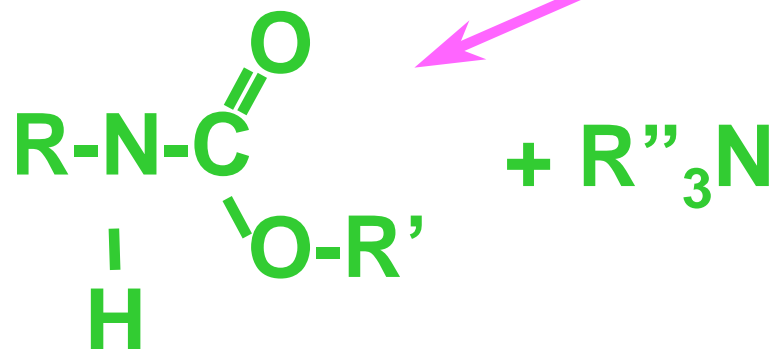
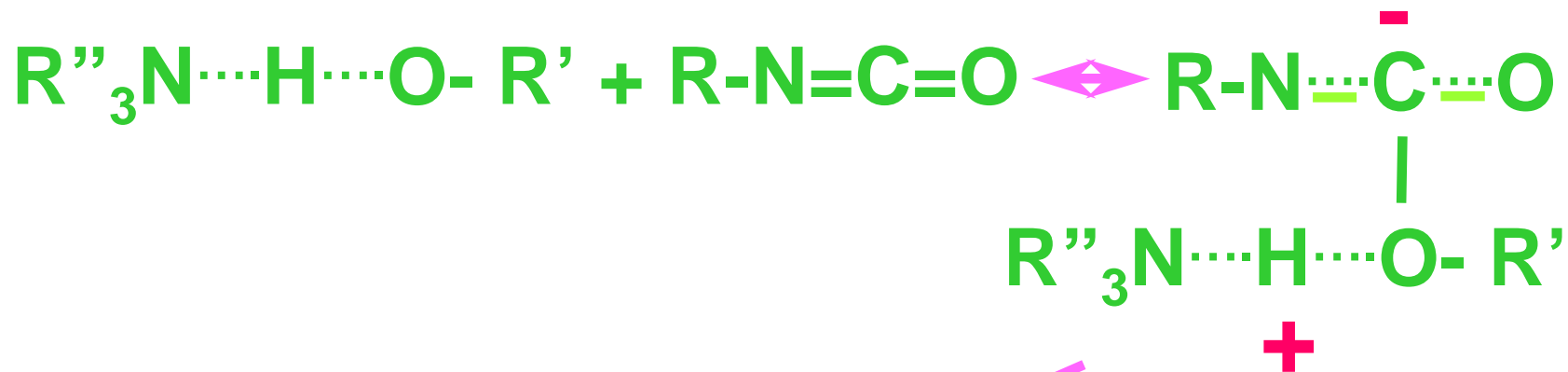
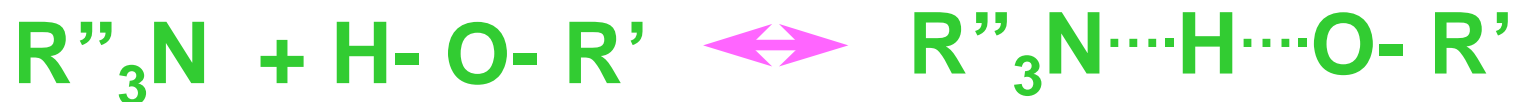
4 HOURS



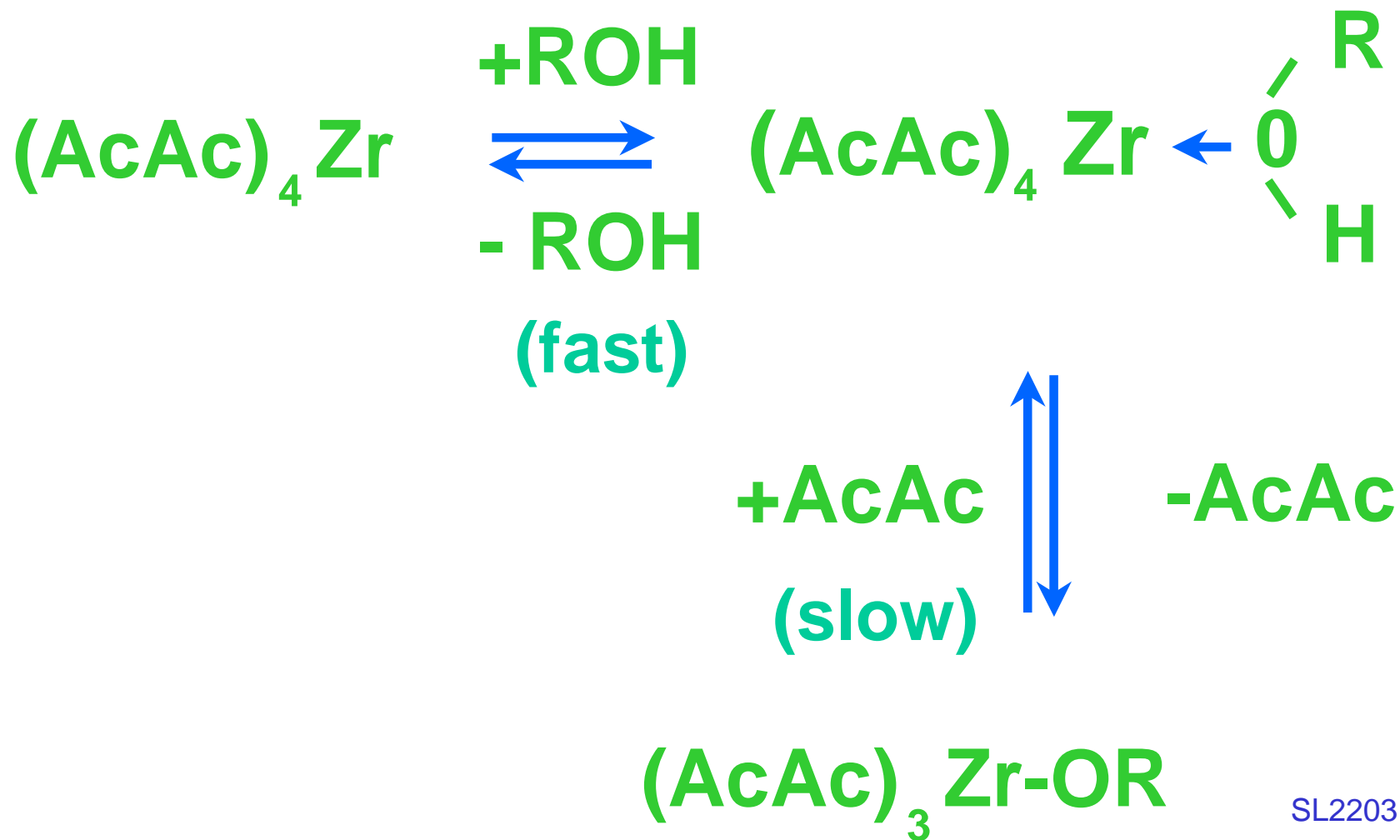
A111 DBTDL 0.5H RT 496-10

1/2 HOUR

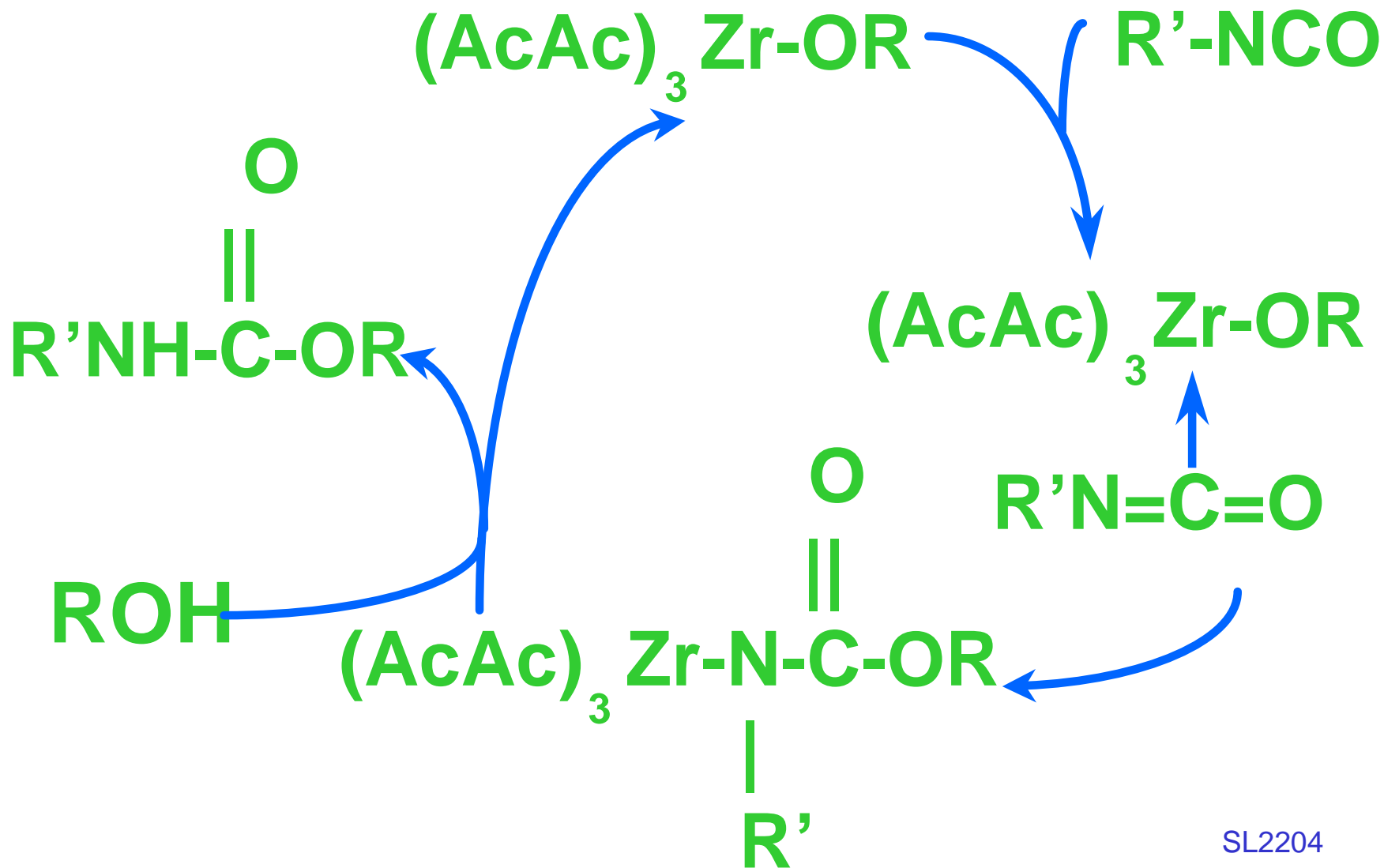
AMINE CATALYSIS



ZIRCONIUM CHELATE CATALYSIS



ZIRCONIUM CHELATE CATALYSIS

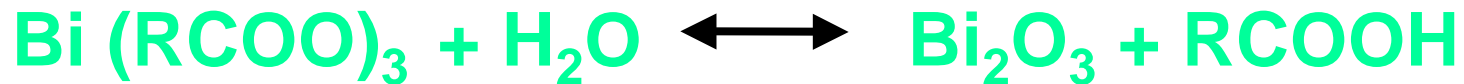


HYDROLYSIS OF Zr CHELATE

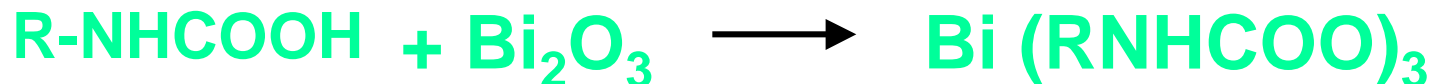
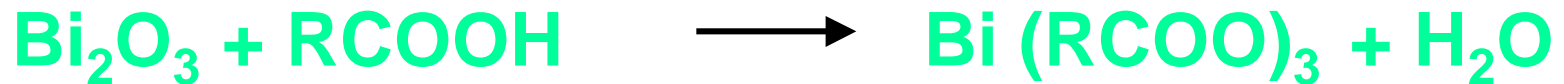


DELAYED ACTION OF BI CARBOXYLATE

DEACTIVATION



ACTIVATION



WHY REPLACE DBTDL

ENVIRONMENTAL

Al, Bi, Zr

POTLIFE - REACTIVITY

Al

PIGMENT ABSORPTION

Al

SELECTIVITY - HYDROXYL vs WATER

Zr

LOW GLOSS HIGH HUMIDITY

Zr

GASSING

Zr

WATERBORNE

Zr

DELAYED REACTION

Bi

SIDE REACTIONS

Zr

HYDROLYSIS OF ESTER GROUPS

Al, Bi, Zr

DURABILITY

Al, Bi, Zr

FORMULATION GUIDE LINES

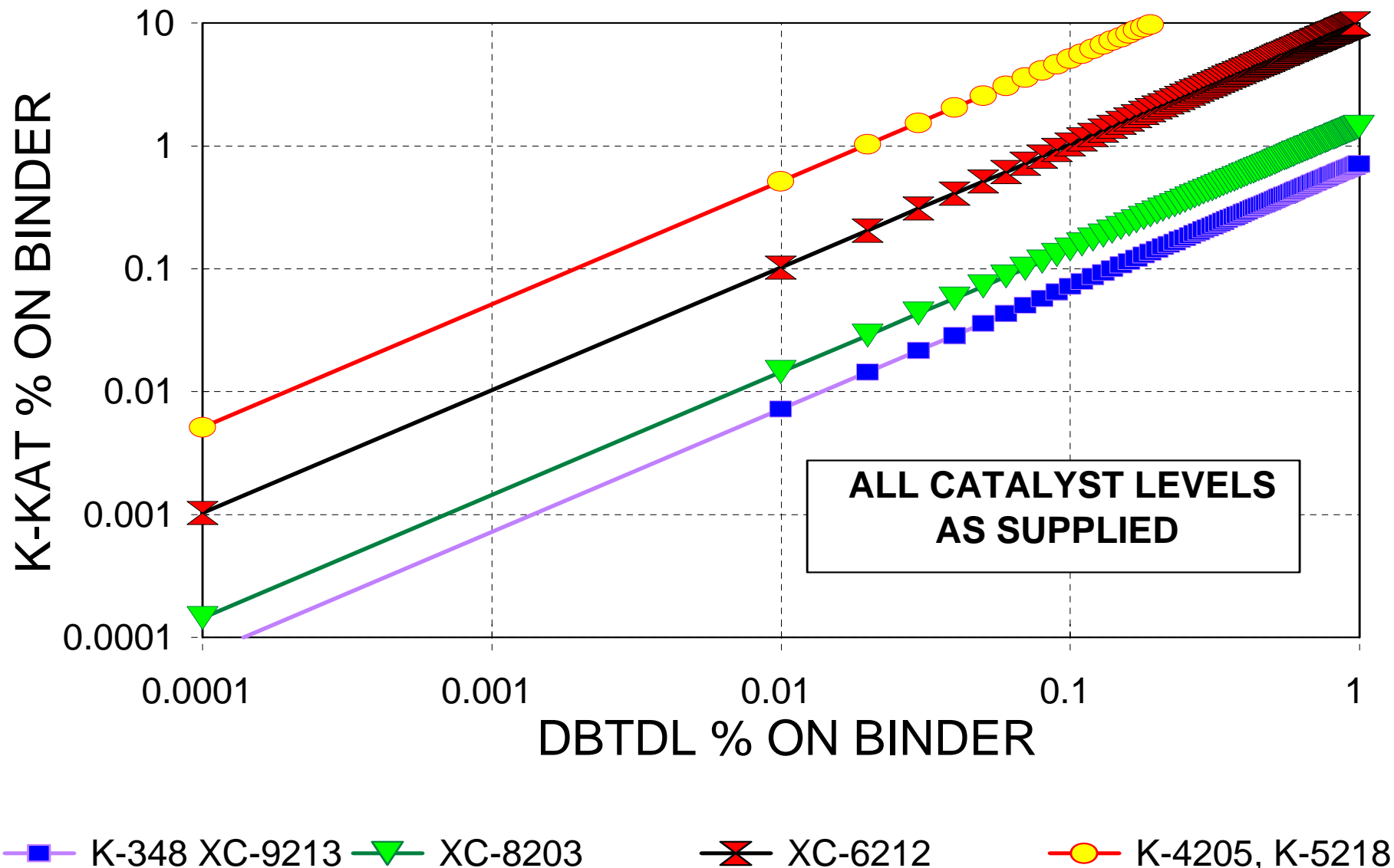
HIGH SOLIDS
POTLIFE - REACTIVITY
SOLUBILITY

WATERBORNE
GASING
CATALYST
HYDROLYSIS

CATALYST INHIBITION - DEACTIVATION
PIGMENT ABSORPTION
WATER
ACID NUMBER
AMINE

K-KAT CATALYST CONCENTRATION

DBTDL REPLACEMENT LEVEL



CATALYSTS FORMULATION GUIDELINE

Zr Chelate XC-6212, XC-9213

Add to isocyanate

Zr Chelate 4205

Water free formulation low in acid number

Bismuth carboxylate K-348, XC-8203

COOH beneficial

Low water content

Dehydrating agents

Al Chelate K-5218

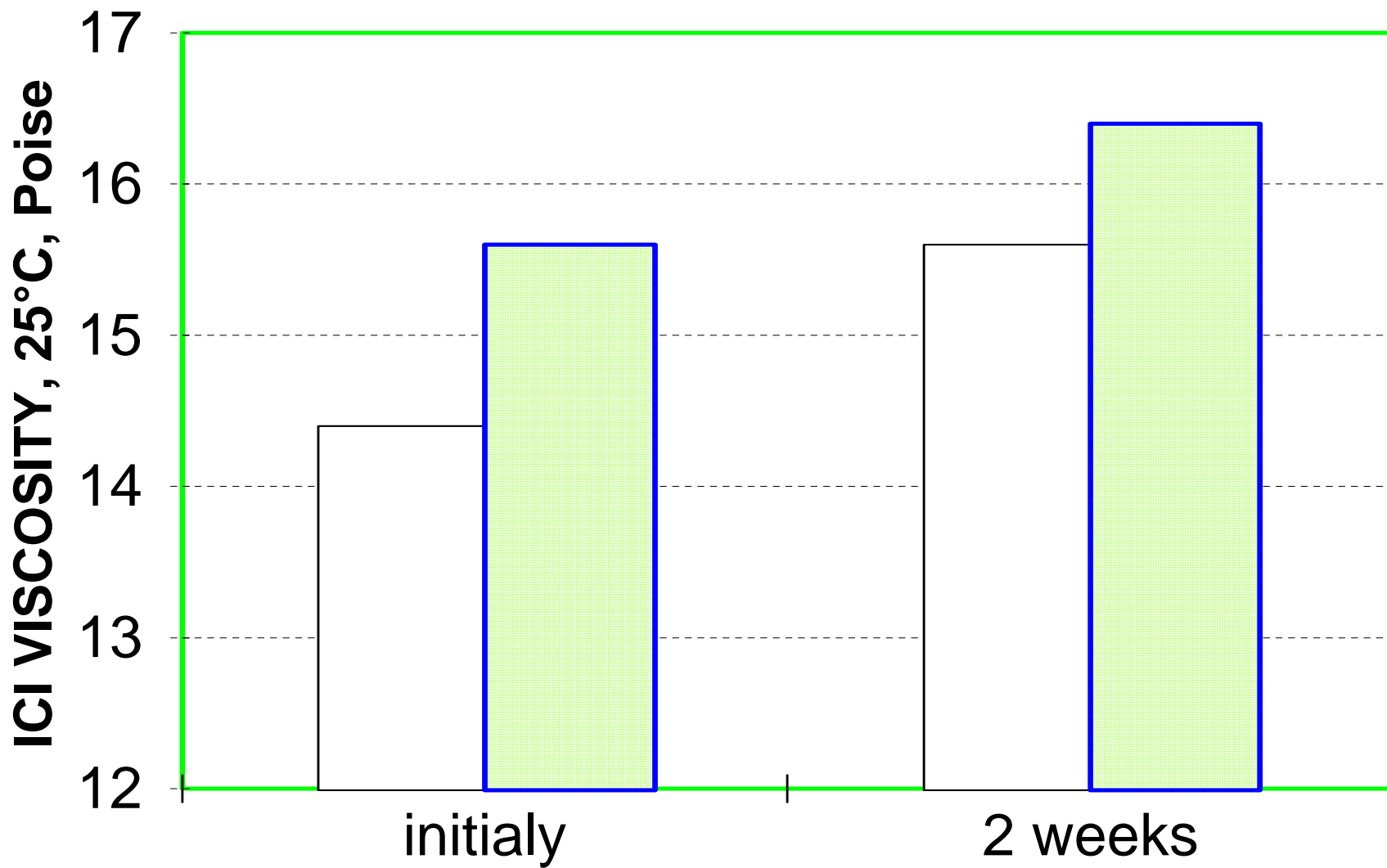
Low acid number, neutralization

Low water content

2,4-pentanedione addition

STABILITY OF HDI-TRIMER 50°C

K-KAT XC-6212 (4%)

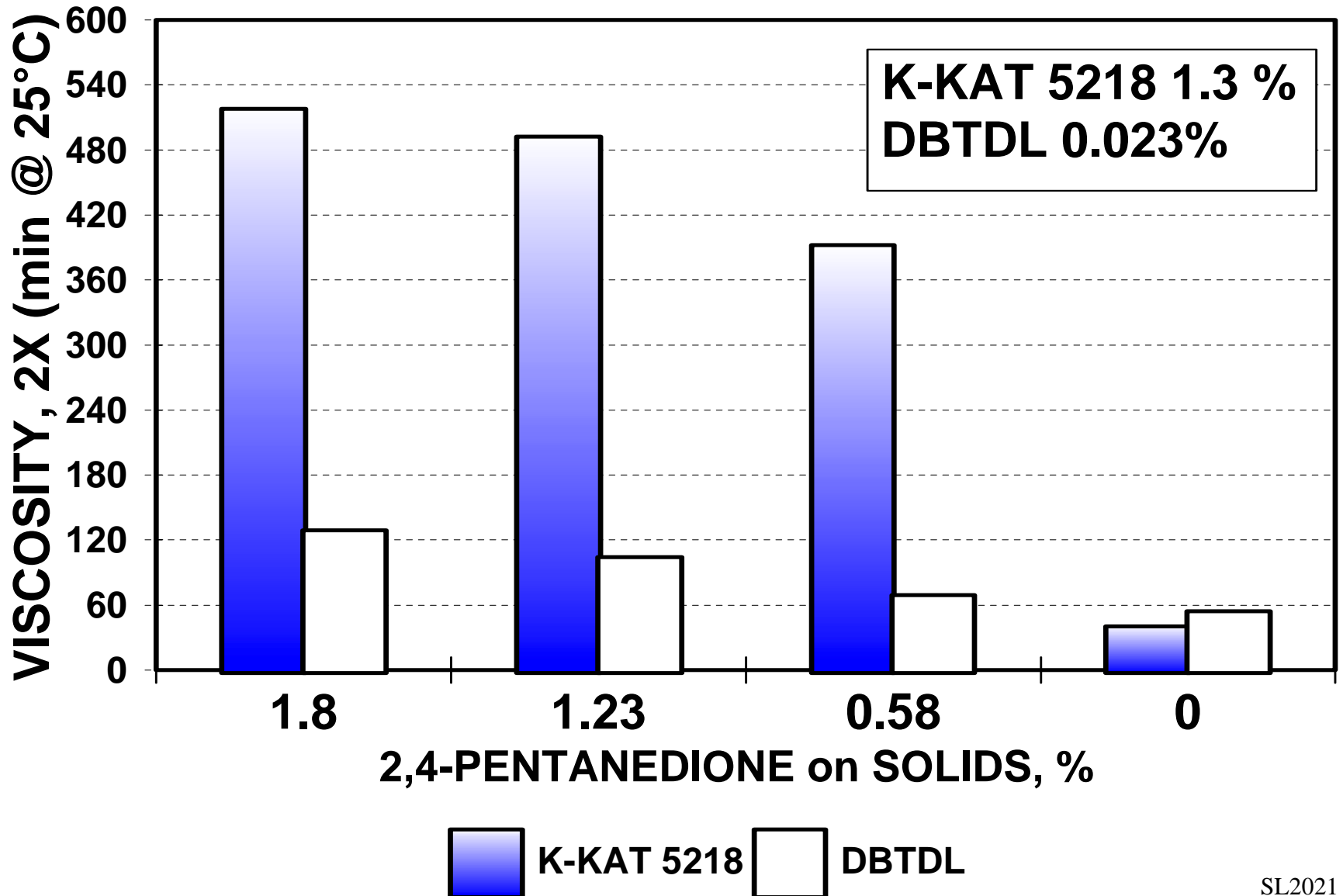


□ CONTROL ■ XC-6212

SL2079

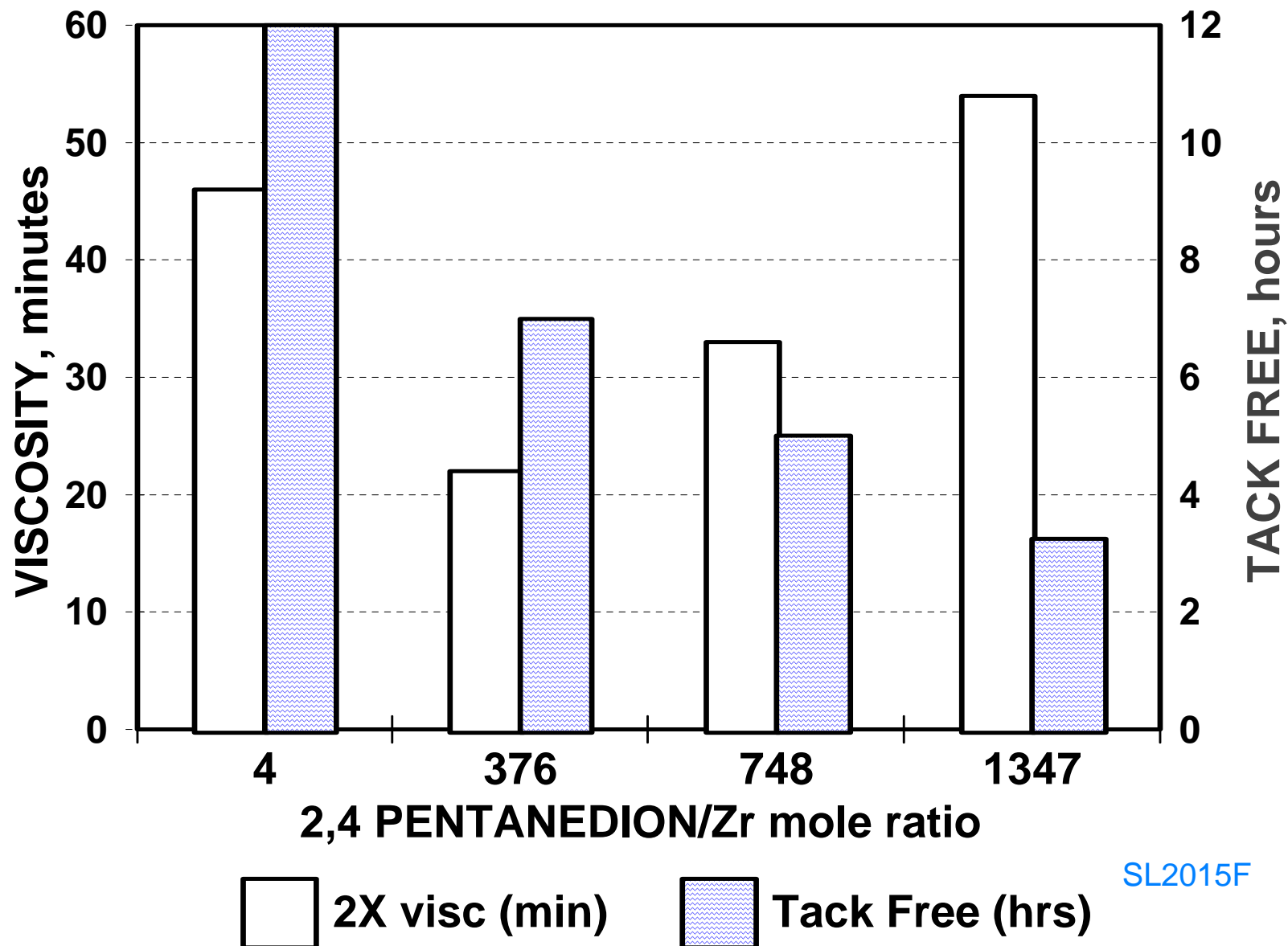
POLYESTER/HDI-TRIMER

TACK FREE TIME 3.0-4.0 HOURS

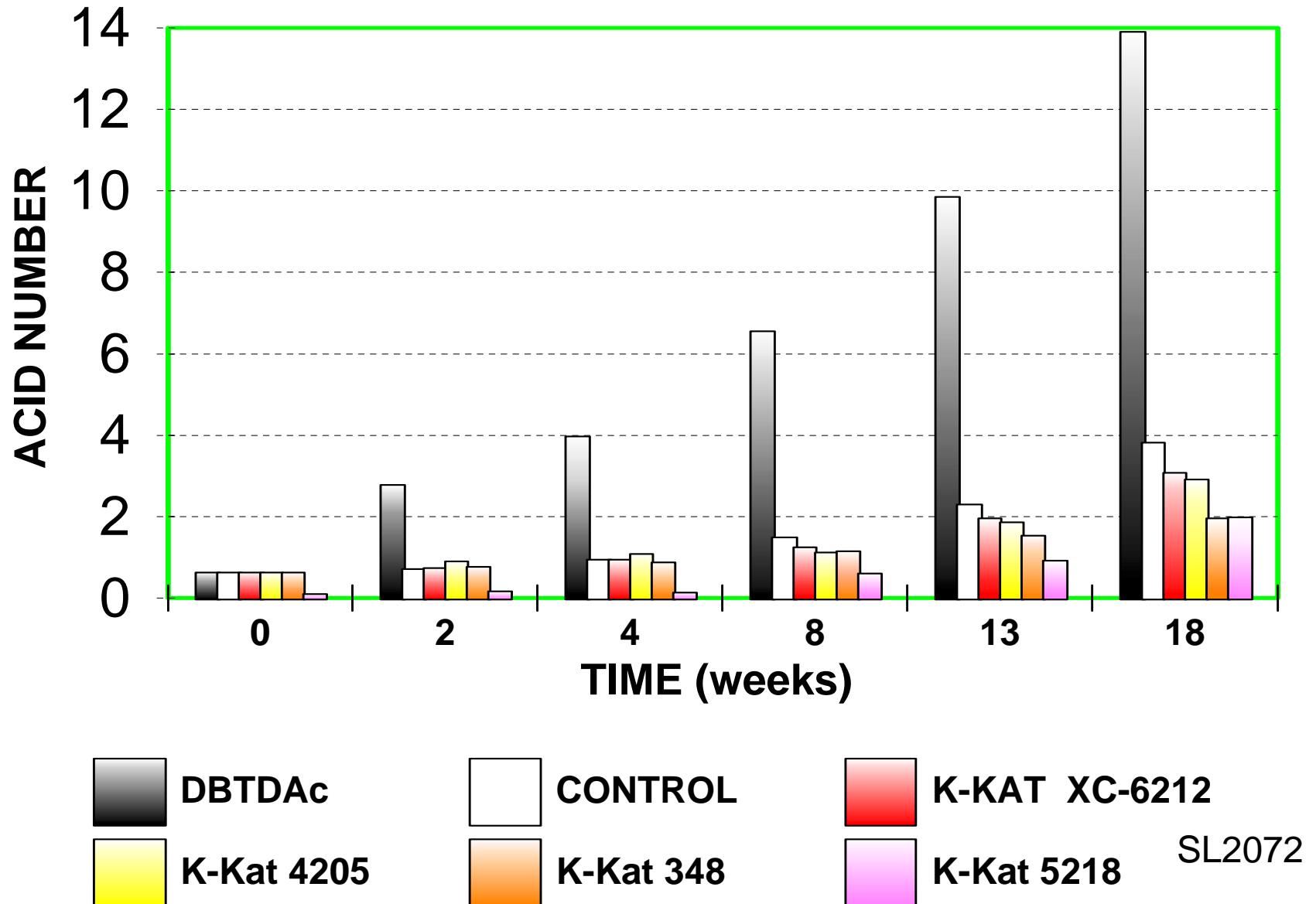


POLYESTER/HDI-TRIMER CATALYST

CATALYST Me 0.0065% ON SOLIDS



Hydrolysis of polyester in presence of catalyst (0.01% on TRS)



SUMMARY

ORGANO TIN FREE COATINGS POSSIBLE

CHOICE OF CATALYST DEPENDS ON APPLICATION

Zr CHELATE CATALYSTS SELECTIVE FOR OH

HIGH REACTION RATES POSSIBLE

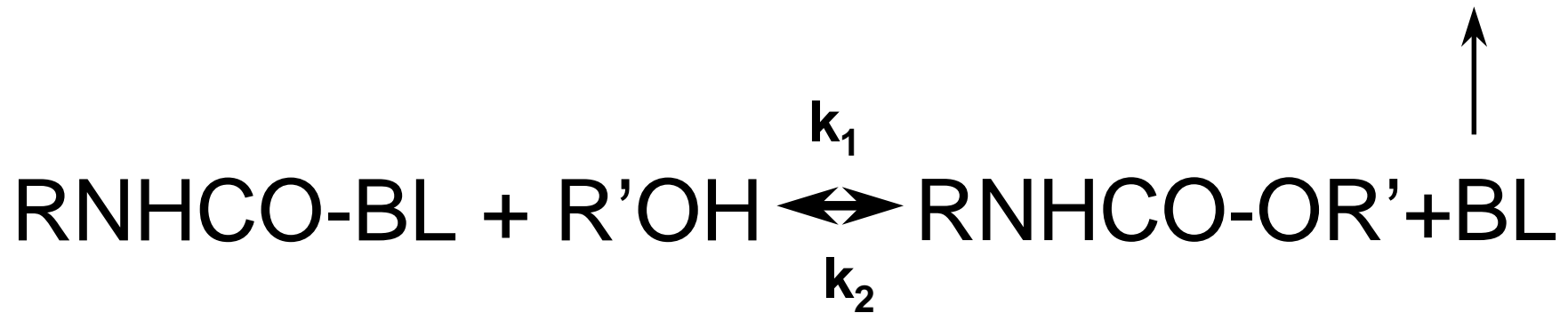
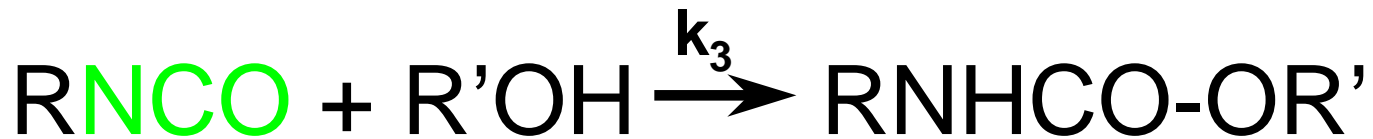
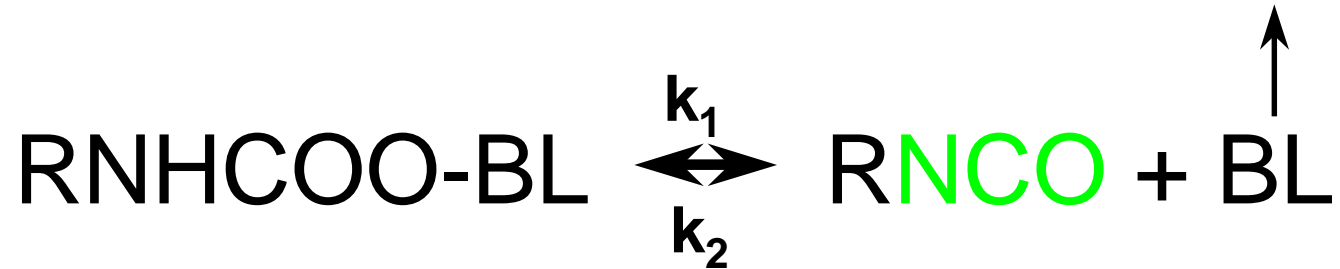
RELATIVE REACTIVITY OF HYDROXYLS DIFFERENT

CATALYSIS OF WATERBORNE COATINGS WITH Zr

POTLIFE - REACTIVITY AI

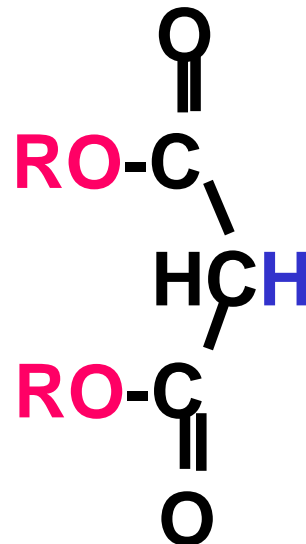
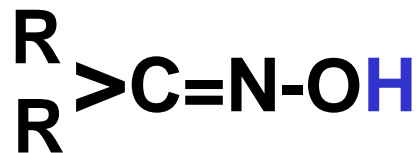
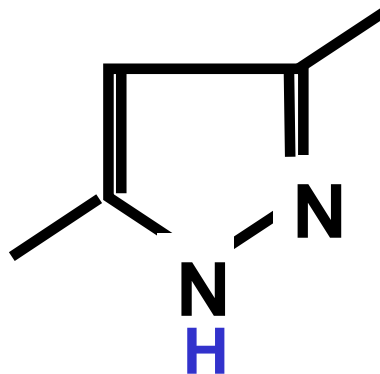
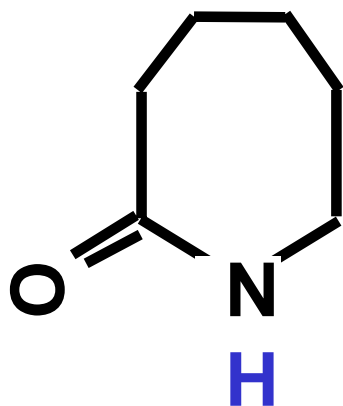
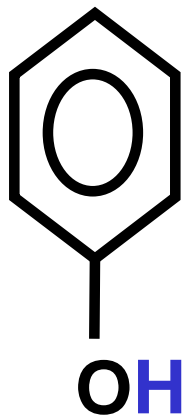
Bi CATALYST SIMILAR TO DBTDL

REACTION OF BLOCKED ISOCYANATE

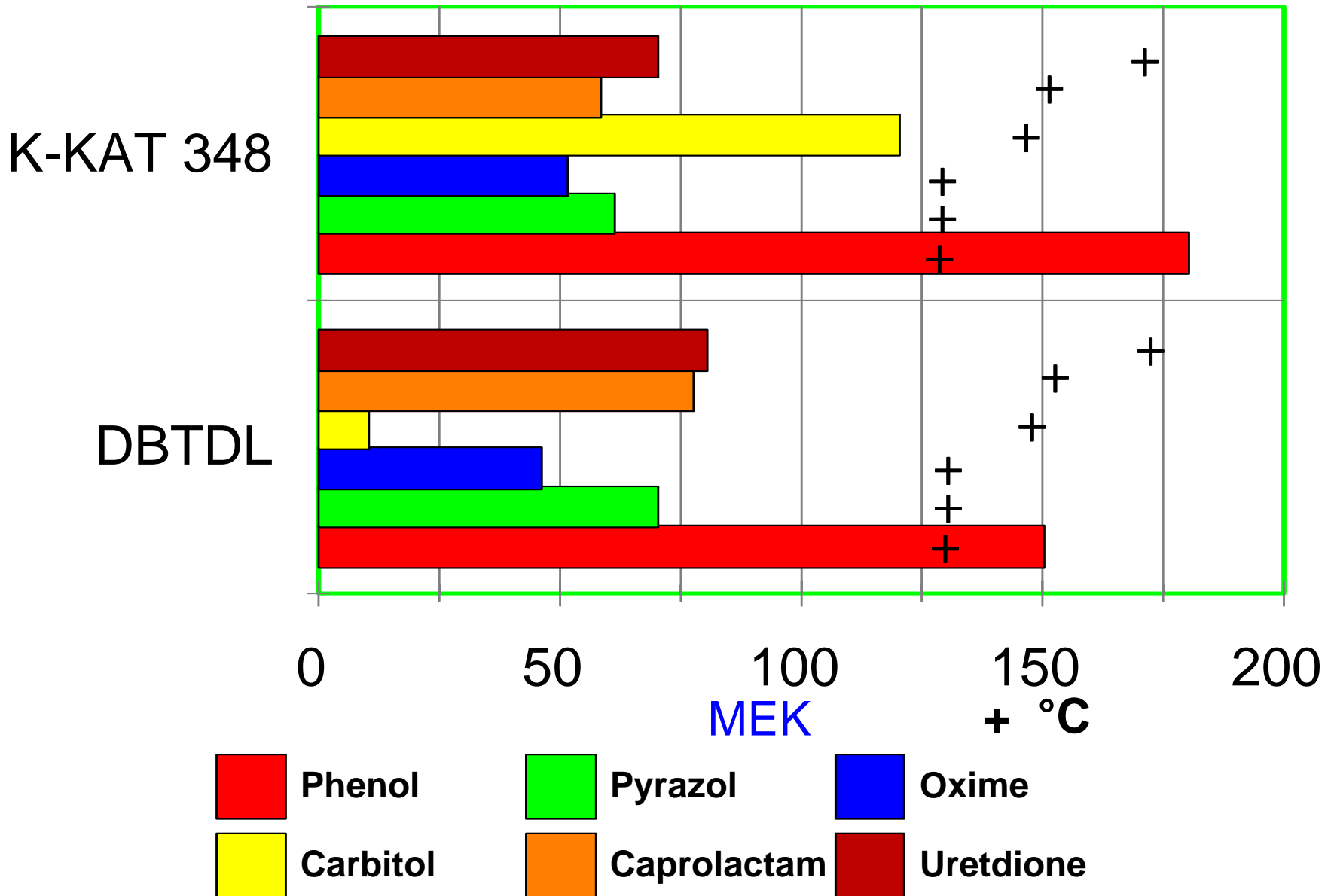


BLOCKED ISOCYANATES

ROH

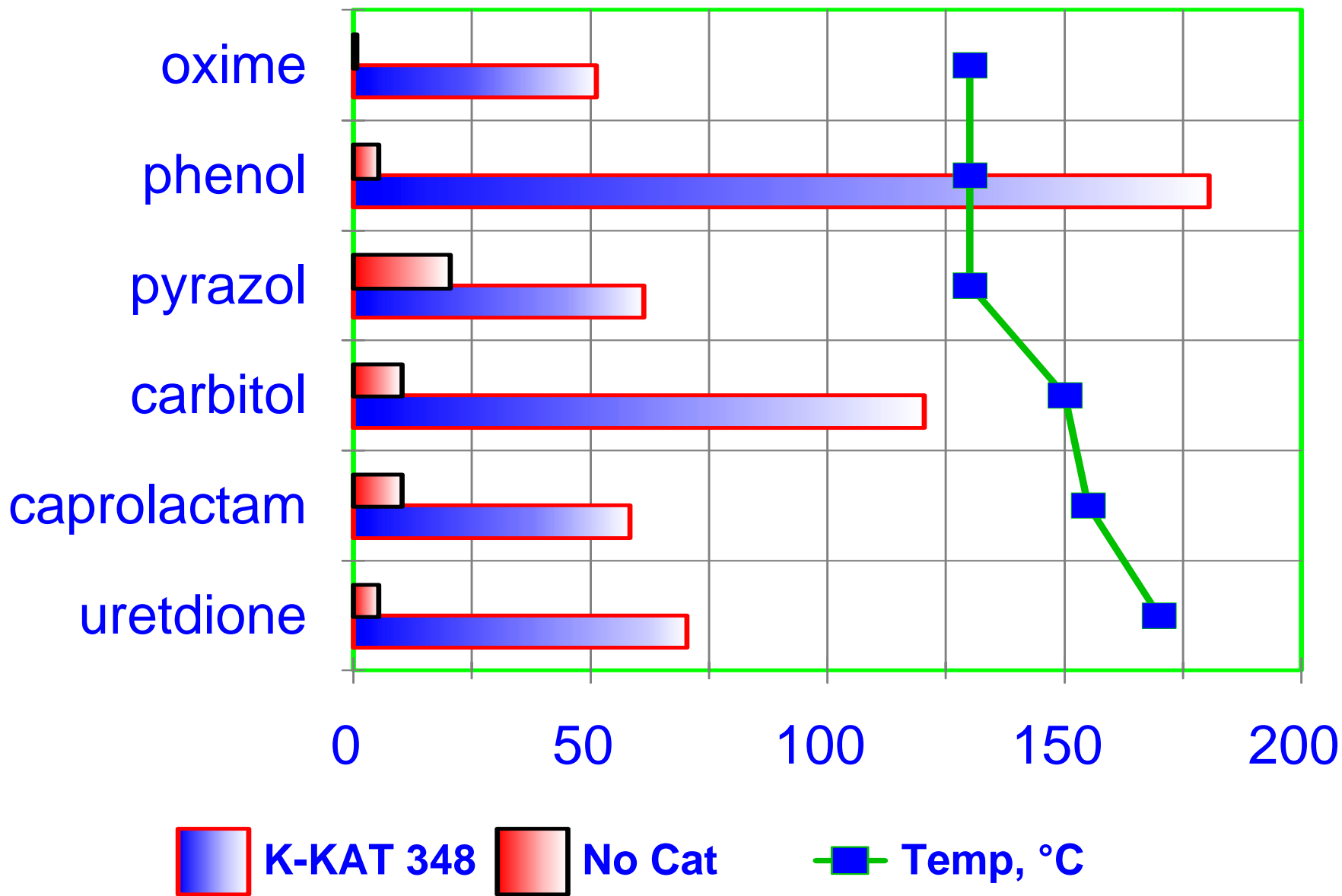


BLOCKED ISOCYANATE



BLOCKED ISOCYANATE

MEK / °C



ACKNOWLEDGEMENT

TECHNICAL SERVICE DEPARTMENT

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www.wernerblank.com

