Catalisi e stabilizzazione di schiume PIR: recenti sviluppi

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Introduction

With high energy costs, increasing importance is being placed on insulation

Polyisocyanurate (PIR) is widely utilised due to it's outstanding insulation and fire properties

Due to the complexity of the chemistry and processing, PIR production is more demanding than PUR production

In this Paper we review PIR technology and introduce main concept to trim reaction profile in order to adapt chemical reaction to various production process issues

Activity & Gel – Blow Selectivity

Urethane and urea reaction follow the same mechanisms

Amine catalysts catalyze typically both reactions

Catalyst differentiate by

- Activity
- Selectivity

The selectivity of the catalyst determines

- Rate of Urethane formation
- Rate of Urea formation

$$\text{Activity} = \frac{\text{C(Standard Catalyst)}}{\text{C}*\text{(Catalyst)}}$$

$*$ To meet reactivity profile

$$\text{Selectivity} = \text{f(time)}$$

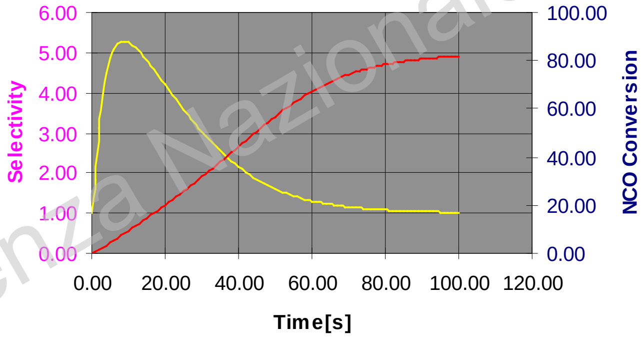
$$\text{Selectivity} = \frac{\text{\%convertedUrea}}{\text{\%convertedUrethane}}$$

Gel - Blow Selectivity Charts

Rigid water co blown Formulation

—Blow- Gel Selectivity

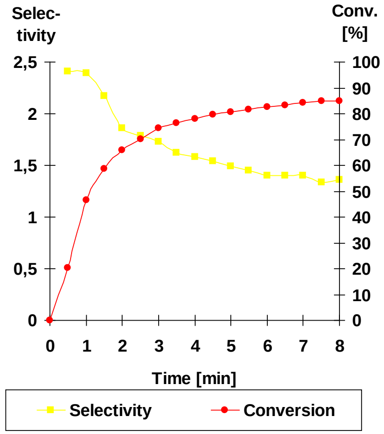
—NCO Conversion



Listemann Model

—Blow Gel Selectivity

—NCO Conversion



Polycat 5

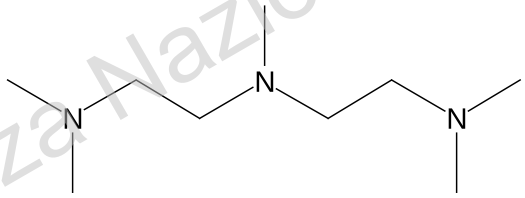
Alias TEGOAMIN® PMDETA

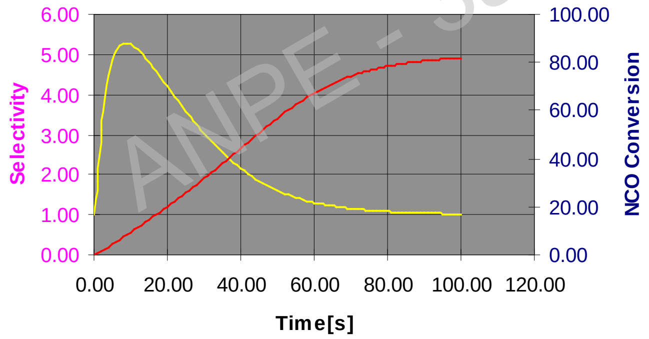
Strong blow catalyst

Improved flowability

Pour-in-place and appliance applications

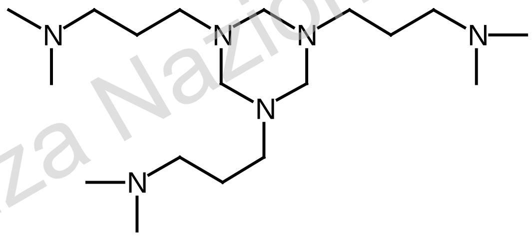
Trimerization co catalyst

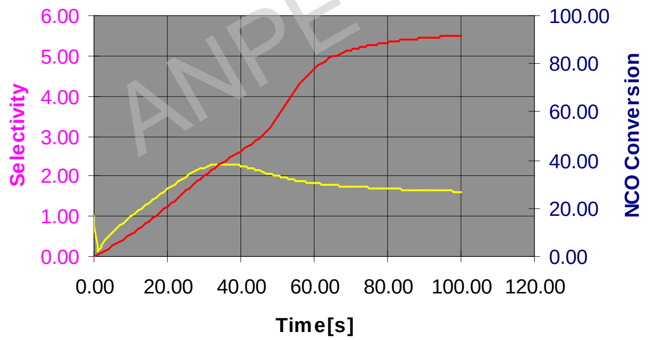




Polycat 41

- Alias TEGOAMIN® 41
- tris-(Dimethylaminopropyl)hydrotriazin
- PUR Catalyst
  - Similar activity as Polycat 8
  - Improved curing
- PIR co Catalyst
  - Delayed frontend





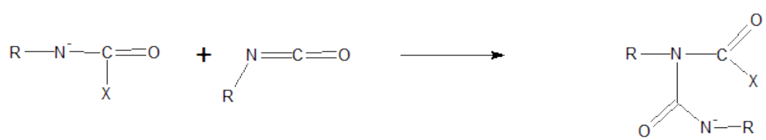
Impact of Gel Blow Selectivity on Physical Properties

	Blow Catalyst	Gel Catalyst
Flowability	higher	lower
Isotropy	higher	lower
Dimensional Stability	higher	lower
Density	lower	higher
Friability	higher	lower
PIR Yields	higher	lower
Carbodiimide	lower	higher
PUR Cure	lower	higher
PIR Cure	higher	lower

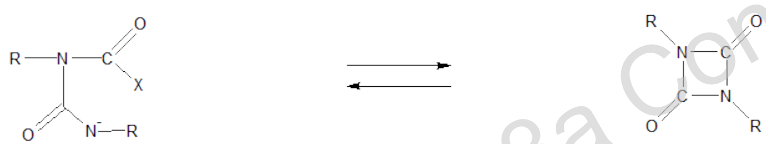
Trimerisation:
Main and Side Reactions

Trimerisation is an Anionic Catalyzed Reaction

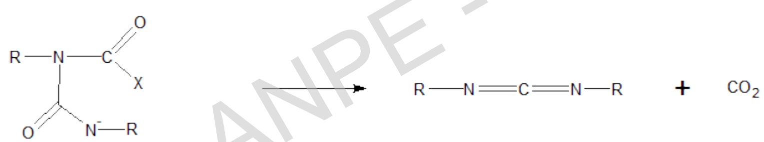
Anion catalyst ion attacks the carbonyl carbon forming an NCO-Catalyst complex.



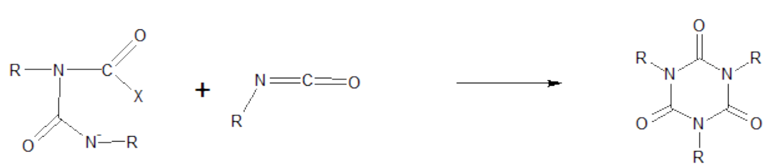
This NCO – Catalyst complex reacts with an other isocyanate. This intermediate can undergo various reactions:



Equilibrium with dimer of isocyanate



Decarboxylate to carbodiimide



React with an other NCO to isocyanurate

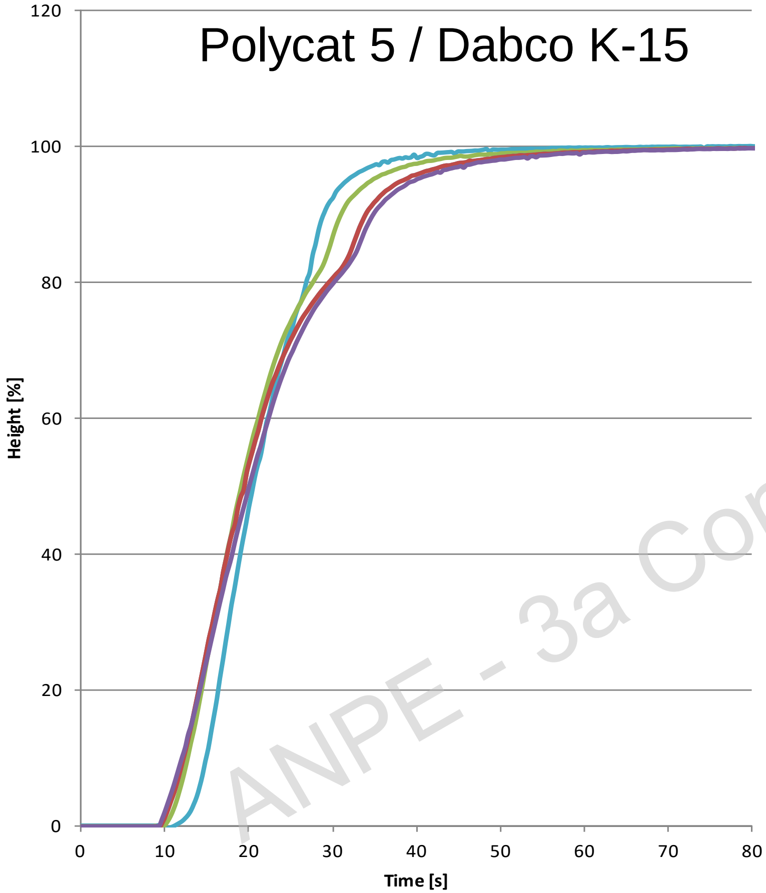
Typical PIR Formulation

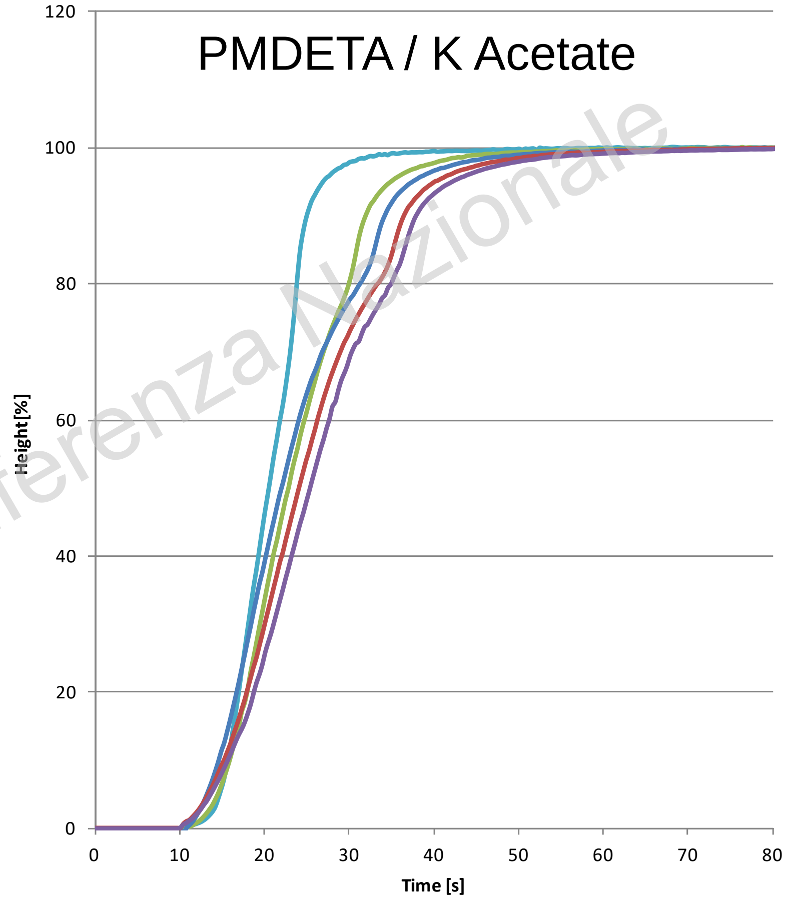
100	Polyester Polyol	Polymer Build
0,5-2,0	Water	Chemical Blowing Agent
10,0-17,0	Pentane	Physical Blowing Agent
2,0-5,0	Silicone Surfactant	Emulsification and Stabilization
0,5-2,0	Amine Catalyst	Catalyze Gel / Blow Reaction
2,0 - 5,0	Trimerisation Catalyst	Catalyze Trimer Formation
150 - 400	Polymeric MDI	Polymer Build

Trimerisation Technical Manual

WATER SENSITIVITY

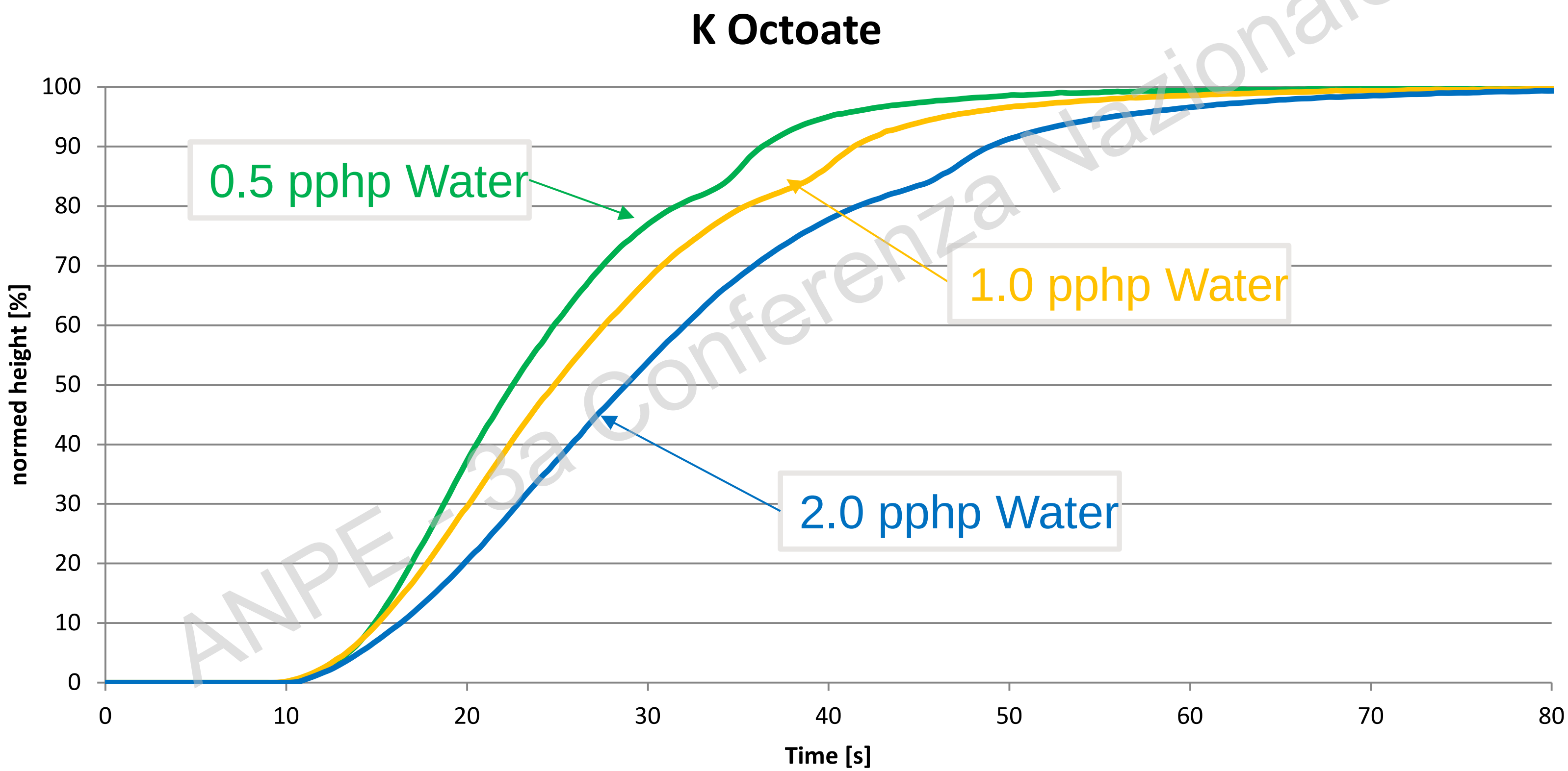
Water Sensitivity





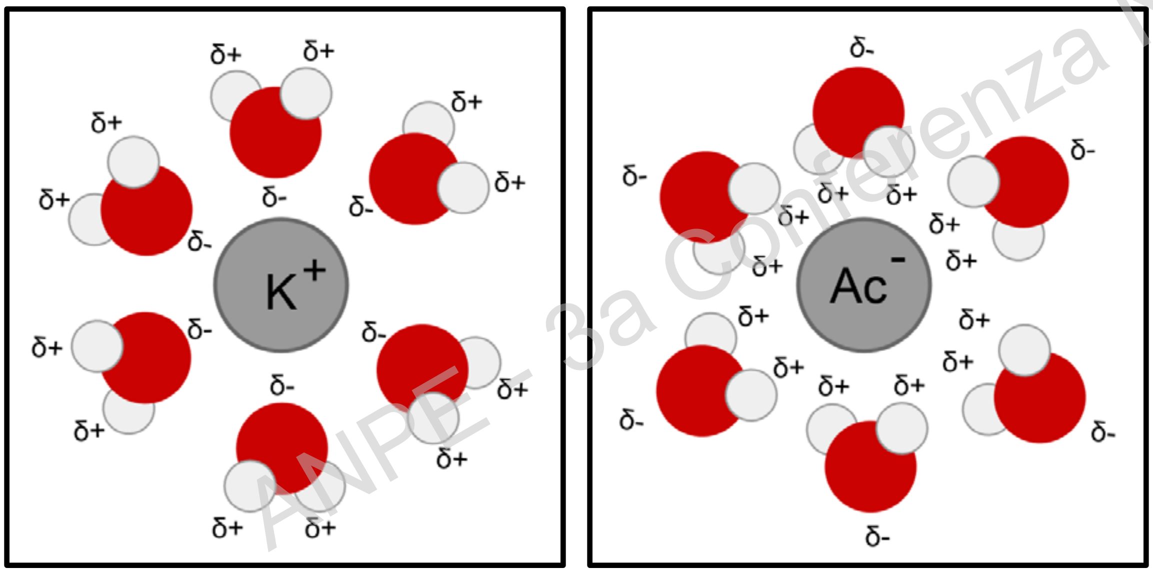
Water content: 0 pphp — 0,5 pphp — 1,0 pphp — 1,5 pphp — 2,0 pphp

Water Sensitivity



Index = constant
C(Catalyst) = constant

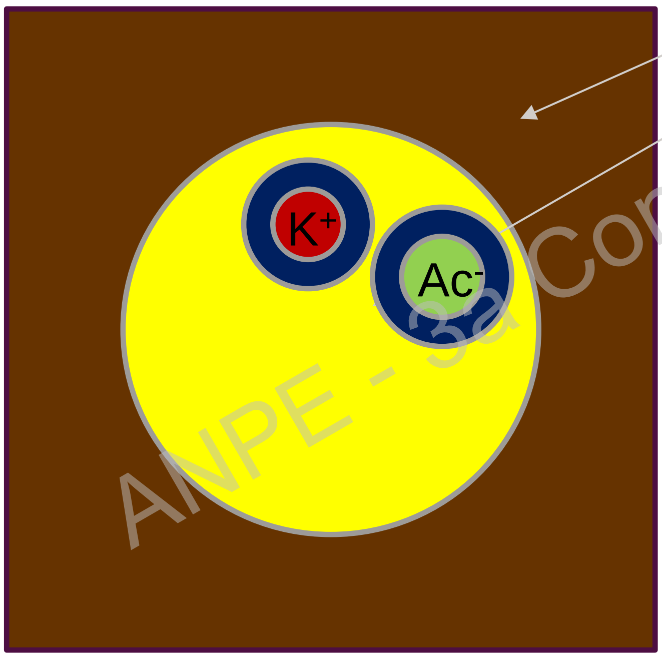
Complexed Ions



Water and MDI

The Reaction Mixture

Isocyanate Polyol Emulsion

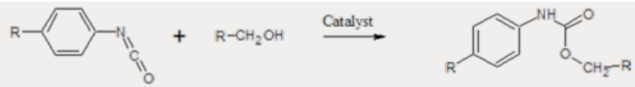
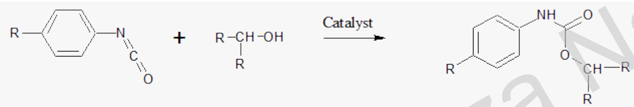
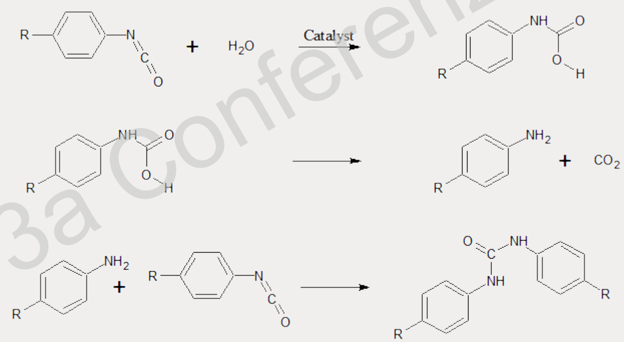
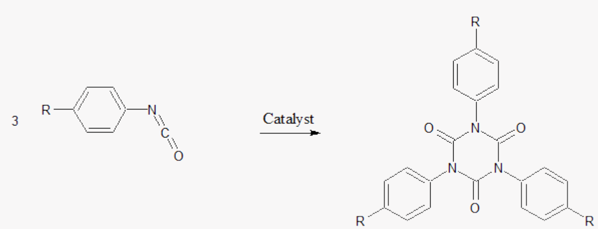


Isocyanate is continues phase

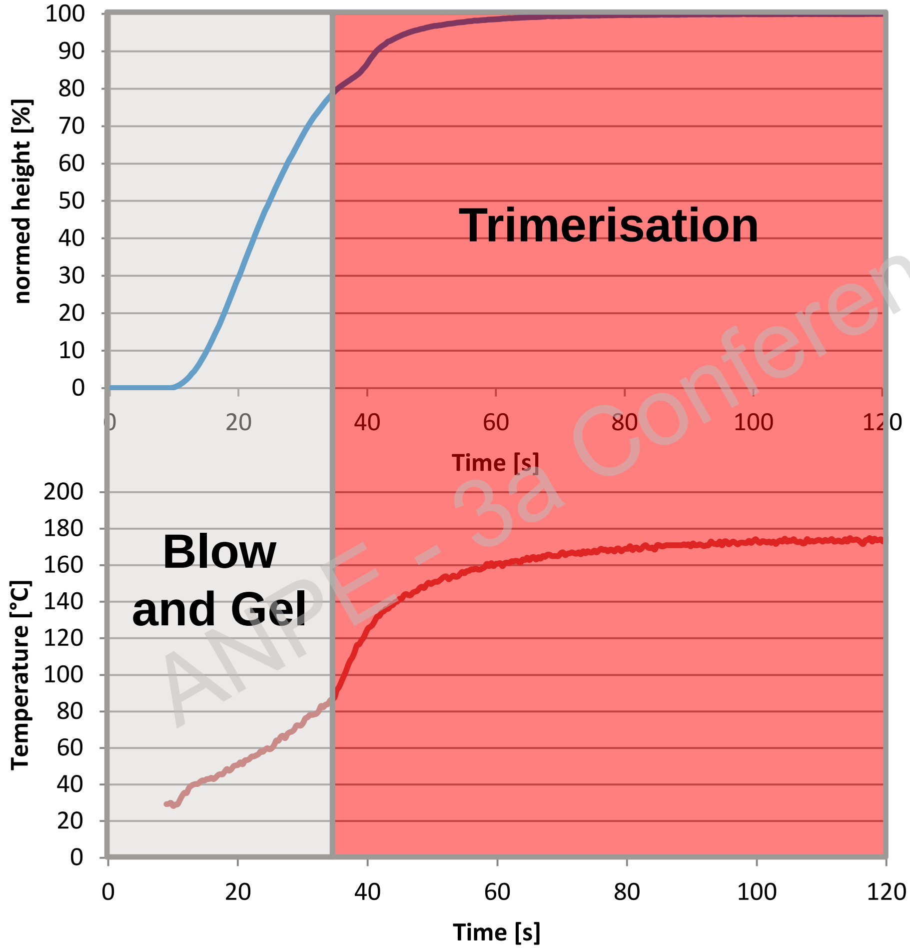
Polyol is emulsified in the isocyanate

Ion	Ion Radius [pm]	M [g/mol]
Li^+	60	7
Na^+	95	23
K^+	133	39
$N(CH_3)_4^+$	260	74
$N(CH_3)_3\ C_3H_6OH^+$	410	105
$HCOO^-$	147	45
CH_3COO^-	153	59
$(CH_3)_3CCOO^-$	280	101
$C_7H_{15}COO^-$	500	143

Foam Reactions

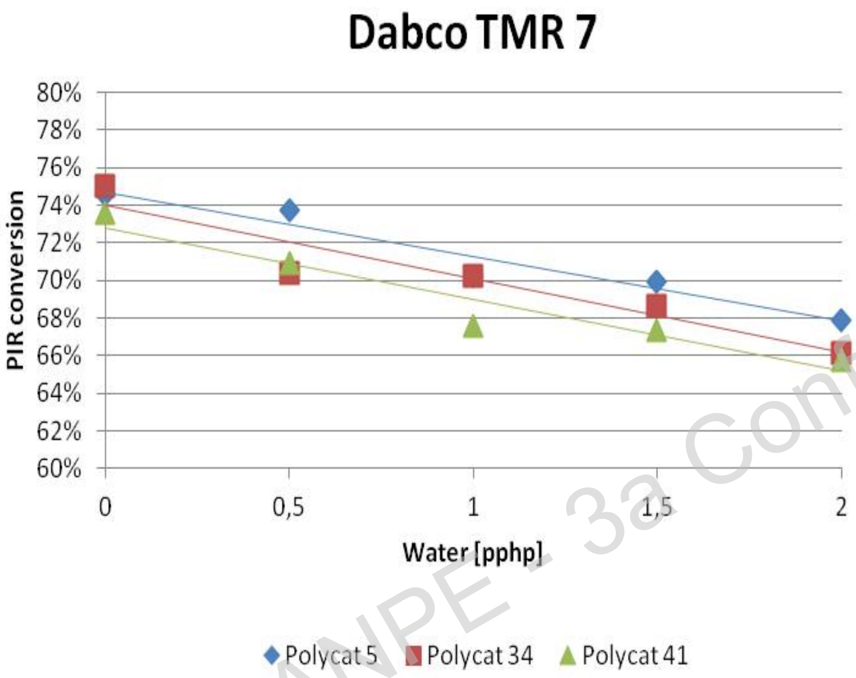
	Reaction	ΔH[kJ/mol]
Urethane		99.3
Urethane		84.7
Urea		91.9
Isocyanurate		201.0

Reaction Segmentation



- Gel and blow reaction is dominating the conversion until the water has been consumed
  - 80% of volume
  - 43% of temperature
- Trimerisation catalyst becomes available
- Trimerisation reaction dominates the backend of the reaction
  - 20% of volume
  - 57% of temperature

Polyisocyanurate Yield



PIR yield decreases with increasing water levels, despite a constant index.

Gel / blow balance of co-catalyst impacts PIR yield

Polycat 5 > Polycat 34 > Polycat 41

Surface Cure

		TFT [s]
Polycat 5	Dabco K-15	87
	Dabco K-2097	38
	Dabco TMR-7	33
Polycat 41	Dabco K-15	37
	Dabco K-2097	38
	Dabco TMR-7	35
Polycat 34	Dabco K-15	84
	Dabco K-2097	79
	Dabco TMR-7	82

Surface cure determined as tack free time (TFT)

- Surface cure is delayed by increasing water level

Polycat 5 is the fastest skin curing co catalyst in the study

Dabco TMR-7 has the highest skin cure potency

Gel Time = 30 s
Water content = 0,5 pphp

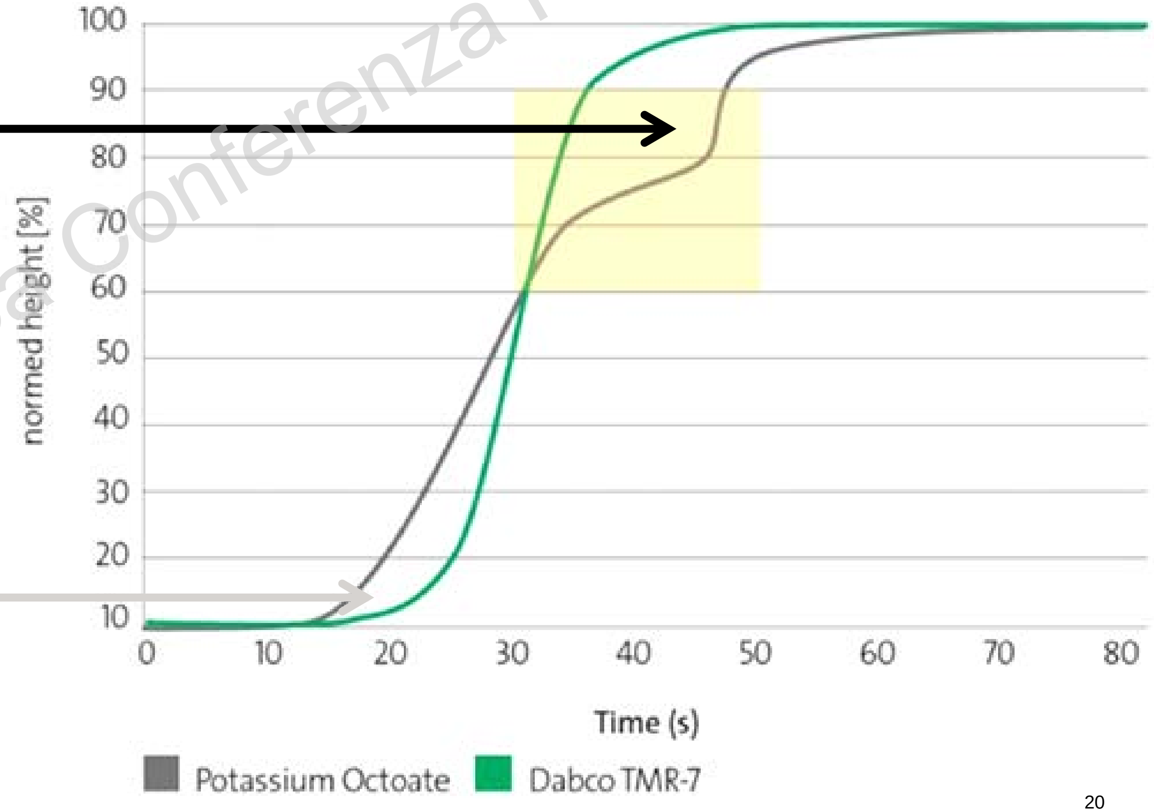
Rise Profile

Important for processing

Key parameter to generate a stable wave in the laminator

PIR kick rise profile

Smooth rise profile



Trimerisation Technical Manual

PRODUCTS

Trimer Catalyst Overview (Air Products Grades)

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Product	Composition	Remarks
Dabco K2097	Potassium Acetate 30% DEG	Standard PIR catalyst
Dabco K17	Potassium Acetate 41% MEG	Standard PIR catalyst
Dabco K15	Potassium Octoate 70% DEG	Standard PIR catalyst
Dabco K15-LV	Potassium Octoate 70% MEG	Low Viscosity
Dabco TMR	Quaternary Ammonium Carboxylate	For smooth reaction profiles
Dabco TMR 2	Quaternary Ammonium Carboxylate	Improved cure and for FA blown sytems
Dabco TMR 3	Quaternary Ammonium Carboxylate	FA modified TMR2
Dabco TMR 7	Quaternary Ammonium Carboxylate	Smooth Reaction Profile
Dabco TMR 8	Quaternary Ammonium Carboxylate	Low Odor TMR2
Dabco TMR 25	Potassium Formate	FA blown systems
Dabco TMR 12	Formulated Carboxylate Catalyst	Universal trimer catalyst
Dabco TMR 13	Formulated Carboxylate Catalyst	For smooth profiles
Dabco TMR 30	Betain Catalyst	Early PIR initiation
Dabco TMR 31	Sodium Carboxylate	Improved cure for PUR and PIR

Commercially available Amine Co-catalysts

Product	Characterisation	Remark
Polycat® 5	Blow catalyst	Suitable for PUR and PIR systems.
Polycat 8	Gel catalyst	Suitable for PUR systems.
Polycat 34	Gel catalyst	Improved EH&S versus DMCHA.
Polycat 41	Delayed action	Suitable for PUR and PIR systems.

Rigid Foam Potassium Catalysts for CLBS - Overview

	KOSMOS® 33	KOSMOS® 33 MEG	KOSMOS® 45 MEG	KOSMOS® 70 LO	KOSMOS® 75 LO*	KOSMOS® 75	KOSMOS® 75 MEG
Active substance	Potassium Acetate	Potassium Acetate	Potassium Acetate	Potassium Octoate	Potassium Octoate	Potassium Octoate	Potassium Octoate
Solvent	DEG	MEG	MEG	OH-free solvent	OH-free solvent	DEG	MEG
Concen-tration	33 %	33 %	45 %	70 %	75%	75 %	75 %
Potassium content	13.1 %	13,1 %	17,9 %	15.0 %	16,1 %	16.1 %	16.1 %
Water content	2,0 %	3,0 %	3,0 %	3.0 %	6,5 %	3.0 %	3.5 %
OH number (incl. water)	815 mg KOH/g	1350 mg KOH/g	1127 mg KOH/g	280 mg KOH/g	405 mg KOH/g	420 mg KOH/g	610 mg KOH/g
OH number (excl. water)	690 mg KOH/g	1160 mg KOH/g	940 mg KOH/g	95 mg KOH/g	0 mg KOH/g	230 mg KOH/g	390 mg KOH/g
Viscosity (25°C)	500 mPa*s	100 mPa*s	150 mPa*s	4000 mPa*s	1000 mPa*s	7500 mPa*s	2600 mPa*s
Comments	Standard potassium acetate catalyst	Low viscosity potassium acetate	High concentrated potassium acetate	Low OH potassium octoate	High performance potassium octoate	Standard potassium octoate catalyst	Low viscosity potassium octoate

Summary

Water and catalyst have significant impact on reactivity and curing behavior

Amine co-catalysts impacts front end reactivity

Trimerisation catalysts control reaction profiles and curing

Evonik today, beside the well know experience and whide portfolio in stabilisers, can offer catalyst solutions to resolve todays challenges in PIR technology