

Polyisocyanates for modern 2K-PU Coatings Systems

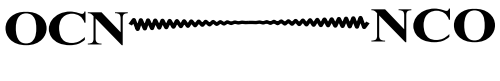
“Ramspec “ – Coatings & Composites

Dr. Ulrich Freudenberg, October, 04th, 2018

Agenda

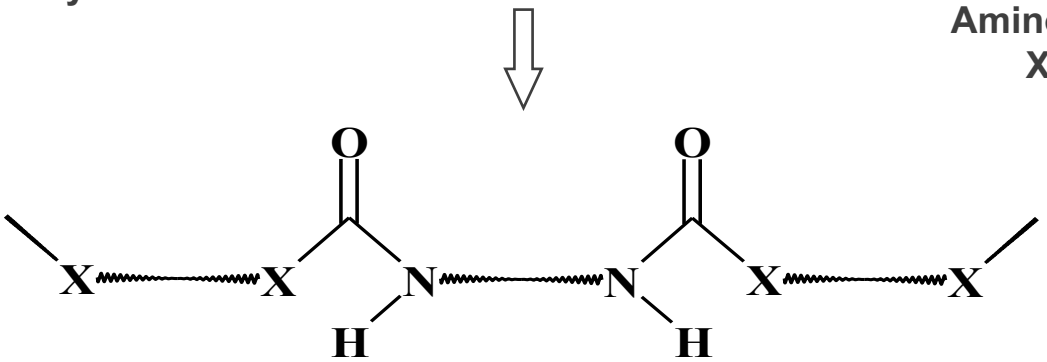
- **Welcome & introduction**
- **Diisocyanates – Basis of PU-chemistry**
- **Polyisocyanates – Standard crosslinkers**
- **New trends of development:**
  - **- low viscous crosslinkers**
  - **- high functional / high elastic crosslinkers**
  - **- low residual monomer content**
  - **- Sustainability**
- **Hydrophilized Polyisocyanates**

Formation of Polyurethanes

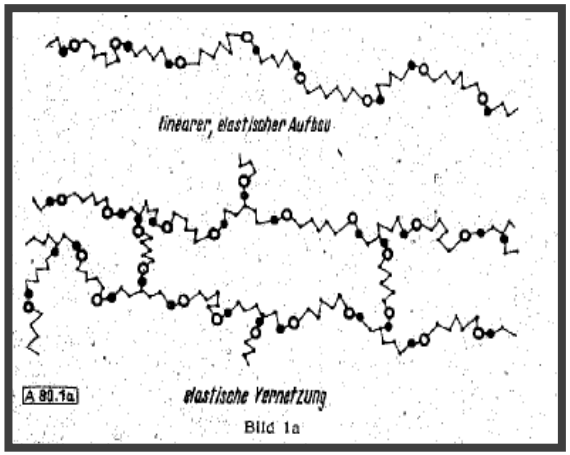


Diisocyanate

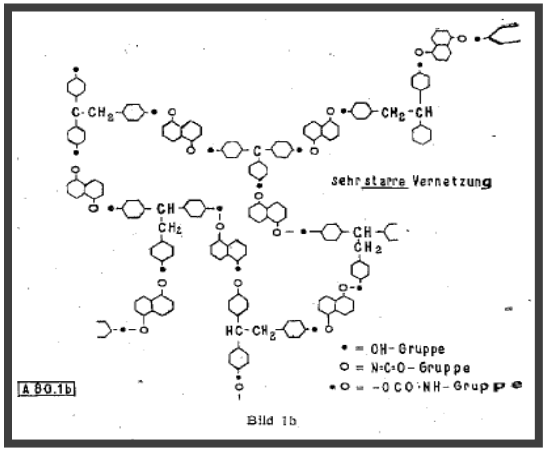
Diol, Diamine,
Aminoalkohol
X = O, NR



Polyurethane (X = O)
Polyurea (X = NR)

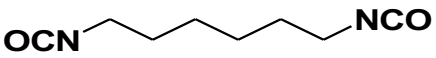


Otto Bayer „Das Di-Isocyanat-Polyadditionsverfahren (Polyurethane)“
Angewandte Chemie, 1947, **59**, 257–288.

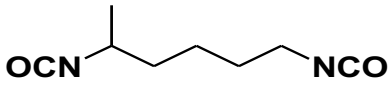


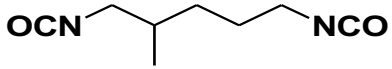
Aliphatic Diisocyanates

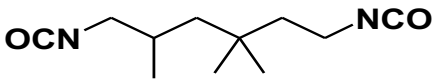
linear aliphatic

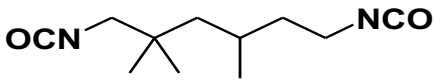


Hexamethylendiisocyanat (HDI),

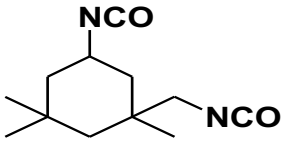




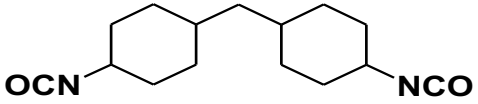




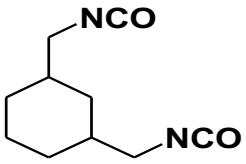
cyclo-aliphatic

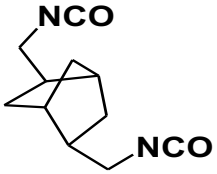


Isophorondiisocyanat (IPDI),

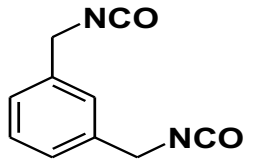


4,4'-Diisocyanatodicyclohexylmethan (H_{12}-MDI),

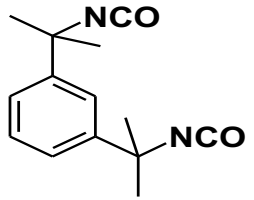




araliphatic

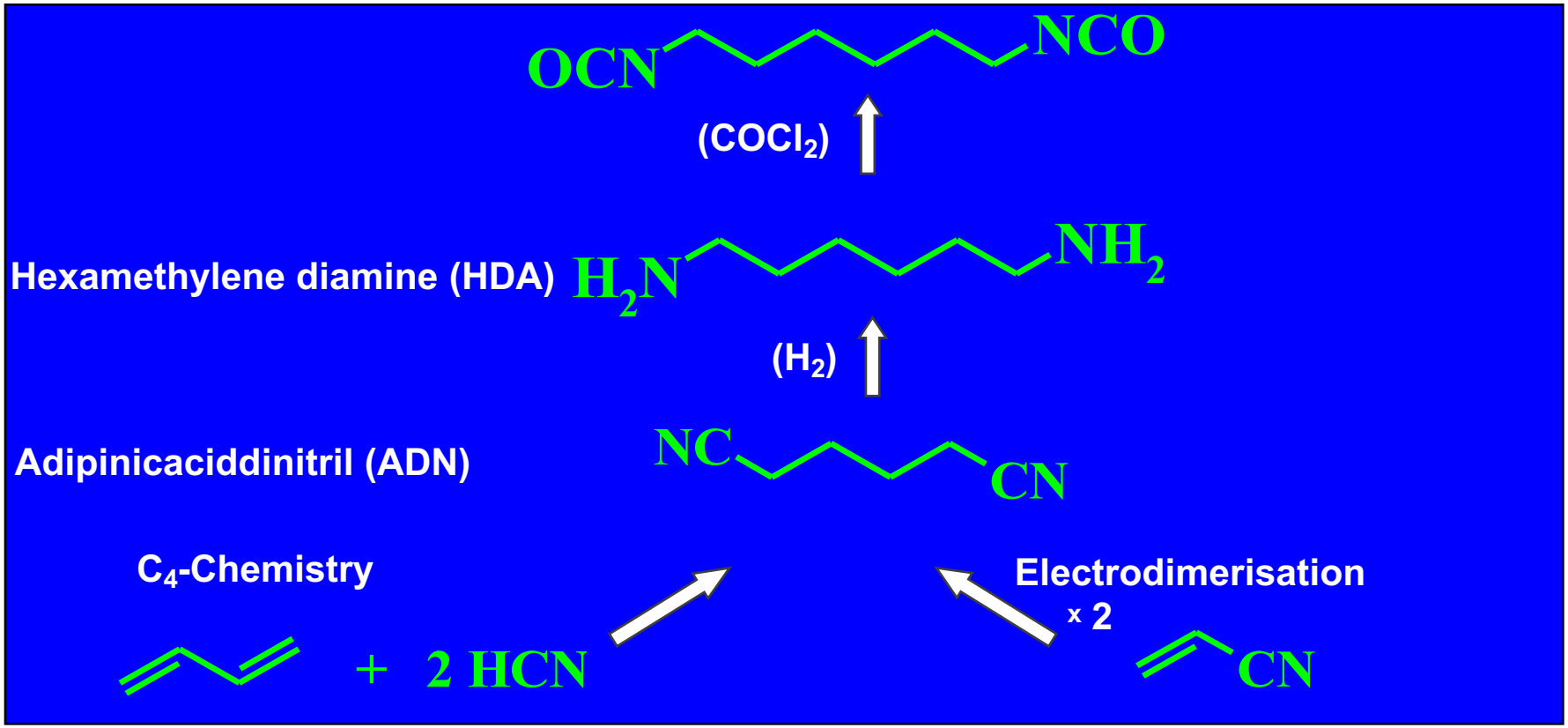


Xylylendiisocyanat (XDI)



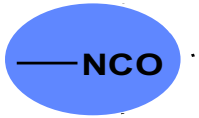
Tetramethyl-
xylylendiisocyanat (TMXDI)

HDI Synthesis

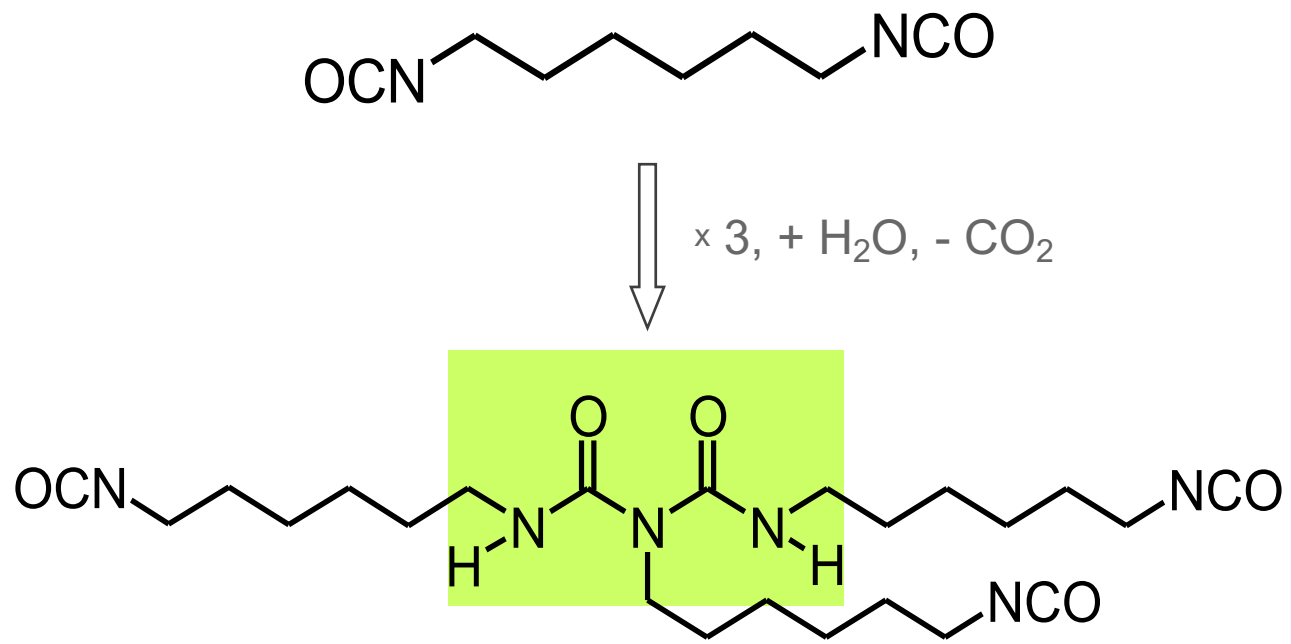


3 steps incl. handling of very toxic raw materials

Main pathways to Polyisocyanates



Aliphatic Polyisocyanates for 2K PUR Coatings (HDI-based)



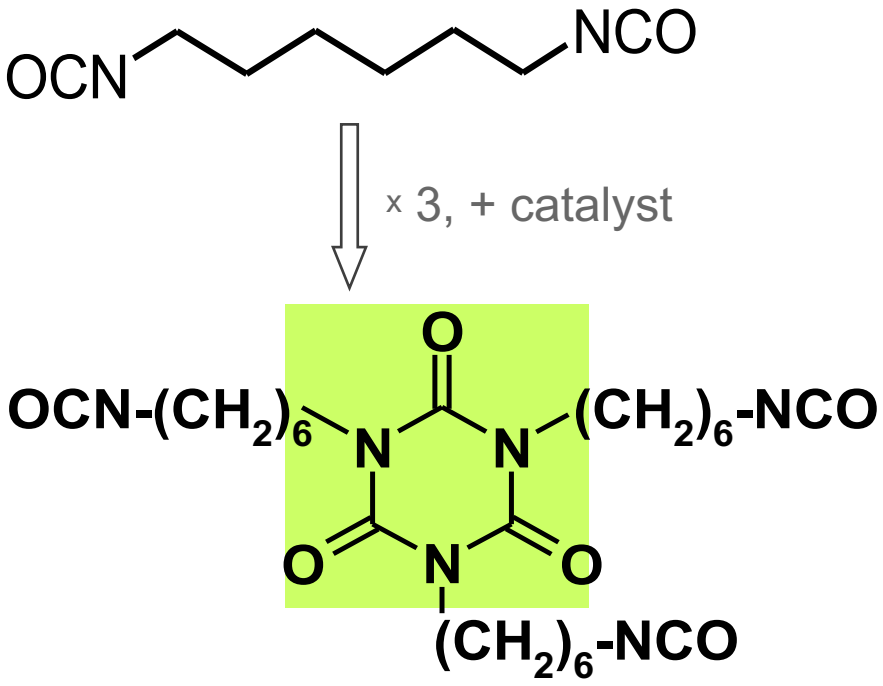
HDI-Biuret

(Desmodur N 100)

***Ideal HDI-Biuret-structure**

Non Yellowing

Aliphatic Polyisocyanates for 2K PUR Coatings (HDI-based)

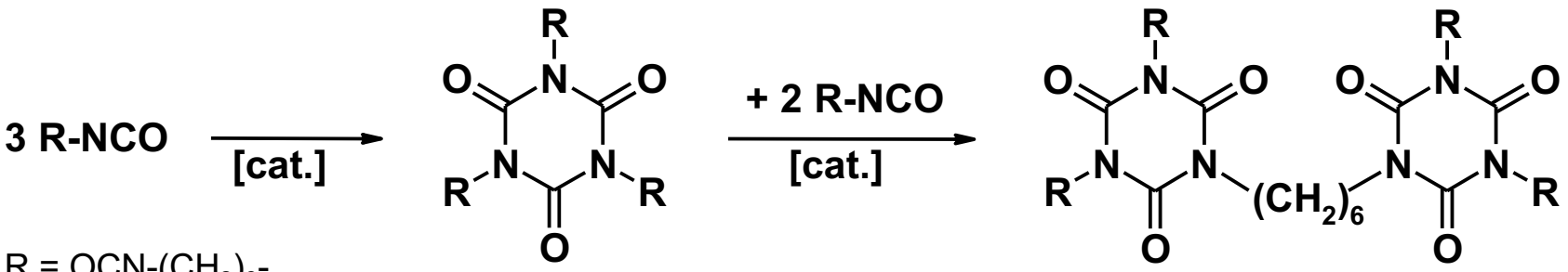


HDI-Trimer

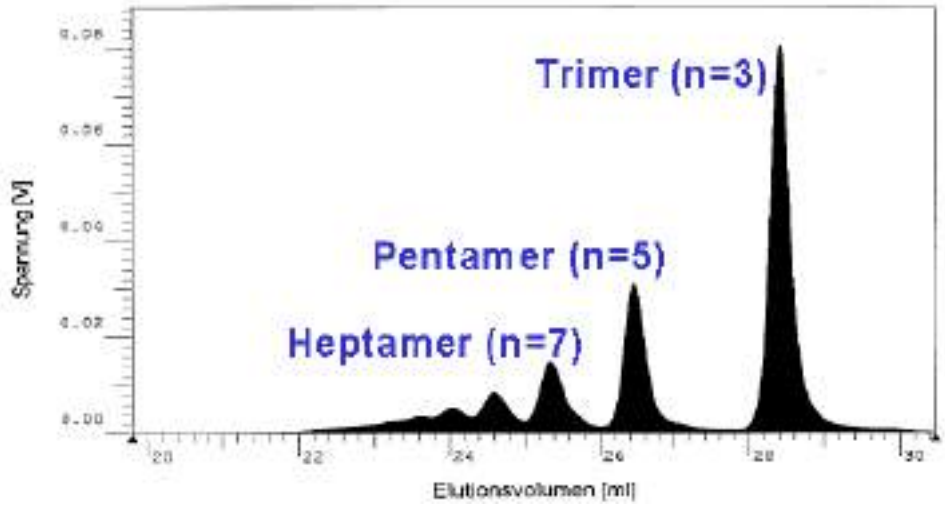
*Ideal HDI-Isocyanurate structure

=> lower viscosity
better monomer stability
vs. technical HDI-Biurets

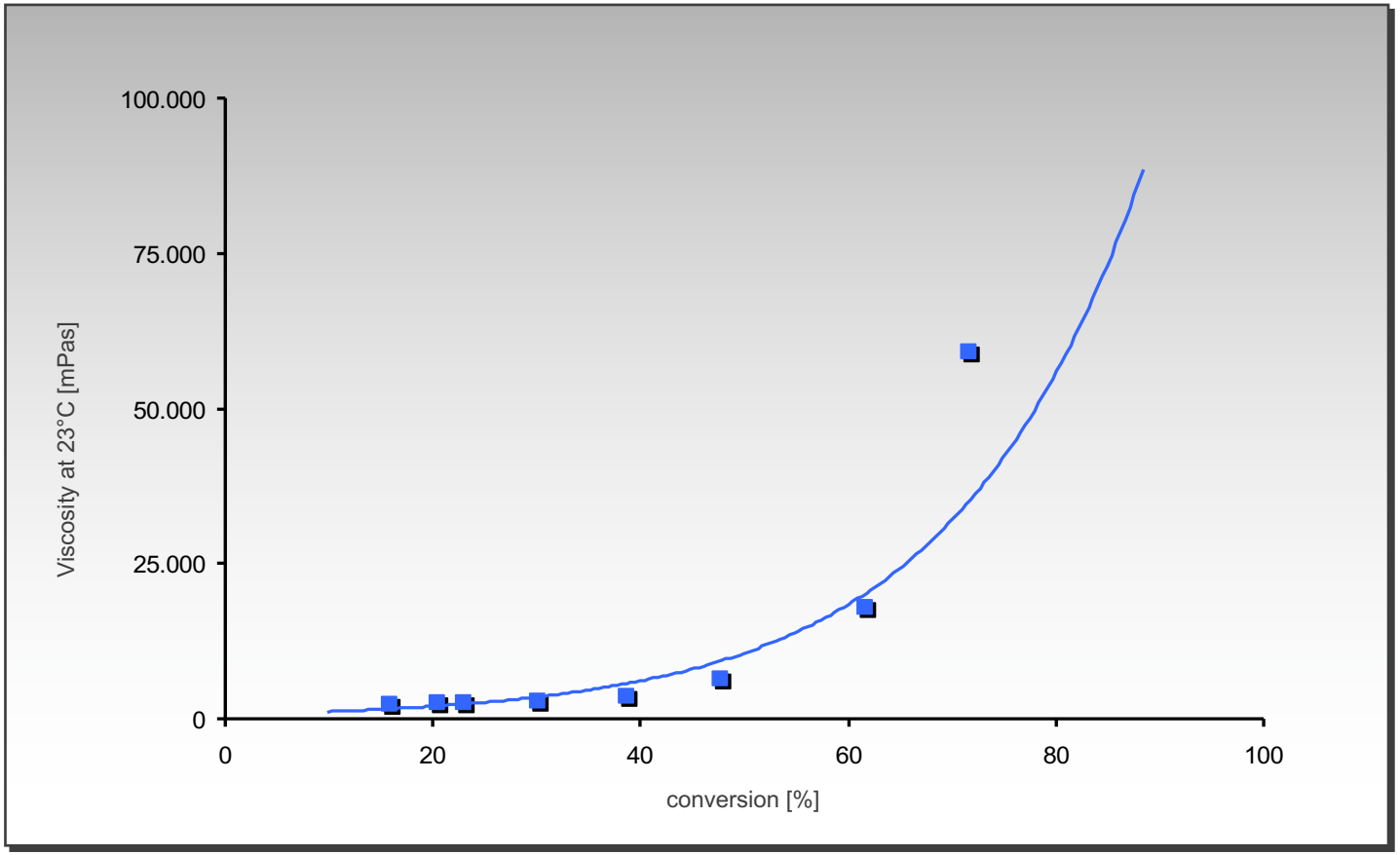
Aliphatic Polyisocyanates for 2K PUR Coatings



n = number of monomeric units incorporated



Manufacturing of polyisocyanates



Aliphatic Polyisocyanates for 2K PUR Coatings

Different oligomer distribution leading to different viscosities and different drying times							
HDI-Trimer	Solid Content	Viscosity [mPas] 23°C	NCO-functionality	Dry Time	Oligomer Distribution		
					n=3	n=5	n>5
standard	100	**3000**	~ 3.5	**+**	**~ 50%**	<20%	<30%
low viscous	100	**1200**	~ 3.1	**o**	**~ 70%**	<20%	<15%

Low viscous Hardener for High Solids and waterborne Systems

Standard PU Hardeners

Biuret **Trimer** **LV-Trimer**

Curing Speed

Decreasing viscosity

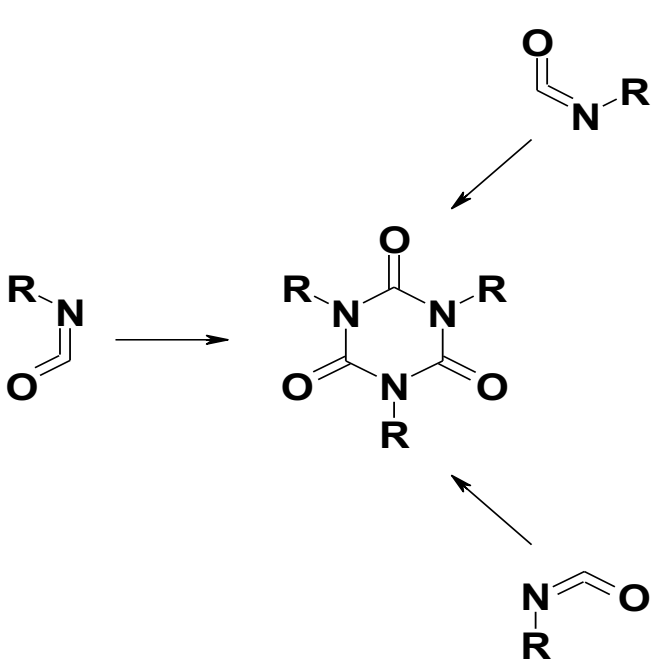
Trends of development:

- Lower viscosity
- Higher functionality / improved properties (p.ex. drying, elasticity)
- Low residual monomer content
- Sustainability
- Hardeners for waterborne 2k-PU-Systems

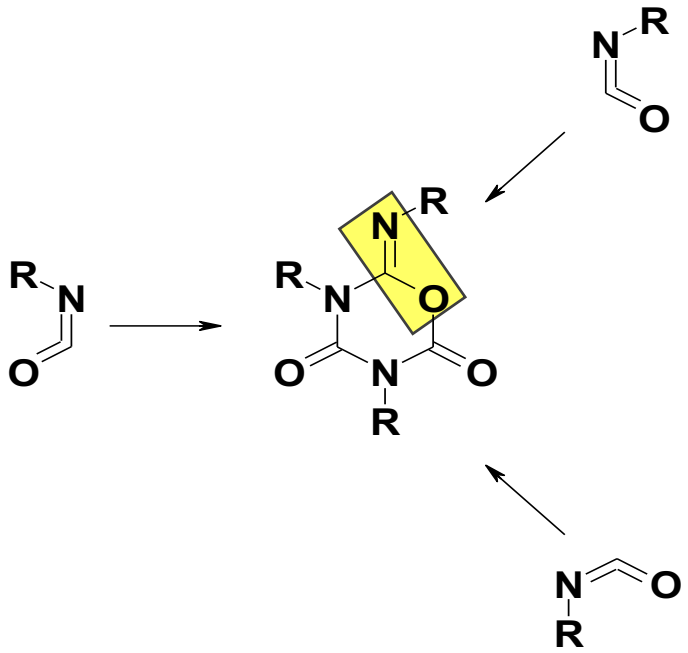
Low viscous crosslinkers

Low viscous Aliphatic Polyisocyanates

Alternative Catalysts lead to Isomeric Trimers:



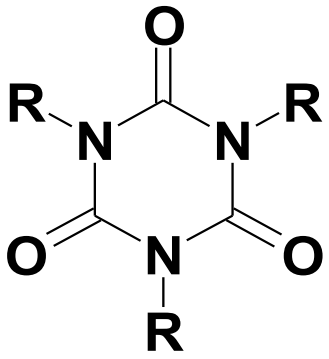
Isocyanurate
(Symmetric Trimer, ST)



Iminooxadiazindione
(Asymmetric Trimer, AST)

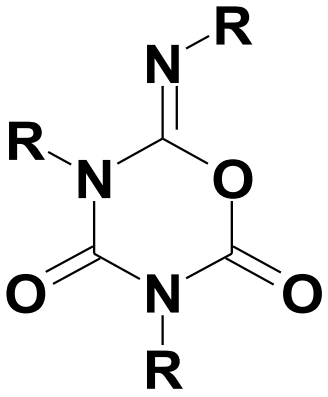
Low viscous Aliphatic Polyisocyanates

Viscosity of the pure Trimers (100% n =3)
(isolated by chromatography)
(model compounds)



Symmetric Trimer (ST)

$R = -(CH_2)_6NCO$



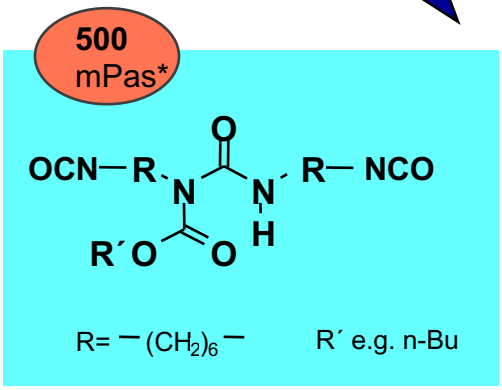
Asymmetric Trimer (AST)

~ 700 mPas

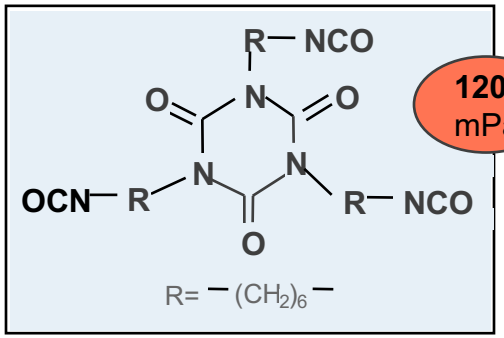
< 400 mPas

Aliphatic Polyisocyanates

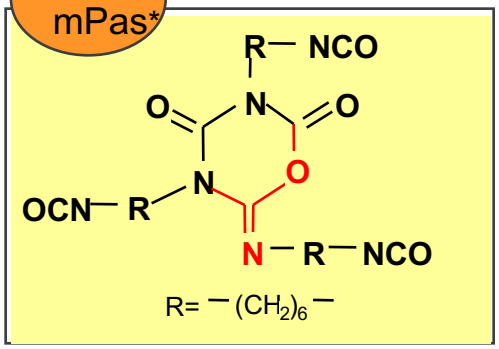
Structures of products with lower viscosity



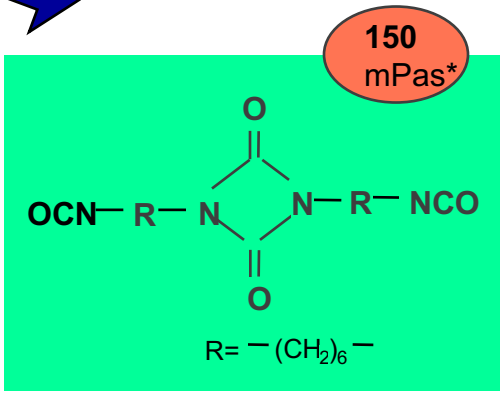
HDI-Allophanate
(Desmodur XP 2860)



Low viscous standard
(Desmodur N 3600)



Low viscous AST
(Desmodur N 3900)



HDI-Uretdione
(Desmodur N 3400*)

*** Ideal structures**

Crosslinkers with high functionality and high elasticity

Aliphatic Polyisocyanates for 2K PUR Coatings

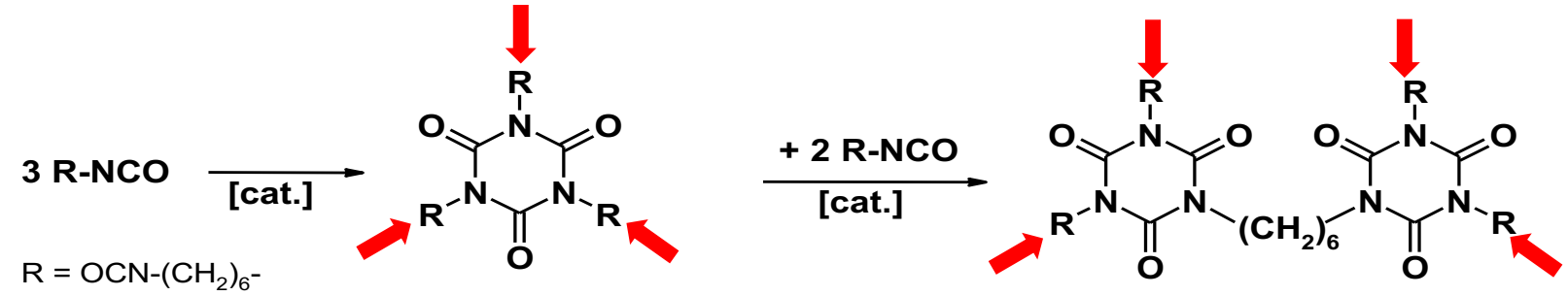
High viscous Hardener for Fast Drying

Different oligomer distribution leading to different viscosities and different drying times							
HDI-Trimer	Solid Content	Viscosity [mPas] 23°C	NCO-functionality	Dry Time	Oligomer Distribution		
					n=3	n=5	n>5
high viscous	100	**15000**	~ 4	**++**	~ 30%	<20%	**~ 50%**
standard	100	**3000**	~ 3.5	**+**	**~ 50%**	<20%	<30%
low viscous	100	**1200**	~ 3.1	**o**	**~ 70%**	<20%	<15%

Low viscous Hardener for High Solids and waterborne Systems

Aliphatic Polyisocyanats for 2K PUR Coatings

Pathways to extremely highfunctional crosslinkers:

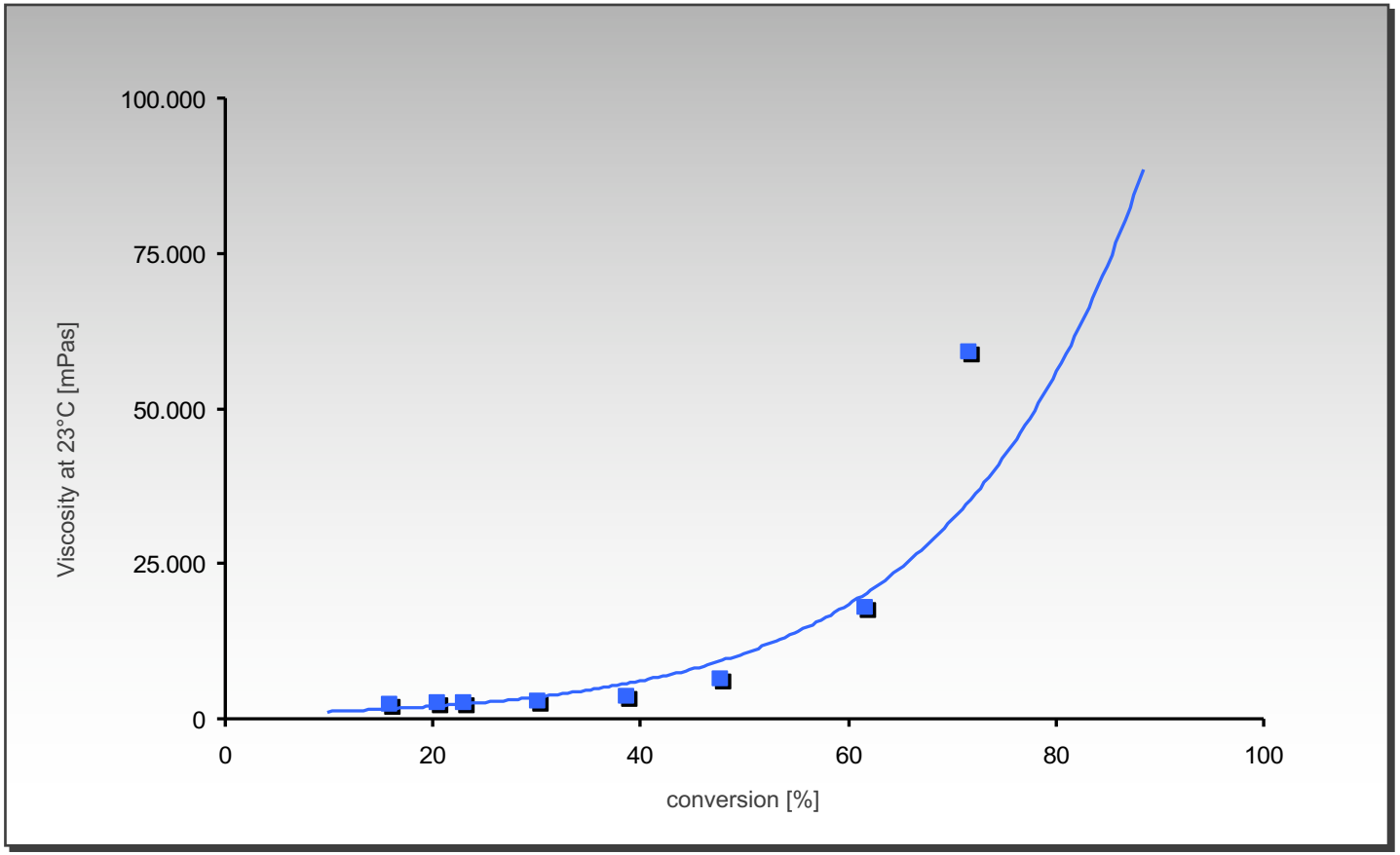


Monomer (n=1) **Trimer (n=3)** **Pentamer (n=5)**

n = number of incorporated monomers

Low residual monomer content

Manufacturing of polyisocyanates

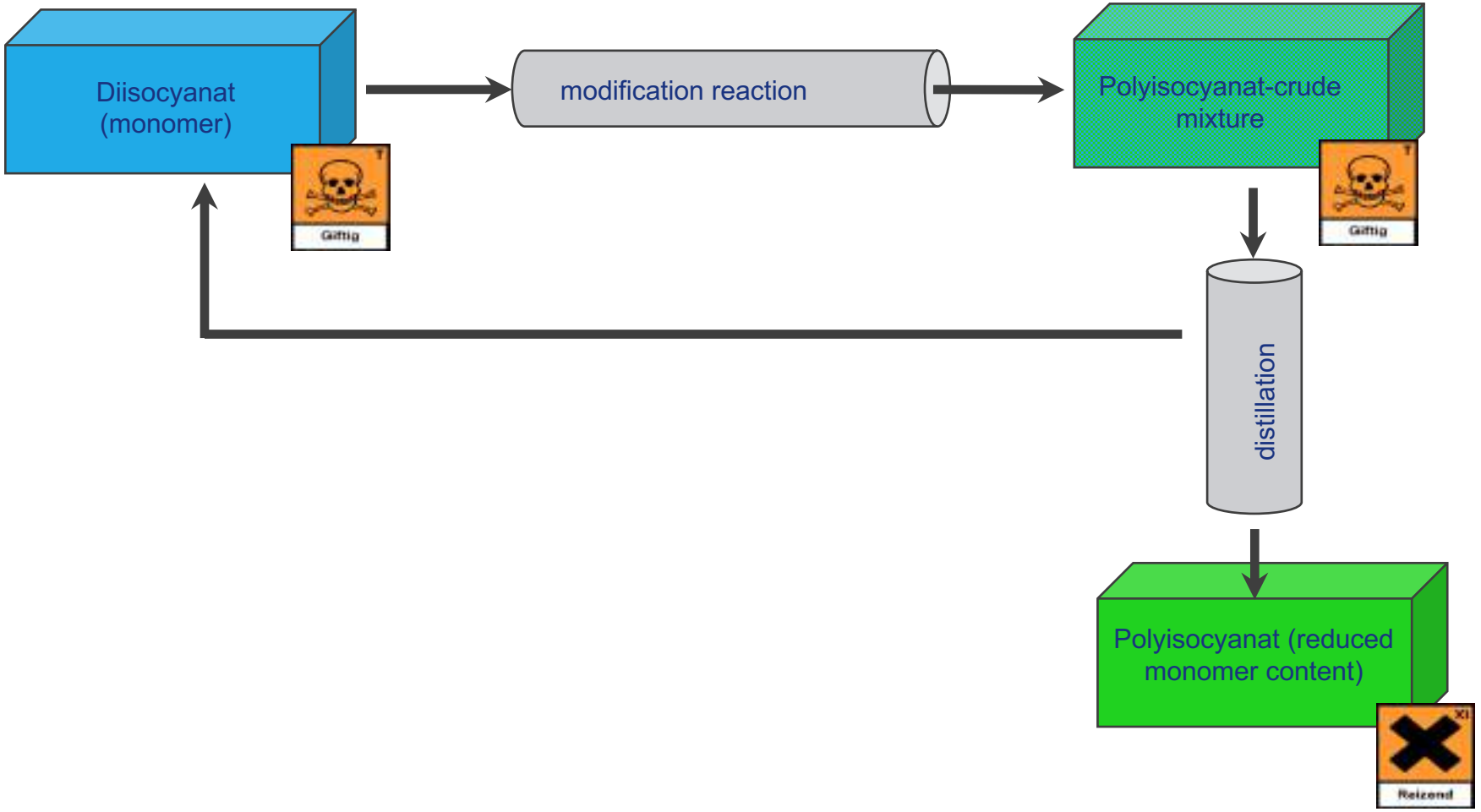


Manufacturing of polyisocyanates – tailoring properties

Increasing conversion / modification means……

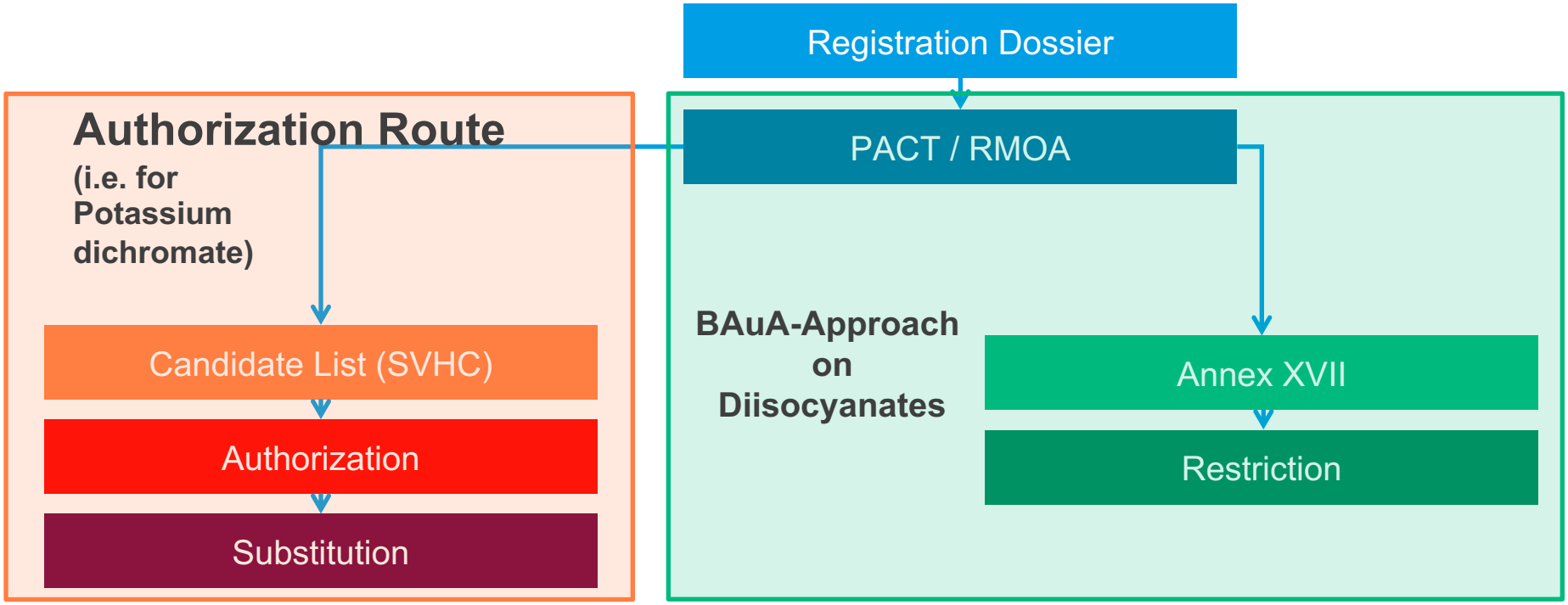
…….. increasing content of higher oligomers
increasing molecular weight
increasing viscosity
increasing average NCO-functionality
increasing crosslinking density
decreasing content of NCO-groups

Scheme manufacturing procedure for polyisocyanates



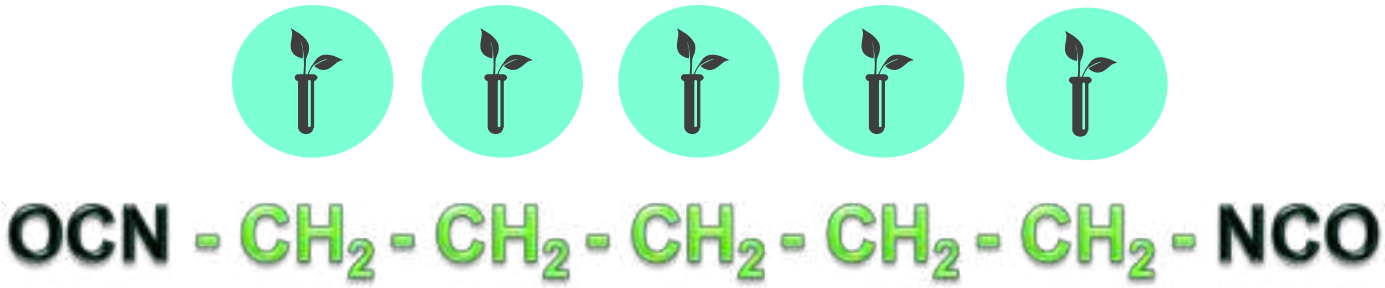
Diisocyanate Restriction is based on REACH

Driven by German Authorities and Supported by Industry Coalition



Sustainability

Pentamethylenediisocyanate (PDI)
A new aliphatic isocyanate with high potential



- The first isocyanate with significant biocontent: **71% renewable carbon***
- The corresponding derivatives are similar to established HDI based products
- The first product: Desmodur® eco N 7300 is a near drop-in to Desmodur ® N 3300

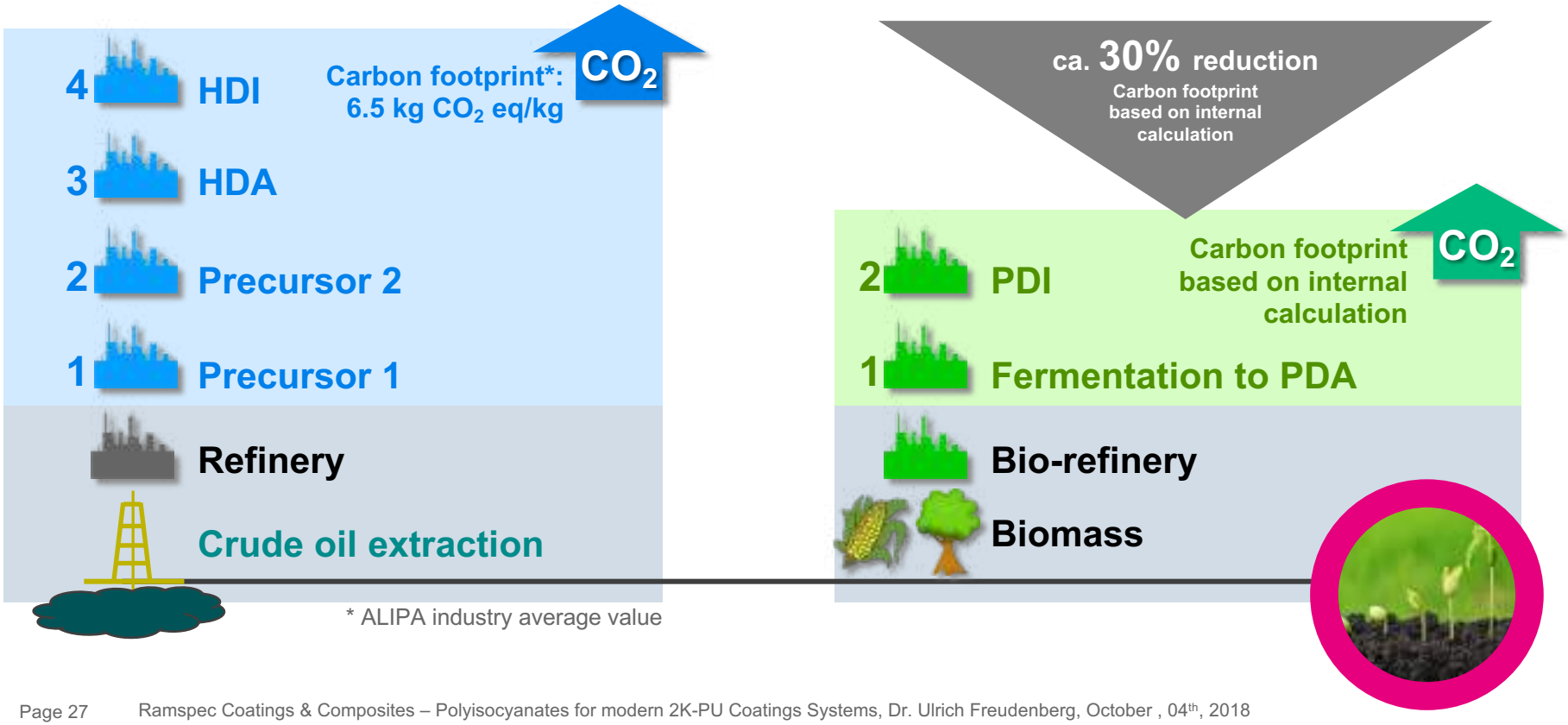
* Confirmed by radiocarbon method ^{14}C measurement according to ASTM-D6866 standard

Desmodur® eco N 7300

Significantly improved carbon footprint

- **Bio-based** and significantly **improved carbon footprint** cradle-to-gate in comparison to standard products
(internal assessment done, external certification in process)
- Bio-based process with significant improvement on **energy efficiency**

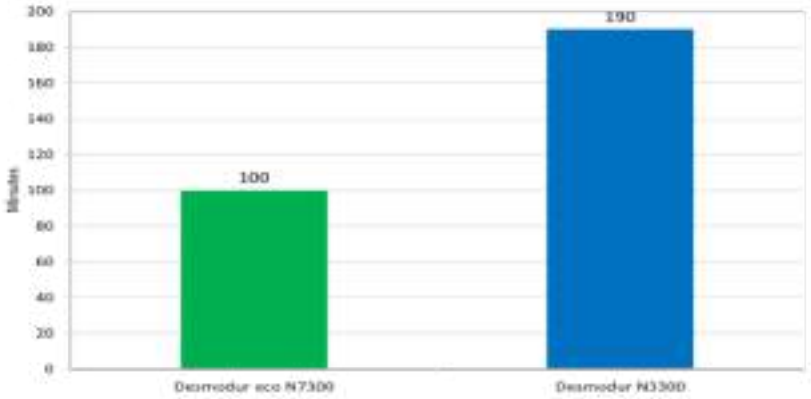
4 step petro-based synthesis vs. **2 step bio-based synthesis**



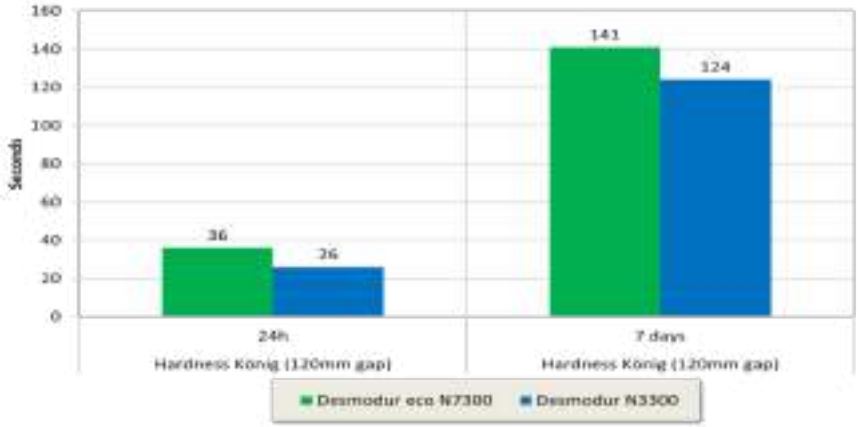
* ALIPA industry average value

Desmodur eco N 7300 versus Desmodur N 3300 in a 2K clear coat formulation for wood

Drying time (T1)



Hardness König



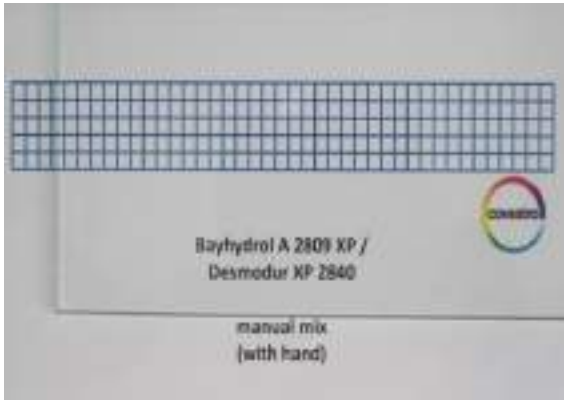
2K formulation based on Desmophen PL 817 and different hardeners at NCO/OH=1

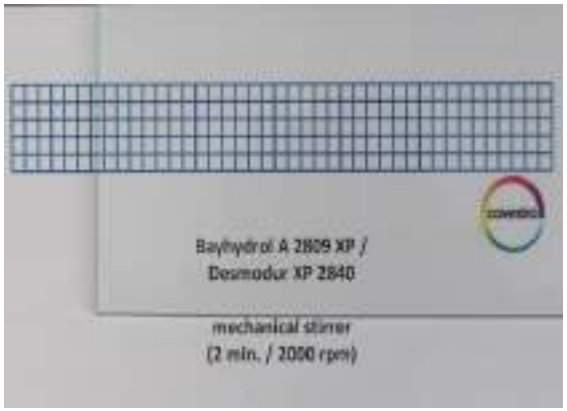
- Advantages of Desmodur eco N 7300 in the early acetone resistance (24h)
- Comparable performance of Desmodur eco N 7300 and N 3300 regarding:
  - Scratch resistance
  - Chemical resistance
  - Gloss

Sirca presented Desmodur eco N based waterborne coating on **bench installation** at Museo Diocesano (Milan)

Hydrophilized Polyisocyanates

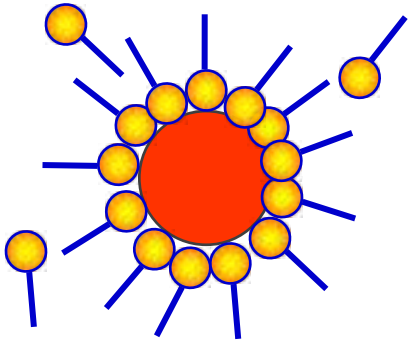
Emulsification of low viscous polyisocyanates in Bayhydrol A 2809



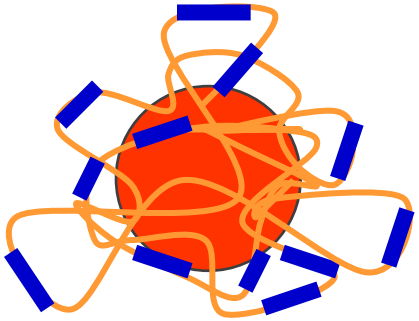


Incorporation of medium viscous polyisocyanates into aqueous dispersions at low shear is critical

Emulsifiers for Polyisocyanates



External Emulsifier



Internal Emulsifier

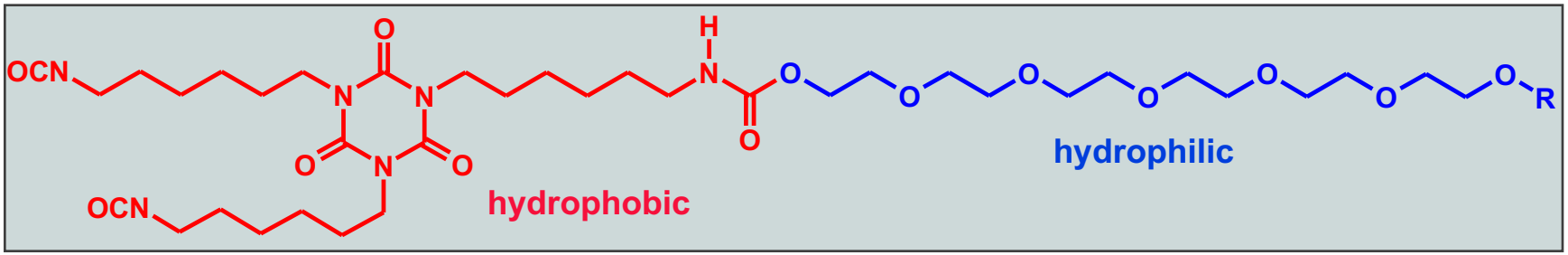
hydrophobic
lipophilic

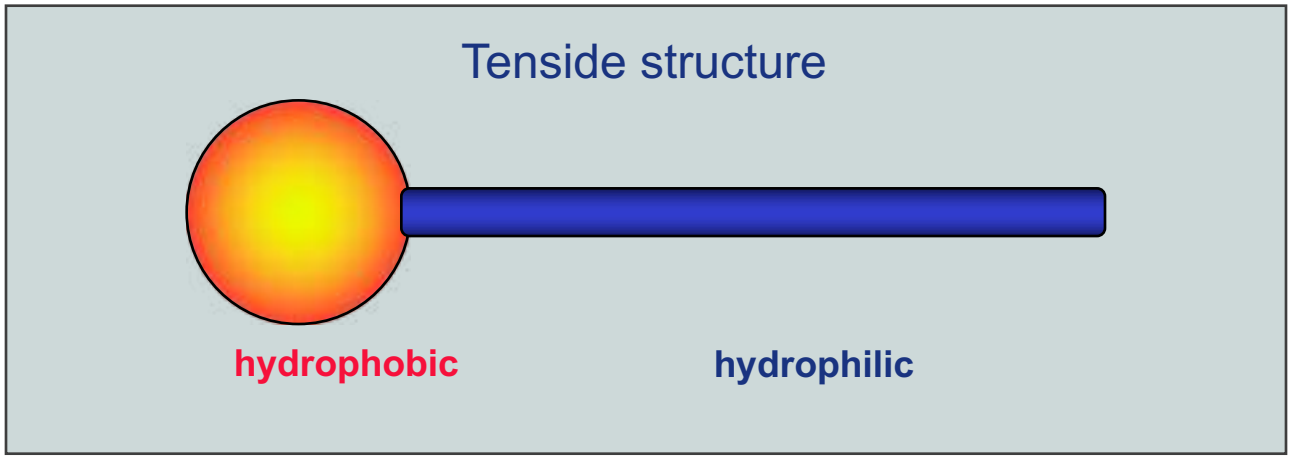
hydrophilic

... have to be:

- non-reactive with Isocyanates (NCO consumption, catalysis)
- free of water
- soluble in isocyanate and coatings film
- reactive with resins
  ⇨ internal emulsifiers / incorporation into PUR network

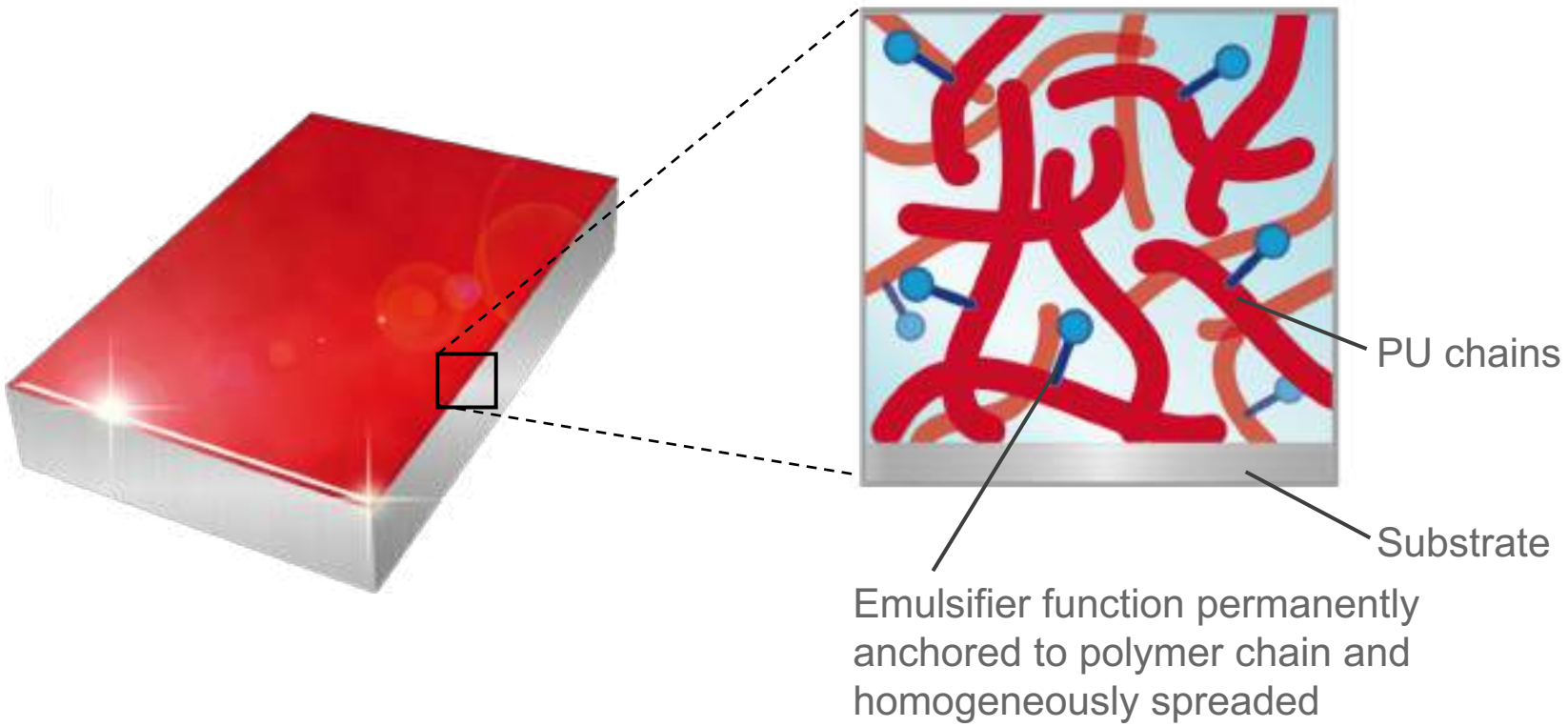
Polyether modified trimer – 1st generation type



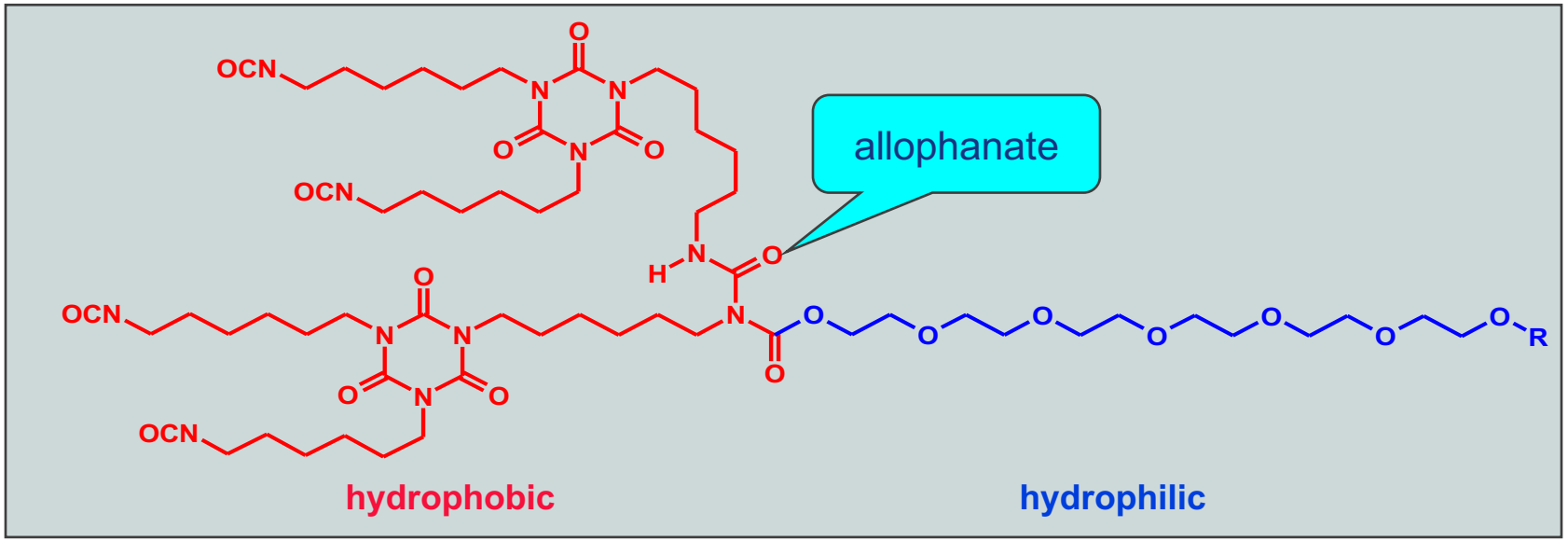


- HDI – based types / IPDI – based types
- Disadvantage: - lower functionality
  - high hydrophilicity

Waterborne PU coating with hydrophilized hardeners



Polyether modified allophanate/trimer – 2nd generation type



- lower hydrophilicity
- higher functionality
- ➔ better resistance
- HDI – based types / IPDI – based types

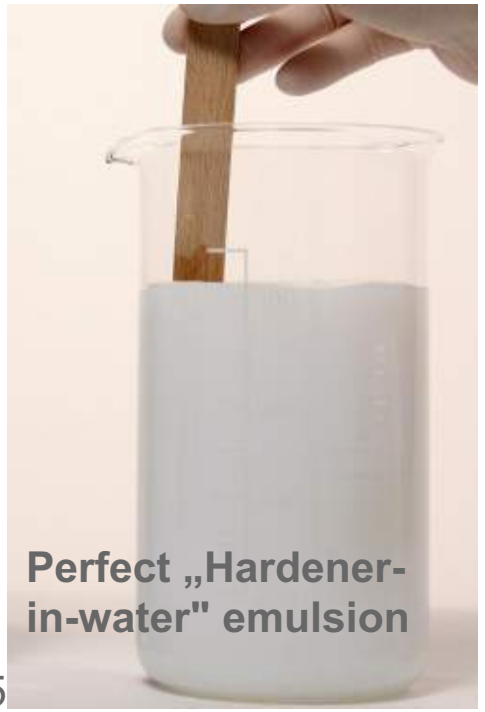
Waterborne PU coating with hydrophilized hardeners – easy to mix

Aqueous phase

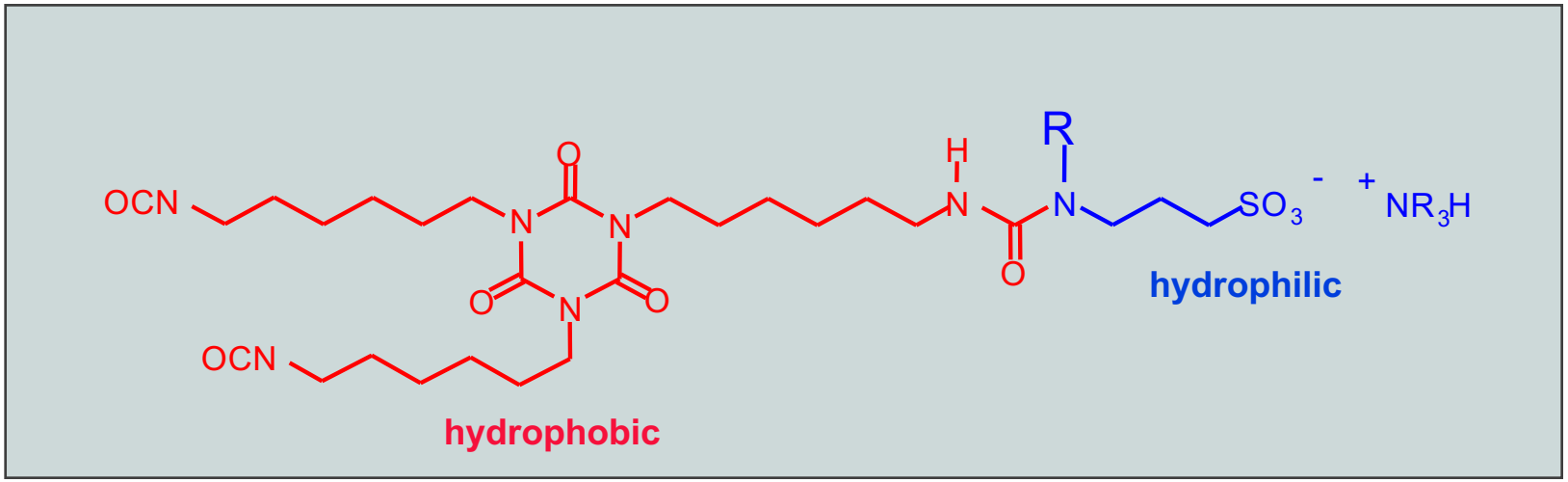
Easy stirring

Spontaneous emulsification

Hydrophilized HDI-hardener Bayhydur® 305 (organic phase)

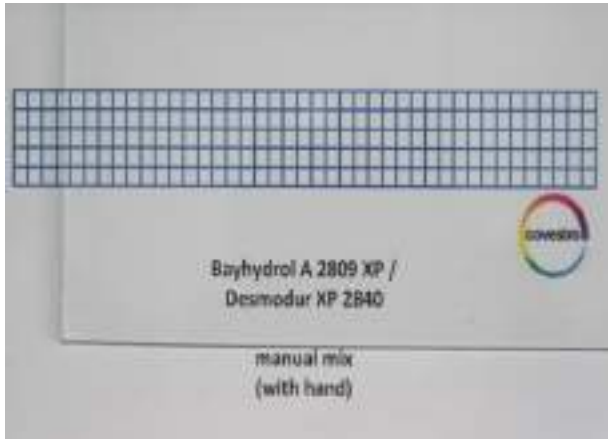


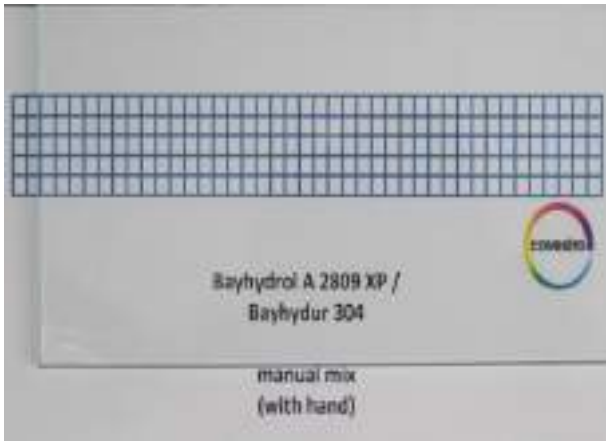
Sulfonic acid modified trimer – 3rd generation type

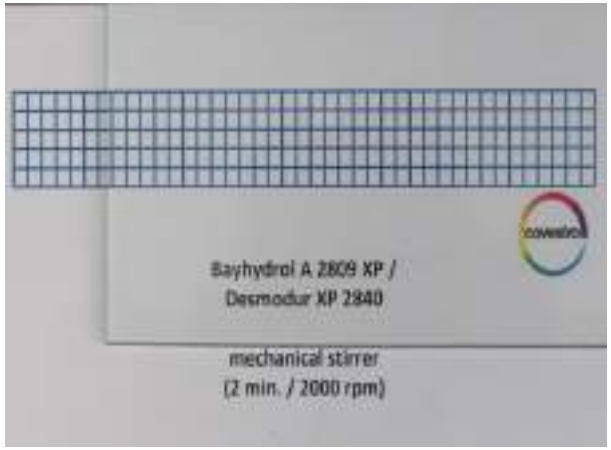


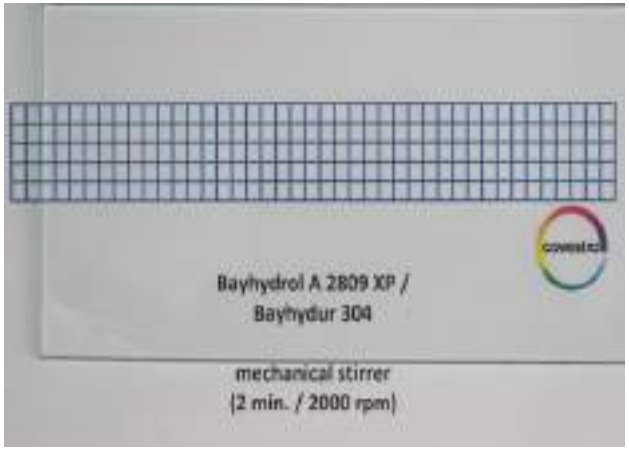
- significantly increased resistance
- HDI – based types

Emulsification of different Polyisocyanates in Bayhydrol A 2809



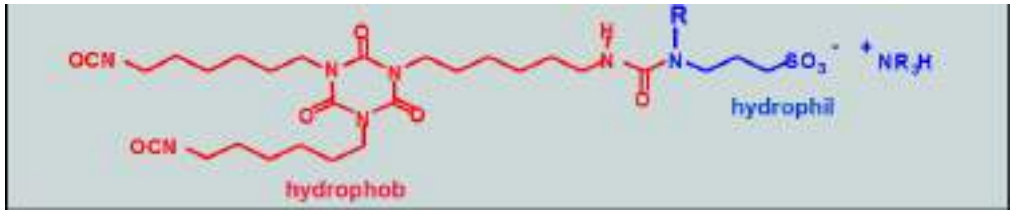






Incorporation of polyisocyanates into aqueous dispersions at low shear is possible through the use of hydrophilic types

Waterborne 2K-PUR-Coatings
…..on the way to even more sustainability



- **HDI / IPDI – mixed products:** **Tailored balance of hardeners and optimal cosolvent enable formulations fulfilling indoor air emission regulations (AgBB)**

- **Use of fatty acid modified polyethers:** **Increase of Bio-content of polyether-modified crosslinkers Building block for low viscous allophanates**

- **PDI – based, hydrophilized hardener:** **Bio-content of crosslinker > 60 %**

Bayhydur® eco 701-90

First biobased hydrophillic polyurethane crosslinker

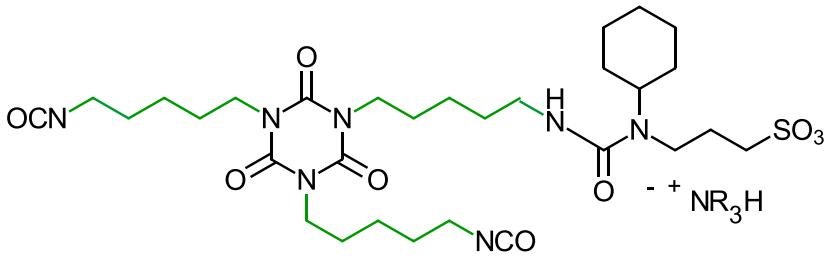
Anionically hydrophilized polyisocyanate from biobased PDI for 2K waterborne polyurethane wood coatings with increased renewable content

	Approx. value
Supply form	90 % in PGDA
NCO	18%
Viscosity	5000 mPa·s
Biobased content*	68 %

* Confirmed by radiocarbon method ^{14}C measurement according to ASTM-D6866 standard

Product highlights:

- Good compatibility with acrylic and polyurethane dispersions
- Easy to mix
- Excellent chemical resistance
- Ready to use possible
- Not flammable
- Low odor



Bayhydur® eco 701-90

2K waterbased PU clear furniture coating

Clear coating, glossy, based on secondary acrylate polyol (Bayhydrol® A 2651)
crosslinking ratio 150%; solid content 40%

Coating based on different hardeners		Bayhydur® eco 701-90	Bayhydur® XP 2655
Hardener solution		**Diluted to 80% in PGDA**	**Diluted to 80% in PGDA**
Mixing process		**manual**	**manual**
VOC content in coating		68 g/l	68 g/l
Bio-based content in coating	on solid	29 %	6 %
Drying time at RT	T1	40 min	60 min
120 µm wet on glass	T4	6.5 h	8.25 h
Hardness [König, s]	1 d, RT	40	45
120 µm wet on glass	16 h, 50°C	110	110
Gloss (GU)	20°	84	84
120 µm wet on black, after 7 days at RT	60°	90	90
	haze	12	14
Chemical resistance			
Water	16 h	5	5
Ethanol 48%	1 h	5	5
Coffee	16 h	5	5
Red wine	6 h	5	5

Bayhydur® eco 701-90 cures faster than the corresponding HDI hydrophilic hardener

covestro

"A new coating has to bring quality and style, but if it creates additional value for consumers as this renewable coating does, this certainly is a great step forward to a more sustainable living"

Matteo Rivolta, CEO RiFRA

"We have been developing bio-based systems for some years now, but most raw materials could not meet the quality level our customers require. Bayhydur® eco boosted the hardness and chemical resistance of the renewable system and contributed to create an outstanding coating"

Maurizio Durante, Vice-President Sirca


Lunch Break ?