



Polyisocyanates for modern 2K-PU Coatings Systems

“Ramspec “ – Coatings & Composites

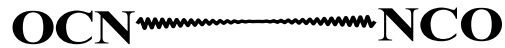
Dr. Ulrich Freudenberg, October, 04th, 2018



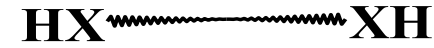
Agenda

- **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**

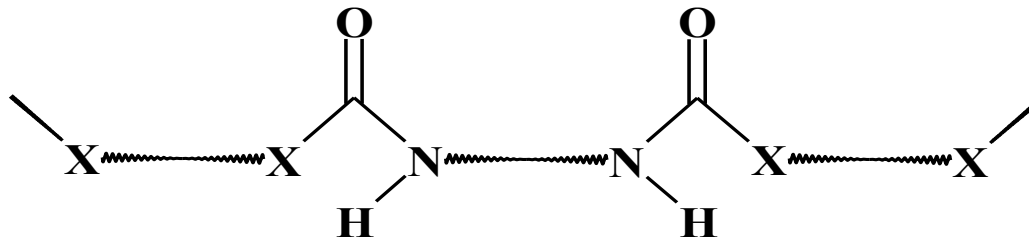
Formation of Polyurethanes



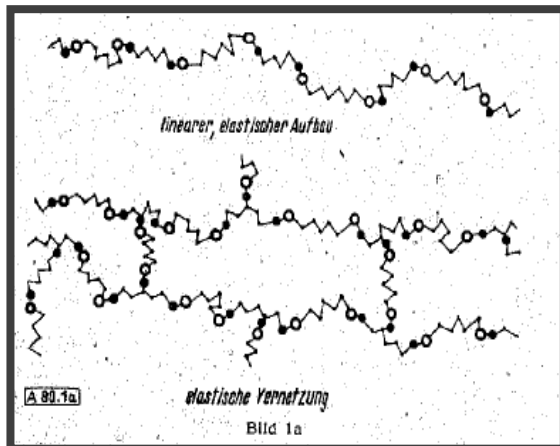
Diisocyanate



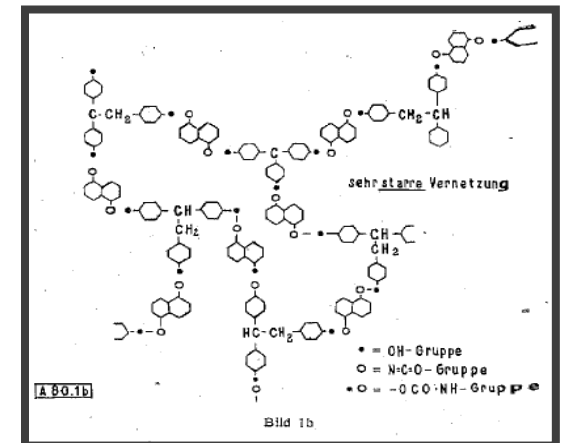
Diol, Diamine,
Aminoalkohol
 $\text{X} = \text{O}, \text{NR}$



Polyurethane ($\text{X} = \text{O}$)
Polyurea ($\text{X} = \text{NR}$)



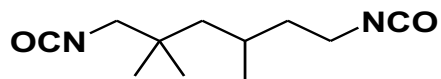
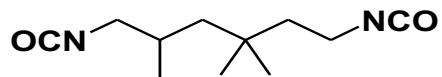
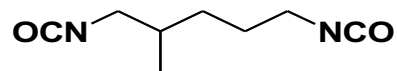
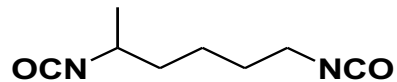
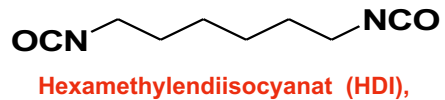
Otto Bayer „Das Di-Isocyanat-Polyadditionsverfahren
(Polyurethane)“
Angewandte Chemie, 1947, **59**, 257–288.



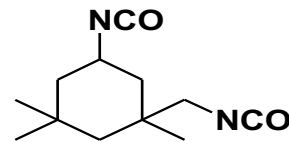
Aliphatic Diisocyanates



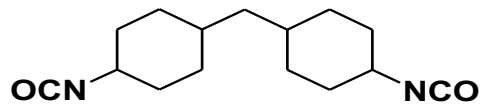
linear aliphatic



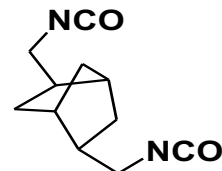
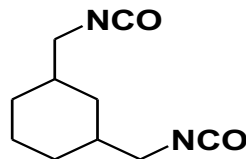
cyclo-aliphatic



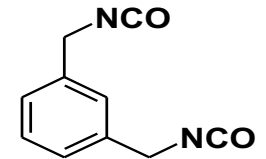
Isophorondiisocyanat (IPDI),



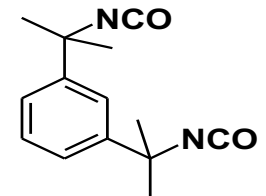
4,4'-Diisocyanatodicyclohexylmethan (H₁₂-MDI),



araliphatic

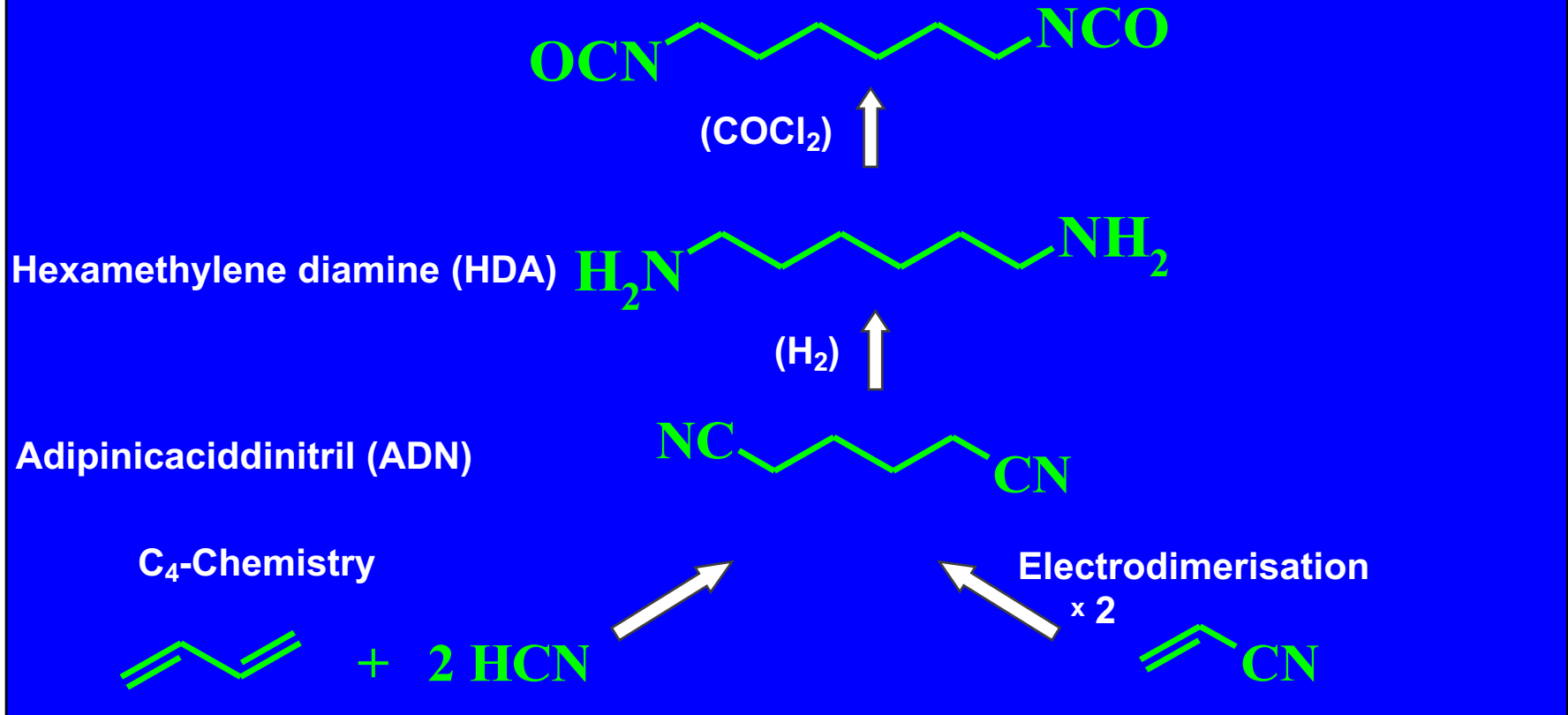


Xylylendiisocyanat (XDI)



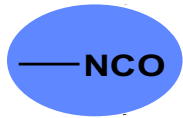
Tetramethyl-xylylendiisocyanat (TMXDI)

HDI Synthesis

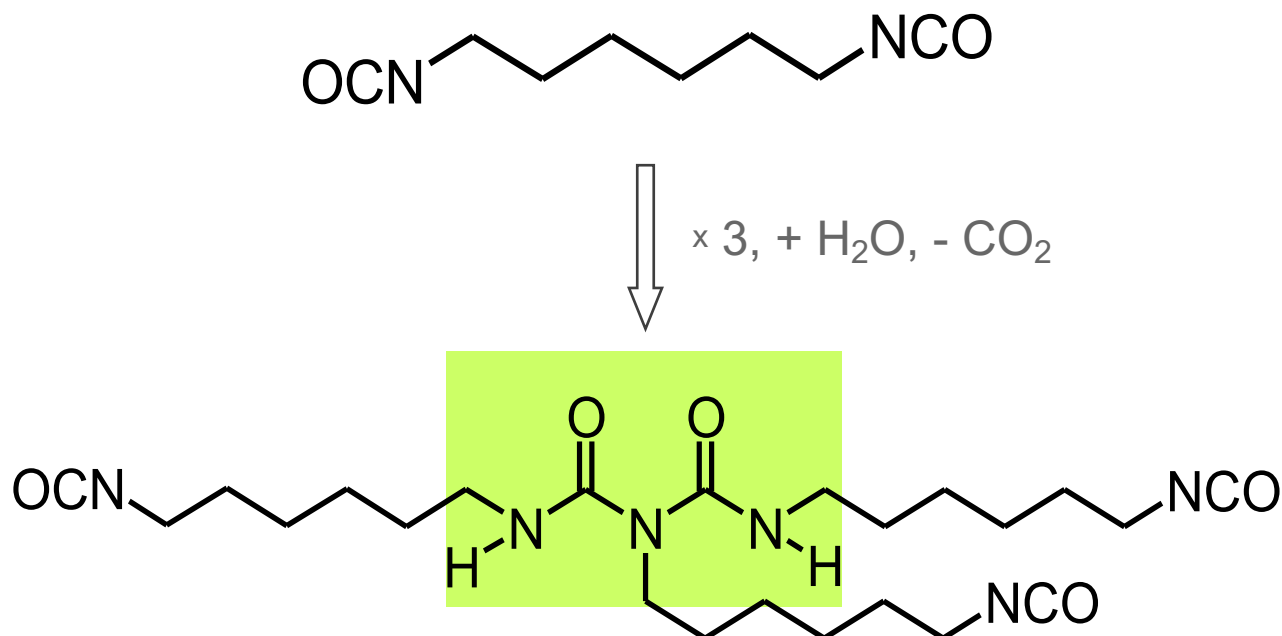


3 steps incl. handling of very toxic raw materials

Main pathways to Polyisocyanates



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



HDI-Biuret

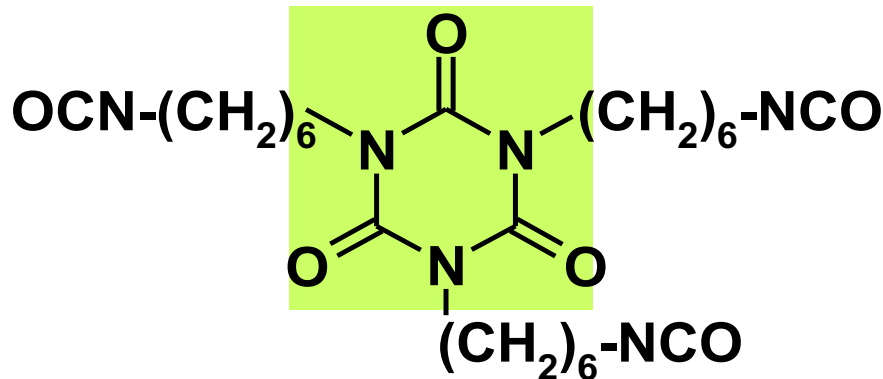
(Desmodur N 100)

***Ideal HDI-Biuret-structure**

Non Yellowing



x 3, + catalyst



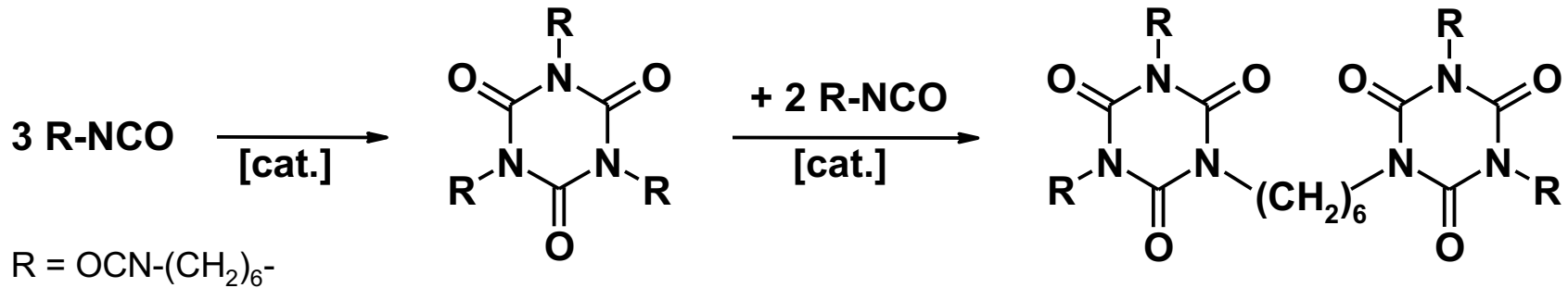
HDI-Trimer

***Ideal HDI-
Isocyanurate
structure**

 $\Rightarrow$

lower viscosity
better monomer stability
vs. technical HDI-Biurets

Aliphatic Polyisocyanates for 2K PUR Coatings

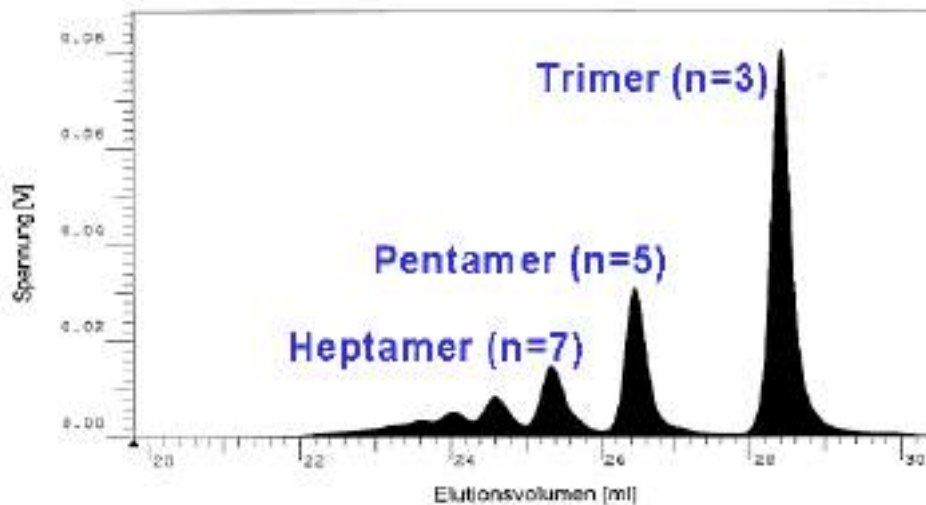


Monomer (n=1)

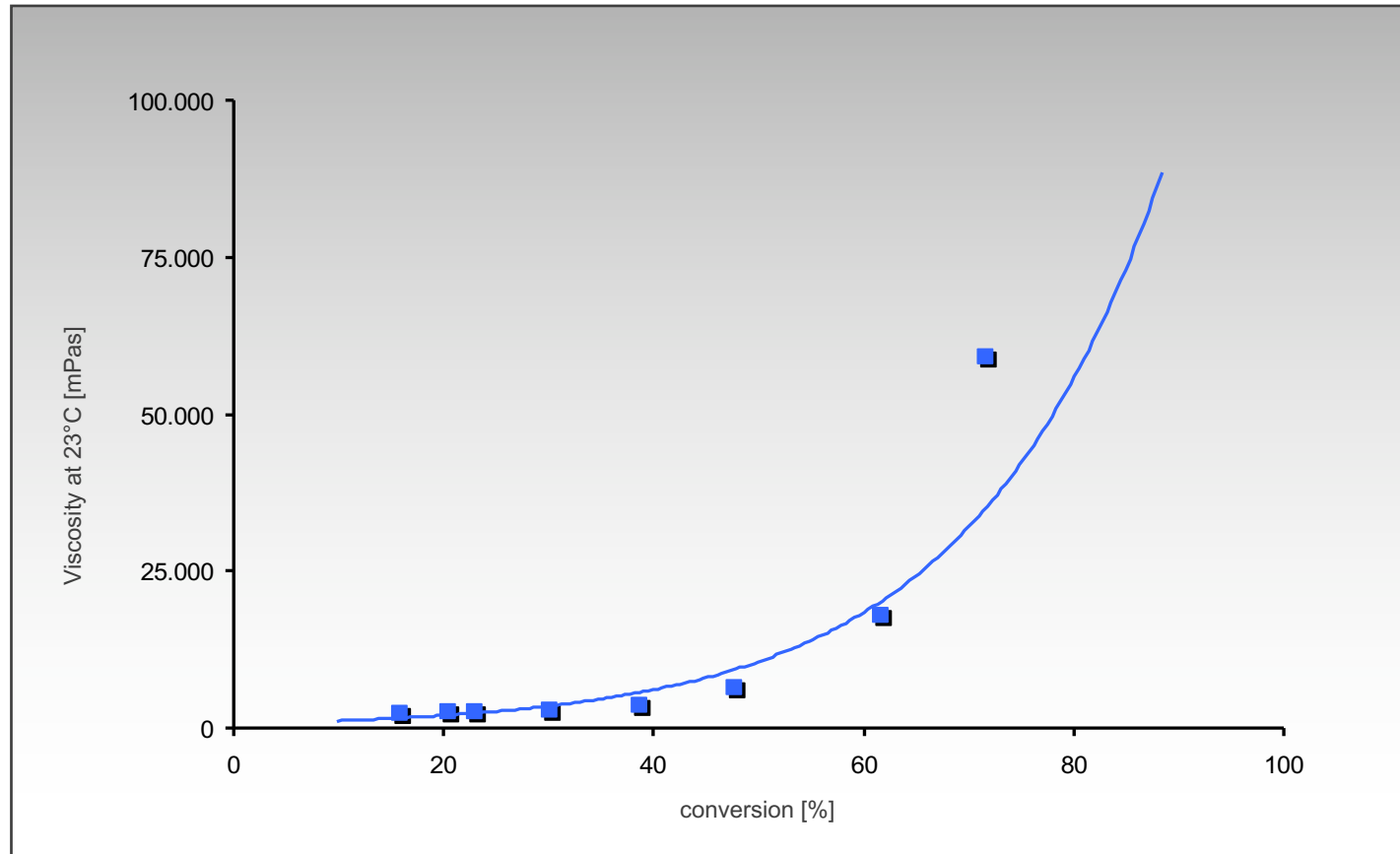
Trimer (n=3)

Pentamer (n=5)

n = number of monomeric units incorporated



Manufacturing of polyisocyanates

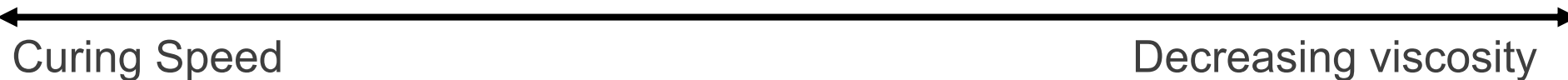


Aliphatic Polyisocyanates for 2K PUR Coatings



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	○	~ 70%	<20%	<15%

Low viscous Hardener for High Solids and waterborne Systems



Trends of development:

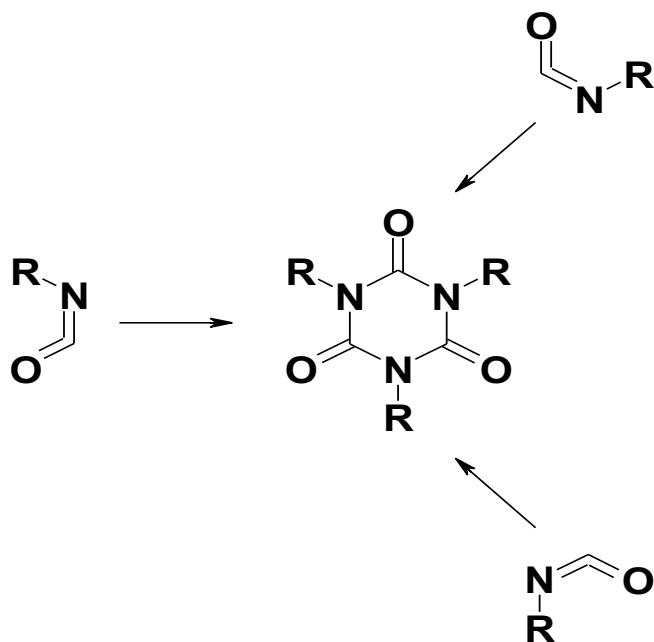
- Lower viscosity
- Higher functionality / improved properties (p.ex. drying, elasticity)
- Low residual monomer content
- Sustainability
- Hardeners for waterborne 2k-PU-Systems

Low viscous crosslinkers

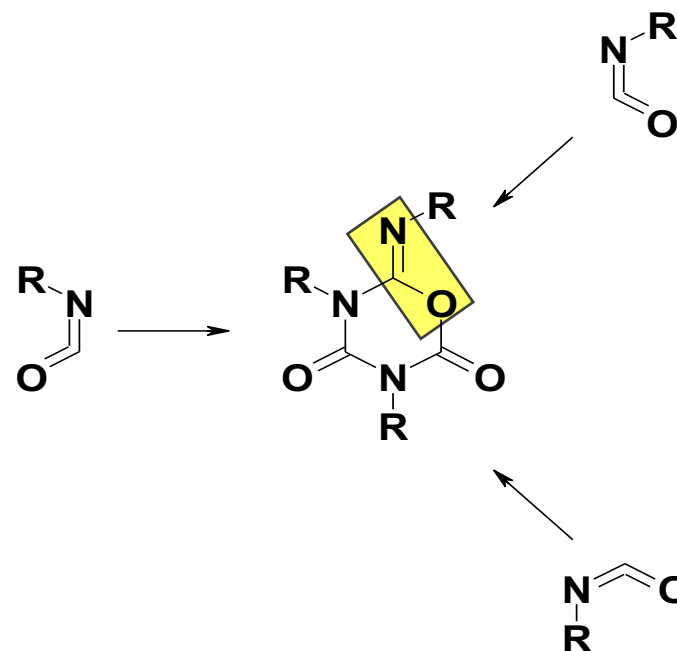
Low viscous Aliphatic Polyisocyanates



Alternative Catalysts lead to Isomeric Trimers:



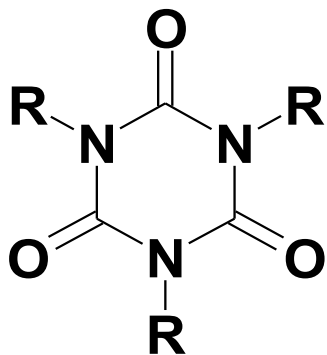
Isocyanurate
(Symmetric Trimer, ST)



Iminooxadiazindione
(**Asymmetric** Trimer, AST)

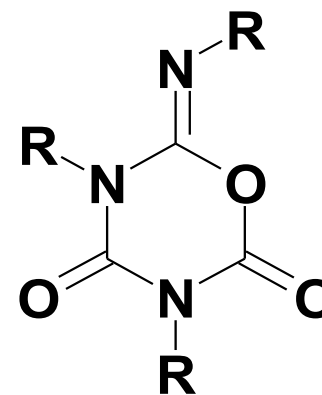
Low viscous Aliphatic Polyisocyanates

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



Symmetric Trimer (ST)

~ 700 mPas



Asymmetric Trimer (AST)

< 400 mPas

Crosslinkers with high functionality and high elasticity

Aliphatic Polyisocyanates for 2K PUR Coatings



High viscous Hardener for Fast Drying

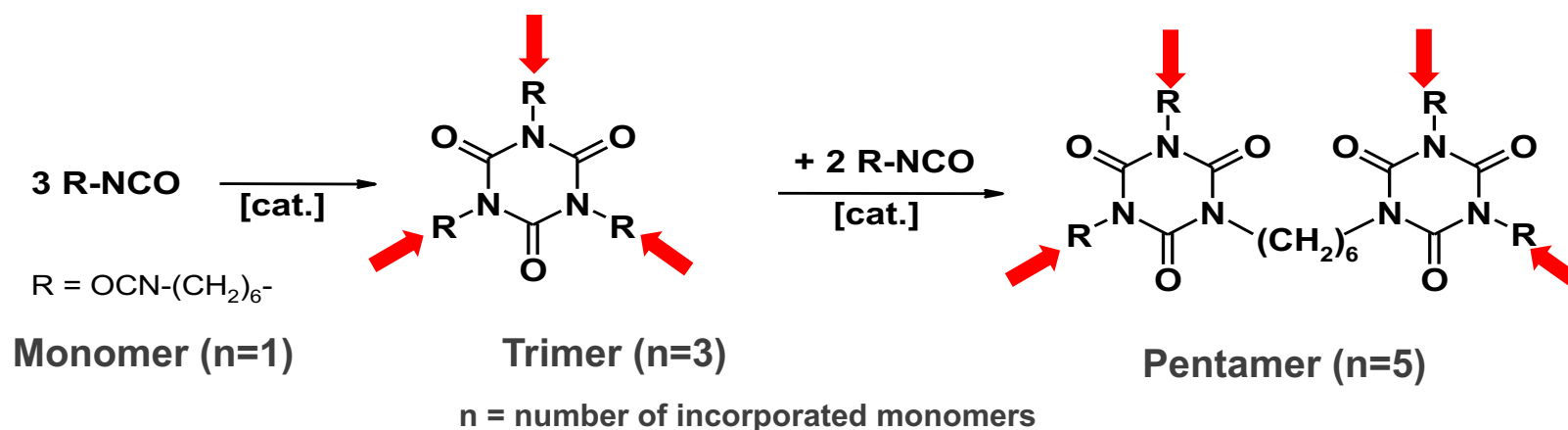
Different oligomer distribution leading to different viscosities and different drying times							
HDI-Trimer	Solid Content	Viscosity [mPas] 23°C	NCO-functionality	Dry Time	Oligomer Distribution		
					n=3	n=5	n>5
high viscous	100	15000	~ 4	++	~ 30%	<20%	~ 50%
standard	100	3000	~ 3.5	+	~ 50%	<20%	<30%
low viscous	100	1200	~ 3.1	0	~ 70%	<20%	<15%

Low viscous Hardener for High Solids and waterborne Systems

Aliphatic Polyisocyanates for 2K PUR Coatings

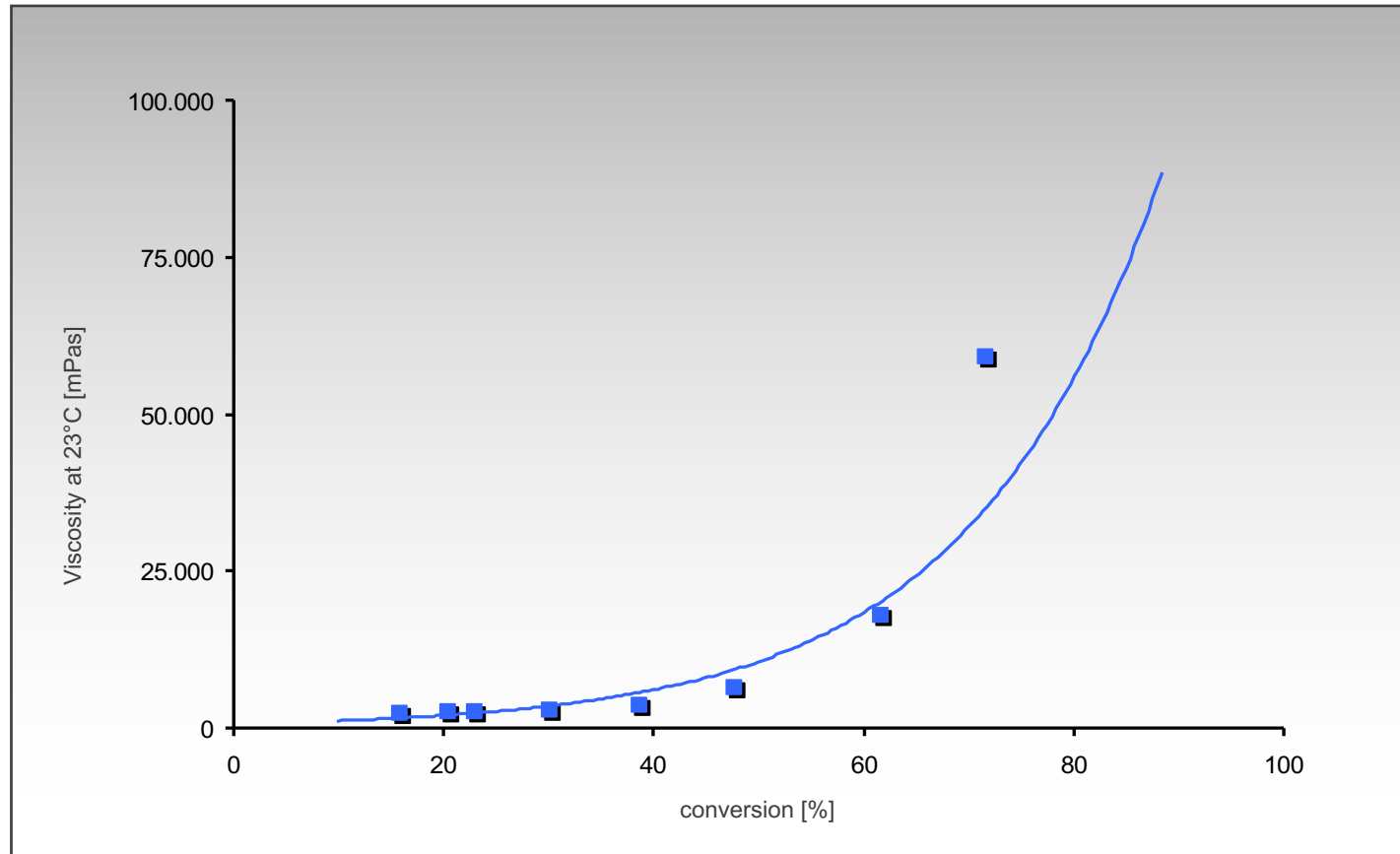


Pathways to extremely highfunctional crosslinkers:



Low residual monomer content

Manufacturing of polyisocyanates



Manufacturing of polyisocyanates – tailoring properties

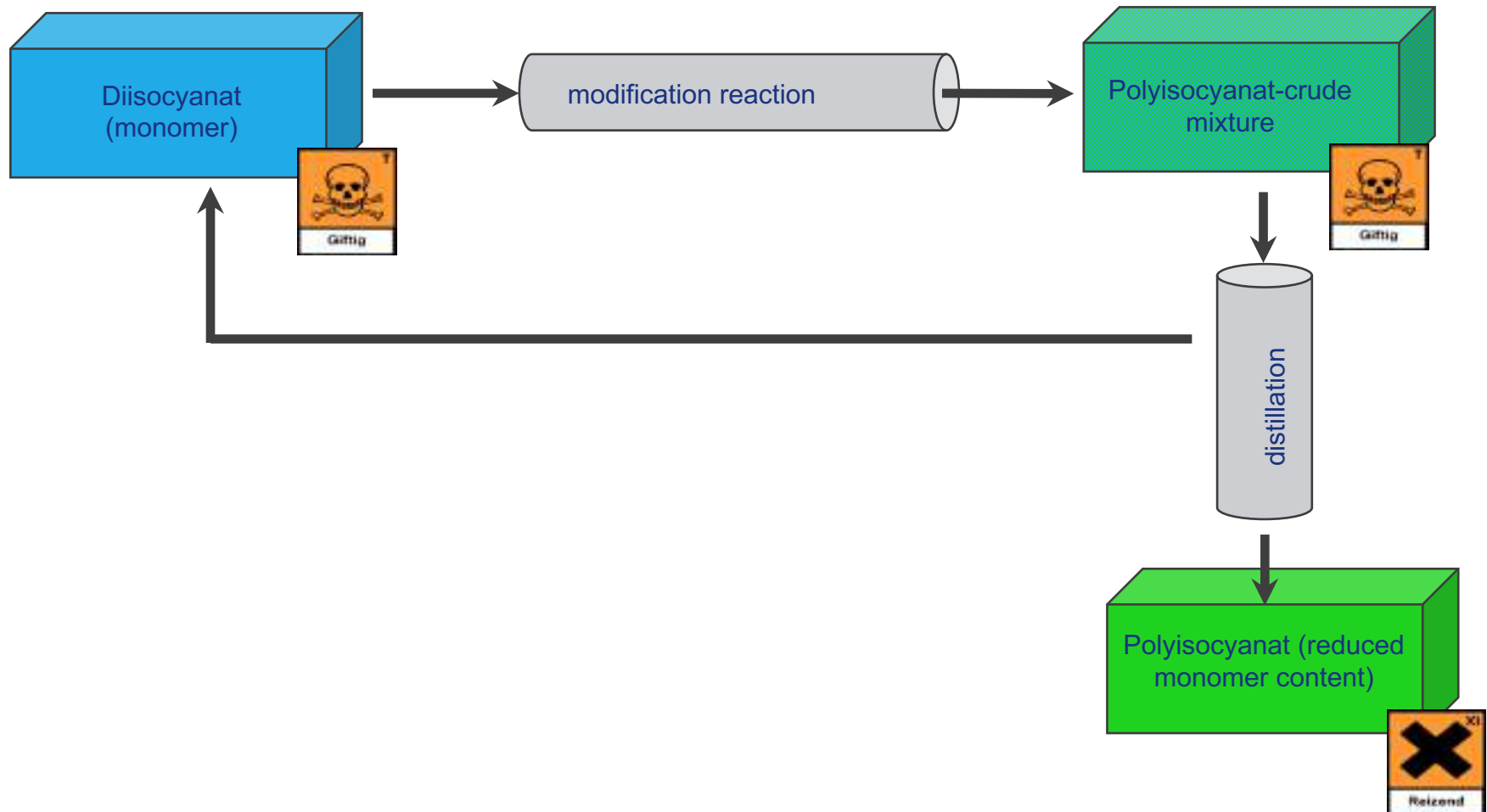


Increasing conversion / modification means.....

.....

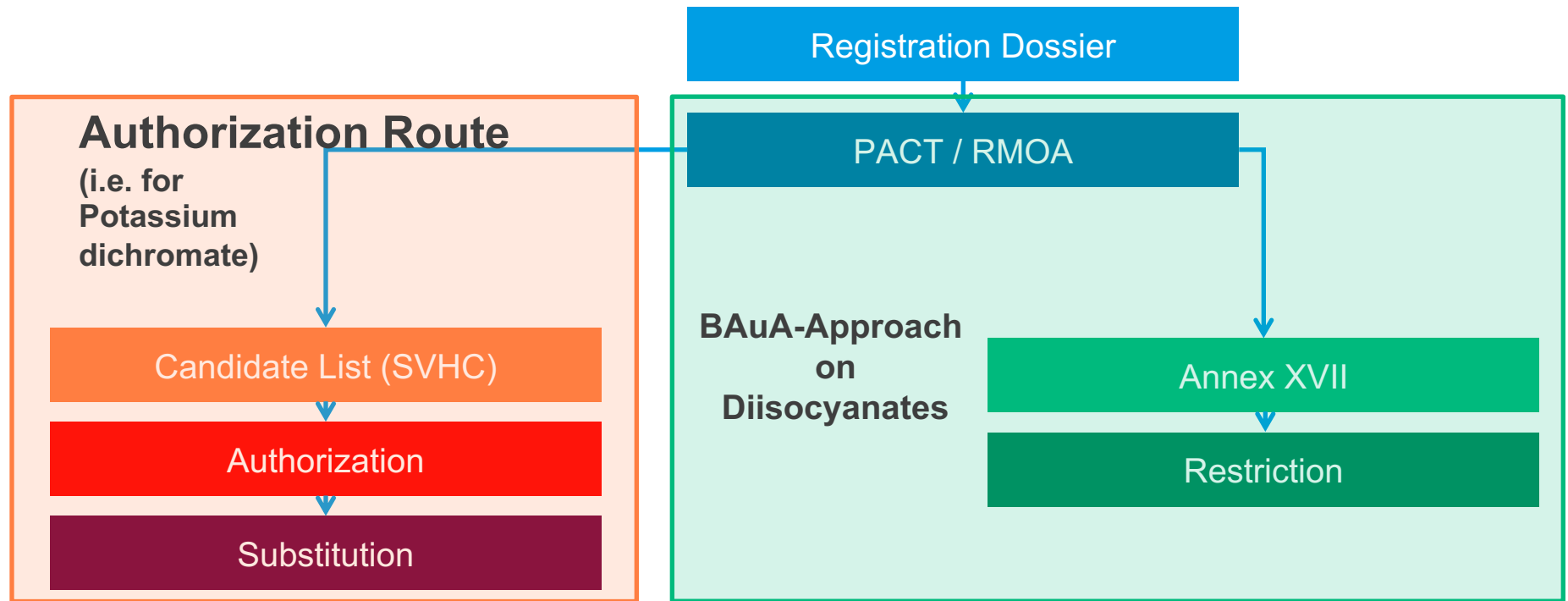
- increasing content of higher oligomers
- increasing molecular weight
- increasing viscosity
- increasing average NCO-functionality
- increasing crosslinking density
- decreasing content of NCO-groups

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 ¹⁴C measurement according to ASTM-D6866 standard

Desmodur[®] eco N 7300



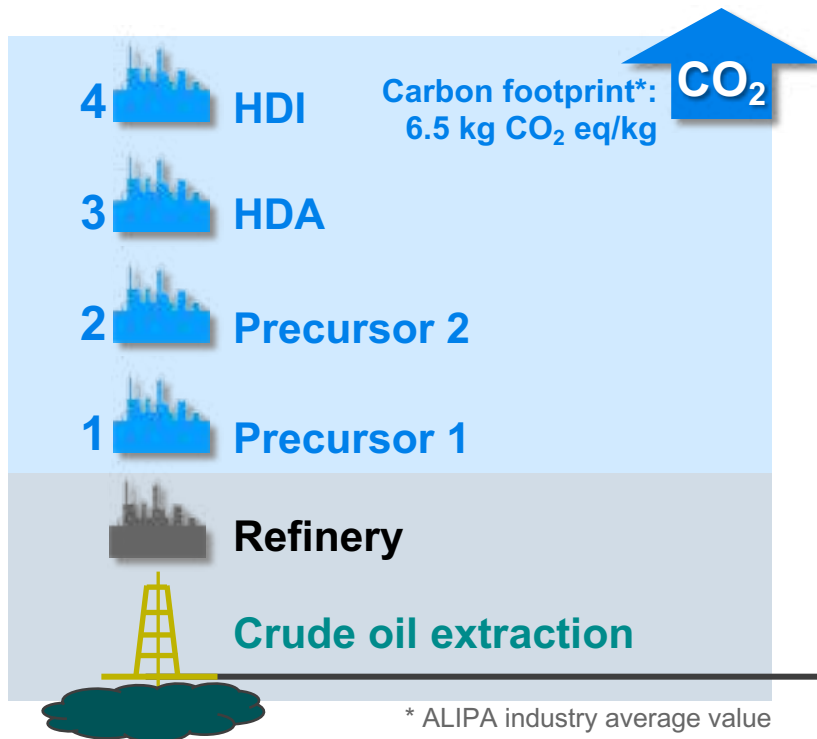
Significantly improved carbon footprint

- **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**

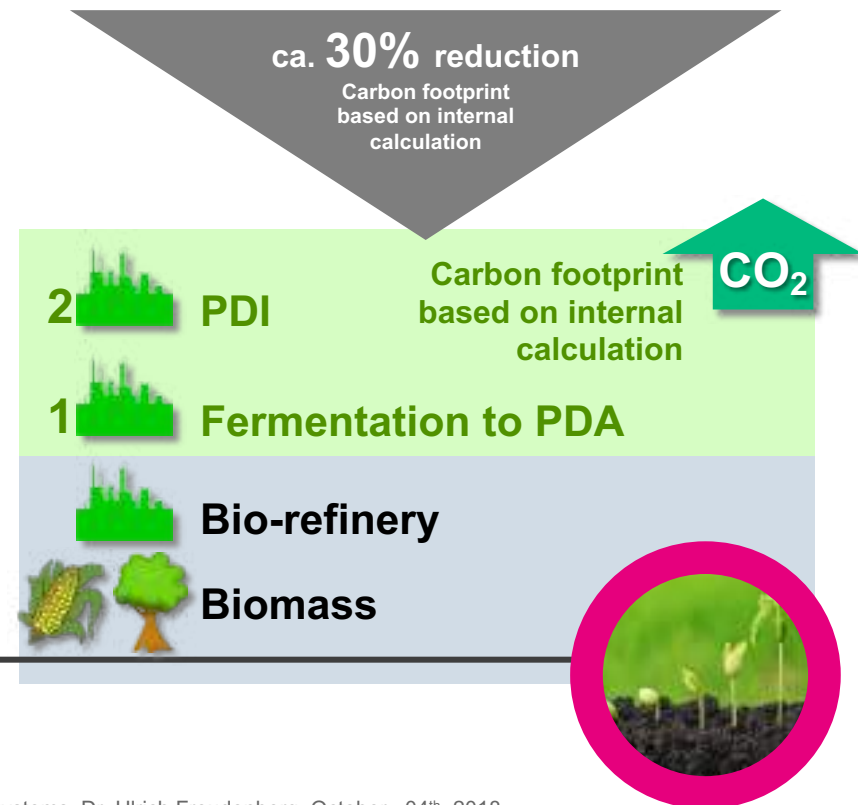
4 step petro-based synthesis

vs.

2 step bio-based synthesis



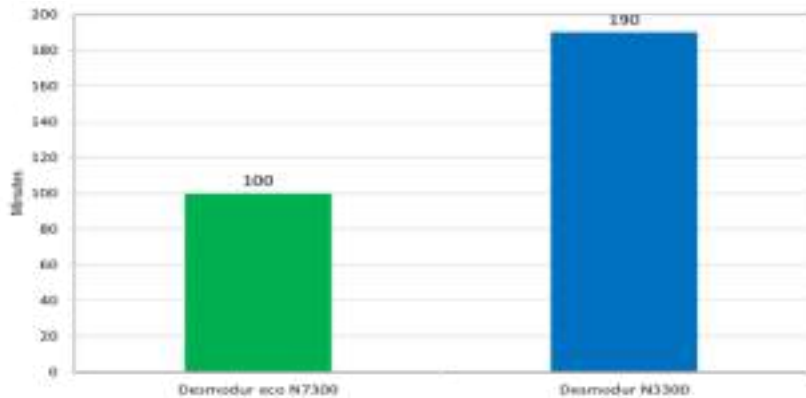
* ALIPA industry average value



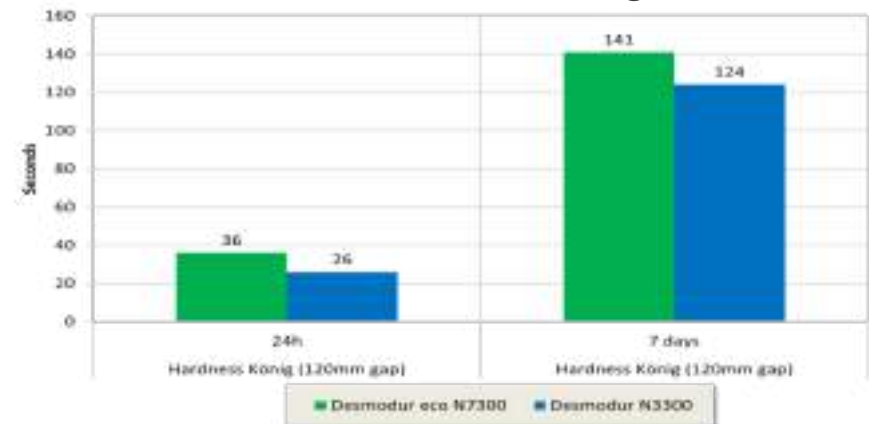
Desmodur eco N 7300 versus Desmodur N 3300 in a 2K clear coat formulation for wood



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



Desmodur® eco

A Desmodur® eco success story: First-ever car painted with a clearcoat with a biobased hardener

How collaboration between three major players along the value chain has made it possible to paint the first car with a clearcoat containing a biobased hardener under near-serial conditions.



Desmodur® eco

High performance enabled by nature

Biobased hardener for automotive clear painting
Automotive OEMs and industrial suppliers are constantly working to reduce energy consumption and CO₂ emissions in their production processes. A project team from BASF Coatings Division, the automotive manufacturer Audi and the materials company Covestro recently achieved a new record: for the first time, Audi GT cars were successfully painted with a clearcoat containing biobased hardener under near-serial conditions at the Ingolstadt plant. BASF developed the Desmodur® eco N based hardener for Desmodur® eco N 7300 from Covestro. "This is a first step towards a car that is not only made from sustainable raw materials, which thus reduces the loss of fossil carbon in the car."



Coating system for near-serial car paint
BASF's biobased hardener
Audi AG, Germany
Kodak

In cooperation with



Biobased hardener for automotive clear painting
Renowned materials are of great importance to Audi. "We are still very much in the early days of using bio-based raw materials," says Thomas Reuter, Head of Technology Development Materials and Process Engineering at Audi. "But the quality of this partnership provides us the making business satisfies our requirements, and the results are promising. This project has given Audi a promising picture of the automotive industry for the future." "This new clear coat enables us to support our customers in achieving their sustainability goals – without having to compromise on quality and performance," says Dr. Rüdiger Schneider, Head of Covestro in Germany and Tobias Dörner at BASF. "This is a collaboration between three major players along the value chain that is an important step to make sustainable automotive painting – and for our understanding of 'Inventing for you'."



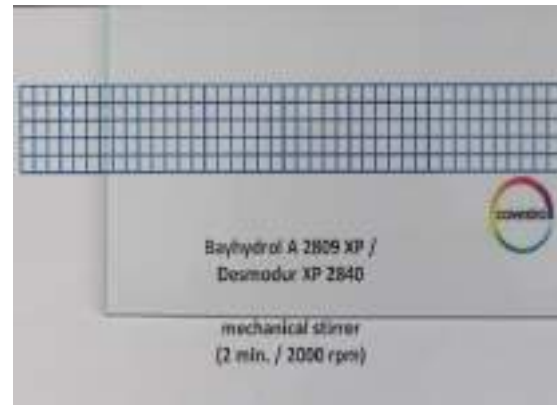
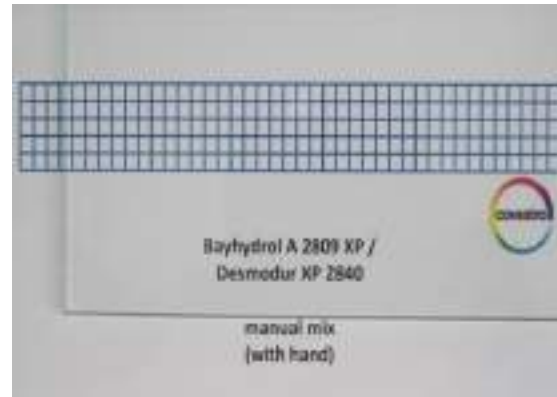
Covestro Clearcoat and All
BASF Coatings Division
Audi AG, Germany
Kodak

The new clear coat is a first step towards a car that is not only made from sustainable raw materials, which thus reduces the loss of fossil carbon in the car. This is a collaboration between three major players along the value chain that is an important step to make sustainable automotive painting – and for our understanding of 'Inventing for you'.

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

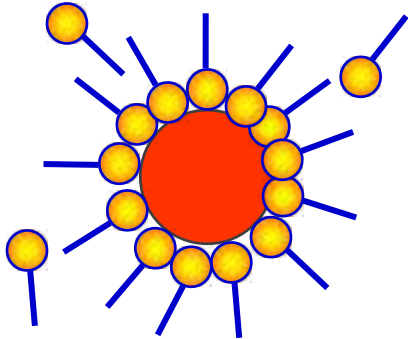
Hydrophilized Polyisocyanates

Emulsification of low viscous polyisocyanates in Bayhydrol A 2809

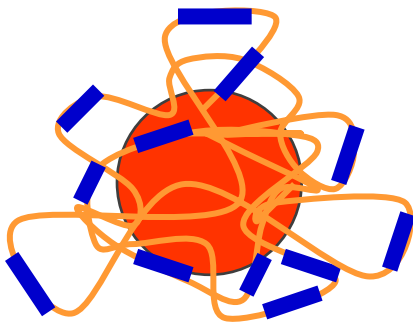


Incorporation of medium viscous polyisocyanates into aqueous dispersions at low shear is critical

Emulsifiers for Polyisocyanates



External Emulsifier



Internal Emulsifier



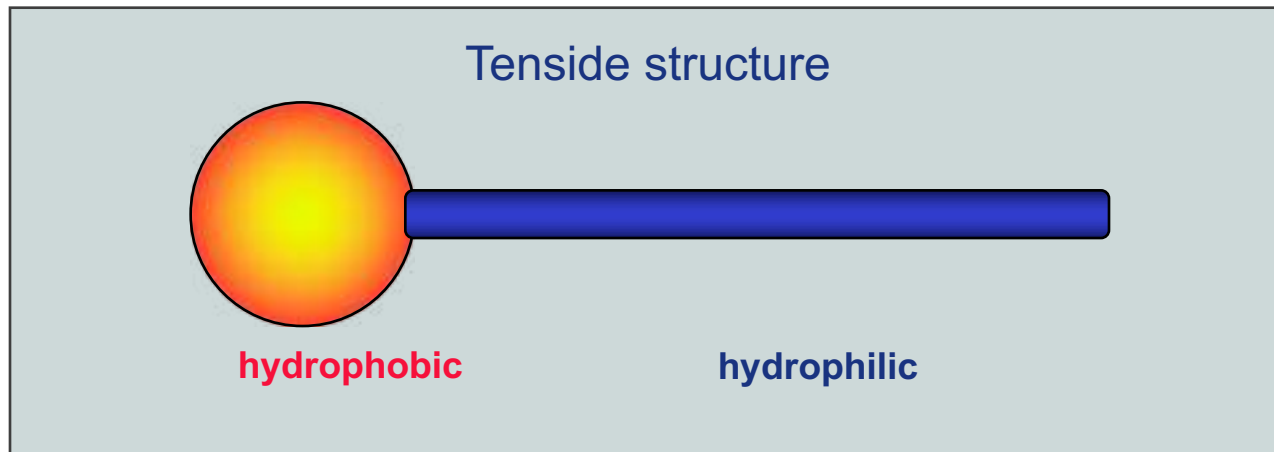
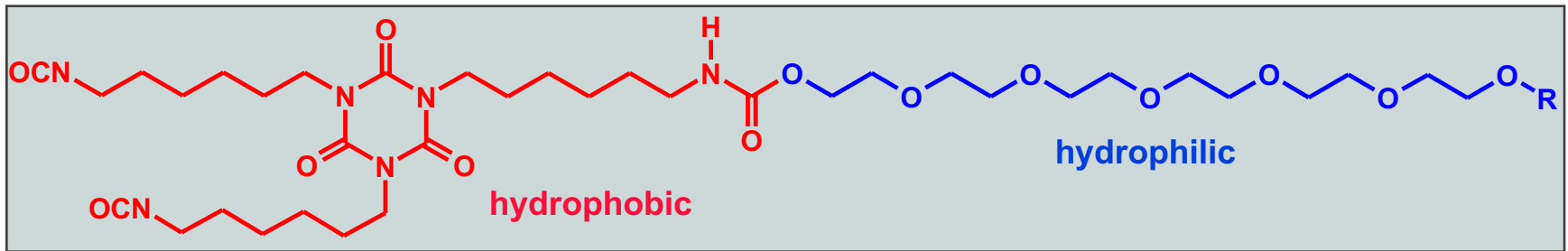
hydrophobic
lipophilic

hydrophilic

... have to be:

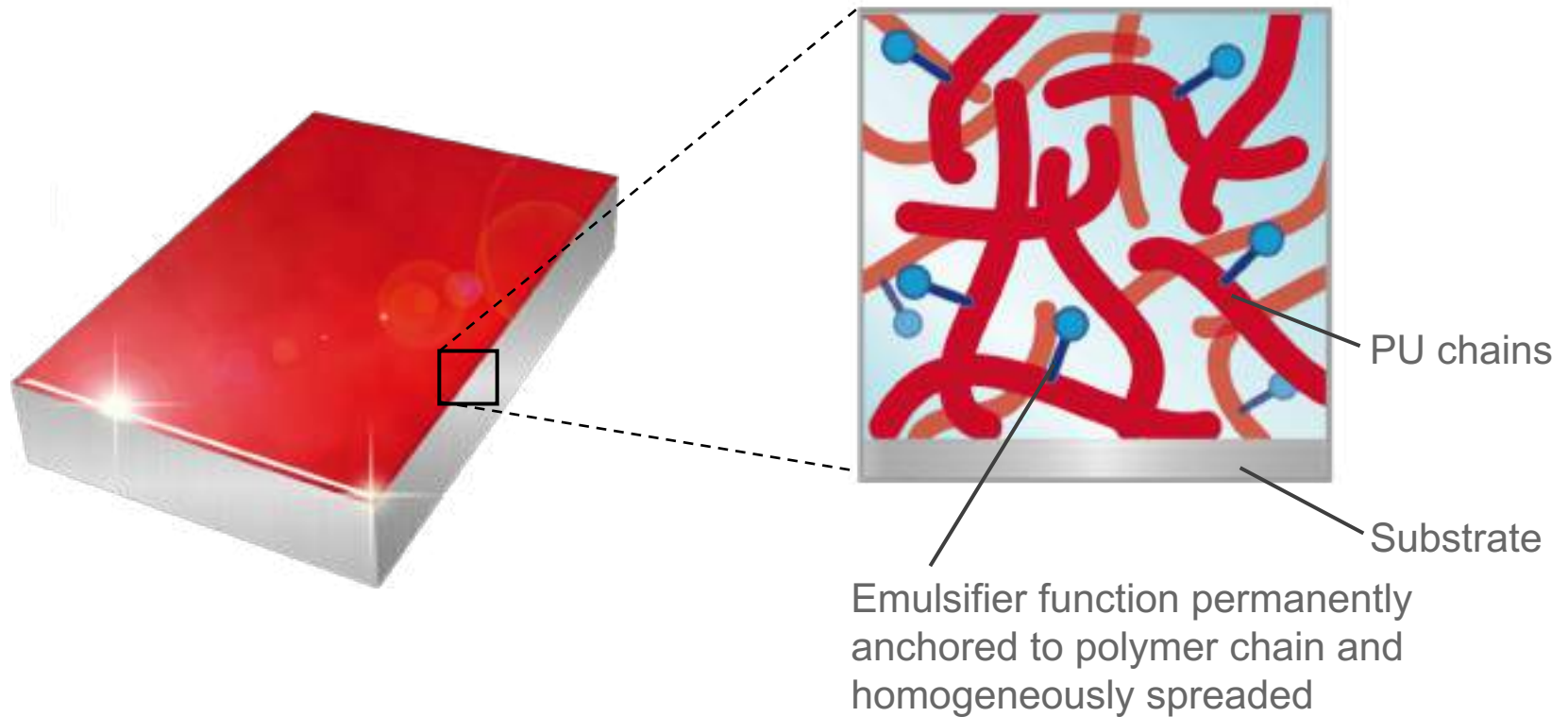
- non-reactive with Isocyanates (NCO consumption, catalysis)
- free of water
- soluble in isocyanate and coatings film
- reactive with resins
⇒ internal emulsifiers / incorporation into PUR network

Polyether modified trimer – 1st generation type

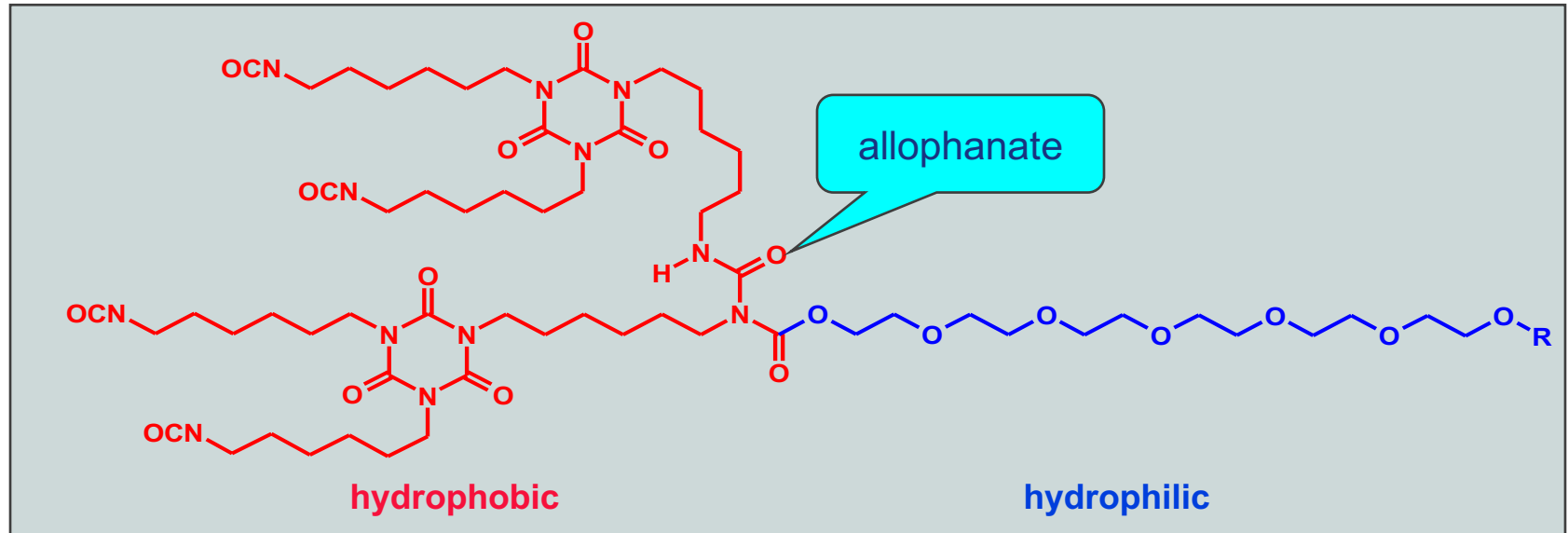


- HDI – based types / IPDI – based types
- Disadvantage: - lower functionality
- high hydrophilicity

Waterborne PU coating with hydrophilized hardeners

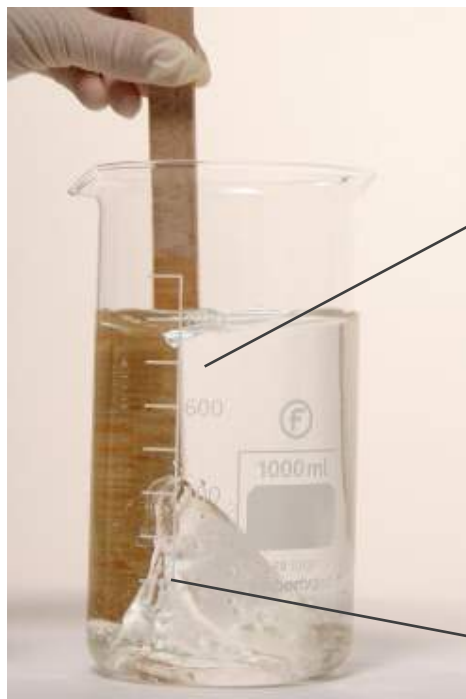


Polyether modified allophanate/trimer – 2nd generation type



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

Waterborne PU coating with hydrophilized hardeners – easy to mix



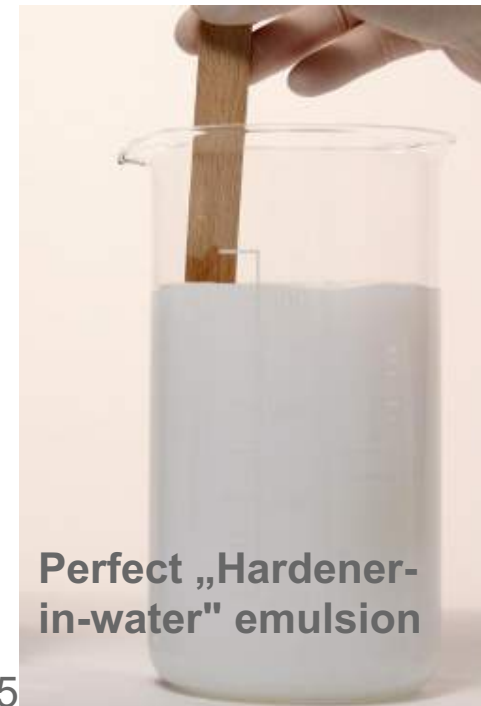
Aqueous phase

Easy stirring

Spontaneous
emulsification

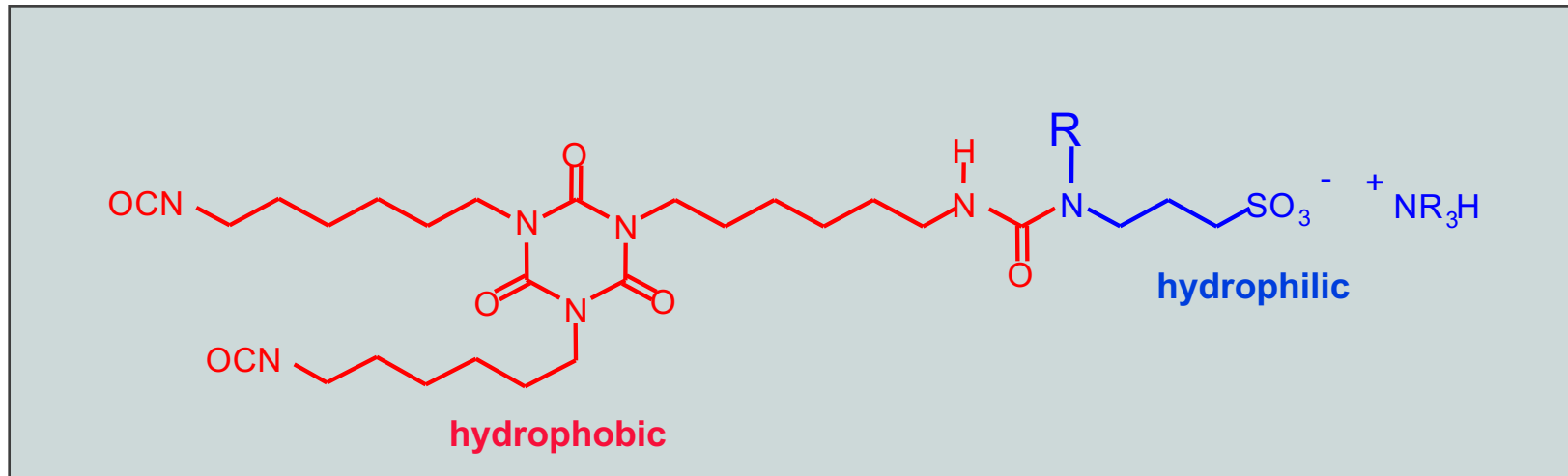
Hydrophilized

HDI-hardener Bayhydur® 305
(organic phase)



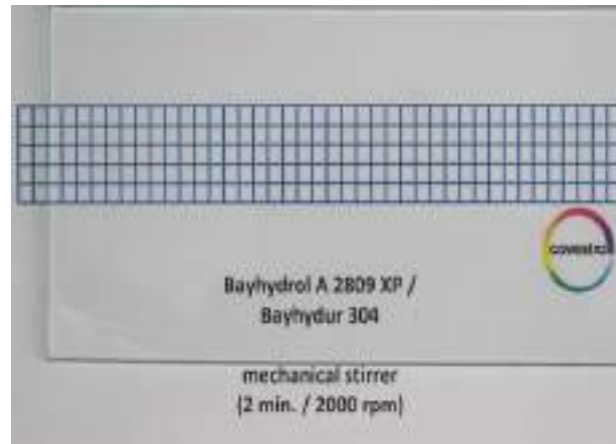
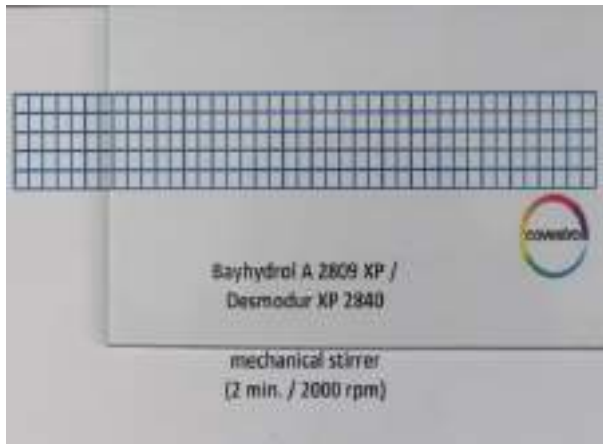
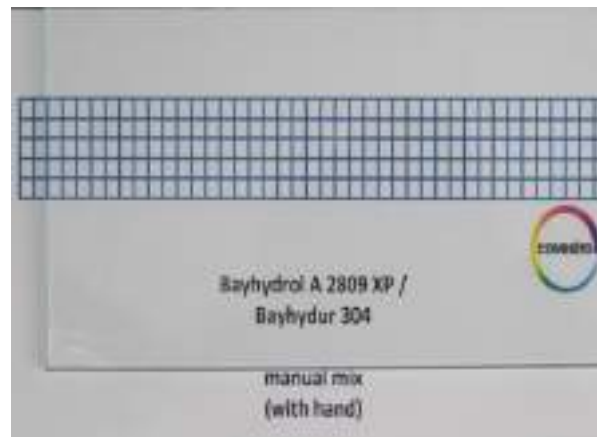
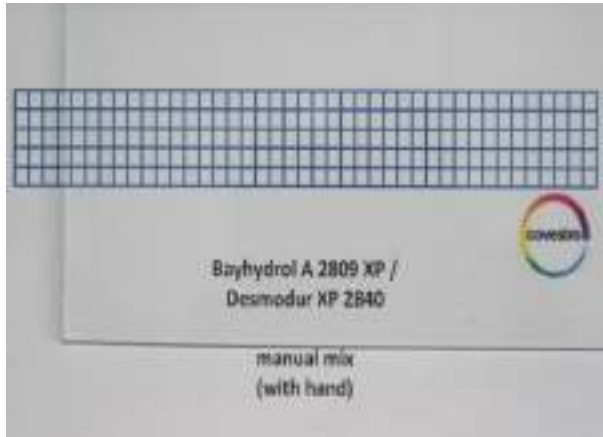
Perfect „Hardener-
in-water“ emulsion

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

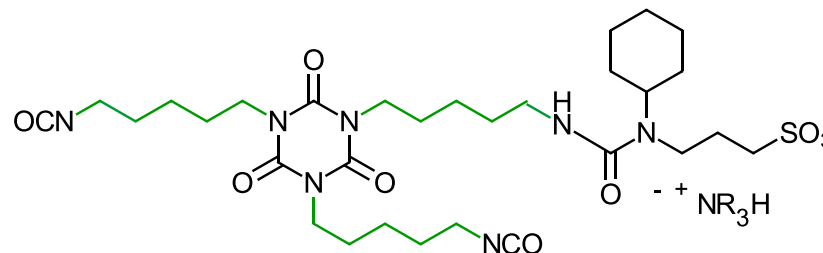
	Approx. value
Supply form	90 % in PGDA
NCO	18%
Viscosity	5000 mPa·s
Biobased content*	68 %

* Confirmed by radiocarbon method ¹⁴C 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

INVENTING
SUSTAINABLE LIVING
FOR YOU



A Bayhydur® eco success story:
Furniture protected by a high-performance
2K bio-based waterborne coating

How Covestro helped an Italian coating manufacturer to develop
a high performance bio-based waterborne coating for one of
Milano's most innovative high-end design furniture brands.

Bayhydur® eco



High performance enabled by nature

Coastal waterborne coating for a sustainable living

Society has generally turned toward the need to reduce greenhouse gas emissions through reducing consumption of fossil resources. This use of natural products (e.g. oils or water) provides a new basis for creating new, durable and sustainable systems to protect your furniture in domestic environments such as bathrooms or bedrooms.

The functional approach has been found in the use of waterborne systems as an alternative to solvent-based systems. However, the latter have been improved even further, as the use of bio-based raw materials has become a reality.

Thanks to this collaboration, we have developed a high-performance 2K bio-based waterborne coating for one of Milano's most innovative high-end design furniture brands.

Coastal waterborne coating for a sustainable living

With its customer, RIFRA, we have developed a high-performance 2K bio-based waterborne coating for one of Milano's most innovative high-end design furniture brands.

The coating system is based on a bio-based waterborne system, which is characterized by high performance and low environmental impact. The system is based on a bio-based waterborne system, which is characterized by high performance and low environmental impact.

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Covestro Coatings Ltd.
Business Unit Coatings
P.O. Box 1000
40000
Germany

coatings@covestro.com
info@covestro.com



“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 and chemical resistance of the renewable system and our customers require. Bayhydur® eco boosted the hardness contributed to create an outstanding coating”

Maurizio Durante, Vice-President Sirca



Lunch Break ?