VESTAMIN® A95

A specialty building block for PUD manufacturing

Nov. 10th, 2022 | Dr. Guido Streukens

EVONIK
Leading Beyond Chemistry

Pioneer in Isophorone Chemistry

Evonik Crosslinkers covers the entire isophorone value chain

With our VESTA products for high-performance solutions, you benefit from our long heritage in isophorone chemistry, operational excellence and our global setup.

Go with the original.

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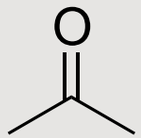
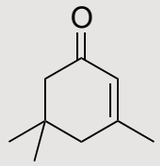
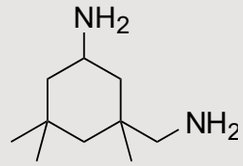
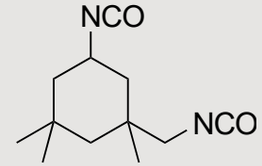
The Isophorone-Chain – Backbone and core competency of Crosslinkers

Raw Materials	Solvents & Intermediates	Diamines	Diisocyanates
			
Acetone	VESTASOL® IP	VESTAMIN® IPD	VESTANAT® IPDI
			

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Crosslinkers' products are used for a large number of different applications

Automotive
- Elastomers
- TPU
- Coatings

Composites
- Wind
- Filament Winding

Solvents & Synthesis
- Vitamin E
- PCMX
- Crop Protection
- Polycarbonates

Industrial Coatings
- Wood
- Flooring

Powder Coatings
- General Metal
- Architectural
- Appliance

PUR Dispersions
- Artificial Leather
- Wood
- Packaging

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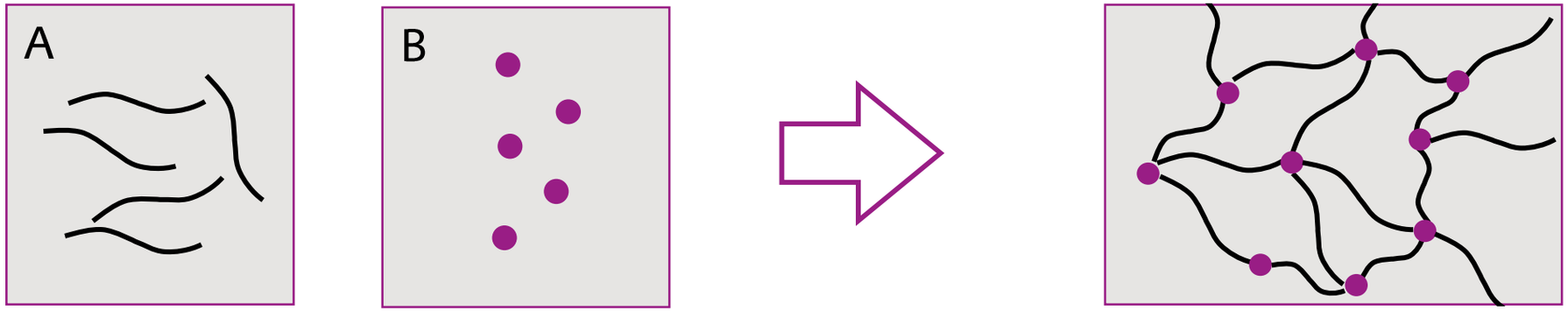
When we think of PUR coatings…

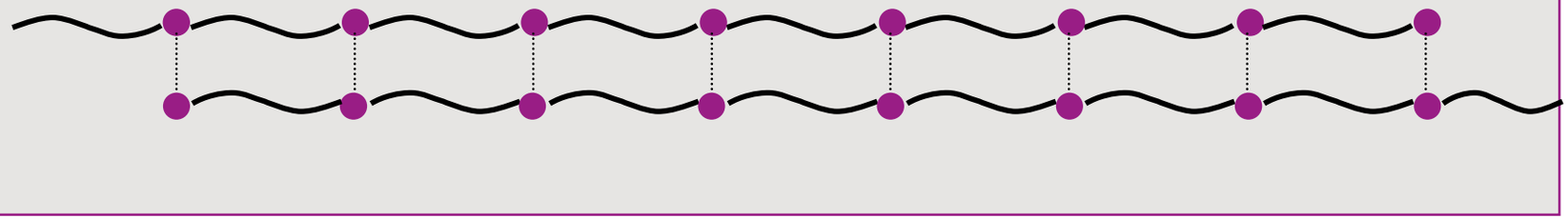
...we usually think of crosslinked systems



- Reactive Systems
- Can be 2K or 1K (blocked)
- Need a chemical curing reaction after application

But PU makes for excellent coatings without additional crosslinking!

TPU – Thermoplastic Polyurethane



TPUs are pre-synthesized thermoplastic polymers

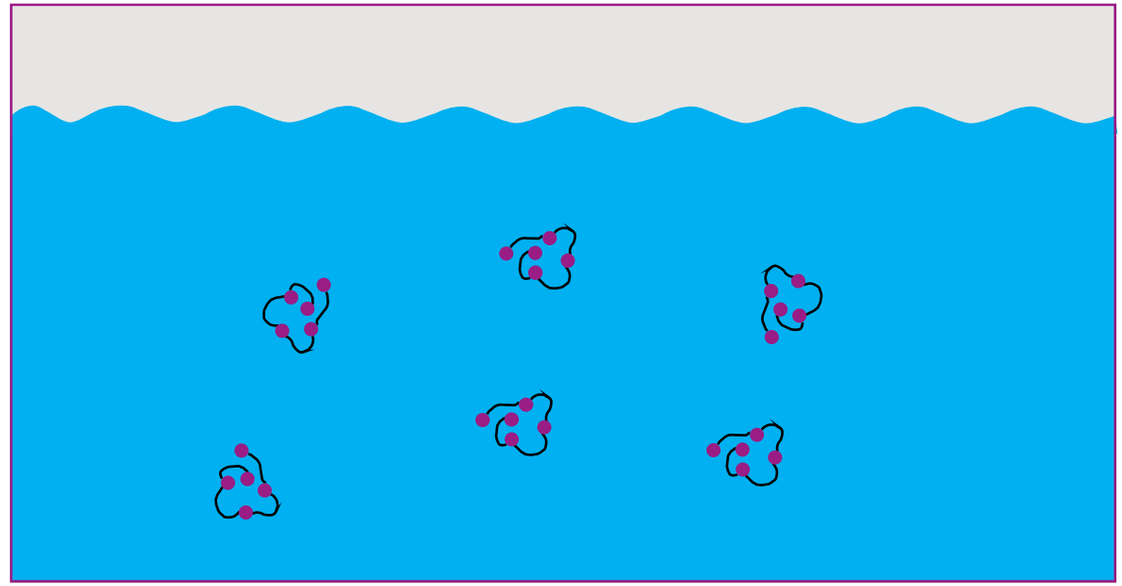
+ Can be dissolved in appropriate solvents
+ After application, only physical drying is necessary
+ Due to hydrogen bonds, still good properties, even if not truly crosslinked

- Molecular weight needs to be high
- Viscosities consequently also very high
- Solid content of the solution is low

This is where PUDs come into play

Polyurethane Dispersions are TPUs dispersed in water

- Viscosity is only determined by particle size, not by molecular weight
- Original development goal was application efficiency and easy handling
- Emission regulations and trend towards low VOC coatings has led to increased importance of PUDs

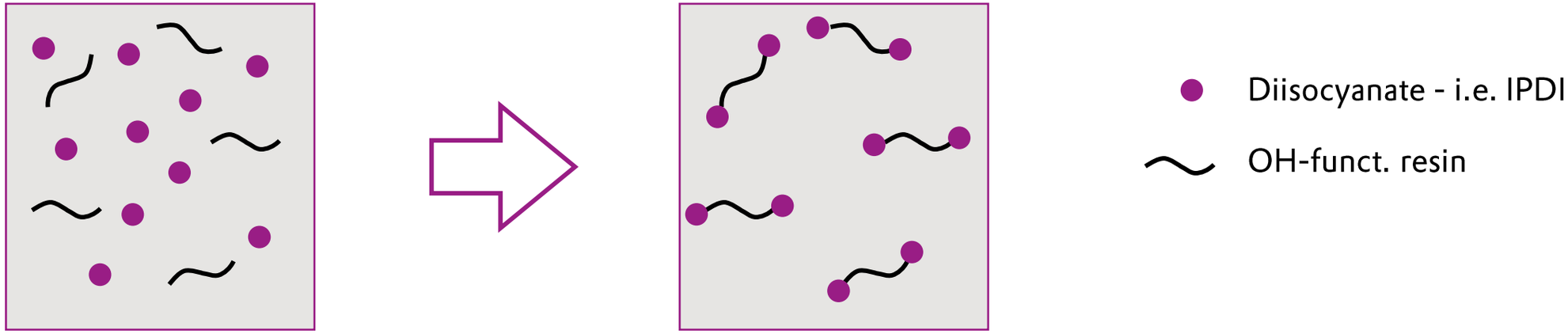


- But to design stably dispersible polymers is not straight forward

Typical applications for PUDs

Synthesis of classical PUDs (Acetone Process)

1. Synthesis of NCO terminated Prepolymer



- Reaction of OH-terminated resin (diol) with appropriate diisocyanates
- Synthesis is carried out in acetone
- Selectivity is important to create
  - Low monomer content
  - Low viscosity

Synthesis of classical PUDs (Acetone Process)

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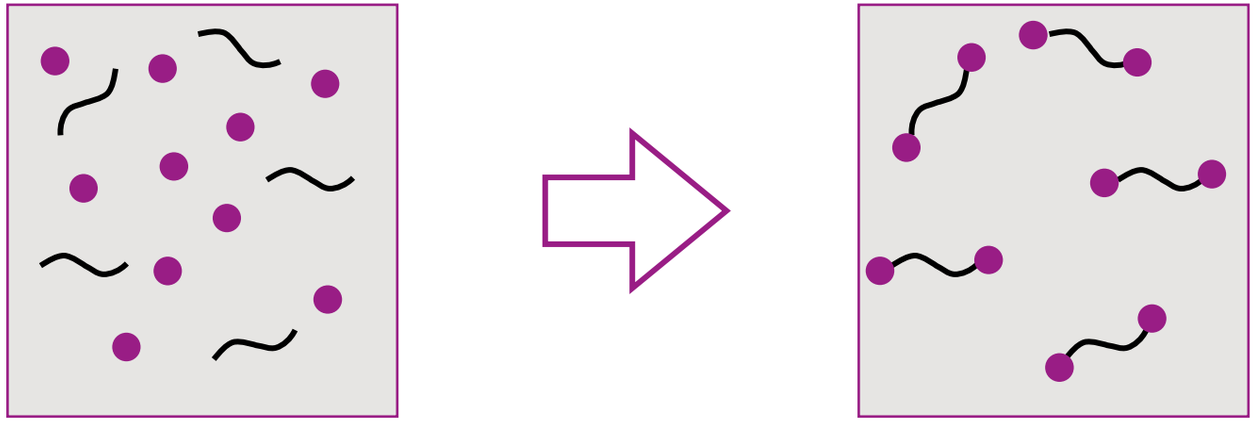
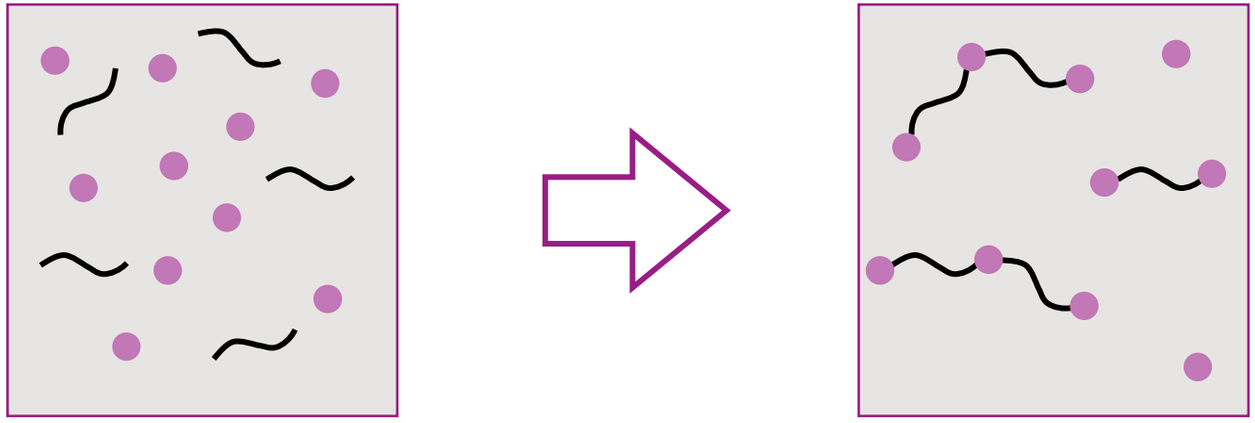


Diisocyanate – i.e. IPDI

OH-funct. resin



Diisocyanate – i.e. H12MDI

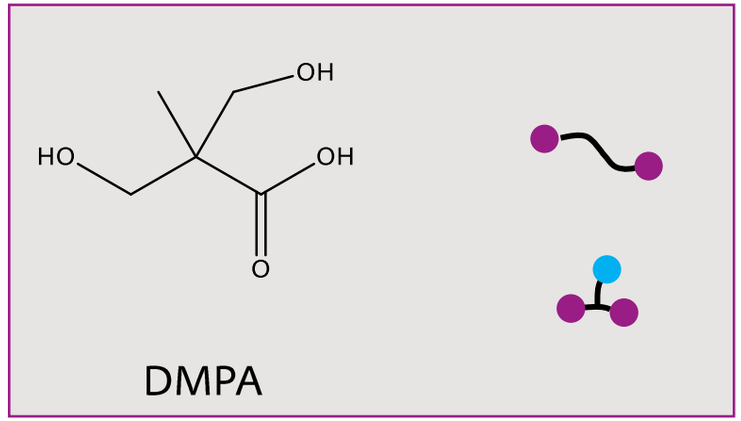
OH-funct. resin

Synthesis of classical PUDs (Acetone Process)

2. Addition of emulsifier to the prepolymer

DMPA is a common emulsifier for PUD synthesis – it is both,

- A diol – so can be built into the prepolymer
- An organic acid – adding hydrophilicity



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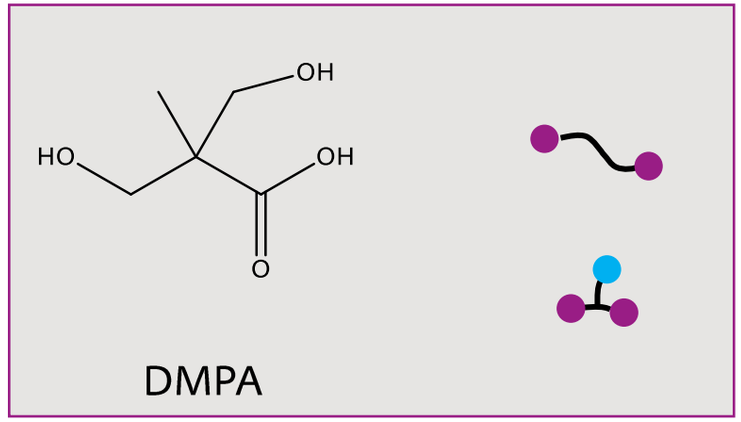
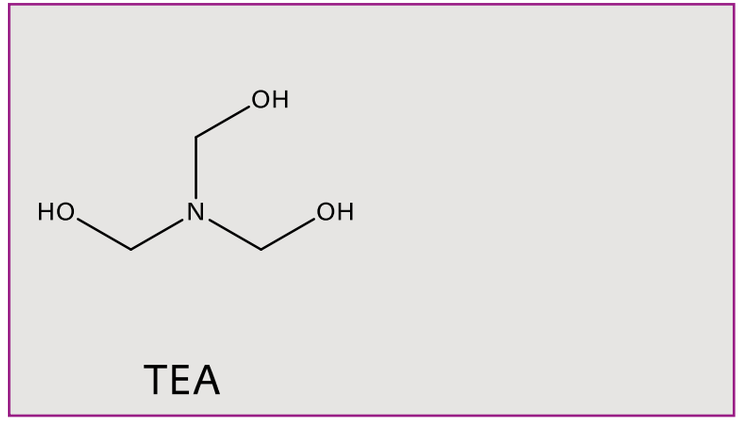


DMPA

3. Neutralization of the acid

After the prepolymer synthesis, TEA is added to neutralize the acidic function of the DMPA



TEA

Synthesis of classical PUDs (Acetone Process)

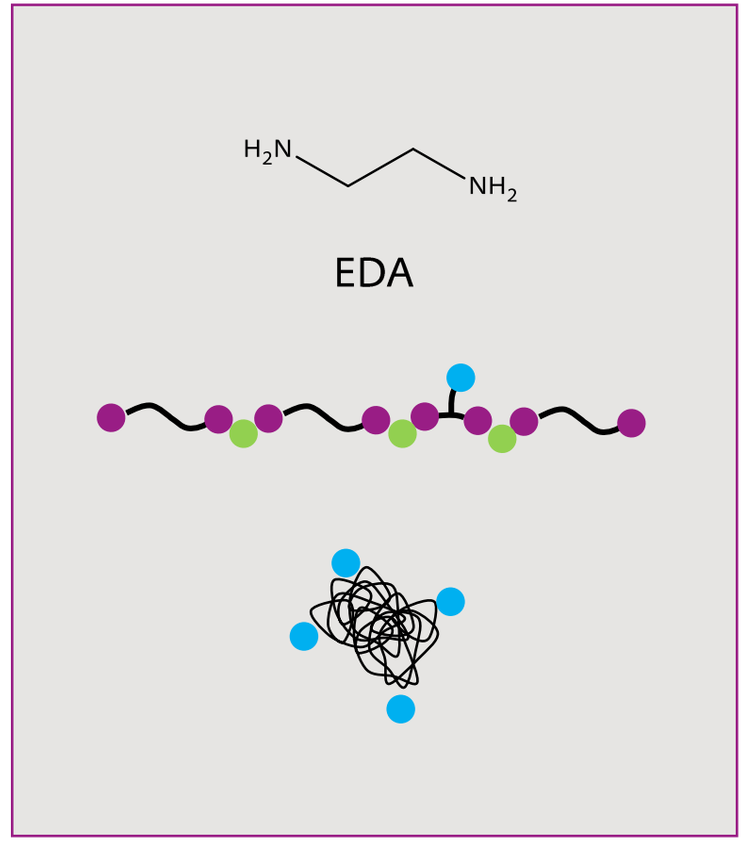
4. Addition of water

and

5. Chain extension

The prepolymers must be connected to long polymers and almost simultaneously be dispersed as fine particles in water.

- Typical chain extenders are simple diamines (ethylene diamine, EDA) to allow for fast reaction
- Reaction of water with isocyanate groups is an unwanted side reaction



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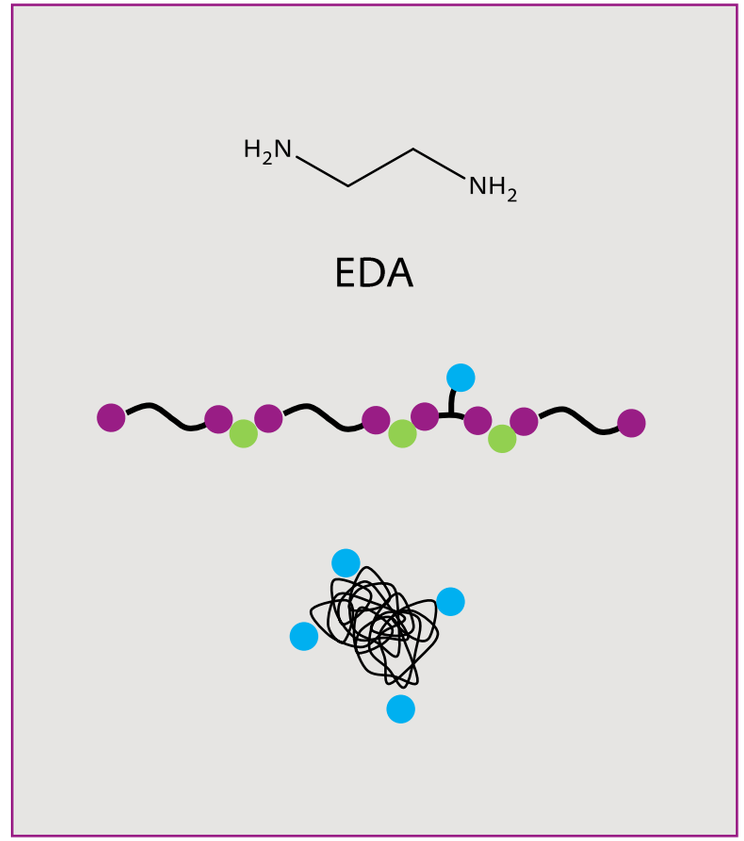
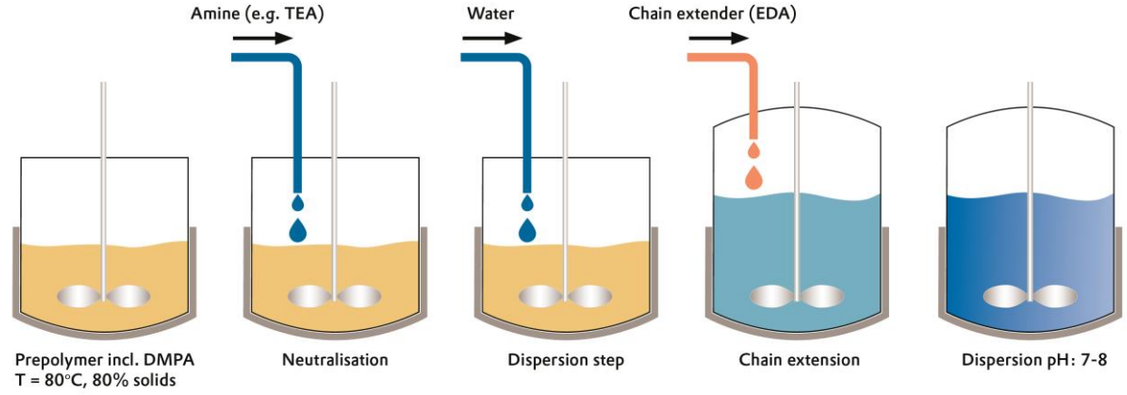
6. Evaporation of Acetone



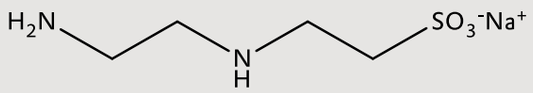
Alternative VESTAMIN® A95 – aminosulfonate process

Downside of the classical Acetone Process

- DMPA is a solid. Dissolving in acetone takes very long (low temperature)
- Hydrophilicity of DMPA is limited, so high amounts needed in the synthesis
- Relatively low solid content achievable



Our alternative: VESTAMIN® A95 – a combination of emulsifier and chain extender



VESTAMIN® A95

- Provided as 50% solution in water – no dissolving
- Increased hydrophilicity – lower amounts needed in synthesis and design freedom for other building blocks
- Increased solid content achievable

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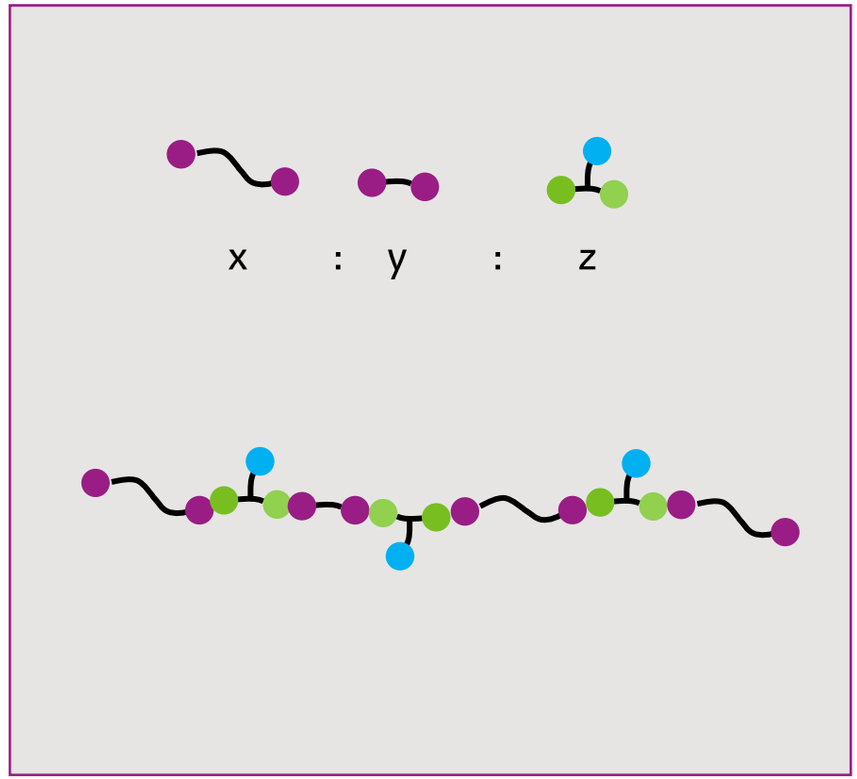
Alternative VESTAMIN® A95 – aminosulfonate process

1. **Synthesis of prepolymer – no change**
2. **Chain extension with VESTAMIN® A95**

- Complete design freedom for hard and soft segments
- Can be combined with classical diamines as well
- No dissolving of emulsifier needed – low process times



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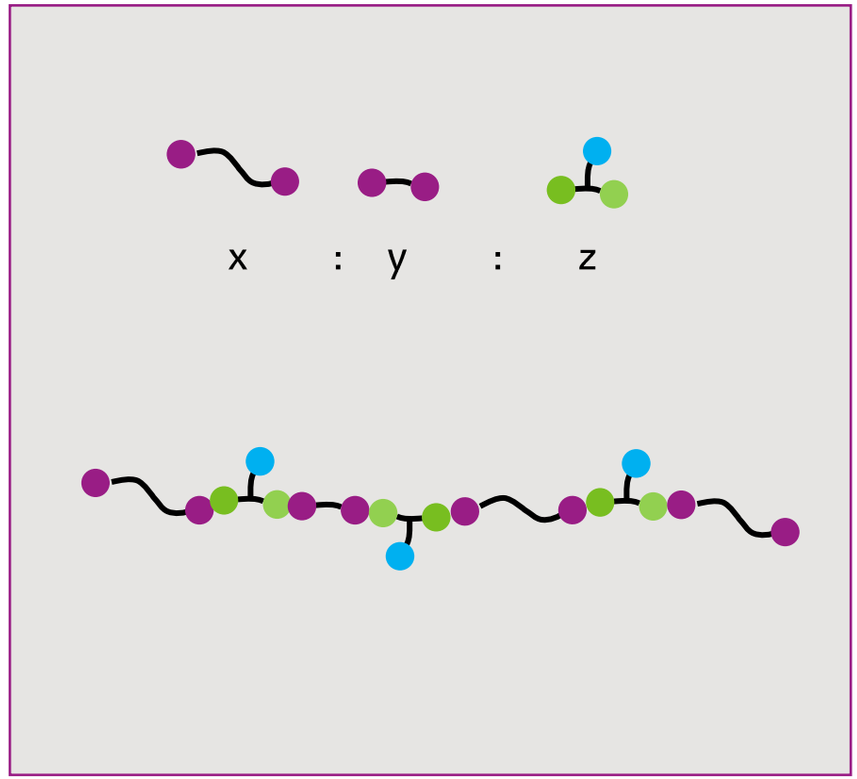


3. **Addition of water – no change**

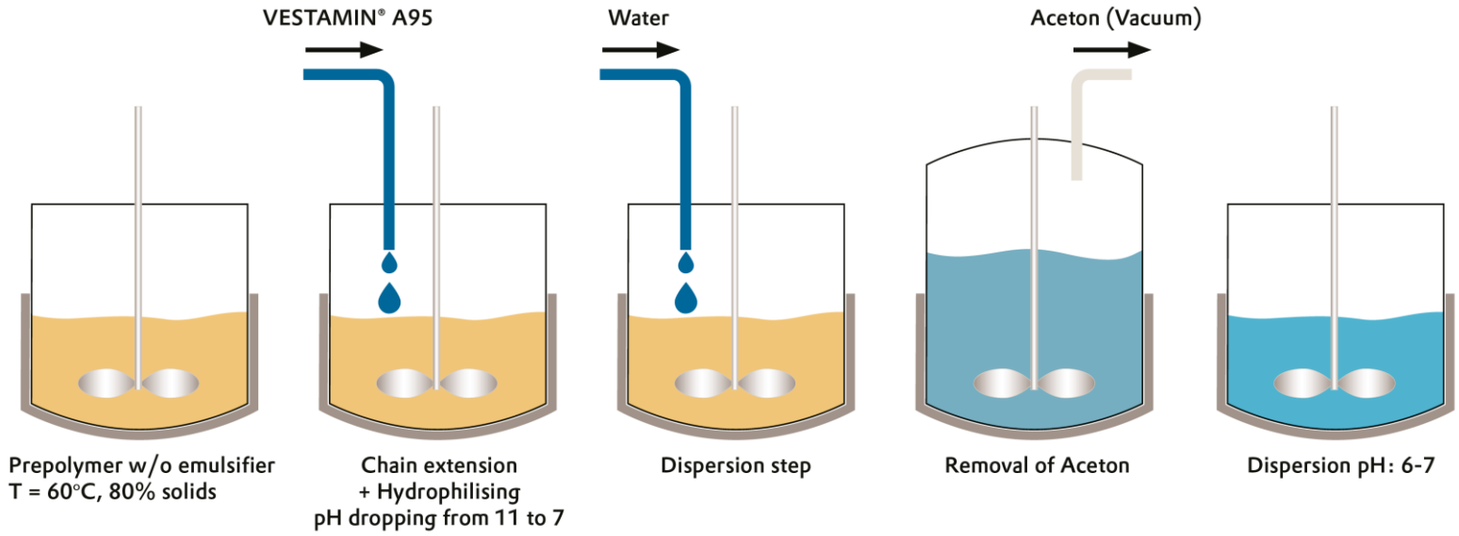
and

4. **Evaporation of acetone – no change**

Alternative VESTAMIN® A95 – aminosulfonate process

Benefits at a glance

- Design freedom
- Lower process time
- Higher solid content
- Less complex process



BUT: How about the performance?

Direct comparison of Dispersions based on DMPA and VESTAMIN® A95

	Prepolymer A DMPA based	Prepolymer B A 95 based
Polyol Mixture		
Oxyester T1136	2.5 eq	2.5 eq
1,4 Butane diol	2.5 eq	2.5 eq
TMP	1.5 eq	1.5 eq
DMPA	3 eq	
NPG		3 eq
Diisocyanate		
Vestanat® IPDI	$NCO:OH_{total}$ 1.5 : 1	
Solvent		
Acetone	30% (70% solids)	

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	Dispersion A DMPA based	Dispersion B A 95 based
Prepolymer		
Prepolymer A/B in 30% Acetone	100%	60%
Add. Acetone		40%
Neutralization		
TEA	1 eq. based on DMPA	
Chain extension		
EDA	NH:NCO 1:1	
EDA: A95 1:15		NH:NCO 1:1
Water addition		
H_2O	33% solids	42% solids

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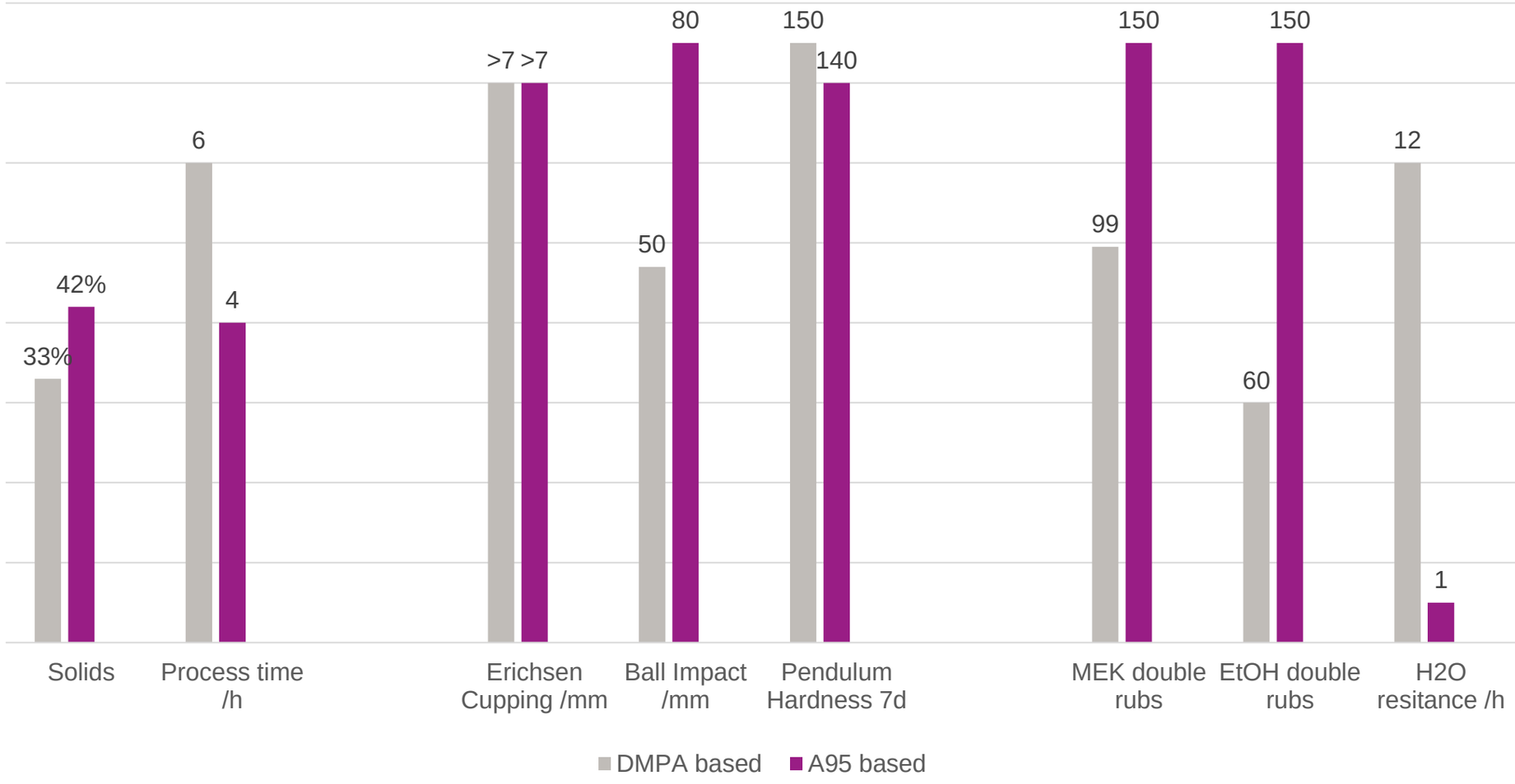

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Even higher solids?

- With the relatively hard formulation A and B, solid content is at the limit
- Even higher solid contents can be achieved with more flexible backbones
- For comparison, we exchanged just the “soft” segment with a even softer one, the hard segments remained unchanged.

	Prepolymer A DMPA based	Prepolymer B A 95 based	Prepolymer C A 95 based
Polyol Mixture			
Oxyester T1136	2.5 eq	2.5 eq	
PolyTHF 2000			2.5 eq
1,4 Butane diol	2.5 eq	2.5 eq	2.5 eq
TMP	1.5 eq	1.5 eq	1.5 eq
DMPA	3 eq		
NPG		3 eq	3 eq
Diisocyanate			
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Solvent			
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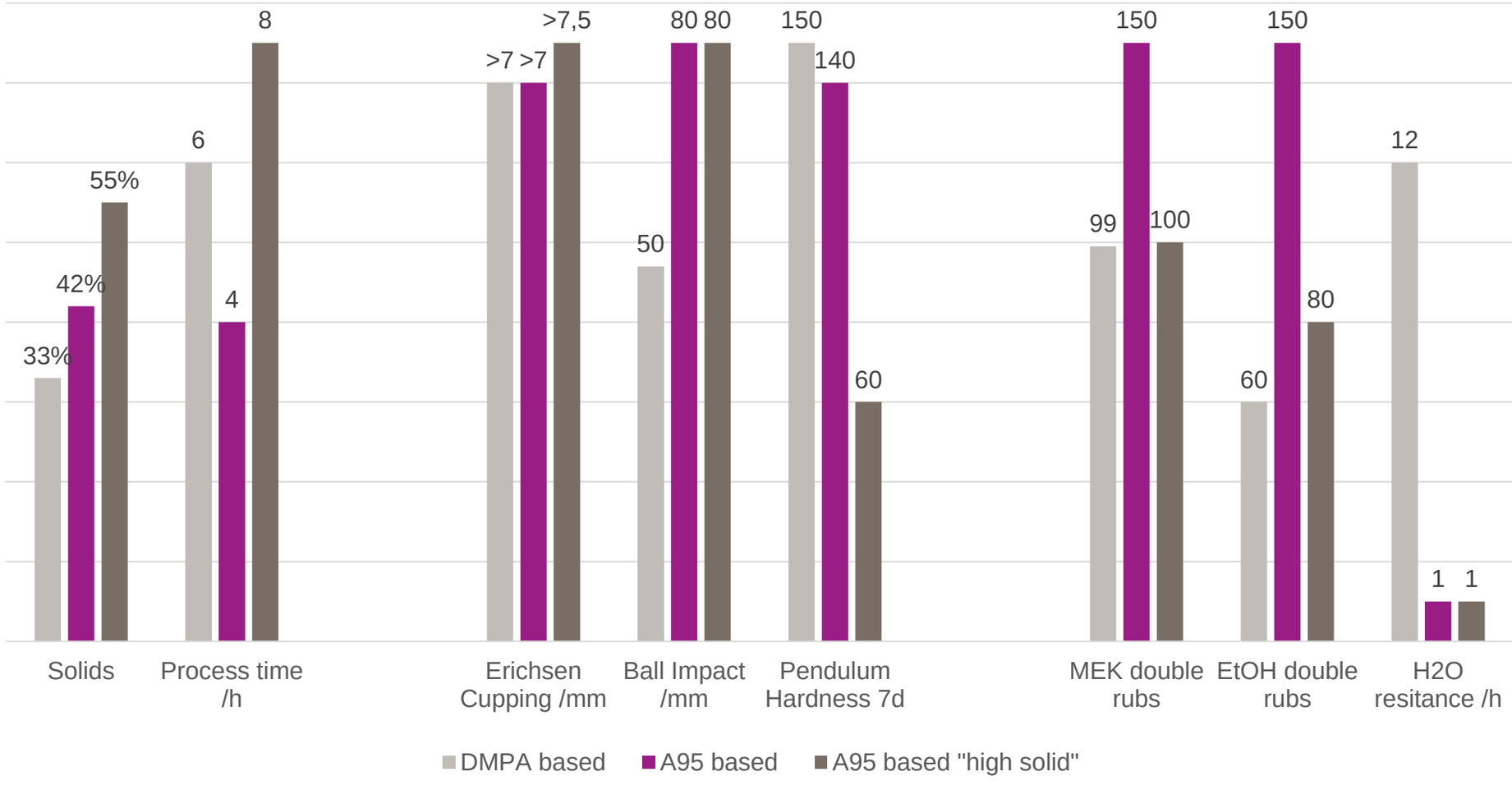
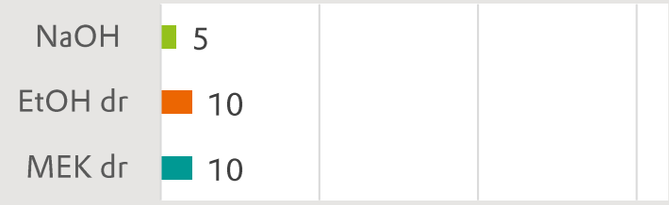
Even higher solids?



Influence on properties – DMPA vs. Vestamin® A95

What has a bigger influence – emulsifier or polyol?

Polyester Mw ~1000
DMPA



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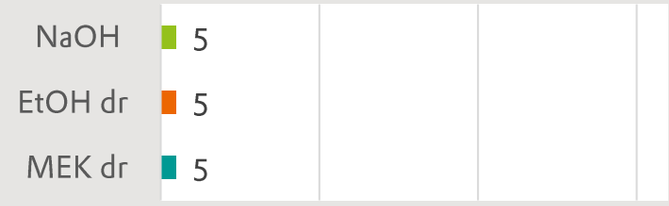

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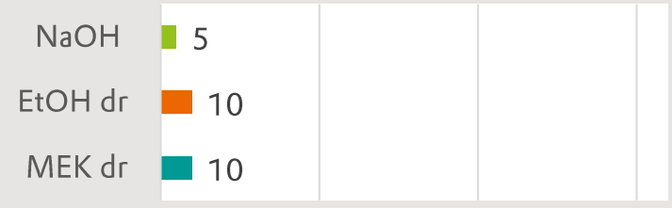
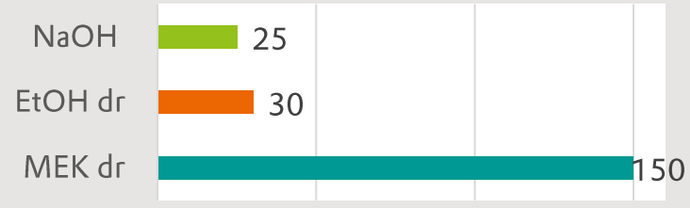


Polyether Mw ~2000
DMPA



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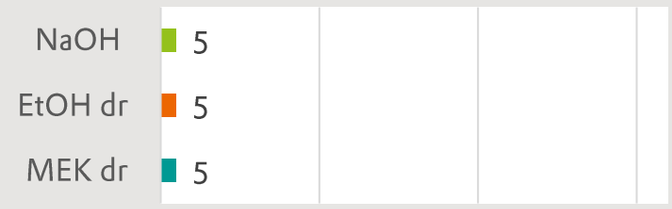

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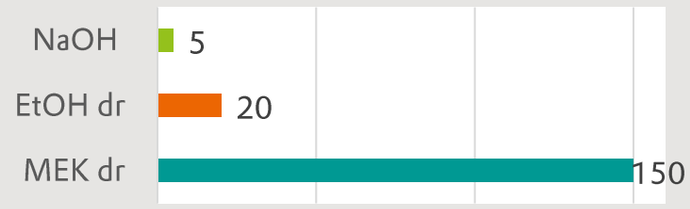

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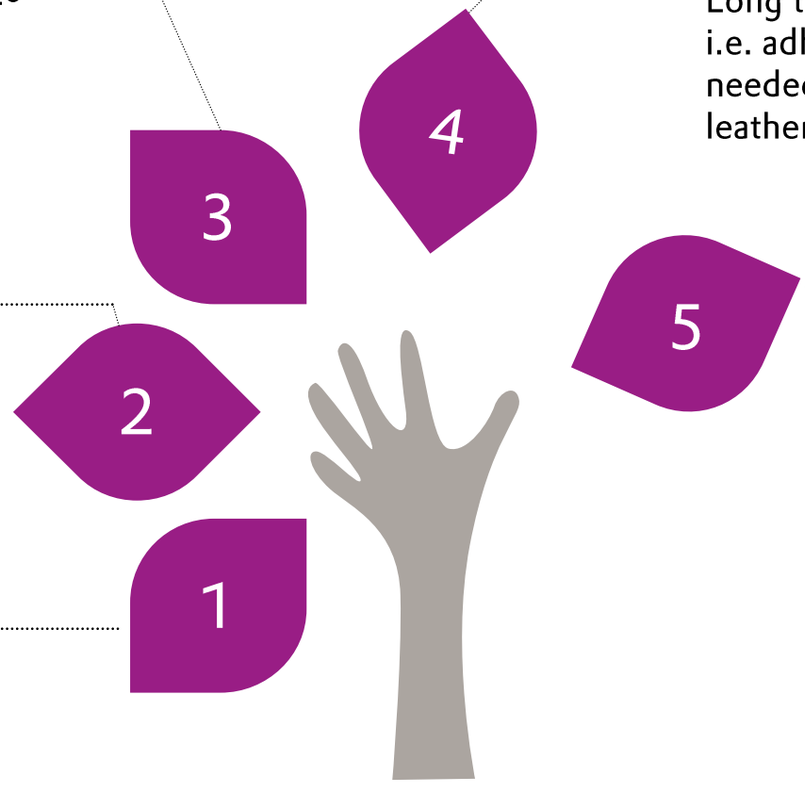
Summary

Convincing properties
Chemical resistance and mechanics are on similar level of state-of-the-art systems – and can be further tuned

Efficient application
High solid content allows for efficient packaging, transport and drying.

Easy process
Processing times are shorter
Design freedom is higher



Water resistance is an issue
Long term water exposure should be avoided – i.e. adhesive layers. Or extra protection is needed – i.e. automotive base coats or artificial leather

If you have questions
Let us know!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