Polyurethane and acrylic dispersions, versatile tools for waterborne, clear coat applications

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High Performance Waterborne Clearcoats II (Berlin)

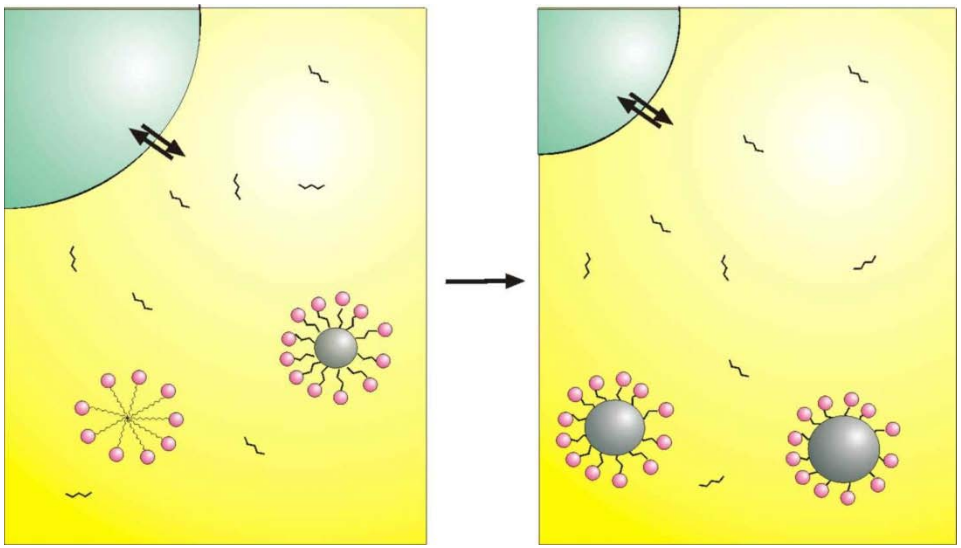
Agenda

- Acrylic dispersions
  - Primary and secondary acrylic dispersions
  - 1K and 2K crosslinking
  - 1K heat curing acrylic for metal and glass coatings
  - 2K acrylic system for automotive and ACE

- Polyurethane dispersions
  - Polyurethane synthesis and dispersion
  - Solventless process (TMXDI)
  - PUD for wood flooring and industrial wood
  - High performance PUD for plastic
  - High gloss UV-PUD for plastic

Acrylic emulsions or primary dispersions

- Monomers
- Surfactants
- Water soluble initiator
- Emulsion polymerization in micelles



Used in wide variety of coating and paint applications

Acrylic dispersions

- **Secondary dispersions**
  - Polymerization in mass or solution
  - Neutralization of carboxylic acid with amines (anionic)
  - Dispersion in water
  - Lower molecular weight (10-50kD vs. 50-500kD)
  - No surfactants
  - Shear stability and improved moisture sensitivity

Acrylic dispersions

- **Crosslinking**
  - Physical drying:
    - Limited properties
    - Glass transition temperature (Tg)
  - Create a 3-dimensional network to improve resistance, hardness, blocking,... compared to physical drying systems
  - Self-crosslinking
  - 2K systems
  - Ambient curing
  - Heat curing (forced drying, baking)

Crosslinking

- **2K Polyurethanes**
  - Hydroxy-functional acrylic + polyisocyanate
  - Crosslinking density: MW, OH-value and stoichiometry NCO/OH

$$\mathrm{OCN{-}R{-}NCO} + \mathrm{H_2O} \longrightarrow \mathrm{OCN{-}R{-}NH{-}COOH}$$

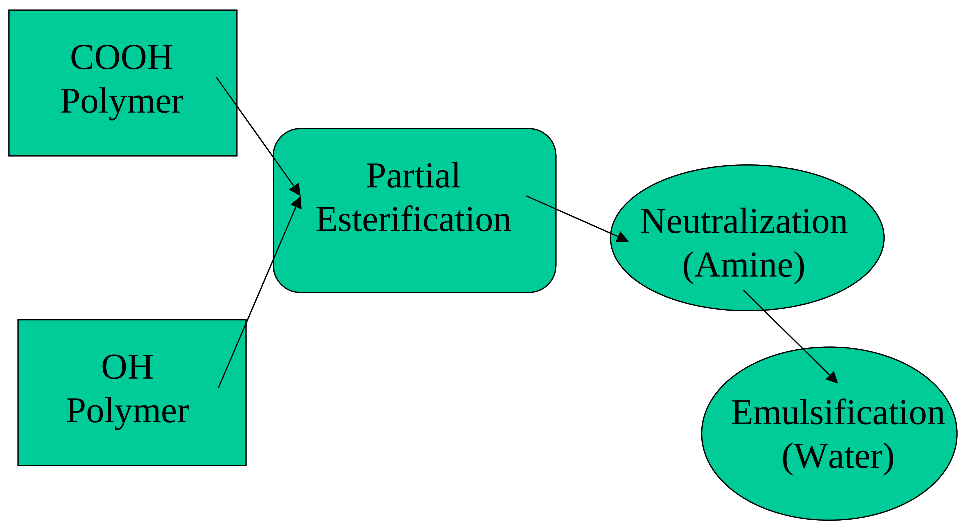
$$\longrightarrow \mathrm{OCN{-}R{-}NH_2} + \mathrm{CO_2}\uparrow$$

$$\mathrm{OCN{-}R{-}NH_2} + \mathrm{OCN{-}R{-}NCO} \longrightarrow \mathrm{OCN{-}R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}R{-}NCO}$$

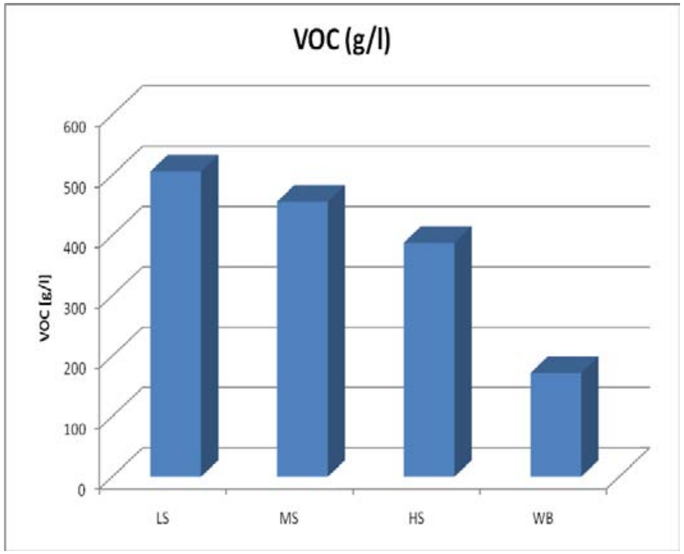
  - Reaction of isocyanate with water
    - 2K application equipment
    - Hydrophilic/hydrophobic isocyanates
    - Segmented hydrophilic/hydrophobic acrylics
  - Water/humidity resistance

- **Segmented hydrophobic/hydrophilic acrylics**
  - 1 Step approach: COOH/OH functional acrylic + epoxy

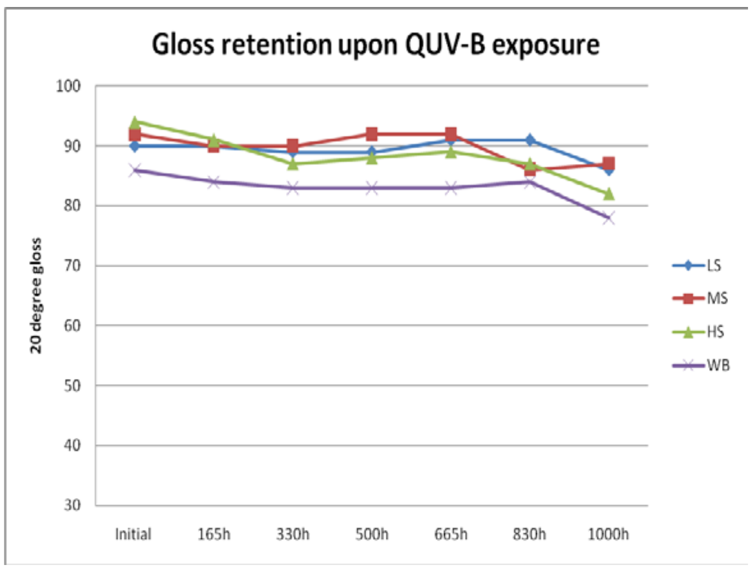
  - 2 Step approach: esterification of OH-acrylic with COOH-acrylic

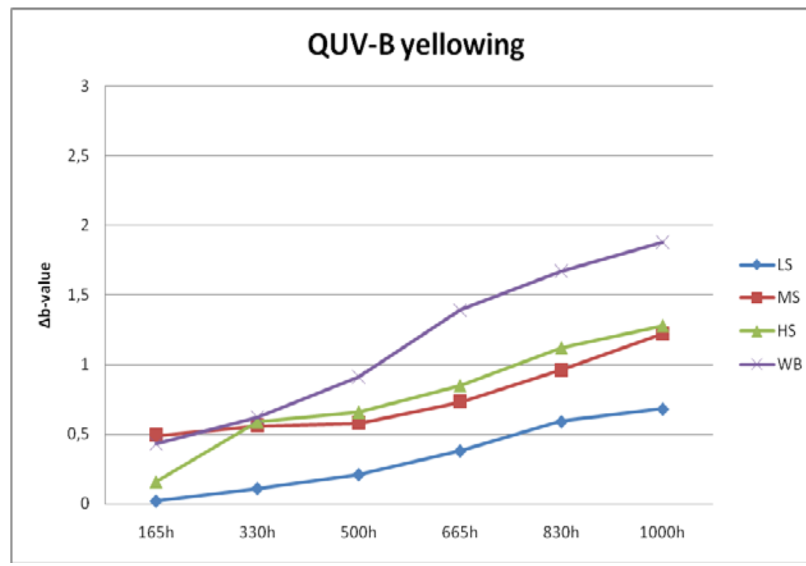


- **Automotive refinish and agriculture and construction equipment (ACE)**
  - 2K cure with isocyanates
  - 42% solids content, OH-value 135 mg KOH/g
  - Comparison with Low, Medium and High Solids Soventborne

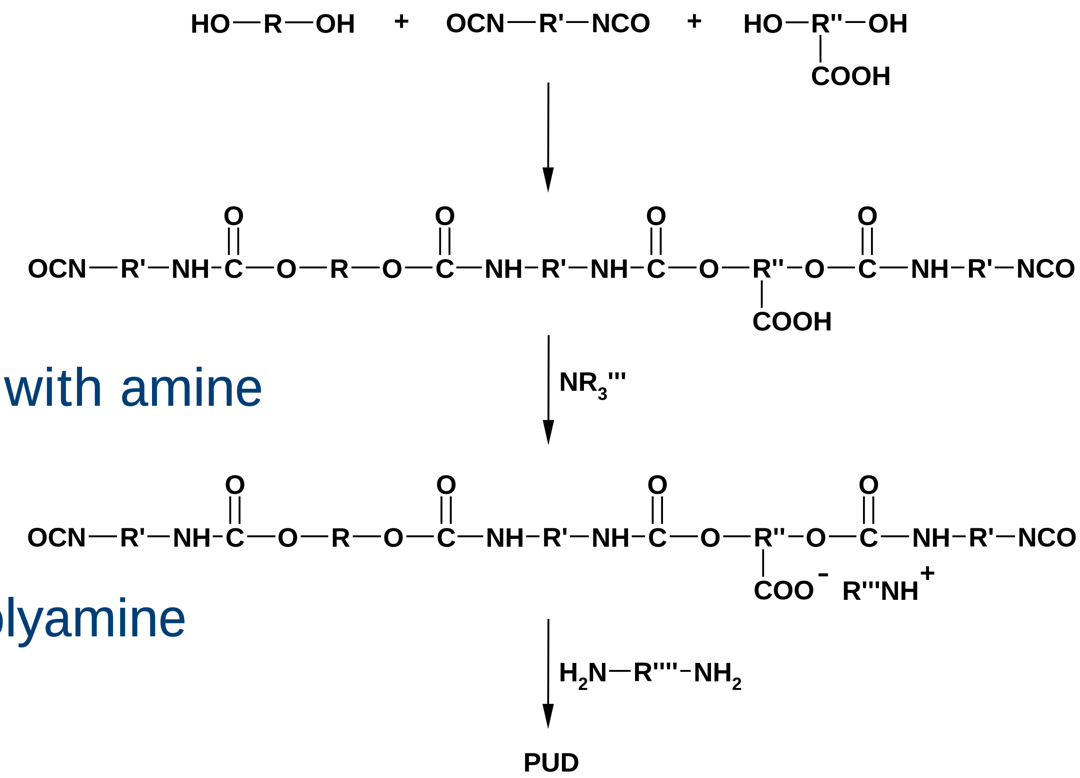


- **Comparison with Low, Medium and High solids Soventborne**
  - Hydrophobic/hydrophilic HDI trimer (1/1)
  - 140% NCO/OH
  - 45 minutes cure at 60C





- **Polyurethane synthesis and dispersion**
  - Polyol + NCO + COOH
  - Neutralization of COOH with amine
  - Chain extension with polyamine
  - Dispersion in water



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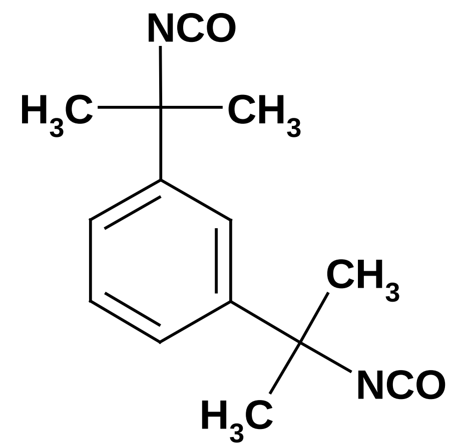
Polyurethane dispersions

- **Polyol + NCO + DMPA (Dimethylol propionic acid)**
  - – Solubility of DMPA
  - – Viscosity increase with molecular weight
  - – Solvent process:
    - Polar, aprotic solvents like acetone, MEK (remove after synthesis)
    - Coalescents like N-Methyl Pyrrolidone (NMP - R61), NEP
  - – Monomer process
    - Acrylate monomers as „solvent“
    - Polymerized to acrylic-PU hybrid or blend
  - – Solventless:
    - Tetramethylxylene diisocyanate (TMXDI)
    - Solvent free, very low VOC

Solventless process

- **Tetramethylxylene diisocyanate (TMXDI)**
  - Aliphatic isocyanate
  - Steric hindrance from methyl groups
  - Reduced reactivity towards nucleophiles
    - Less side reactions with water
    - Better stability at higher temperature
  - Reduced hydrogen bonding of urethane groups
    - Lower viscosity
    - Higher flexibility and adhesion



Polyester	Butylene adipate			Hexamethylene adipate		
Isocyanate	TMXDI	IPDI	H12MDI	TMXDI	IPDI	H12MDI
Viscosity @ 90°C (mPa.s)	7710	19500	34300	8260	16400	40000

Polyurethane dispersions

- **Wood flooring and industrial wood applications**
  - Solvent-free, aliphatic PUD
  - 35% solids
  - Flooring, furniture, kitchen cabinets,...
  - Excellent clarity
  - Natural wood aspect
  - Very good abrasion resistance
  - 1K or 2K curing
  - Aziridine or isocyanate curing at ambient T

- **Wood flooring and industrial wood applications**

		PUD 1K	PUD + isocyanate	PUD + aziridine
Set to touch		30 min	33 min	30 min
Tack free time		40 min	55 min	55 min
König Pendulum Hardness (150µ wet)	5hrs	48 sec		
	1 day	83 sec	110 sec	115 sec
	1 week	140 sec	155 sec	150 sec
Chemical resistance 1=worst, 5=best	Ethanol 1h	2	5	5
	Ammonia 2 min	5	5	5
	Water 16h	5	5	5
	Red wine 6h	4	5	5
	Coffee	3	3	4
Abrasion resistance CS17, 1000 cycles, 1 kg weight	Weight loss	30 mg	20 mg	15-20 mg

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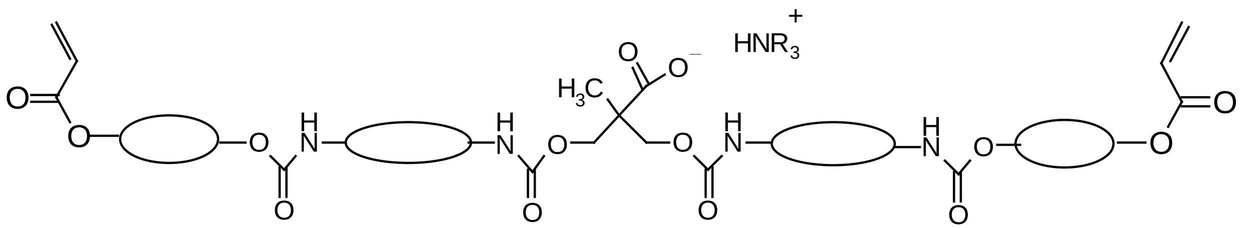
Polyurethane dispersions

- **High performance plastic applications**
  - Solvent-free, aliphatic PUD
  - 41% solids
  - High OH value (175 mg KOH/g) for 2K isocyanate curing
  - Excellent adhesion on a variety of plastic substrates
  - High gloss
  - Excellent chemical resistance, including marker pens
  - High water and humidity resistance
  - Outdoor resistance

Adhesion (cross cut with peel off test):		Pendulum hardness (König): 172 sec	
ABS	GT = 0		
PVC-h	GT = 0	Chemical resistance (Acetone): > 3 min	
PC	GT = 0	Hydrolysis test (72h, 90°C, 95% RH, ABS):	GT = 0/0
PP_{fl}	GT = 0	Humidity chamber (10 days, ABS):	GT = 0/0
PET	GT = 0	Water test (16 h/ 40 °C):	GT= 0/0

Polyurethane dispersions

- **UV-curable polyurethane dispersions**
  - Low viscosity compared to 100% UV systems
  - High molecular weight (10-20 kD) compared to 100% UV
  - No need to add a lot of monomers (skin irritation)
  - Spray applications
  - Physical drying before UV-curing (tack-free or not)
  - UV-radiation decomposes photoinitiators and creates radicals
  - This starts a radical polymerization of the acrylate double bonds and the end of the PU chain



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UV-curable PUD

- **High gloss plastic coating**
  - – Aliphatic, polyurethane dispersion
  - – 45% solids content
  - – 15 min drying at 40 °C
  - – 5 m/min with 80 W/cm Hg lamp
  - – Very good adhesion on plastic
  - – High gloss and mirror effect
  - – Excellent hardness
  - – High chemical resistance

Film properties	**UV-PUD**
Adhesion PVC	5B
Steel wool scratch	Pass
Persoz hardness	320 s
Stain resistance	5=no visible stain
Mustard	5
Coffee	3,5
Wine	5
Cola	5
Oil	5
Detergent	5