Ymer™ N-120

Time to change your Polyurethane Dispersions !

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Perstorp in brief

- 130 + years. Swedish HQ. 14 manufacturing sites globally, ca. 1,800 employees .
- World’s market leader in pentaerythritol, trimethylolpropane, speciality polyols, 2-ethylhexanoic acid, DMPA, ε-caprolactone/polycaprolactone and formaldehyde manufacturing technology.
- Strong emphasis on bio-based RM initiatives today.

Coating resins and paint- Perstorps offer

- Pentaerythritol, phthalic anhydride, isophthalic acid for alkyd resins
- Micronized Pentaerythritol and Di-Pentaerythritol for intumescent coatings.
- For PUD: Polycaprolactones (Capa™), Polycarbonate diols (Oxymer™), DMPA (BisMPA™) Non-ionic Diol(s).
- Polyols, Dendritics and Alkoxylates for Radcure systems.
- Trimethylol Propane, Neopentylglycol (Neo™) , BEPD, Di-TMP, for Polyester Resins.
- Capa™ as a reactive diluent in 2K PU.

Polyurethane dispersions

High molecular weight polyurethane dispersed in water

- Versatile products both in coatings and adhesives
- High performance system, flexible and tough
- Allows formulation of soft flexible or hard durable systems
- Environmentally friendly – low volatile organic content (VOC)
- Suitable for wide range of substrates e.g. wood, plastic, metal, leather & textiles

Where are PUD's used?

- Coatings
  - Metal
  - Wood
  - Glass
  - Concrete
  - Basecoats
  - Flooring
- Adhesives
- Leather finishes
- Textile Coatings
- Glass fiber sizings
- Film barriers




Polyurethane dispersions

Current developments

- NMP free PUDs
- Reduce solvent –> solvent free PUDs
- Increasing solid contents > 40 %
- Reduction of the use of amines
- Development of UV PUDs

Perstorp products for polyurethane dispersions

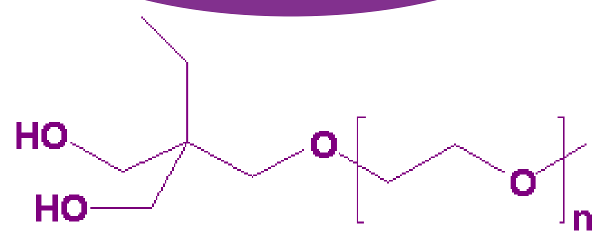
- Perstorp offers a wide palette of products for polyurethane dispersions

Bis-MPA™

Di-methylol propionic acid

Ymer™ N-120

Non-ionic diol



Capa™

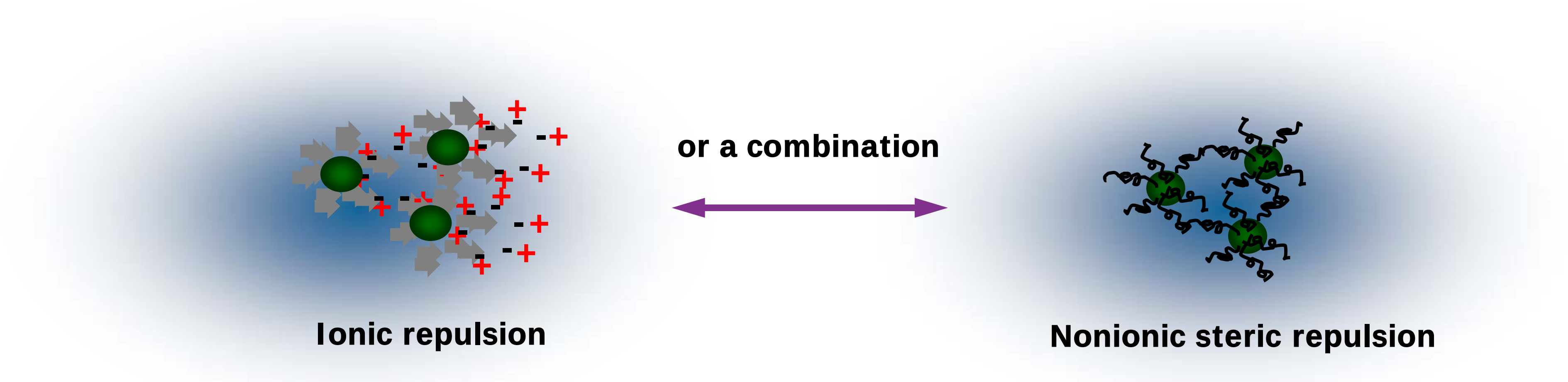
Polycaprolactones

Oxymer™

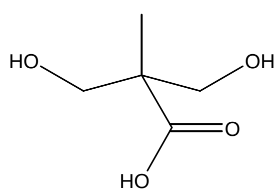
Polycarbonate diols

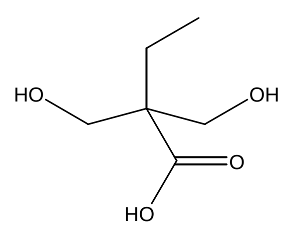
Internal stabilization of Polyurethane dispersions

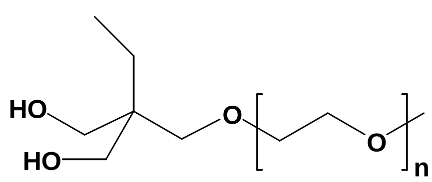
- Stabilization can be achieved using either ionic or nonionic (hydrophilic) segments



- **Ionic stabilization (anionic or cationic)** → neutralized di-hydroxy acids, e.g. dimethylol propionic acid (Bis-MPA) or dimethylol butanoic acid (DMBA)
- **Nonionic stabilization** → most common are polyethylene glycols



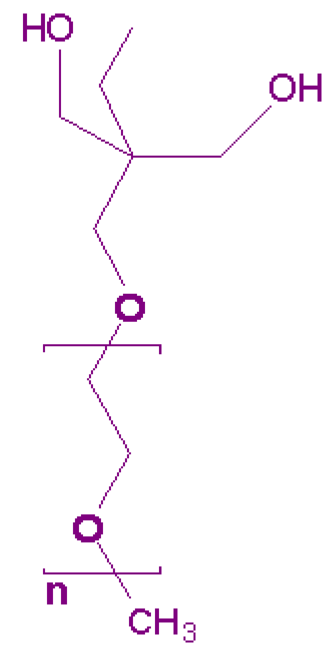




Ymer™ N-120 product characteristics

Diol with a long ethoxylated capped side chain which provides non-ionic segments in lateral positions along the polymer backbone

Appearance at RT:	white, waxy solid
Melting range:	20 – 40°C
OH-number:	100-120 mg KOH/g
Molecular weight:	~ 1,000 g/mol
Colour (liquid) Hazen:	< 100 APHA



Ymer™ N-120

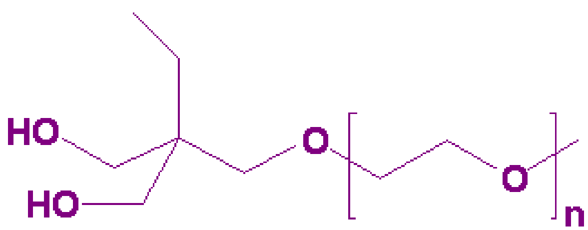
Non-ionic diol

Fulfills European polymer definition (exempted from Reach registration)

Advantages of Ymer™ N-120

Provides non-ionic segments in lateral position along the polymer backbone

- Ready to use, no additional synthesis step required, e.g. compared to adduct process
- Low viscosity product, decreases the need of co solvents during the prepolymer synthesis
- Two hydroxyl groups enables incorporation along the polymer backbone
  - No end capping of the polymer
  - Suitable in e.g. polyurethanes, polyesters and alkyd resins
- Contributes with increased stability towards pH variations
  - Highly increased stability towards electrolytes (salts)
  - Increased freeze/thaw stability



Ymer™ N-120

Non-ionic diol

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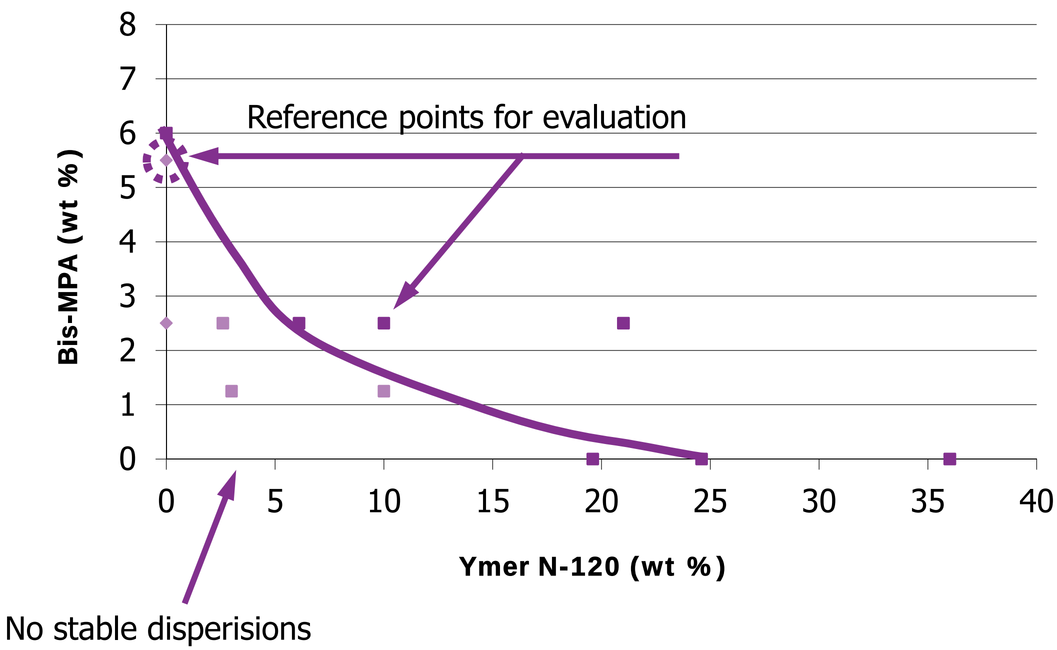
Formulation – content nonionic and anionic

Recommended content of Ymer™ N-120 and bis-MPA



➡ Recommended range: ≈ 10 wt % Ymer™ N-120 with 2.5 wt % bis-MPA[1]

[1] Stabilizer loading depends on formulation and dispersion technique.

Combination of Ymer™ N-120 and Bis-MPA

Combination of non-ionic and anionic stabilization

- The non-ionic stabilizer Ymer™ N-120 offers reduced prepolymer viscosity and lower amount of anionic stabilization required
- 4-10 wt %* of Ymer™ N-120 together with 3-4 wt %* of Bis-MPA in the prepolymer enables possibility to synthesize solvent free PUDs (NCO/OH > 1.5)
- Charge the diol, Bis-MPA and Ymer™ N-120, heat to obtain a homogeneous mixture, cool to suitable reaction temperature and charge the isocyante(s)
- Incorporation of Ymer™ N-120 in the PUD increases flexibility of the PUD, maintained chemical resistance but reduced hardness

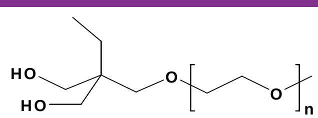
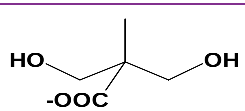
* Formulation dependant

PUD formulation

A comparative study between non-ionic co-stabilized PUD and a purely anionicly stabilized PUD

- PUD's prepared using the prepolymer melting process
- Polyester macro diol (hexane diol – adipic acid polyester)
- $H_{12}MDI$ (NCO/OH = 1.8), solid content of 35 wt %
- Non-ionic PUD is solvent free, anionic contains NMP (~ 4 %)
- The non-ionic PUD is co-stabilized with bis-MPA
  - Reduced water sensitivity and softness of the coating
  - Less non-ionic content needed

Wt % based on dry

Stabilizing	Non-ionic	Anionic
	10.3	
	2.5	5.5

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Materials

Prepolymer (step 1)	Non-ionic[1]	Anionic[2]
$H_{12}MDI$ Hexanediol adipate Ymer N-120 Bis-MPA DBTL NMP	37.8 49.0 10.6 2.6 0.04	39.4 44.7 5.1 0.04 10.8
Total	**100.0**	**100.0**
PUD synthesis	**Non-ionic**	**Anionic**
Prepolymer from step 1 Triethyelene amine Water Diethylene amine	33.7 0.6 64.7 1.0	35.8 1.3 61.7 1.2
Total	**100.0**	**100.0**
NCO/OH ratio Degree if neut. % NH/NCO molar ratio	1.8 90 0.8	1.8 90 0.8

- 4,4-dicyclohexylmethane diisocyanate
- Polyhexanediol adiapate (1,000 g/mol)
- NCO/OH=1.8
- NH/NCO=0.8
- Solid content = 35 wt %
- Dibutyltin dilaurate (catalyst)
- Triethylamine (neutralizing base)
- Ethylene diamine (chain extender)
- N-methyl pyrrolidone (NMP)

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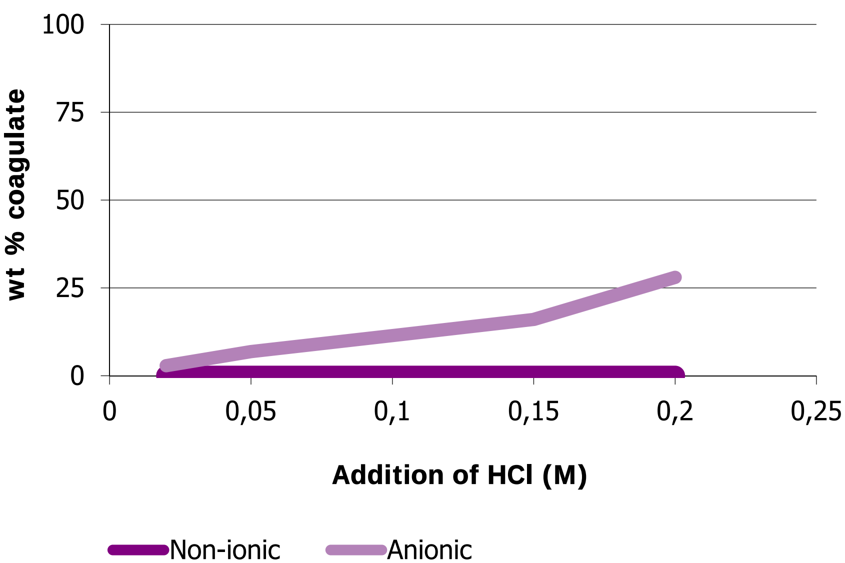
Synthesis and processing

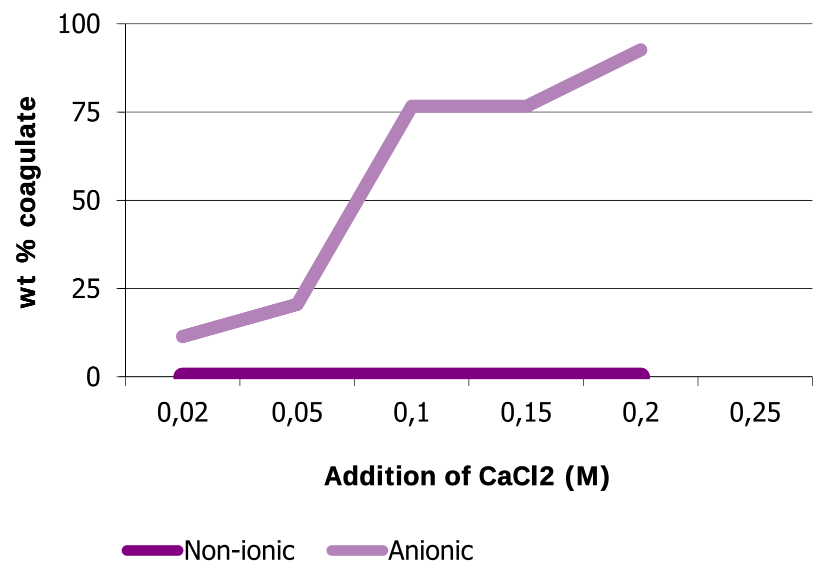
	Non-ionic	Anionic
Consolvent in synthesis	No	NMP (11 wt % on dry)
Appearance	Milky white	Transparent blueish
Viscosity mPas	7.8	13
pH	6.6	9.8
Stability	3 months 50°C	3 months 50°C

- Ymer™ N-120 enables synthesis of solvent free PUD's
- Equal stability of the non-ionicly co-stabilized PUD compared to the anionicly

Dispersion stability – electrolytes

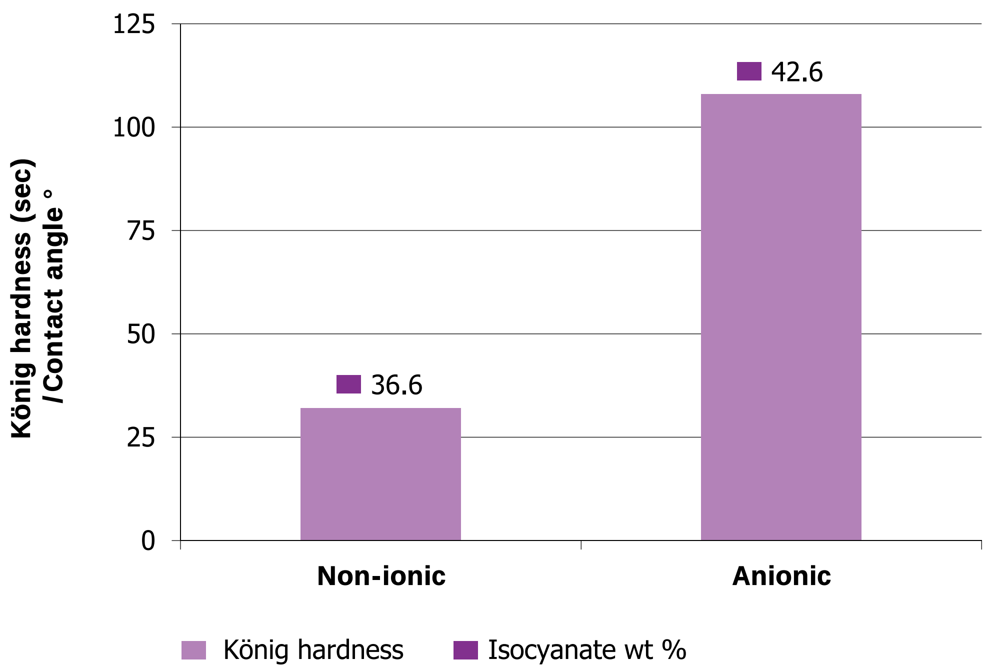
Hydrochloric acid (HCl)(aq) or Calcium Chloride ($CaCl_{2)}$ (aq) was added dropwise to the PUD with a maximum addition corresponding to 0.2M. Thereafter the PUD was filtered and any coagulate was collected, dried in the oven for 24 hours at 50°C and weighed.





➡ Non-ionic stabilized PUD's displays very low sensitivity towards pH and salt variations

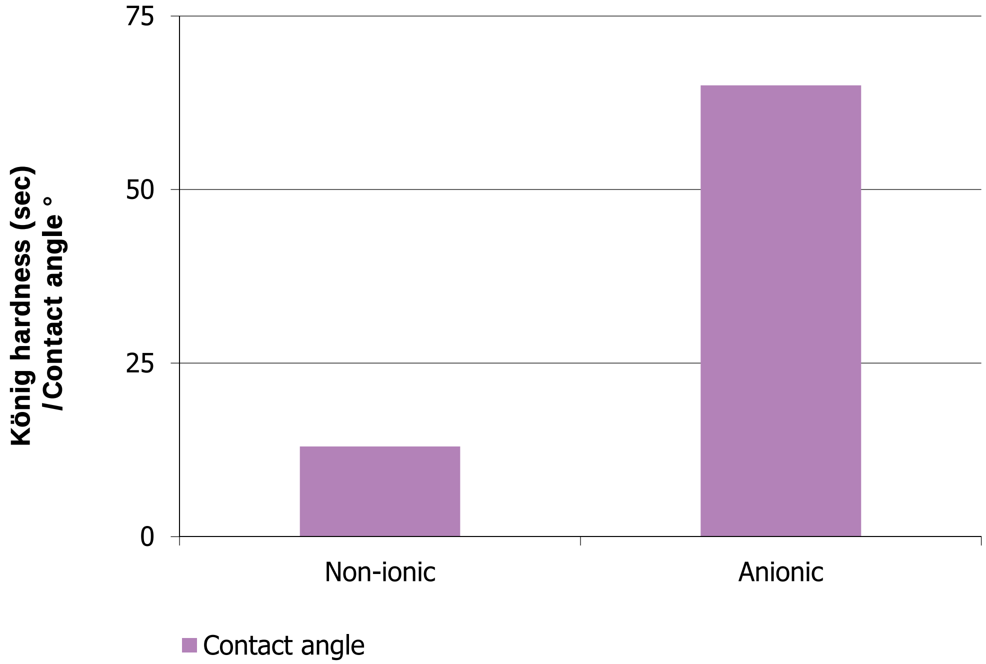
Coating hardness



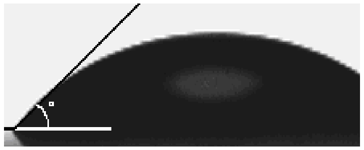
Pendulum hardness:
Coating tests were performed after a drying period of 72 hours at 23°C and 50 % RH. Dry film thickness was about 30 µm.

- Nonionic co-stabilization reduces the coating hardness – ethoxylates are flexible
- The non-ionic PUD use less content of cycloaliphatic polyisocyanate (weight basis)

Surface energy of the coatings

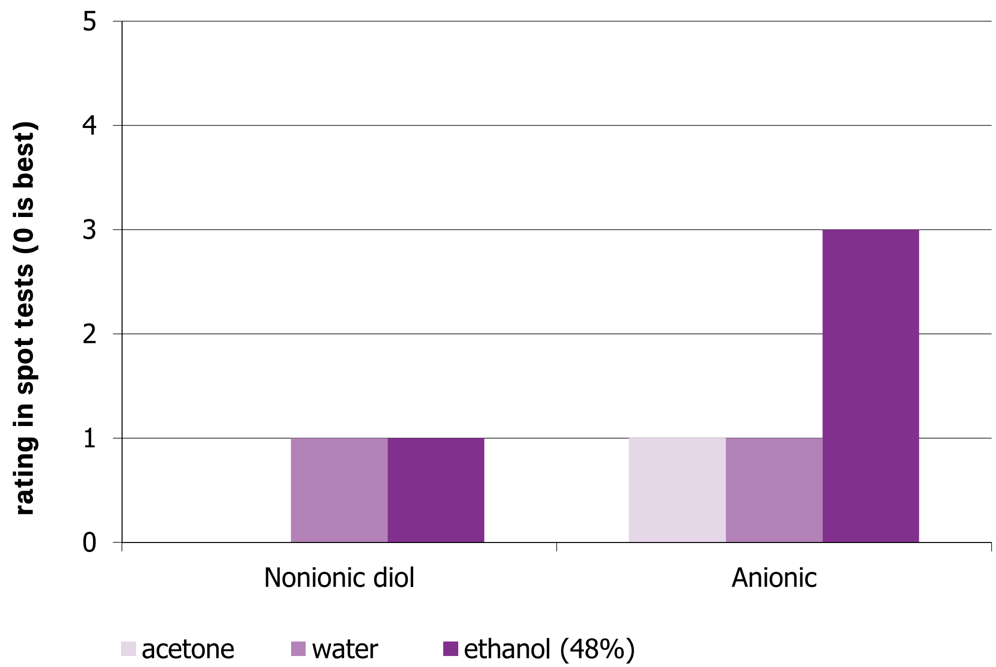


Contact angle:
Coating tests were performed after a drying period of 14 days at 23°C and 50 % RH.



- Non-ionic co-stabilization decreases the water drop contact angle – ethoxylates have high surface energy

Coating solvent resistance



Covered spot tests:
2 minutes (acetone), 24 hours (water) and 6 hours (ethanol), recovery 2 hours.

0 = no effect on the coating

5 = sever damage.

- Despite the higher fraction of hydrophilic segments nonionic co-stabilization show higher solvent and water resistance

Tensile properties – impact of water treatment

- Free films were immersed in water for 24 hours

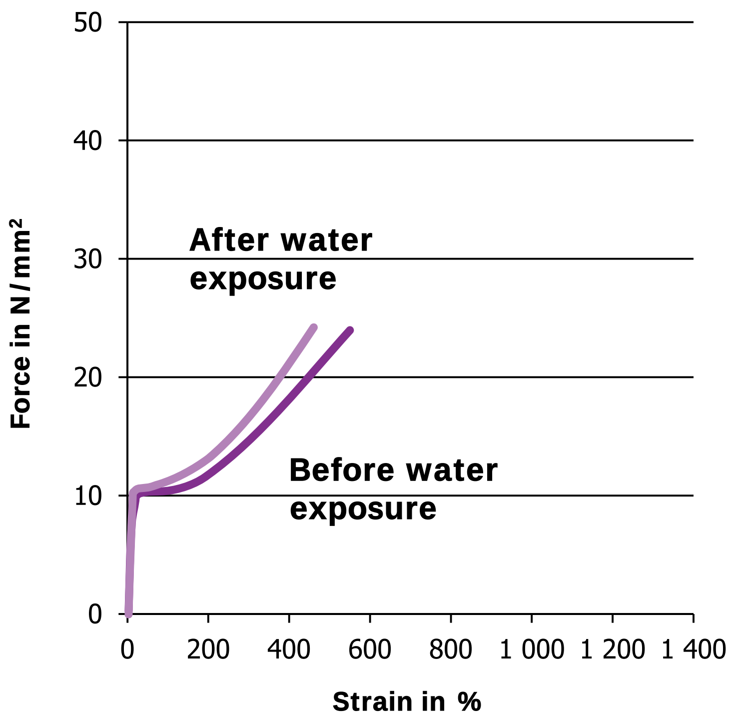
24 in water resulted in:
Nonionic: 17 wt % water
Anionic: 9 wt % Damaged

- Softer and flexible coatings with higher surface energy absorb more water
- A flexible structure reduces the build-up of internal stresses due to swelling

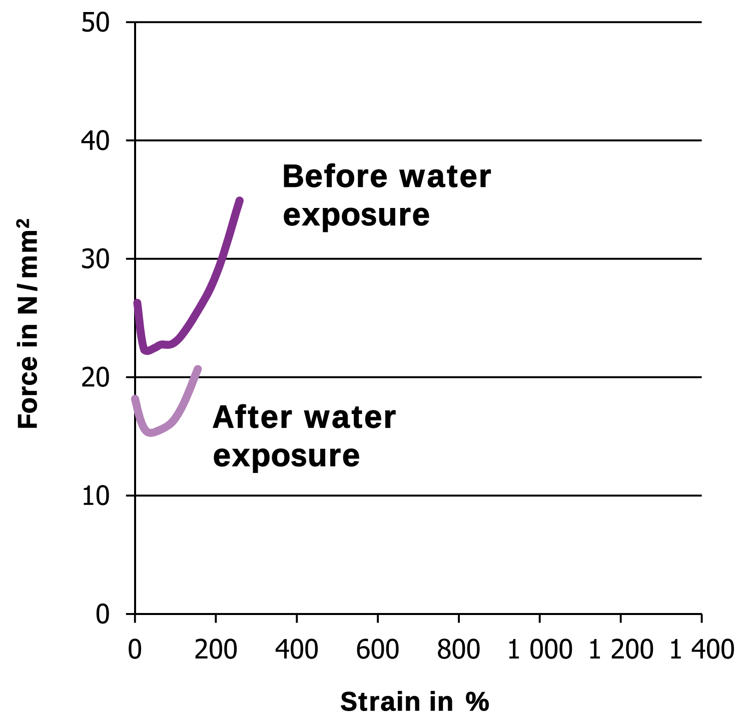
Tensile properties – impact of water treatment

- Nonionic co-stabilized PUDs form tough and flexible films

Non-ionic



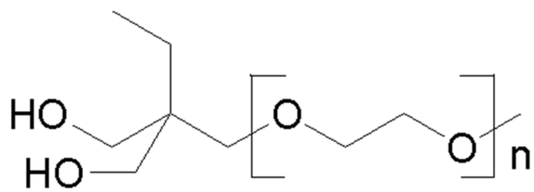
Anionic



- Tensile properties measured before and after water treatment
- Immersion in water 24 hours, 2 hour recovery, deformation rate 500 mm/min

Concluding remarks

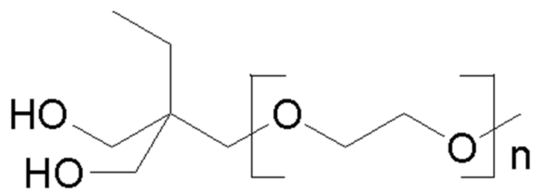
Ymer™ N-120



- Ease of processing, no adduct synthesis required
- Less/no neutralizing amine
- Reduced/no need for co-solvent
- Reduced content of isocyanates
- Increased stability in electrolytes
- Insensitive to pH variations
- Shear stable
- Freeze/thaw stable

Further concluding remarks

Ymer™ N-120



- Easier to incorporate than other non-ionics e.g PEG 600, MPEG 1000 due to lower M.Pt.
- Cost/Performance advantage over other high-end non-ionics.
- Well suited to softer, flexible substrates e.g leather & textile but also suitable for wood PU lacquers where Urea bonds content is high (> 1.8).
- Can assist pigment wetting and dispersion stability (TiO2)
- Perstorp have studied alternative ‘n’ values to deliver different properties.

Solvent free PUD

To obtain solvent free PUDs a reduced prepolymer viscosity is desired together with solubilized Bis-MPA

Possible ways towards solvent free PUDs

- Pre-neutralized Bis-MPA
  - Salts of Bis-MPA show highly improved solubility
- Combination of low viscous polyols together with a higher NCO/OH ratio
- Combination of Ymer™ N-120 and Bis-MPA
- Use of acetone process
  - Removal of acetone renders a solvent-free PUD

Thank you for your attention !

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Visit us at stand # 7A-623.

Ymer™ N-120

Non-ionic diol