Novel renewable polyesterimide-based alkyd resins for coating applications


Polycondensation 2016, Moscow/St.Petersburg, September 11-15, 2016
Our Strategy: based on global societal trends
Focus on innovation includes sustainable coating solutions

- Waterborne China Platform
- Discovery™
- Ultra™ NeoPac
- DSM-Niaga™
- LCA; B4↑; WB↑; SB↓; VOC ↓; Fully recyclable carpets
- AGI UV curable resins
Unique business positions of DSM Coating Resins to enhance sustainability

Among global leaders in resin systems for industrial and decorative and frontrunner in sustainable resins:

- Pioneer & Market leader in Resins for Water-Borne Coatings
- Pioneer & Market leader in Resins for Powder Coatings
- Emerging player in resins for 100% UV curable Coatings (DSM-AGI)
A real transformation to sustainable coatings

- Solvent borne coatings
- Water borne coatings
- UV curable coating
- Powder coatings


Acquisition and Divestment Events:
- NeoResins
- DSM - AGI
- Synres
Why go bio-based?

- One way to be more sustainable, next to cleaner processes & recycling (*NOTE: bio-based doesn’t inherently imply sustainable and low CFP!*)
- Decreasing fossil feedstock (*and fluctuating oil prices*)
- Become politically less dependent on oil producing countries
- Stricter environmental impact regulations (*legislation*) demand for higher sustainability and reduced Carbon Footprint
- New materials obtainable, sometimes with enhanced performance, with entirely new chemistry and unprecedented combinations of properties

*Scientific, environmental, economic & political reasons*

**BUT:** Customer asks for performance; Bio-based is (still) ‘nice to have’
Alkyd resins

Alkyd resins are polycondensates based on:

- Fatty acids or vegetable oils 30-70%
- Polyols like glycerol/pentaerythritol/TMP 10-30%
- Polyacids like phthalic anhydride/IPA 10-40%
- (Benzoic acid as $T_g$ booster/chain stopper 0-20%)

Characteristics

- Broad molecular weight distribution; branched structure
- Residual hydroxyl and carboxyl groups for wetting properties
- Versatility in design
- Renewable monomers
- Auto-oxidative curing of fatty acid residues using metal-based dryers as catalyst (e.g. Fe)

[Chemical structure of alkyd resin]

$\text{Mn} = 5 \text{ kD}$
$\text{Mw} = 100 \text{ kD}$
Renewable alkyd resins

Our goal: Develop ≥ 80% renewable alkyd resin emulsion:

- Oils & fatty acids

- Polyols: glycerol, pentaerythritol available
Renewable alkyd resins

Our goal: Develop $\geq 80\%$ renewable Alkyd resin emulsion:

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Renewable alkyd resins

Our goal: Develop ≥ 80% renewable Alkyd resin emulsion:

- Oils & fatty acids
- Polyols
- Polyacids (+ monoacid)

Problem: hard, Tg boosting renewable (aromatic or cycloaliphatic) acids are currently not available at large scale
Renewable hard polyacids

→ Future solutions (> 2016) (non-exhaustive):

1) 2,5-furandicarboxylic acid (dimethyl ester)
   *Too late/IP for alkyds/branched polyesters owned by Perstorp!/
   *No enhanced properties w.r.t. phthalic anhydride-based alkyds*

![Chemical Structure]

2) Bio-based (tere)phthalic acid in the pipeline
   *Too late for short term solution and product development*
Novel *biobased* imides as renewable building blocks

**Target**
- To replace high-$T_g$ phthalic anhydride, benzoic acid and IPA/TPA by *biobased* alternatives
Novel *biobased* imides as renewable building blocks

**Target**
- To replace high-$T_g$ phthalic anhydride, benzoic acid, IPA and TPA with *biobased* alternatives

**How?**
- Using imides prepared *(in situ)* from natural amino acids and bio-based succinic acid and citric acid:

  - phenyl alanine
  - glycine
  - lysine
  - succinic acid
  - citric acid
Amino acid + citric acid $\rightarrow$ dicarboxylic acid replacing PA

Amino acid + succinic acid $\rightarrow$ monocarboxylic acid replacing benzoic acid

$\text{R} = \text{H}$ is glycine succinimide;  
$\text{R} = \text{benzyl}$ is phenyl alanine succinimide
Synthesis of imide compounds using xylene azeotrope

Citric acid was reacted at elevated temperature in appropriate amounts of xylene (*azeotropic water removal*) with phenylalanine (R = benzyl) or with glycine (R = H), furnishing the dicarboxylic acid structure (1).

A similar reaction in xylene of succinic acid with phenylalanine or with glycine yielded the mono-functional carboxylic acid structure (2) (R = H for glycine; R = benzyl for phenylalanine).

Succinic acid with lysine in xylene furnished the mono-functional carboxylic acid structure (3).
Lysine disuccinimide

Of desired reaction product:
Left imide ca. 100% formed
Right imide ca. 82% formed
(Rest in amic-acid form)
Residual succinic acid present
Glycine succinimide

Desired reaction product: 82% (of which imide/amide ratio is 89/11)
Residual succinic acid
Phenylalanine succinimide

Of desired reaction product (ignoring xylene traces):
Imide/amide/residual succinic acid = 87/8/5
1H-NMR of citric acid/(D/L)phenylalanine reaction product

Main product (89%, two isomers, D/L)

Dehydrated-1
3% (6.56 ppm)

Dehydrated-2
1% (5.66 ppm)

Dehydrated/Decarboxylated 1 and 2
3% (6.56 ppm)
1% (6.21 + 5.66 ppm)

Conclusion: appr. 4% monocarboxylic acid; also 2-3 % amide (amic-acid)
Possible side reactions at high T & synthesis alkyds

Possible decomposition routes for citrimides

So, T polyester-imide alkyd resin synthesis as low as possible
Melt polycondensation temperature: 180-220 °C (only at end 220 °C); reaction water azeotropically removed using xylene/Dean-Stark trap.
Resin characteristics of ca. 80 wt% bio-based polyesterimide-based alkyds from soybean fatty acid, bio-based pentaerythritol and either phthalic anhydride (PA) or benzoic acid (BA) or one or more of the following imide building blocks:

* Voxtar™ M100 (Perstorp);
Succinimides based on Biosuccinium™ (Reverdia)
Paint preparation from xylene-based systems

From the obtained xylene-dissolved resins, paints were produced by mixing in a Cowless dissolver:

- resin solution (44 g solid resin)
- 28 g of Tioxide TR 92 (pigment)
- 0.30 g of Nuosperse FA 601 (dispersant)

and milling them into a mill paste.

To this paste were added under stirring:

- 0.31 g Borchi OXY-Coat (iron drier)
- xylene to give a suitable application viscosity.
# White paint properties of xylene-cast resins

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DMTA of typical, xylene-cast, ca. 80 wt% bio-based resins

Physical & chemical drying

Alkyd comprising:
- PA
- Voxtar pentaerythritol
- Lysine succinic diimide from Biosuccinium
- Soya Fatty acid or
- Soya Fatty acid/conjugated SOFA 75/25

$T_g = 18.2 \, ^\circ\text{C}$

Modulus, $G^*$ [Pa]

$T$ [$^\circ\text{C}$]

Phyiscally dried 1 day drying

Tg commercial alkyd Uradyl AZ 760: 12 $^\circ\text{C}$
Preparation emulsions (SAD process)

Reference Resin, Resin 3 and a 50/50 wt/wt mixture of resins 3 and 4:

- dissolved in acetone
- part of the carboxylic acid groups were neutralized with a non-amine base
- the neutralized resin solution was mixed with water
- the acetone was removed by distillation

NOTE: the milky alkyd emulsions were stable

Reference: Soybean fatty acid, bio-based pentaerythritol, PA and BA
Resin 3: Soybean fatty acid, bio-based pentaerythritol, PA, lysine disuccinimide
Resin 4: Soybean fatty acid, bio-based pentaerythritol, PA, phenylalanine succinimide
Towards more sustainable systems: Polyester-imide alkyd emulsions

Via SAD process, no emulsifier, non-amine base for neutralization of COOH groups of the resin. Volume-average Particle Size: 81 nm
Paint preparation from emulsified resins

Pastes were produced by mixing in a Cowless dissolver:

- 5 g of demi water
- 22.5 g of TiO\textsubscript{2} (Tioxide TR 92)
- 1.1 g of Disperbyk 2015 (dispersant)
- 0.1 g of Byk 028 antifoam agent

and subsequently mixing these compounds into a mill paste.

To this paste were added under stirring:

- the resin emulsion (25 g solid resin)
- 0.88 g Borchi OXY-Coat 1101 iron drier (diluted 10 times in demi water)
- 7.2 g of Acrysol RM2020 (thickener)
- demi water

resulting in a solids content of 48%.
### White paint properties of emulsion-based coatings

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Summary/Main conclusions - 1

Our work on novel polyesterimide-based alkyd resins with high renewable contents of appr. 80 wt% (*higher is possible*) showed the following:

- Novel imide-containing renewable building blocks for alkyd resins can be manufactured from naturally occurring amino acids and bio-based succinic and citric acid.

- Incorporation of these building blocks into alkyd resins is possible using standard condensation polymerization chemistry and technology.

- The polyester-imide alkyds can be dissolved in xylene or emulsified in water and from the resulting solutions and emulsions coatings can be made that dry faster and show enhanced hardness compared to the corresponding coatings based on a reference alkyd (ca. 40 wt% biobased).
Summary/Main conclusions - 2

- The polyesterimide-based alkyd resins exhibit a slightly higher initial color and a somewhat more pronounced yellowing in the dark compared to a phthalic acid and benzoic acid-based reference alkyd.

- For the emulsion based on lysine disuccinimide the water resistance is a point of attention. For the phenylalanine succinimide based systems this is OK.

- Data taken from: WO2015/052342A1 to DSM IP ASSETS B.V., Polymer and composition
Problem to be solved with faster drying imide containing alkyd resins!!

Picture: https://richardtommycampion.files.wordpress.com/2013/10/1229935_506772539411812_2051790592_n.jpg
Acknowledgements

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