biosuccinium®

sustainable succinic acid

enabling sustainable materials

RESINS AND COATINGS
DATA SHEET

enabling sustainable materials

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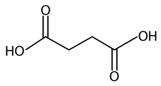
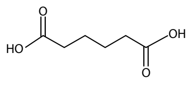
INTRODUCTION

Biosuccinium™ sustainable succinic acid is a 100% bio-based succinic acid that enables you to manufacture resin and coating products with lower environmental footprints. Biosuccinium™ offers an alternative to traditional chemicals such as fossil-based succinic acid, adipic acid or terephthalic acid which are conventional raw materials used for resins, coatings, adhesives, and sealants.

This data sheets aims at showing some examples of uses of bio-based succinic acid in resins and coatings to illustrate potential opportunities. The examples are taken from different sources and references are given for more information.

Table 1: Properties of succinic and adipic acid

	Succinic acid	Adipic acid
Molecular structure		
Molecular formula	$C_4H_6O_4$	$C_6H_{10}O_4$
Molecular mass [g/mol]	118,09	146,14
Melting temperature [°C]	184	152

POLYESTER RESINS

Topic: Succinic acid use in polyester resins

Author: Dow Chemical

Presentation: ANTEC® 2011

Key findings: The polyester resin was based on neopentyl glycol, trimethylolpropane, isophthalic acid and either adipic or succinic acid. A comparison was made between the succinic and adipic based resin, and the following observations were made:

- Higher T_g of resin (by 8-18 °C than adipates for this specific formulation), higher viscosity
- Dramatically higher hardness
- More gouge resistance, similar or slightly lower scratch resistance
- Similar acid resistance
- Similar high gloss and clarity

Reference: Materials from Succinic Acid – A Renewable Resource, S. Guillaudeu, M. Sonnenschein, B. Wendt, J. Argyropoulos, O. Uzun, ANTEC®, Society of Plastics Engineers, May 3, 2011

POLYURETHANE DISPERSIONS

Topic: Succinic acid use in polyurethane dispersions

Author: Bayer Material Science

Presentation: 2013 European Coatings Congress

Abstract: The carbon footprint of polyurethane dispersions can be significantly lowered by using renewable polyester polyols that can be synthesized by a typical condensation of diacids and diols. By using renewable succinic acid with 1,3-propanediol or 1,4-butanediol it was possible to synthesize polyester polyols with a molecular weight between 1650 and 1900 g•mol-1 and a renewable content up to 100 wt%. The polyols were used in the synthesis of aliphatic polyurethane dispersions for two different application areas. For a thermo activated adhesive a semicrystalline polyol should be used and for waterborne aqueous PU leather an amorphous polyol is necessary. It could be shown that both product types can be made from renewable polyols with comparable application properties compared to standard products. This path opens new possibilities for a new more sustainable generation of PU systems.

Reference: Hans Georg Grablowitz, Bayer MaterialScience, Sustainable solutions with bio based PU-dispersions, European Coatings Congress, Nürnberg, Germany, March 18+19 2013

DIMETHYL SUCCINATE – PROVICHEM® 2511 Eco

Topic: Use of Dimethyl Succinate, a chemical derivative of succinic acid, as a solvent and a raw material for specific pigment (see general properties of Dimethyl Succinate in table 2).

Author: Reverdia

Presentation: Internal

Table 2: General Properties of Dimethyl Succinate

Parameter	Value	Unit
Boiling point	196	°C
Hansen solubility parameter		
Dipolar intermolecular forces delta P	7,7	-
Dispersion forces delta D	16,1	-
Hydrogen forces delta H	8,8	-
Melting point	21,9	°C
Refractive index	1,41 – 1,43	- (at 20 °C)
Dielectric constant	5,1	- (at 20 °C)
Specific gravity	1,11	kg/l (at 25 °C)
Water solubility	8,5	g/l (at 20 °C)

Use as Solvent

Applications for Dimethyl Succinate as solvent often compare its performance versus so called DBE solvents. DBE is a byproduct from the nylon production process and is a blend of 3 esters: succinate, glutarate and adipate. Basic properties of DBE and Dimethyl Succinate are quite similar; both are colorless liquids with a specific density of about 1,1 kg/l, refractive index of ~ 1,42 and viscosity at 40 °C of 1,7-1,8 cSt. Typical applications for DBE are cleaning solvents for example for paints and inks. First indicative lab testing showed similar or better performance of Dimethyl Succinate for cleaning of paint and grease.

Use as Raw Material for Pigments

The use of biobased Dimethyl Succinate as raw material for pigments leads to a renewable content in the pigment of about 40% in the case of quinacridones. In addition, the carbon footprint of the pigment can be reduced. Pigments that are based on Dimethyl Succinate are:

- PV-19 (color index number 73900)
- PR-122 (color index number 73915)
- PR-202 (color index number 73907)

Another group of pigments—Diketo-Pyrrolo-Pyrroles, DPP—is based on another ester of succinic acid, being di-isopropyl succinate.

Availability: Biobased Dimethyl Succinate has been commercialized by Proviron under the name Provichem® 2511 Eco. For more information visit www.proviron.com or contact Reverdia.

Reference: Reverdia internal data

POLY-ISOSORBIDE-SUCCINATE FOR POWDER RESINS

Topic: Resin system based on succinic acid and isosorbide

Author: Dutch Polymer Institute (Noordover and coworkers)

Presentation: 2013 European Coatings Congress

Abstract: Co- and terpolyesters based on succinic acid and isosorbide in combination with other renewable monomers such as 2,3-butanediol, 1,3-propanediol, and citric acid were synthesized and characterized. Linear polyesters were obtained via melt polycondensation of nonactivated dicarboxylic acids with OH functional monomers. Polymer end functionality (i.e., hydroxyl or carboxylic acid) was controlled by adjusting the monomer stoichiometry. The glass transition temperatures of the resulting polyesters could be effectively adjusted by varying the polymer composition and molar mass. By adding polyfunctional monomers such as trimethylolpropane or citric acid, polyesters with enhanced functionality were obtained. These biobased polyesters displayed functionalities and Tg values in the appropriate range for (powder) coating applications. The polyesters were cross-linked using conventional curing agents. Coatings from branched polyesters - hydroxyl as well as acid functional - showed significantly improved mechanical and chemical resistance compared to those formulated from linear polymers. These renewable polyesters proved to be suitable materials for coating applications with respect to solvent resistance, impact resistance, and hardness.

Reference: Co- and Terpolyesters Based on Isosorbide and Succinic Acid for Coating Applications: Synthesis and Characterization, B.A.J. Noordover, V.G. van Staalduinen, R. Duchateau, C.E. Koning, R.A.T.M. van Benthem, M. Mak, A. Heise, A.E. Frissen, J. van Haveren, Biomacromolecules, Vol. 7, No. 12, 3407, 2006)

ALKYD RESINS WITH INCREASED RENEWABLE CONTENT

Topic: Succinic acid use in high solid alkyd resins

Author: Nuplex Resins BV

Presentation: 2013, Seminar Green and Biobased Paints

Abstract: Alkyd resins generally consist of multifunctional polyols (like pentaerythritol) and polyacids (like phthalic acid or it's anhydride), modified with fatty acids. The fatty acid fraction leads to an "intrinsic" renewable content.

The work presented here highlights the development of alkyd resins and paint formulations with an increased renewable content. The traditional polyols and polyacids are replaced with renewable monomers, like succinic acid. Using various types and combinations of biobased polyols and polyacids, the biobased content of the alkyd resin could be increased from 66% to 96%.

As an additional step, the traditional solvent (D40) has been replaced with the biobased solvent DMS (dimethyl succinate). The viscosity of the paint was not affected by the different solvent, but the drying characteristics improved significantly with a reduction in drying time of up to 40%.

Furthermore, the alkyd based on Biosuccinium-D40 combination showed a significantly higher Persoz Hardness (10-15s higher). The alkyd based on Biosuccinium-DMS combination showed a similar hardness compared to the reference, but hardness developed faster over time.

Reference: Dirk Mestach, Nuplex Resins BV, Sustainable Binders for the Paint Industry, Seminar Green and Biobased Paints, Nieuwegein, the Netherlands, May 28 2013

UV CURABLE POLYESTER ACRYLATES

Topic: Succinic acid use in UV-curable acrylates

Author: DSM Coating Resins BV

Presentation: DSM Coating Resins BV, Internal

Abstract: UV-curable acrylates were synthesized using commercially available biobased monomers, and fossil-based acrylic acid. The objective was to synthesize resins with as high a renewable carbon content as possible, and to evaluate such resins on curing speed and final film properties.

An oligomeric polyester acrylate was made based on bio-pentaerythritol and Biosuccinium; this resin has a renewable carbon content of 44%. Both curing speed and final film properties are very good.

Additionally, a reactive diluent was made based on bio-based 1,3 propanediol and Biosuccinium; this resin has a renewable carbon content of 63%, and a good curing speed . Due to the linear nature, the hardness however is relatively low, and this reactive diluent is probably best to be used in combination with an oligomer of higher functionality and molecular weight.

Reference: Philip Davies/Hans Groen, DSM Coating Resins BV, UV-curable Resins based on Biosuccinium, Internal report, September 2013

Table 3. Properties of Biosuccinium-based UV Curable Acrylates

		Example 1	Ref 1	Example 2	Ref 2
Parameter	Unit	Oligomer		Reactive diluent	
Monomers (*= biobased)		Pentaerythritol* Succinic acid* Acrylic acid	Neorad P-60 (Fatty acid* modified poly-ester acrylate)	1,3 propanediol* Succinic acid* Acrylic acid	Tri-propylene glycol Acrylic acid
Renewable carbon content					
Biosuccinium fraction	%	12		25	
Total		44	40	63	0
Functionality	-	6	6	2	2
Molar mass, theoretical	g/mol	678	1100	342	300
Viscosity	mPa.s	24.000	8-10.000	79	10-16
Cure speed (double MEK rubs) 1*300mJ/cm2	-	> 200		> 200	
Film properties	-	Good		Good	
Film hardness	König seconds	119		31	

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