Lubricant Fluids from Bio Succinic Acid

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INTRODUCTION

BioAmber is a next generation chemicals company, with a portfolio of renewable chemicals; a C4 Platform, based on bio succinic acid and its derivatives, including bio 1,4-butanediol, and a C6 Platform, which includes bio adipic acid and other bio-based C6 chemicals. BioAmber was first to market with commercial scale bio-based succinic acid, and is currently serving customers from a plant in France. Based on growing market demand for bio-based chemicals, BioAmber is constructing a large-scale plant in Ontario, Canada, to supply industrial scale bio succinic acid. As a platform chemical, BIO-SA™ succinic acid has a wide range of applications, including as an intermediate for bio based synthetic ester lubricants.

Dibasic acid esters generally have low pour points, good thermal stability and excellent solvency.[1] These diesters are classified as synthetic lubricants, and are often based on petroleum derived adipic acid. Adipate diesters are used in a variety of lubricant formulations including crankcase lubricants, compressor oils, textile lubricants, military lubricants, gear oils, circulating oils, metal working fluids, and hydraulic fluids.[2] Adipate esters are often used in combination with polyalphaolefins (PAOs) for applications such as screw compressor oils, gear and transmission oils, automotive crankcase oils, and hydraulic fluids. They are also used as the sole base stock when biodegradability is desired, or high temperature cleanliness is critical.

Succinic Acid has emerged as one of the most competitive of the new bio based chemicals. BioAmber bio-based succinic acid process technology is carbon neutral at industrial capacity. The Sarnia, Ontario plant will generate a savings of >100% greenhouse gas emissions, and uses 60.9% less energy compared to petrochemical production of adipic acid kilogram per kilogram.[3] The use of BIO-SA™ from BioAmber immediately reduces the overall footprint of any product, when used as a direct replacement for energy and carbon intensive petrochemicals.

Diesters from BioAmber's BIO-SA™ are bio based alternatives to petroleum based adipate esters for lubricants. They provide low pour points, relatively high viscosity indices, and high flash and fire points. Succinate esters are soluble in mineral oil, and may be used as an additive, or as the sole base stock fluid. Due to their low pour points, they may also be used to modify bio based lubricant base stocks. The low viscosity makes the succinate esters suitable for Industrial Fluids, and is particularly attractive as metal working fluids.

EXPERIMENTAL

A series of five succinate diesters were synthesized by reacting BioAmber's BIO-SA™ with the corresponding alcohols (Figure 1). These diesters were selected in order to screen the lubricant properties across a range of molecular weights, with both branched and linear diesters. Isoamyl alcohol, ethylhexyl alcohol, isononyl alcohol, and isodecyl alcohol were used to synthesize pure diesters of succinic acid. A mixture of octyl and decyl alcohol was used to synthesize the mixed ester, octyl decyl succinate (ODS). This succinate ester has the potential to have up to 100% bio based carbon as defined by ASTM D6866, if the alcohol stream is sourced from plant feedstocks.

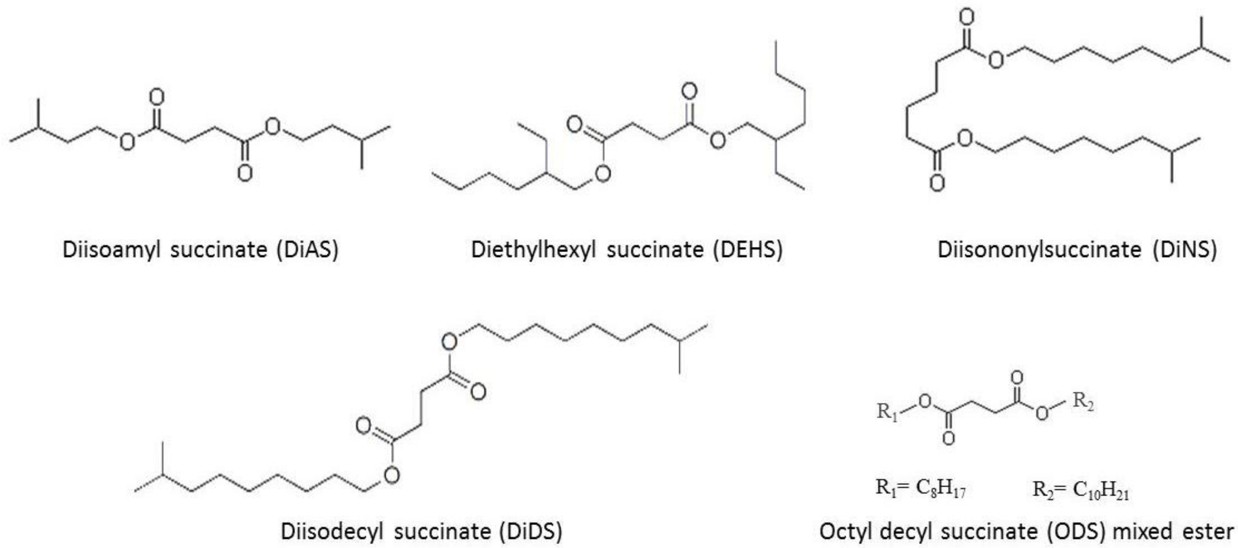

Figure 1. *Succinate Esters for Lubricant Fluids*

The succinate esters were evaluated at the University of Northern Iowa National Ag Based Lubricants Center for a number of key lubricant properties using standardized test methods. Diethylhexyl adipate (DEHA) at 97% purity was used as a benchmark for property comparison. All diesters were tested without additives or addition of other base fluids. Table 1 summarizes the test methods used to measure lubricant performance of succinate esters.

Table1. Experimental Test Methods for Lubricant Performance Evaluations

Property	Method
Viscosity	ASTM D445
Viscosity Index	ASTM D2270
Four Ball Wear	ASTM D4172
Load Wear Index	ASTM D2793
Weld Point	ASTM D2783
Pour Point	ASTM D97
Flash Point	ASTM D92
Fire Point	ASTM D92
Cloud Point	ASTM D5772
RPVOT Oxidation	ASTM D2272

RESULTS AND DISCUSSION

Table 2 summarizes the viscosity profiles of the succinate esters and diethylhexyl adipate benchmark. Viscosity at both 40 °C and 100 °C increases with increasing diester chain length. Diethylhexyl succinate has very similar viscosity profile to diethylhexyl adipate indicating that succinate esters are viable replacements for petroleum based adipic acid esters. Overall, viscosity indices are high, indicating limited change in viscosity with temperature.

Table2. Viscosity Properties of Succinate Ester Lubricants

Diester	Viscosity at 40 °C (cSt)	Viscosity at 100 °C (cSt)	Viscosity Index
DiAS	6.05	1.38	-
DEHS	7.58	2.2	90
ODS	9.15	2.65	132
DiNS	9.99	2.71	110
DiDS	12.13	3.06	112
DEHA	7.55	2.01	120

Table 3 summarizes the physical properties of BIO-SA™ based diesters. Succinate esters exhibit excellent pour points, with most diesters having pour points <65 °C. The one exception is the octa decyl succinate mixed ester, which shows a higher pour point of 1 °C. The higher pour point is most likely the result of using linear alcohols versus branched alcohols for the succinate diesters. Flash and fire points are near or above 200 °C for all diesters with the exception of diisoamyl succinate, the lowest molecular weight diester.

Table3. Physical Properties of Succinate Diester Lubricants

Diester	Pour Point (°C)	Flash Point (°C)	Fire Point (°C)	Cloud Point (°C)
DiAS	<-65	138	142	-18.8
DEHS	<-65	198	206	<-65
ODS	1	220	224	17.3
DiNS	<-65	209	220	
DiDS	<-65	215	236	
DEHA	-53	201	229	

Wear properties of succinate esters and the adipate diester benchmark are shown in Table 4. While ODS has a higher pour point compared to the other succinate esters, it exhibits the best wear properties as measured by the four ball wear test. ODS also has a higher Load Wear Index compared to other succinate esters tested, as well as the adipate ester benchmark. Diisodecyl succinate has a Load Wear Index similar to the adipate diester benchmark, while DiAS, DEHS and DiNS have slightly lower Load Wear Index. The minimum weld points were higher for all BIO-SA™ based diesters compared to the adipate diester benchmark.

Table4. Wear Properties of Succinate Diester Lubricants

Diester	Four Ball Wear Max (mm)	Load Wear Index Min (kg)	Weld Point Min (kg)	RPVOT Oxidation (minutes)
DiAS	0.96	15.6	126	39
DEHS	0.84	17.3	126	33
ODS	0.47	25.6	126	32
DiNS	0.76	17.0	126	37
DiDS	1.00	20.8	126	32
DEHA	0.96	21.1	100	48

Oxidative stability for the succinate esters was measured by the RPVOT Oxidation test and reported in minutes. The succinate esters range from 32-39 minutes, while the adipate diester was 48 minutes. Often, antioxidants are used to improve the oxidative stability of lubricant formulations. 4 ppm of t-butylhydroquinone (THBQ) antioxidant was added to ODS, and tested for oxidative stability. The RPVOT oxidation increased from 32 minutes to 128 minutes.

CONCLUSION

BioAmber's BIO-SA™ is a carbon neutral replacement for adipic acid as a raw material for lubricant esters. Succinate diesters all show a high viscosity index. Viscosity increases with increasing ester chain length, with diethylhexyl succinate having essentially the same viscosity at 40 and 100 °C as diethylhexyl adipate. Compared to DEHA, succinate esters have similar to improved wear performance, as measured by the Four Ball Wear Test. Succinate esters with branched alcohols show lower pour points compared to the DEHA benchmark. Oxidative stability as measured by RPVOT Oxidation is slightly lower than DEHA, but is improved with the addition of anti-oxidants. Additionally, succinate diesters have high flash and fire points, and minimum weld points that are higher than DEHA. Succinate esters are soluble in mineral oil, and may be used as an additive, or as the sole base stock fluid. The unique combination of properties and positive environmental footprint makes succinate esters ideal candidates for Industrial Fluids.

BioAmber

BioAmber is a next generation chemicals company. Its proprietary technology platform combines industrial biotechnology, an innovative purification process and chemical catalysis to convert renewable feedstocks into chemicals for use in a wide variety of everyday products including plastics, food additives and personal care products. BioAmber produces bio-succinic acid in what it believes to be one of the world's largest bio-based chemical manufacturing facilities. For more information visit the company's web site at www.bio-amber.com.

REFERENCES

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BIOGRAPHY

Tara Mullen is the Manager of Application Engineering and Technical Support at BioAmber Inc. She received a B.S. in Chemistry from St. Norbert College, and a Ph.D. in Polymer Science and Engineering from the University of Southern Mississippi. Prior to joining BioAmber in 2012, Tara held Application and Commercial Development roles at Segetis, and also spent 5 years at GE Plastics in a Product Development role.