The Development and Commercialization of Oleic Estolide Esters

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Recent Milestones

In 2011, due to widespread interest in the technology, LubriGreen received a sizeable amount of funding from one of the world's largest oil companies, TSCA registered its chemicals, filed twelve patents surrounding estolide technologies, demonstrated effective new catalysts for production that will be recoverable and reusable, and received positive test results from an engine test where oleic estolide esters were included as >50% of the formulation.

EPA Award Eligibility

LubriGreen's technology is eligible for the small business award as sales do not exceed $40M annually.

Award Focus Areas

LubriGreen's technology falls under three EPA award focus areas: (1) the use of greener synthetic pathways, (2) the use of greener reaction conditions, and (3) the design of greener chemicals.

Extent of US Contribution

Oleic estolide esters were originally developed and patented by Dr Steven Cermak and Dr Terry Isbell the US Department of Agriculture (USDA) in Peoria, IL, and since been exclusively licensed to LubriGreen Biosynthetics, headquartered in Irvine, CA. Since the licensing of these patents, LubriGreen has managed and overseen the development and optimization of the technology, working in conjunction with the USDA, American universities, and other domestic third-party labs.

Nominated Award Recipients

Research around the core technology began at the USDA with Dr Cermak and Dr Isbell; the core patents have since been exclusively licensed to LubriGreen. LubriGreen has since lead all research and development efforts to optimize the product for industrial use. Because of contributions from Dr Cermak, Dr Isbell, and LubriGreen, we would like to nominate all parties as potential recipients of the award.

Abstract

In the lubricant industry it has been recognized that naturally occurring vegetable oils, triglycerides, provide excellent lubricity and have high viscosity indexes, while being both biodegradable and nontoxic. While economically and environmentally attractive, vegetable oils have not been successful at displacing petroleum-based products in industry due to their oxidative and hydrolytic instability, and poor cold temperature properties. These deficiencies exclude them from being used in severe applications, including passenger car motor oils (PCMOs) and cold temperature environments. When fatty acids from triglycerides are derivatized into estolides, however, the inherent disadvantages of vegetable oils are overcome and the favorable properties preserved. Patented oleic estolide esters, oligomers of fatty acids, are at the core of LubriGreen's technology. The mechanism proceeds via an acid-catalyzed S_N1 addition of the carboxyl of one fatty acid to the site of unsaturation on another. Post-estolide

formation, the free acid estolides are subsequently esterified. The novel structure of oleic estolides gives them excellent lubricity, high viscosity indexes, good cold temperature properties, allows them to be biodegradable, nontoxic, and have good oxidative and hydrolytic stability. In turn, estolides are viable for the most severe lubricant and industrial applications, including PCMO, hydraulic fluids, greases, gear oils, metal-working fluids, dielectric fluids, and others. Estolides have biodegradability and toxicity ratings on par with triglycerides, hence their particular benefit in environmentally sensitive settings. The size of the global base oil market is approximately 11B gallons annually, and there is current high demand for a product that is both (i) comprised of sustainable carbon and (ii) robust enough for demanding lubricant applications. Industry and EPA estimates indicate 2.4B gallons of lubricants are used annually in the US. Of this volume, 1B gallons are consumed in operation (emitted as CO_2 or released into the environment), 800M gallons are burned, 400M gallons are improperly disposed, and 200M gallons are re-refined. As a sustainable, biodegradable, nontoxic and high performing alternative, oleic estolides have the potential to displace a significant portion of this market, reducing emissions and the release of hazardous chemicals into the environment. LubriGreen is currently working with the world's largest formulators, lubricant distributors, teams of chemists and engineers, moving toward commercialization of this novel line of products by the end of 2013.

I. Product Description

A. Chemical Structures

Triglycerides

In the lubricant industry naturally occurring triglycerides have been sought after as a sustainable alternative to petroleum-based products based on their excellent lubricity, high viscosity indexes, biodegradability, and nontoxicity. Albeit economically and environmentally attractive, the effectiveness of vegetable oil for use as a lubricant, however, has been limited due to its oxidative and hydrolytic instability and poor cold temperature properties. To this day, few additives have been able to address any of these issues. For even moderately-severe applications, the few additives that are relevant to vegetable oils have shown to be insufficient.

Oleic Estolides

The USDA has exclusively licensed to LubriGreen its patents on oleic estolides, oligomers of fatty acids. Because the patents encompass the structure of the oleic estolide ester, LubriGreen is currently the only company working on this technology. The mechanism for estolide oligomerization proceeds through an acid-catalyzed S_N1 addition of the carboxyl of one fatty acid to the site of unsaturation on another.

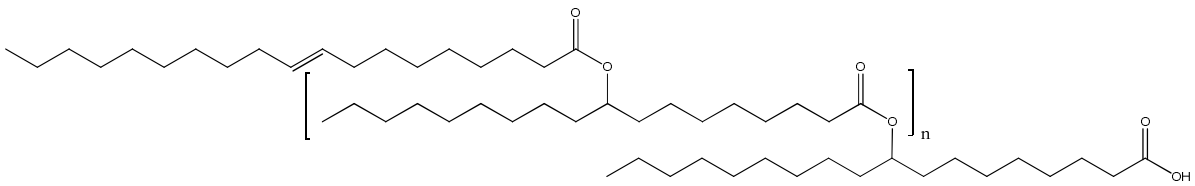


Figure 3. Structure of a free acid oleic estolide, where n is an integer ≥ 0.

Oleic Estolide Esters

For improved stability and better cold temperature properties, the free acid oleic estolide is esterified with a branched alcohol.

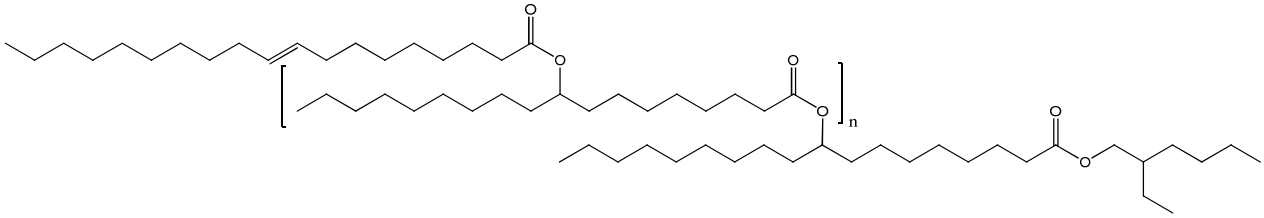


Figure 5. Structure of a pure oleic estolide 2-ethylhexyl ester, where n is an integer ≥ 0.

B. Properties of Estolides

There is high demand in industry for a product that is both (i) comprised sustainable carbon and (ii) robust enough for severe lubricant applications. Because triglycerides provide excellent lubricity, are renewable, biodegradable, and nontoxic, they have been sought after as an environmentally friendly alternative to petrochemicals. To overcome their inherent deficiencies, however, traditional petroleum additives have proved to be ineffective. As such, triglyceride base stocks are only used in very mild lubricant applications where pour point, oxidative stability, and hydrolytic stability are of little concern.

Exclusively licensed to LubriGreen, patented oleic estolide esters are a novel biobased solution that address the shortcomings of vegetable oil. In conjunction with LubriGreen, Dr Steven Cermak and Dr Terry Isbell at the USDA have optimized estolide esters to have improved oxidative stability, hydrolytic stability, and good cold temperature properties that allow them to be used in a much wider range of applications.

Sites of unsaturation are susceptible to free radical attack and are a major contributor to the oxidative instability of triglycerides. One novel aspect to the estolide chemistry is the mechanism of estolide oligomerization itself, where each estolide bond formed leads to the reduction of an alkene, inherently reducing the overall olefin content of the oil. Any remaining double bonds may be eliminated through hydrogenation. An alternative to hydrogenating the material is to "cap" the estolide by intentionally adding saturated fatty acids to the raw feed. Because saturated fatty acids may only act as nucleophiles, once "capped" with a saturate the estolide will cease to grow, be fully saturated, and have further increased oxidative stability.

To verify oxidative stability, LubriGreen conducted the rotating pressure vessel oxidative test (RPVOT, ASTM D2272) in conjunction with the USDA to compare the oxidative stability of oleic estolide esters with that of other lubricant products in the market. Results from the test indicated that estolide esters respond better to oxidative stability additives than triglycerides.

Another unique aspect to estolide structures is their ability to resist hydrolytic attack. Known for their hydrolytic susceptibility, most esters undergo degradation in the presence of water and an acid or base catalyst. Because estolide bonds are secondary esters, a steric barrier is formed

around the carbonyl to which water has difficulty penetrating. At this sterically hindered carbonyl site, hydrolysis is less likely to occur. Vegetable oils are comprised of primary esters; lacking the steric protection provided by estolides, these esters are susceptible to hydrolysis under even mildly catalytic conditions.

Another novel property of oleic estolides is their distinguished cold temperature properties in contrast to triglycerides and many petroleum base oils in the market. On a molecular level, esters formed at the 9 and 10 carbons of the oleic acid substrate create a high degree of branching, disrupting nucleation and subsequent crystal growth necessary for solidification. As such, oleic estolide esters require lower temperatures to freeze, giving them characteristically low pour points. These low pour points further broaden the ability of LubriGreen's compounds to be used in applications where sustainable lubricant and industrial products have traditionally not been an option.

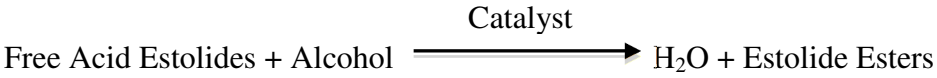
In recent years, LubriGreen has developed various viscosity grade products based on estolide technologies. This is a valuable property in contrast to triglycerides, since vegetable oils naturally come in a narrow range of kinematic viscosities (KV), typically 8-9 cSt at 100°C. LubriGreen's low viscosity product, SE6, has a KV at 100°C of 6 cSt. SE6 has generated the largest demand in industry, formulating to fit the 5W30 motor oil specification. LubriGreen also has medium and high viscosity products with KVs at 100°C of 11 cSt and 20 cSt, respectively.

II. Process Description

Oleic estolide esters are synthesized using a two-step process:

(1) ***Oligomerization***

(2) ***Fischer Esterification***



When the oleic estolide patents were licensed to LubriGreen, the oligomerization step required the use of a perchloric acid catalyst and a reaction time of 24 hours. On a commercial scale the generation of perchlorate salts has the potential to be extremely hazardous to the environment; special handling would have been required for its use and disposal. Furthermore, a 24 hour reaction time would have required voluminous amounts of energy, enough to at least partially negate the environmental benefits of the product.

Through extensive research efforts, LubriGreen has developed proprietary methods to address these concerns (patents pending). After LubriGreen's evaluation of numerous catalysts, a recoverable and reusable organic superacid has been identified to catalyze high yields of estolide formation in less than one hour (>80% conversion). Not only does this eliminate the energy required to catalyze a 24 hour reaction, but it also dismisses the need for perchloric acid or any

other toxic derivative. Regarding the esterification step, combining industry knowledge with novel proprietary methods developed at LubriGreen, a catalyst and conditions have been identified that effectively esterify free acid oleic estolides within one hour.

III. Product Applications

Research has long been underway to overcome the deficiencies of vegetable oil in the lubricant industry. To date, research has failed to yield a triglyceride-based product robust enough to work in the majority of lubricant applications. However, by converting the fatty acids into oleic estolides, sustainability and performance are able to coexist. Therefore, this novel line of compounds has been able to be use in wide array of industries.

Some of the world's largest motor oil manufacturers and distributors are currently in the process of testing and certifying passenger car motor oil (PCMO) formulations using estolide esters as the base oil. Typically considered the most difficult test to pass for PCMO certification, Sequence IIIG engine testing was carried out jointly between LubriGreen, potential customers, and third-party labs. Formulations having >50% of LubriGreen's product passed the most rigorous industry standards, either matching or surpassing higher-end synthetics available on the market. Data indicated that the engine ran much cleaner, with minimal sludge/engine deposits, and there was less degradation to the oil than with traditional formulations. These promising results suggest that oleic estolides may not only be a sustainable replacement to petroleum-based PCMOs, but also have advantages with regard to performance and fuel efficiency.

In addition to PCMO, LubriGreen is working with other potential customers to formulate, test, and certify a variety of sustainable lubricant and industrial products. With characteristically high flash and fire points, oleic estolides have distinct advantages over petrochemicals for use as dielectric (transformer, insulating) fluids. The current biobased product on the market is a triglyceride base stock. Because estolide esters have much better cold temperature properties and oxidative stability, however, they may be used in a much broader range of transformer fluid applications. Other lubricant and industrial products currently being investigated with LubriGreen affiliates are hydraulic fluids, greases, gear oils, and metal-working fluids.

Aside from lubricants and industrial products, oleic estolides are also being tested as a component in plastics, cosmetics/personal care products, paints and coatings, and other chemical applications where either renewable, nontoxic, or biodegradable substitutes are desired. Due to their superior properties in comparison to many petroleum-based products, LubriGreen's novel oleic estolide esters have key performance advantages in a variety of applications.

IV. Market/Environmental Impact

Due to the enormity of the global base oil market, oleic estolide esters have the ability to make a tremendous impact on the market and environment by displacing a sizeable portion of petroleum-based products.

The size of the global base oil market is approximately 11B gallons annually. Industry and EPA estimates indicate 2.4B gallons of lubricants are used annually in the US. Of this volume, 1B gallons are consumed in operation, 800M gallons are burned, 400M gallons are improperly disposed, and 200M gallons are re-refined.[1] LubriGreen's sustainable, robust, and high performing estolide-based product has the potential to enter nearly every facet of this industry.

In the US, 2.2B gallons of lubricants are released into the environment each year; either transformed to CO_2 via combustion or otherwise leaked into the environment (from engines, improperly disposed of, etc). As a biobased option, any CO_2 derived from the combustion of oleic estolide esters would be naturally sequestered into the carbon cycle, leading to a zero net increase of greenhouse gases. While a significant portion of lubricants are burned either in operation or as fuel, a larger portion is merely released into the environment. According to the Mississippi Department of Environmental Quality, 40% of fresh water pollution in the US comes from used motor oil; EPA estimates indicate that 1 gallon of motor oil is enough to contaminate up to one million gallons of drinking water.[2,3] In attempt to understand the toxicity of oleic estolide esters, LubriGreen conducted an OECD 203 acute toxicity test on the products. To find the LC50 of the oil, concentrations >50,000 mg/L were achieved without endpoint determination. Thus, the LC50 value remains unknown; oleic estolides are considered nontoxic. Furthermore, per OECD 301D and 302D, oleic estolides biodegrade at a rate near to that of canola oil (ultimately biodegradable).

Table 1. OECD 301D/302D biodegradability testing for oleic estolide esters SA9 and SA14, as compared to natural canola oil.

Material Tested	Biodegradability (%)	
	OECD 301D	OECD 302D
Canola Oil	86.9	78.9
SA 9 (Estolide ester)	76.4	76.6
SA 14 (Estolide ester)	64.0	70.9

Thus, in contrast to petroleum, release of these biobased, nontoxic, and biodegradable chemicals into the environment, as CO_2 or the base fluid, would be considered nonhazardous and cause no harm to surrounding ecosystems.

The potential for oleic estolides goes far beyond lubricants, however. Commonly used as plasticizers, phthalates are highly toxic to both humans and the environment. They have been connected to damage of the kidneys, liver, cardiovascular and reproductive systems, lungs and

[1] U.S. Department of Energy. *Used Oil Re-Refining Study to Address Energy Policy Act of 2005 Section 1838*. 2005.
[2] Mississippi DEQ. *Proper Disposal of Motor Oil*. Mississippi Department of Environmental Quality. Pollution Prevention Program, Jackson, MS. No Date.
[3] USEPA. 2000. *Used Oil Management Program*. U.S. Environmental Protection Agency, Office of Solid Waste. [www.epa.gov/osw/conserve/materials/usedoil/index.htm]. Accessed February 2, 2011.

developing fetuses.[4] LubriGreen is currently working with a global chemical company to develop a nontoxic oleic estolide-based product that has the potential to displace phthalate plasticizers. Annual use of phthalate plasticizers in the U.S. is estimated at 2B pounds.

Dielectric/transformer/insulating oils are used at an annual rate of around 500M gallons worldwide. Many applications have a risk of fire, explosion, and toxic spills due to contact between volatile mineral oils and electrical currents. Oleic estolide esters show promise in this market due to their nontoxic and biodegradable characteristics. LubriGreen is jointly developing products for distribution with the largest transformer manufacturers in the world.

V. Conclusion

The introduction of a sustainable alternative to petroleum in the lubricant industry has long been desired, but not at the detriment of performance. Naturally occurring triglycerides initially seemed favorable, but failed even in mild environments due to their oxidative/hydrolytic instability and poor cold temperature properties. Thanks to LubriGreen's research and development efforts, oleic estolide esters have been optimized to meet the rigors of nearly any lubricant or industrial application. Oleic estolides are manufactured from a renewable source, are ultimately biodegradable, nontoxic, provide excellent lubricity, have a high viscosity index, good cold temperature properties, and have both oxidative and hydrolytic stability. They have shown to be successful as PCMOs, hydraulic fluids, greases, gear oils, metal-working fluids, dielectric fluids, and others. They are also being investigated for use as plasticizers, cosmetics/personal care products, paints and coatings, and a variety of other chemical applications. LubriGreen is working in the direction of improving fuel economy, decreasing carbon emissions, reducing pollution of toxic chemicals, and displacing a sizable portion of the hazardous petrochemical lubricant industry by taking this novel line of products to market. American farmers, the USDA, global oil companies, lubricant distributors, formulators, PhD chemists and chemical engineers worldwide are working with LubriGreen to show industry that performance does not have to be sacrificed at the hands of sustainability.

[4] DiGangi, J., et. al. Health Care Without Harm. *Aggregate Exposures to Phthalates in Humans*. 2002.