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California start-up says its novel technology makes its renewable esters suitable for use in engine oils.

加州的创业企业称其新技术使可再生酯用于发动机油

作者：Blaine Denton

HIP ESTERS

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THE SEARCH FOR RENEWable base oils has long been faced with a number of challenges due to the complex and varied needs of the market, especially in the engine oil space.

Traditionally, base oils from vegetable oils have been used in industrial applications only. That's about to change, as California start-up Biosynthetic Technologies gets ready to launch commercial production of its bio-synthetic base oil products, known as estolides, which Chairman and CEO Allen Barbieri describes as a "novel disruptive technology." The company is in the final engineering phase for a full-scale commercial plant to be built in Houston, Texas.

The company wants to compete against Group IV and V base stocks. Barbieri says that its demonstration plant, which was built and is operated by Baton Rouge, La.-based Albemarle Corp., has proven "that our cost of manufacturing in our first commercial plant will be lower than PAO manufacturing costs."

"Further, through extensive testing by over 40 major lubricant manufacturers, top tier additive companies and industry leading equipment OEMs, we have data that shows our products perform better than Group IV and Group V base oils in several key criteria. Therefore, while we fully expect we will capture significant market share from Group V base oils solely on price, we also expect we will be able to capture a certain amount of market share from PAOs based on price and performance," he says.

Oxidation stability has always been a problem for vegetable-derived base oils.

The structure of many bio-lubricants renders these products susceptible to atmospheric oxygen due to the presence of two or more carbon double bonds. Oxidation can lead to a number of problems, most notably decomposition, an increase in acid number and an increase in viscosity. Decomposition, combined with increased acidity, leads to significant levels of sludge build-up. Viscosity increases lead to similar problems with regards to heat, as such increases will slow the oil's circulation speed, which then decreases the rate of heat dissipation.

Because of these shortcomings, bio-based lubricants have not taken as significant a foothold as they could have.

So far, additives have been the preferred method of addressing the shortcomings of bio-based lubricants, but this approach has its own limitations. First, additives provide limited improvement in oxidative stability. For example, a 2% mixture of additives placed into castor oil only resulted in an increase of from 15 to 100 minutes using the Rotating Pressure Vessel Oxidation Test (RPVOT)[1]. Further, additives cost money, and given the finite potential for

increased stability, may not be the most cost-effective solution. Also, there have been successful attempts to increase the oxidative stability of soybean-based oils through hydrogenation. Such processes have seen improvements in the oxidation stability index from 9.4 to 15.3.

A study from Biosynthetic Technologies showed that biosynthetic estolide base oils displayed much higher oxidative stability than polyol ester, polyalkylene glycol or high-oleic canola oil, with 1,468 minutes of stability compared to 989, 444 and 52 minutes, respectively, using a 1% antioxidant treat rate.

As such, estolides have emerged as an elegant solution to address both the issues of oxidative stability and performance. Developed by the U.S. Department of Agriculture (USDA), estolides are "new functional fluids made from renewable vegetable and animal-based oils."

Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form oligomeric esters[2].

According to the U.S. National Center for Agricultural Utilization Research (NCAUR), estolides are very promising because they have excellent lubricity, oxidative stability and biodegradability. Barbieri explained that the company's estolides are excellent with over 70% biodegradable within 28 days, a characteristic that can make a huge difference within the lubricant industry.

Speaking at the 7th Asia-Pacific Base Oil, Lubricant & Grease Conference in Bangkok in March, he cited a statistic from the U.S. Environmental Protection Agency (EPA) that estimates that more than 200 million gallons of used motor oil is disposed of improperly each year in the United States. Much of this is dumped down storm drains, ending up in rivers, lakes and oceans, he said.

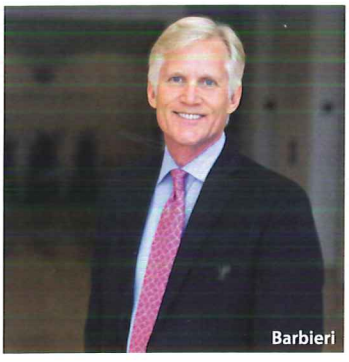
Jakob Bredsguard, chief technology officer, said that biosynthetic estolides overcome the traditional shortcomings of bio-based oils, with fewer additives, and in some cases even exhibit a natural detergency, which helps prevent the build-up of varnish, sludge and deposits on pistons and equipment surfaces. Given their biological origins, estolides have the potential to be safer than their synthetic counterparts, he added.

Tyler Housel, vice president of the Lexolube Division at Inolex Chemical Company, noted in a white paper that, "In general, synthetic esters have an excellent health and safety profile. For example, many synthetic esters are approved by the FDA, CFIA, and other regulatory bodies as appropriate for food processing lubricants where incidental contact with food products is possible."

In 2011, synthetic base stock production reached 2,600 kilotons, 13% of which were synthetic esters, and that number continues to grow.

Such growth can be attributed to a number of factors, including continued improvements in bio-based fluid technology. Bio-synthetic estolides are likely to contribute to the growth once they hit the market, as they have the ability to outperform traditional bio-based fluids in almost all

[1] Product Performance Data Rev. 3, Biosynthetic Technologies
产品性能数据，第三版，Biosynthetic Technologies
[2] Cermak and Isbell 2003
Cermak 和 Isbell 2003


Barbieri


Bredsguard

由于市场需求的复杂性和多样性，特别是在发动机领域，对可再生基础油的探索一直以来面临着诸多挑战。

一般而言，源自植物油的基础油仅用于工业应用。这种情况将发生改变，加州的创业企业Biosynthetic Technologies已准备进行生物合成基础油产品的商业化生产，该产品被称为"estolides"（交酯），公司董事长兼CEO Allen Barbieri称之为一种"新的突破性的技术"。公司将在德州休斯顿建设全尺寸商业装置，目前已进入最终工程设计阶段。

公司希望以该产品与四类和五类基础油进行竞争。Barbieri说，由Baton Rouge, La.-based Albemarle Corp.建设并运行的示范装置已证明"我们第一座商业化装置的生产成本将低于PAO的生产成本。"

"此外，通过由40多家主要的润滑油生产商、一流添加剂公司和业内领先的设备OEM的广泛试验，我们的数据表明我们产品的部分关键性能优于四类和五类基础油。因此，我们深信，仅凭我们的价格就可以从四类油的市场上夺取显著的份额，并且凭借我们的价格和性能在PAO市场上也能取得一定的份额。"

植物油基础的历来最大问题就是氧化稳定性。

由于存在两个或多个碳双键，许多生物润滑油的结构使得产品在大气氧环境中不稳定。氧化会带来一系列问题，最主要的是分解，酸值增加，粘度增加。分解再加上更高的酸度会形成大量油泥。粘度增加会引起类似问题，如粘度增加会使油品的循环速度下降，降低散热效率。

由于这些缺点，生物润滑油没有取得它们应有的市场地位。

到目前为止，解决这些缺点主要是采用添加剂，但这种方式也有其自身的局限。首先，添加剂对氧化稳定性的改善有限。如，蓖麻油中加入2%的添加剂只能使旋转氧弹法（RPVOT）[1]的成绩提高15-100分钟。此外，使用添加剂会增加成本。考虑到对提高氧化稳定性的有限效果，并不是一种成本有效的解决方案。同时，曾经尝试对豆油进行加氢，成功地提高了氧化稳定性。这种工艺可以使氧化稳定性指数从9.4 提高到15.3。

Biosynthetic Technologies的一项研究表明，生物合成交酯基础油表现出比聚酯、聚二醇、高油酯菜籽油更高的氧化稳定性，在采用1%抗氧化加剂量时其氧化稳定性成绩为1,468分钟，而聚酯仅为989分钟、聚二醇为444分钟，高油酯菜籽油为52分钟。

由此，交酯成为解决氧化稳定性和性能问题的出色方案。由美国农业部开发的交酯是"从可再生植物和动物基油品生产的新的功能液体。"

交酯是由一种脂肪酯中的羧酸功能团与另一种脂肪酯中未饱和部分发生交链形成的低聚酯。[2]

据美国国家农业应用研究中心（NCAUR），交酯由于具备出色的润滑性、氧化稳定性和生物可降解性，极具潜力。Barbieri解释说，公司生产的交酯具有出色的生物可降解性，70%在28天内降解，这对润滑油行业来说是一种巨大的变化。

三月份在曼谷召开的第七届亚太基础油、润滑油和润滑酯大会上，他在发言中引用了美国环保署的统计数据，据估计，美国每年有约2亿加仑的发动机废油处置不当。这当中相当一部分是直接倒入雨水管道，最终流入江河湖海。

首席技术官Jakob Bredsguard说，生物合成交酯克服了生物基础油的传统缺点，只需更少的添加剂，甚至在有些场合下具有天然清净性，可以防止活塞和设备表面形成漆膜、油泥、沉积。由于交酯源自植物，因此较其同类的合成物可能更安全。

Inolex Chemical Company公司Lexolube部副总裁Tyler Housel在其白皮书中说，"一般而言，合成酯具有出色的健康性和安全性。例如，许多合成酯获得了FDA，CFIA及其他监管机构的批准，可用作食品加工润滑剂，这些应用中有可能会与食品发生偶尔的接触。"

2011年的合成基础油产量达到了260万吨，其中有13%是合成酯，这个比例还是不断上升。

这种增长得益于若干因素，包括生物油技术的不断发展。生物合成交酯一旦进入市场，有可能为进一步的增长作出贡献，因为他们在大部分领域都要优于传统的生物基油。Bredsguard说。

公司成立于2006年，位于加州Irvine，获得了来自位于St. Louis的农业巨头孟山都公司和英国石油巨头BP公司的资金。除了这些股权投资以外，与孟山都公司还有一些其他安排，包括许

areas, said Bredsguard.

Based in Irvine, Calif., the company, which was founded in 2006, has received funding from St. Louis-based agricultural giant Monsanto Co., and British oil major, BP. In addition to their equity investment, the arrangement with Monsanto includes a license for the production of Monsanto's Vistive® Gold high-oleic soybeans.

One of the most often cited benefits of bio-based oils are their environmental impact and their renewability. With regards to the former, bio-based oils surpass their traditional counterparts because "In regular engine operations, most of the emissions come from the lubricant. Oil vapors that don't get burned condense on the solid particles of soot that fly out through the exhaust pipe. Vegetable oil doesn't evaporate as easily as petroleum-based oil, so less finds its way out of the engine."[3]

The basic function of a lubricant is to prevent metal-on-metal contact while transferring heat from friction away from contact points; petroleum-based oils generally require modification to achieve this, while vegetable oils are "excellent in terms of functionality without chemical modification." [4]

One promising class of bio-synthetic estolides is those containing saturated capped estolides of oleic acid. These tend to do well in cold temperatures with pour points (the lowest temperature at which a fluid will pour or flow) of between minus 15°C and minus 29°C, as well as good oxidative stability. Some seed oils show promise, albeit with a limited availability. The lesquerella auriculata seeds, for example, contain 32% oil, 96% of which are estolides.

Estolides have potential uses in a wide variety of lubricant applications such as food-safe (incidental contact), cooling fluids, crankcase and drive line lubricants, hydraulic fluids, dielectric fluids, metalworking fluids, gear oils, marine oils and electrical insulation oils (EIOs) in transformers.

A number of companies, including Chevron, Dow Chemical and Petrobras, have patents on file relating to estolides.

Bruce Marley, senior vice president of sales and marketing for Biosynthetic Technologies, explained that engine oils can be formulated using a combination of estolides, Group III base oils and PAOs, depending upon what characteristics are needed. The company's work has "cast aside all past perceptions that base oils derived from natural feed stocks such as vegetable oils aren't viable" in the motor oil market. More specifically, Marley sees estolides competing with Group III base oils in performance and with Group IV and V base oils on both performance and price.

Generally, combining PAOs with an ester will lead to better stability under heat while maintaining high compatibility with mineral oils. Some high-performance motor oils contain up to 20% by weight esters.[5]

A concern with estolides, however, is their low-temperature properties. It appears the degree to which estolides can perform at low temperatures has to do with the oil from which they were produced. A study from Evonik, one of the world's leading specialty chemical companies, found that estolides provide much better cold-temperature performance than the more commonly used olefin copolymers.

Soybeans are being used as the current feedstock of Biosynthetic Technologies. The company has a license and supply agreement with Monsanto, an important step toward launching "domestically-sourced, renewable bio-synthetic lubricants," Barbieri said.

可生产孟山都的Vistive® 金色高油酸大豆(Gold high-oleic soybeans)。

生物基础油的最大好处是其环境影响和可再生性。对于前者,由于"在普通发动机运行中,大部分的排放物都来自润滑油。没有燃烧的油蒸汽在由排气管排出的碳黑颗粒上冷凝。植物油不如石油基础油那么容易蒸发,因此很少从发动机中排出"[3],生物基础超过了其他所有的类似产品。

滑润油的基本功能是防止金属与金属的接触,并将接触点摩擦所产生的热带走;石油基础油一般需要通过改性才能做到这一点,而植物油"在无需化学改性的情况下就具有出色的性能"。[4]

有一类具有潜力的生物合成交酯是含有饱和油酸交酯。这些交酯有着良好的低温性能,倾点在-15C到-29C之间;和氧化稳定性。有些植物油也很有潜力,但供应量有限。例如,lesquerella auriculata的种子,含油量32%,其中96%是交酯。

交酯可用于多种应用,如食品安全(偶尔接触)、冷却液、曲轴箱和驱动系统润滑油、液压油、绝缘油、金属加工油、齿轮油、船用油和变压器中的电气绝缘油(EIO)。

多家公司,包括雪佛龙、陶氏化学、巴西国家石油公司,都申请了与交酯相关的专利。

Biosynthetic Technologies的销售和市场高级副总裁Bruce Marley解释到,发动机油可以采用交酯、三类油和PAO的混合配方,这取决于需求什么特性。公司在工作中"抛弃了源于植物等天然原料所生产的基础油在发动机油市场上不可行"这个观点。具体而言,Marley认为交酯可以在性能上与三类基础油竞争,在性能和价格上与四类和五类基础油竞争。

把PAO与酯进行混合可以获得更好的热稳定性,同时又保持着与矿物油的兼容性。一些高性能的发动机油最高含有20%(重量)的酯。[5]

但是交酯有一个问题是其低温性能。交酯的低温性能取决于原料作物。世界领先的特种化学品公司Evonik的一项研究发现,交酯的低温性能较常用的烯烃共聚物要好得多。

Biosynthetic Technologies目前采用大豆为原料。"公司与孟山都签有许可和供应协议,这是推出"以国内原料生产的可再生生物合成润滑油"的重要一

[3] Boehman, A.L., et al. 1998
[4] Johnson, Rhodes, and Allen 2002
Johnson · Rhodes和Allen 2002
[5] R.H. Schlosberg, J.W. Chu, G.A. Knudsen, E.N. Suciu and H.S. Aldrich, High stability esters for synthetic lubricant applications, Lubrication Engineering, February 2001, pp. 21-26
R.H. Schlosberg · J.W. Chu · G.A. Knudsen · E.N. Suciu和H.S. Aldrich · "合成润滑油应用的高稳定性酯" · 《润滑工程》(Lubrication Engineering) · 2001年2月号 · 第21-26页

But, because of the higher cost of vegetable oil, Barbieri says the company plans to release its estolide at or below PAO prices. He says it is unlikely that they can compete with Group III prices.

Biosynthetic Technologies' CTO believes that "The greatest obstacle in the adoption of estolides thus far has been validating the performance of these new oils in the multiple formulations in a wide variety of applications. Formulating, testing and certifying can be a lengthy process."

Nonetheless, Marley said that the PCMO market is attracting great interest from global oil companies, automotive OEMs and finished fluid marketers. While several of these companies are working on their own formulations, Biosynthetic Technologies is working with a major additive company to get ILSAC GF-5 approval for a motor oil formulation, which should be completed before year end. The formulation will be made available to lube marketers interested in selling environmentally friendly, high-performance fully synthetic motor oil.

The company uses a "simple, catalyst-driven chemical reaction process. As such, the company could partner with numerous chemical plants around the world to manufacture these products using common chemical equipment," Barbieri said.

It will take years "before we know all of the applications where these new chemicals can impact and improve lubricants and other chemical sectors," said Marley. But the future is promising as researchers continue to find ways to utilize the products' novel performance and environmental characteristics, he said.

"Things are moving quickly for us and we continue to be excited about the prospects of this novel disruptive technology," Barbieri said.

步。"Barbieri说。

Barbieri又说，但由于植物油较高的成本，公司计划以低于PAO的价格进行销售；不大可能与三类油的价格进行竞争。

Biosynthetic Technologies的首席技术官认为"目前看来采用交酯的最大障碍是在不同应用的多种配方中验证其性能。配方研制、测试和认证可能是一个很长的过程。"

虽然如此，Marley说，全球的油品公司、汽车制造商和成品油销售商对PCMO市场表示了极大的兴趣。其中有些公司正在开发自己的配方，Biosynthetic Technologies正在与主要的添加剂公司进行合作，获取发动机油配方的ILSAC GF-5批准，预计可以年底前完成。这些配方将提供给有兴趣销售环境友好、高性能全合成发动机油的销售商。

公司采用一种"简单、催化驱动的化学反应工艺。如此，公司可以与世界各地无数的化工厂进行合作，以常用的化工设备来生产这些产品。" Barbieri说。

Marley说，"要知道这些新的化学品在哪些应用中可以一展身手、提升润滑油和其他化工领域"还需数年的时间。但，这些新产品具有新的性能和环境友好特性，研究人员将不断找到新的利用这些产品方法来，未来充满希望。

"事情的发展快于我们的预期，我们对这种新的突破性的技术的未来充满信心。" Barbieri说。


Marley