Estolides a Developing Versatile Lubricant Base-stock

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Vegetable oil based lubricants have made steady progress in the penetration of the lubricant market because they offer up good lubrication properties, low volatility and good biodegradability. However, they are often plagued with poor performance in oxidative stability, cold temperature attributes and until recently more expensive than traditional mineral based lubricants. Various derivatives of vegetable oils can reduce unsaturation to improve oxidative stability and when the branching is introduced in the molecule can also improve cold temperature properties as well. One such developing basestock with these chemical moieties is a class of compounds termed estolides. Estolides are oligomeric esters either from the addition of a fatty acid to a hydroxyl containing fat or by the condensation of a fatty acid across the olefin functionality of a fat. The secondary ester makes the molecule more resistant to water hydrolysis as compared to underivitized triglycerides.

Estolides which are synthesized from the addition of a fatty acid across the olefin of a second fatty acid are currently undergoing commercialization by Biosynthetic Lubricants Inc. This class of molecules can be synthesized from any monounsaturated fatty acid with the second fatty acid originating from virtually any type of fatty acid. Therefore, the two fat groups in the oligomer can be tailored to meet the physical properties of the application of interest and the cost of production. Lower cost fatty acids which are typically less refined or have a wide range of fatty acid chain lengths and unsaturation tend to give lower cost estolides with lower performance characteristics. More highly refined or high purity fatty acids yield higher purity estolides and improved performance properties.

As a comparison, estolides synthesized from tallow fatty acids provide relatively inexpensive starting materials with modest physical properties as compared to estolides synthesized from high oleic sources in combination with decanoic fatty acids. The tallow estolides have pour points of -15^{o}C whereas the oleic-decanoic estolides have pour points of -39^{o}C. The tallow estolides have a RPVOT time of 274minutes as compared to the oleic-decanoic RPVOT time of 305 minutes. These cold temperature properties compare well to fully formulated petroleum 4-cycle base-stocks which have pour points of -27^{o}C and RBOT times of 223minutes. Two more key benefits of the vegetable based estolides is their higher molecular weight and good lubricity. The higher molecular weights of these vegetable based materials yield lower evaporative loss values compared to similar viscosity grade oils. Estolides have **<1%** evaporative loss compared to fully formulated crankcase oils which typically have evaporative losses of **30%.** Vegetable oils are known for their low coefficient of friction and good lubricity characteristics. The estolides preserve that performance characteristic and demonstrate wear scars of **0.3mm** in an unformulated **4-ball wear test**. This value compares well to a wear scar of **0.5mm** for a fully formulated commercial crankcase lubricant.

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This class of compounds do to the ester linkages in the molecule is **readily biodegradable with 80% degradation in 30 days.** Lastly, the viscosity of the estolide can be tailored across a wide range from 30cSt to >500cSt (40^{o}C) depending on the carboxylic ester functionality and the degree of oligermization. Typically short chain and branched esters give lower viscosities as well as lower oligomer numbers. Viscosity indices remain high for all oligomers and esters with values between 160-180.

The next three classes of estolides have been studied but not commercialized. The first class are estolides found in nature (natural estolides) most commonly found in the genus *lesquerella*, a hydroxy containing triglyceride. The natural estolides of *lesquerella auriculata* can be as high as five ester groups per triglyceride also called a fully capped estolide do to the fact that all of the hydroxy groups in the molecule are esterified. The natural estolides have not been characterized because of their limited availability to date.

The second class is synthetic triglyceride estolides which model the natural estolides and can be readily made from the hydroxy moiety of lesquerella or the commercially available castor oil. The reaction can be carried out on the intact triglyceride or from the hydroxy fatty acids. When oil is used, essentially a fatty acid of any functionality can undergo condensation with the hydroxyl to form an estolide. The properties of the resulting estolides can vary widely by choice of capping fatty acids and the level of estolide formation (capping) from single capped molecules to fully capped oils containing up to six ester linkages. Cold temperature properties can range from solids with melting points as high as 38^{o}C to pour points as low as -36^{o}C depending on the capping fatty acid. RBOT oxidatative stability values ranged from 29 minutes up to 242minutes for monounsaturated and fully saturated capping fatty acids respectively.

The third class are the hydroxy fatty acids are used they can self oligomerize to form estolides with an average of 5 repeating units. Conversely, the hydroxy fatty acids can be capped with non-hydroxy fatty acids to form a wide variety of estolides and their associated unique physical properties are partially dictated by the capping fatty acid group. These estolides have very good cold temperature properties with pour points down to -54^{o}C and RBOT values as high as 403 minutes.