Chapter X

Estolides: A Bioderived Synthetic Base Oil

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Abstract

One novel technology to reach the lubricant market in recent years are estolides, a class of high-performance, environmentally acceptable lubricant base oils. Estolides have been tested against a set of similar competing base oils from the marketplace, and the results show they have excellent performance in the areas of oxidative stability, hydrolytic stability, evaporative loss (volatility), viscosity index, and wear protection, in addition to environmental benefits including high renewable content, biodegradability, and non-bioaccumulative nature. These benefits, among others, have lead formulators to begin using estolides in a variety of industrial and automotive lubricant applications. In addition, a high-performance estolide-based motor oil formulation has been certified by the American Petroleum Institute (API) as having met the most current performance specifications for motor oils, API SN-RC (ILSAC GF-5). In addition, a field trial using estolide-based formulations was conducted in Las Vegas, Nevada where estolides demonstrated their ability to keep engines looking clean with minimal varnish. Furthermore, an estolide-based motor oil underwent environmental testing to determine the effect on biodegradability, if any, of (1) blending the estolide base oil with additives and (2) using the formulation in an engine. The results show that blending the base oil with additives did not have an effect on biodegradability of the estolide, and using the formulation in an engine appeared to slightly improve the biodegradability of the estolide.

Keywords: Estolides, biosynthetic, motor oils, environmentally acceptable lubricants (EALs), biodegradable, bio-based, renewable, lubricants, synthetics, engine cleanliness.

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1.1 Introduction

One exciting technology to reach the lubricant market in recent years are estolides, a class of high-performance, environmentally acceptable lubricant base oils. Estolides are currently being used in a variety of industrial and automotive lubricant applications, and have garnered recent attention for their use in high-performance motor oil formulations. In addition, they are renewably sourced, biodegradable, and non-bioaccumulative, making them also suitable for environmentally sensitive applications.

Estolides are oligomers of fatty acid monomers derived from the splitting of triglycerides, or vegetable oils. Fatty acid monomers can be synthesized into estolide oligomers using one of two pathways. The first option is to use monounsaturated fatty acids as feed (e.g. oleic acid), whereby a mineral acid is used to catalyze the electrophilic addition of the carboxyl of one fatty acid to the alkene on another (see Figure 1).[1] The second is to use hydroxyl fatty acids as feed (e.g. ricinoleic acid or 12-hydroxystearate), whereby a mineral acid is used to catalyze a series of condensation reactions (Fischer esterifications) to generate estolide oligomers.[2] The product from either method will have a free carboxylic acid which can be esterified with an alcohol to further optimize the compound for use as a lubricant.[3]

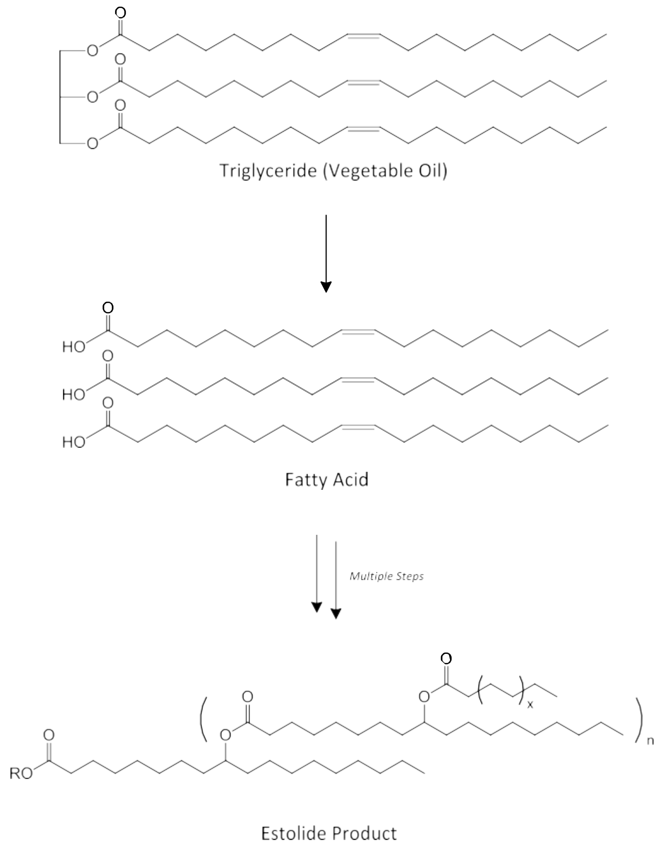

Figure 1 – Reaction schematic, vegetable oil to estolide.

From the perspective of performance, estolides offer a number of advantages. When compared to a set of similar competing base oils from industry, estolides showed to have strengths in the areas of oxidative stability, hydrolytic stability, evaporative loss (volatility), viscosity index, and wear protection, to name a few.

In addition, estolides are a tremendously versatile class of synthetic compounds, and can be designed to fit just about any application. Oligomerization can be minimized or maximized, molecules can be functionalized with various moieties, and properties such as oxidative stability, hydrolytic stability, and cold temperature flow can be tuned to meet specific needs.

Aside from performance, estolides also have superior environmental profiles, making them ideal for environmentally sensitive applications. Increased environmental regulations and legislation in the industry have formulators seeking ingredients which do not fit the traditional "performance versus environment" tradeoff. With characteristics of a high-performance synthetic, along with high bio-content, good biodegradability, and non-bioaccumulative nature, estolides represent one such option for formulators.

The product described throughout this chapter, Biosynthetic SE7B, is a high-performance estolide base oil which is making rapid advances in the industry. It is being tested by numerous companies to formulate the next generation of synthetic lubricant products. The product is currently being used in the development of various formulations, including engine oils, hydraulic fluids, gear oils, greases, metalworking fluids, compressor fluids, and dielectric fluids. Recently, estolides have attracted much attention for their ability to keep engines clean when used in motor oil formulations. These properties, among others, lead to the first certified estolide motor oil formulations (5W-20 and 5W-30) by the American Petroleum Institute (API) which meet industry's current motor oil standard, API SN-RC (ILSAC GF-5).[4] In addition, biodegradability tests on an estolide motor oil formulation showed that the estolide base oil in the formulation maintained its biodegradability when blended with additives, and tested in an engine for thousands of miles.

The performance properties, environmental properties, and chemical versatility of estolides not only make them attractive to developers of environmentally friendly products, but also to the oil industry at large. Increasingly stringent performance specifications, along with tighter environmental legislation and regulation in the sector, are all reasons why estolides are poised to take a significant share of the lubricant base oil market in the coming years.

1.2 Performance Characteristics

Estolides naturally exhibit a number of performance properties that make them ideal as lubricant base oils. This allows them not only to compete with conventional petroleum products, but also with high-end synthetic lubricants. In each of the following sub-sections, we discuss results of estolides being compared against a set of common lubricant base oils from industry. Table 1 provides a brief description of the different products used in the comparison studies, and Table 2 provides some basic properties these base oils.

Base Oil	Description
Group II Mineral Oil	API Group II – Refined, hydrotreated crude
Group III Mineral Oil	API Group III – Refined, hydroisomerized crude
Polyalphaolefin	Highly branched isoparaffinic polyalphaolefin
Polyalkylene Glycol	Oil soluble polyalkylene glycol
Diester	Adipate diester containing long-chained branched alcohols
Polyol Ester	Dipentaerythritol ester
Biosynthetic SE7B (Estolide)	Estolide product

Table 1 – Description of the base oils tested and evaluated in this work.

	Units	*Method*	Group II Mineral Oil	Group III Mineral Oil	Polyalpha-olefin	Polyalkylene Glycol	Diester	Polyol Ester	Biosynthetic SE7B (Estolide)
Kinematic Viscosity, 100°C	cSt	D445	6.6	6.5	7.0	6.5	5.5	8.6	7.2
Kinematic Viscosity, 40°C	cSt	D445	44	37	38	32	28	53	35
Viscosity Index	-	D2270	102	130	146	164	135	135	173
Pour Point	°C	D97	-13	-15	-43	-57	-60	-51	-18
Flash Point	°C	D92	230	256	264	216	243	282	280

Table 2 – Basic properties of the base oils tested and evaluated in this work.

1.2.1 Oxidative Stability

Vegetable oils have been used as lubricants for centuries, but they have always come with a marked deficiency in the area of oxidation resistance. The ability of a fluid to resist oxidation, also referred to as oxidative stability, is one of the primary indications used to predict the lifespan of a lubricant. On a molecular level, the instability of vegetable oil originates from the sites of unsaturation, or olefin content of the oil. Vegetable oils high in unsaturates tend to have good cold temperature properties (remaining liquid to temperatures <0°C), but poor oxidative stability.[5] If the olefins are reduced through hydrogenation, many vegetable oils become solid at room temperature, thus rendering them ineffective as a lubricant. For example, while the melting point of soybean oil is -7°C, the melting point of fully hydrogenated soybean oil is 71°C.[6] This tradeoff between oxidative stability and cold temperature performance is one of the main reasons the use of vegetable oils in lubricants has remained limited to a niche set of applications.

Because estolides have a high level of saturation, the oxidative stability of these fluids is similar to other high-end synthetics (see ASTM D2272 result for the estolide product in Figure 2).[7,8,9] In addition, because the molecular structure is branched at each of the estolide positions, the oligomers have difficulty crystallizing as temperatures are reduced, resulting in good cold temperature flow despite low levels of unsaturation.

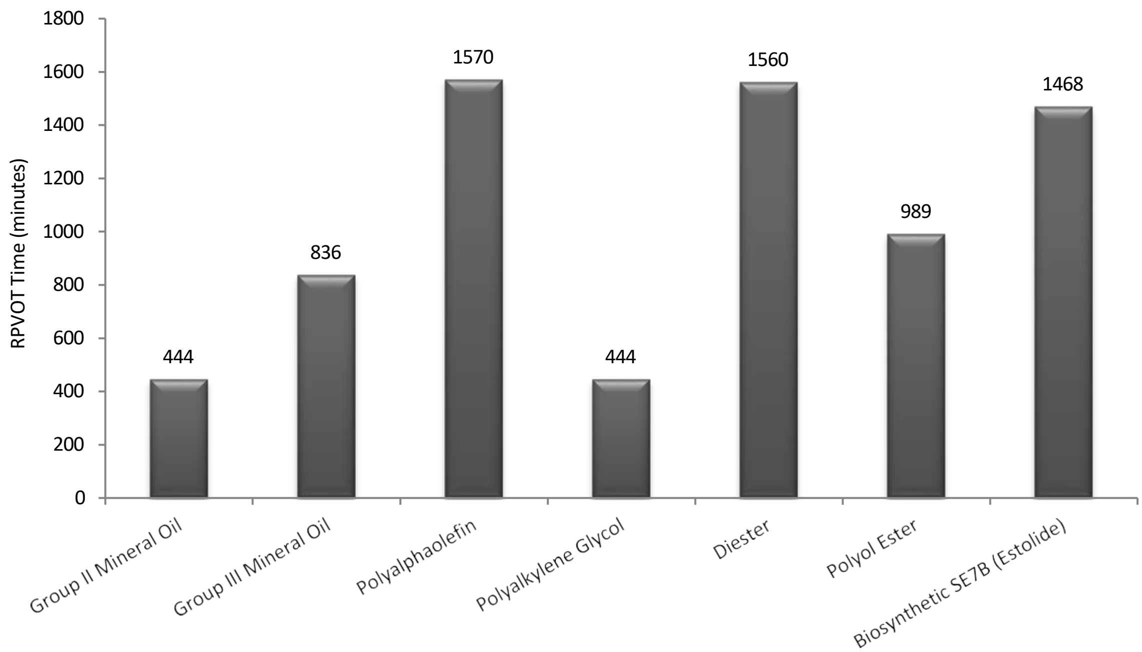

Figure 2 - Oxidative stability of estolides (Biosynthetic SE7B, 7 cSt at 100°C) compared to similar viscosity (6 to 8 cSt at 100°C) base oils, according to ASTM D2272, RPVOT (minutes). Base oil samples contain 1 wt% aminic/phenolic antioxidant blend (1:1 weight ratio).

1.2.2 Hydrolytic Stability

In the presence of water and a small of amount of catalyst, esters can degrade to form acidic byproducts that can cause corrosion to various metals used in bearings, engines, and other equipment. With respect to estolide esters, however, large hydrophobic branches on both sides of each estolide link provide a steric barrier that protects the esters from hydrolytic attack.

To demonstrate this trait, a modified ASTM D2619 hydrolytic stability test (Figure 3) was performed, where the test duration was extended from 48 to 144 hours to exaggerate test results – all other test parameters followed method guidelines. As shown in Figure 3, these hydrophobic barriers provide estolides with better hydrolytic stability than the synthetic esters tested, making their performance more comparable to refined mineral oils and synthetic hydrocarbons.

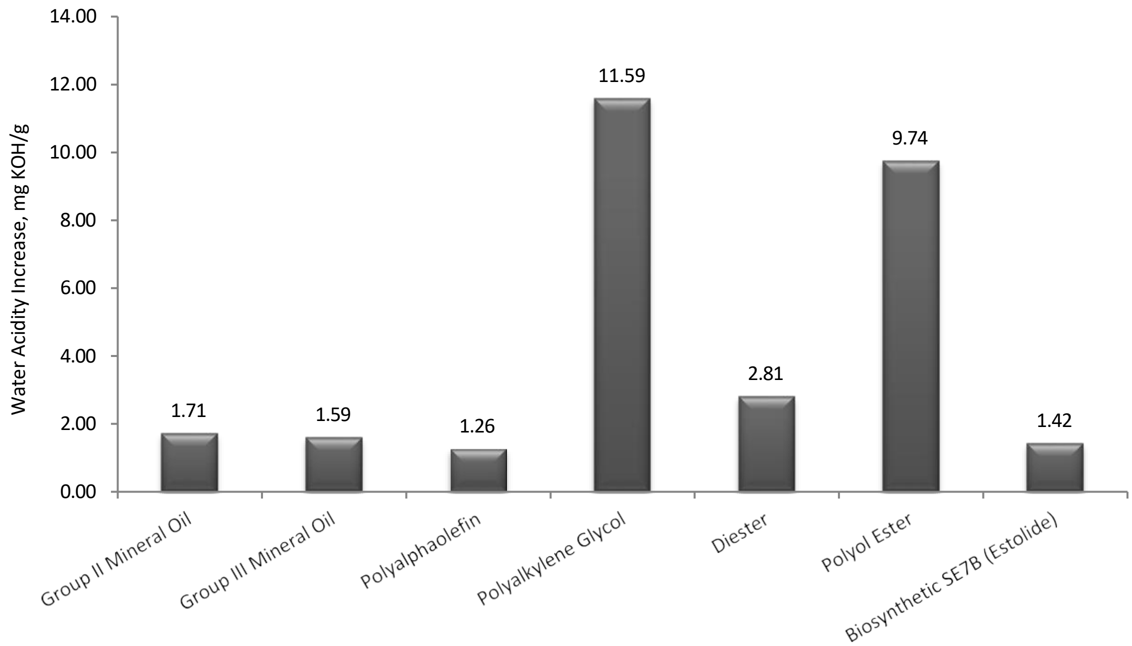

Figure 3 - Hydrolytic stability of estolides (Biosynthetic SE7B, 7 cSt) compared to similar viscosity (6 to 8 cSt at 100°C) base oils. Modified ASTM D2619, measures water acidity increase after 144 hours (mg KOH/g). Base oil samples were tested without additives.

1.2.3 Evaporative Loss (Volatility)

Another performance characteristic of estolides is low volatility, resulting in reduced evaporative loss as compared to other high-performance base oils (per the Noack standardized test method, ASTM D5800). Results for this test are often referred to as the "Noack" of an oil or lubricant formulation. Noack is the weight percent of a fluid evaporated after exposure to 250°C for 60 minutes, and is a critical parameter for lubricants as it indicates the level of evaporative loss a lubricant might experience while in high-temperature service. This characteristic is of particular importance in motor oils, where the heat of an engine can vaporize the lower molecular weight components of the fluid, thereby changing its composition. As the molecular weight distribution of the lubricant changes, the viscosity of the fluid can increase, resulting in poor engine oil circulation, and therefore reduced fuel economy. In addition, another effect of lubricant loss to the atmosphere is that the fluid must then be replaced, or "topped off," in between oil changes. In this way, higher evaporative loss can result in increased oil consumption. As shown in Figure 4, the estolide product measured has a lower Noack value than competing base stocks with similar viscosities.

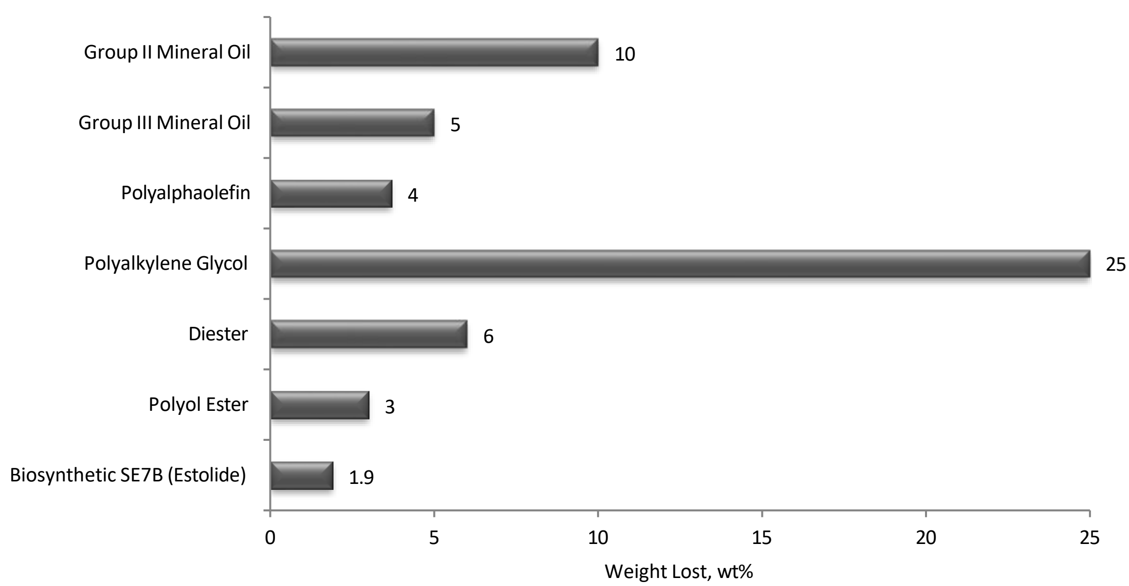

Figure 4 - Evaporative loss (Noack) of estolides (Biosynthetic SE7B, 7 cSt at 100°C) compared to similar viscosity (6 to 8 cSt at 100°C) base oils, according to ASTM D5800 (weight percent lost during testing). Base oil samples were tested without additives.

1.2.4 Viscosity Index

Viscosity index (VI) is defined as the ability of a fluid to resist drastic change in viscosity as the temperature of the fluid is either increased or decreased. Because estolides have higher VIs than most products (see Figure 5), they have a number of advantages over other base oils. Higher VI fluids provide increased film thickness at elevated temperatures, resulting in better protection, and in many cases reduced wear. At lower temperatures, high VI base fluids display a lower rate of viscosity increase resulting in reduced viscous drag on moving parts, leading to higher horsepower output and increased energy efficiency.[10] In addition, formulations containing high VI fluids require less VI improver additives to meet minimum VI requirements – thus, the higher the VI of the lubricant base stock, the less such additives are required.

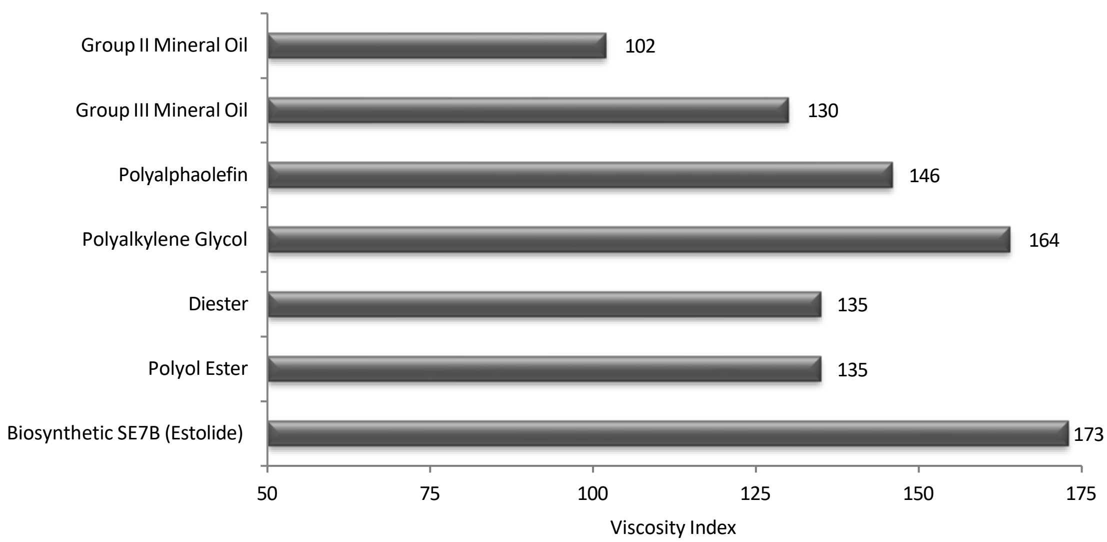

Figure 5 – Viscosity index of estolides (Biosynthetic SE7B, 7 cSt at 100°C) compared to similar viscosity (6 to 8 cSt at 100°C) base oils, according to ASTM D2270. Base oil samples were tested without additives.

1.2.5 Wear Protection

Estolides also exhibit unique properties in the area of wear protection. Because the compounds are polar, they have an increased affinity for metal surfaces, allowing them to form protective barriers between moving parts. This attraction to the metal surface fortifies the surface against wear, as shown in Figure 6.

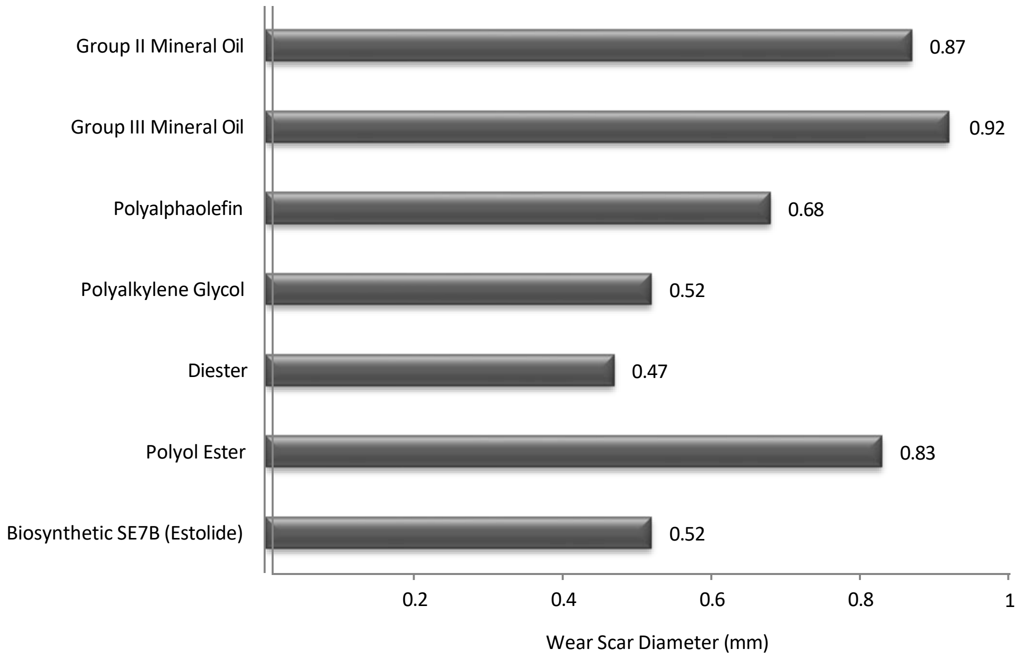

Figure 6 – 4-Ball wear properties of estolides (Biosynthetic SE7B, 7 cSt at 100°C) compared to similar viscosity (6 to 8 cSt at 100°C) base oils, according to ASTM D4172 (wear scar diameter, mm). Test parameters were 1 hour, 75°C, 1200 rpm, 40 kgf. Base oil samples were tested without additives.

1.3 Environmental Properties

Governments from around the globe are paying more and more attention to the environmental impact of lubricants, leading to increased regulation and legislation in the sector.

Examples of such programs are the US EPA's Vessel General Permit (VGP), the BioPreferred program, and Europe's EcoLabel, to name a few. These requirements are forcing many lubricant manufacturers to begin investigating alternative ingredients for their formulations. With an environmental profile favorable to many traditional base oils, estolides represent one such alternative to formulators developing environmentally acceptable lubricants (EALs).

1.3.1 Renewable Content

Estolides are one of the few lubricant base oils with high levels of bio-content. Refined mineral oil products, including Group I-III base stocks, are sourced directly from petroleum, and thus do not contain renewable bio-based carbon. In addition, current feed streams for other synthetic hydrocarbons, including PAOs and PAGs, are also petroleum-sourced and do not have renewable content. There are some new technologies being developed, however, which can produce bio-based raw materials for products similar to Group III (farnesene-based) and PAO (decene derived from vegetable oil metathesis). Other widely used products with high bio-content include esters that are based on fatty acid or fatty alcohol chemistries, including polyol esters and diesters.

Because estolides are oligomers of fatty acid monomers derived from plant, animal, or algal oils, they can have very high levels of bio-content. In fact, estolides can be entirely renewably sourced if the alcohol chosen to terminate oligomerization is also derived from bio-based carbon (e.g. bio-based ethanol, n-butanol, fatty alcohols, etc).

1.3.2 Biodegradability

Another unique characteristic of estolides is their ability to rapidly biodegrade once released into the environment. As shown in Figure 7, OECD 301 evaluation shows neat estolide base oils have a higher potential for biodegradation than many base oils with similar viscosities.

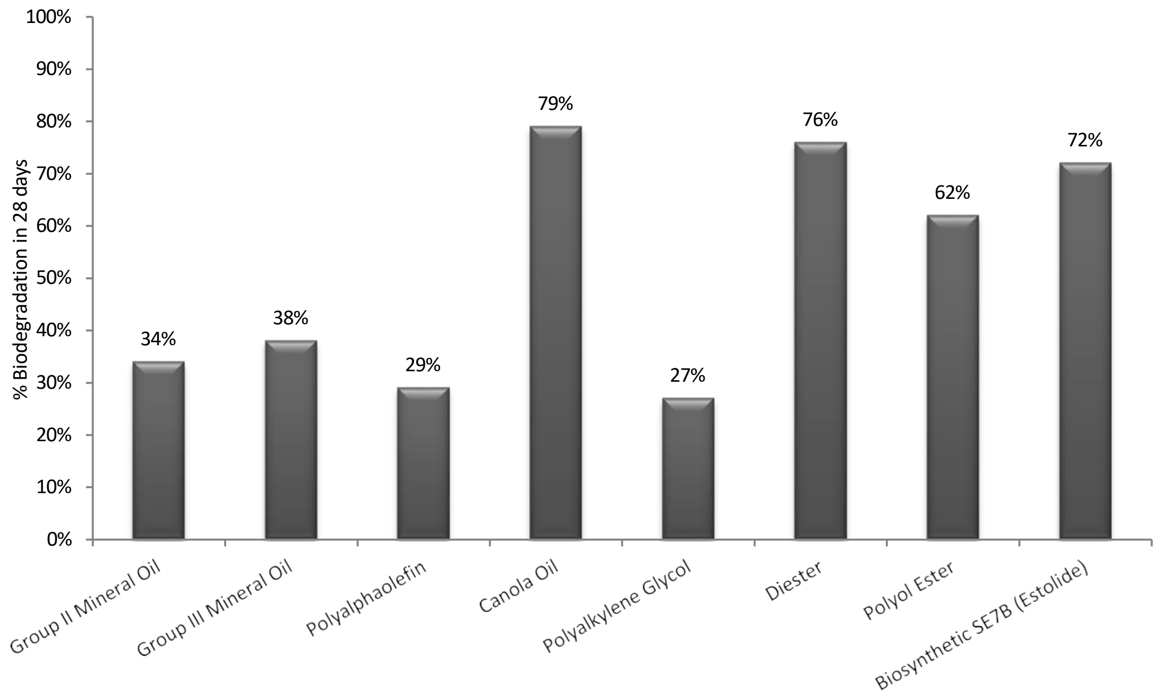

Figure 7 – Biodegradability of estolides (Biosynthetic SE7B, 7 cSt at 100°C) compared to similar viscosity (6 to 8 cSt at 100°C) base oils, OECD 301B (% biodegradation in 28 days). Base oil samples were tested without additives.

In a follow-up study on the biodegradability of estolide-containing motor oil formulations, it was determined that the individual components of a formulation biodegrade independently from one another. Findings from this study indicated that the estolide fraction of the formulation maintained a proportional amount of biodegradability, even after being used in an engine. See section 1.4.2 for more detailed information.

1.3.3 Bioaccumulation

Bioaccumulation refers to the accumulation of a contaminant in the tissues of a living organism via any route, including respiration, ingestion, direct contact, sediment, or other means.[11] Thus, a bioaccumulative compound has a rate of tissue uptake which exceeds the rate of elimination. Bioaccumulation is a critical environmental property because compounds with very low environmental concentrations (e.g. water or soil concentration) can build up in the tissues of living organisms, eventually reaching harmful or lethal levels.

The tendency of a substance to bioaccumulate depends on the lipophilicity, size or molecular weight, and chemical stability of the compound. First, lipophilic (non-polar) substances can more readily be absorbed into fatty tissues, potentially promoting the bioaccumulative process. However, highly lipophilic substances can also readily diffuse out of an organism's tissues. Therefore, for a compound to have bioaccumulative potential, its lipophilicity must be sufficient enough in order to penetrate fatty tissue, but not so lipophilic that it readily diffuses out from the tissue once absorbed. Second, regarding molecular weight, small molecules can readily enter and exit an organism's tissue, whereas large molecules cannot enter tissue at all. Thus, similar to lipophilicity, mid-range molecular weight compounds tend to favor bioaccumulation. Third, a bioaccumulative compound must also be very stable in biological systems. In other words, once it enters an organism, it must be resistant to the biological processes by which the organism would naturally remove contaminants.[12]

The primary test methods used to determine bioaccumulative potential are OECD 107 (Shake Flask Method) and OECD 117 (HPLC). Both methods are ways to estimate the partition coefficient for a substance between water/n-octanol phases ($P_{OW} = [solute]_{octanol} / [solute]_{water}$) as a means for determining the degree of lipophilicity of the compound.[13,14] A substance which favors the aqueous phase will yield a small P_{OW} and shows that the substance tested is more polar, or non-lipophilic. Alternatively, favoring the n-octanol phase will yield a large P_{OW} and shows that the substance tested is more non-polar, or lipophilic.

According to the US EPA, a substance is non-bioaccumulative if the Log P_{OW} of the sample per OECD 117 is <3 or >7 (not lipophilic enough to bioaccumulate, or too lipophilic to bioaccumulate, respectively). In addition, in some regulations such as the Vessel General Permit, there are exclusions for compounds above a certain molecular weight or molecular diameter.[15] A sample of low viscosity estolide product (Biosynthetic SE7B) obtained a result of Log P_{OW} >7 per these guidelines, indicating that the material is predicted to be too lipophilic to accumulate in the tissues of living organisms.

1.4 Estolide-Based Lubricant Formulations

Estolides can be used in a wide range of lubricant formulations, including for engine oils, hydraulic fluids, gear oils, greases, metalworking fluids, compressor fluids, and dielectric fluids.[16,17,18] In addition, due to their favorable environmental profile, they are of particular interest in ecologically sensitive lubricants for the marine, forestry, mining, and petroleum drilling fluid market segments. The focus of this section will be on the use of estolides in Passenger Car Motor Oil (PCMO) formulations.

1.4.1 Estolide-Based Motor Oils

A variety of PCMO field trials have been conducted using lubricants with estolide base oils, in both hot and cold climates. Common to each of these tests has been the observation of enhanced engine cleanliness with estolide-based as compared to conventional petroleum-based motor oil formulations. Even after a field trial of over 100,000 miles, engines using estolide-based motor oils displayed high levels of cleanliness. In fact, in a formulation containing Group II base oil, replacing just 10% of the base stock with an estolide product showed significant improvements on the engine cleanliness measurements of a Sequence IIIG engine test. In Figures 8-10, we compare a set of images from two engines (Chevy Impala, 3.5 liter V6) after an 18 month and 150,000 mile field trial in Las Vegas, NV. The reference engine (top) was run using a standard quality GF-5 motor oil formulation while the test engine (bottom) was run using an estolide formulation. As shown in the images, the reference engine showed levels of varnish consistent with what is expected from a standard motor oil formulation. The test engine with the estolide formulation, however, showed outstanding overall cleanliness and minimal varnish.

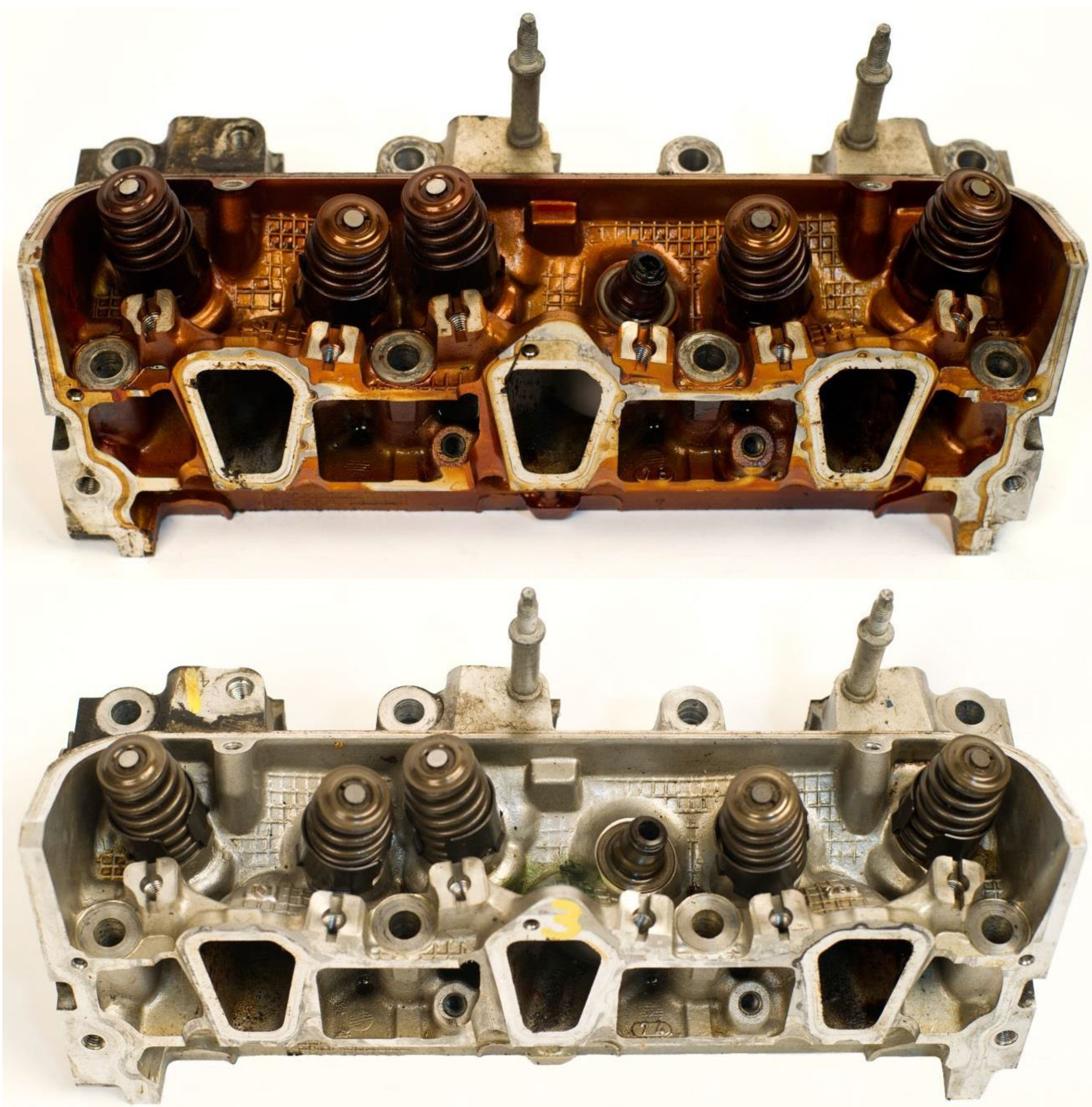

Figure 8 – Cylinder heads from two Chevy Impala 3.5 liter V6 engines used in an 18 month 150,000 mile field trial in Las Vegas, NV. The conventional motor

oil formulation (top) had a typical level of varnish at the end of the test, while the estolide formulation (bottom) showed a high degree of overall cleanliness and minimal varnish.

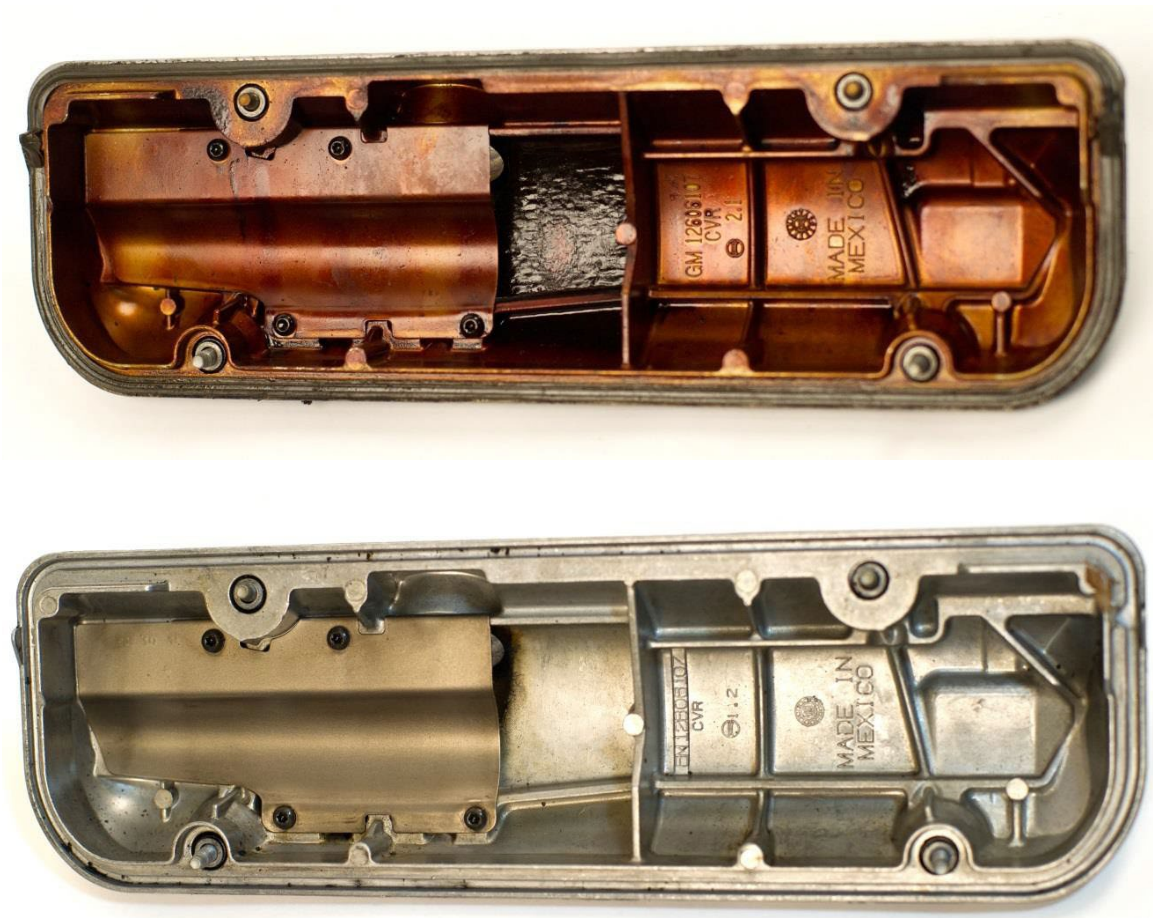

Figure 9 – Valve covers from two Chevy Impala 3.5 liter V6 engines used in an 18 month 150,000 mile field trial in Las Vegas, NV. The conventional motor oil formulation (top) had a typical level of varnish at the end of the test, while the estolide formulation (bottom) showed a high degree of overall cleanliness and minimal varnish.

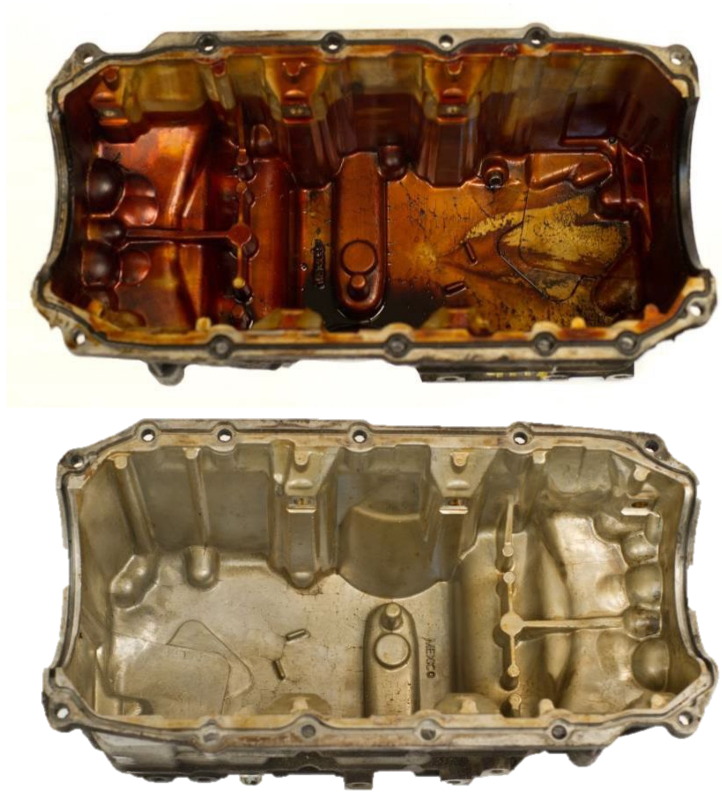

Figure 10 – Oil pans from two Chevy Impala 3.5 liter V6 engines used in an 18 month 150,000 mile field trial in Las Vegas, NV. The conventional motor oil formulation (top) had a typical level of varnish at the end of the test, while the estolide formulation (bottom) showed a high degree of overall cleanliness and minimal varnish.

Both 5W-20 and 5W-30 motor oil formulations containing estolide base oils have been certified by the American Petroleum Institute (API) and met the most current specifications for motor oils, ILSAC GF-5, thus achieving the API SN-RC designation (see Figure 11).

Figure 11 – Two motor oil formulations (5W-20 and 5W-30) containing estolide base oils have recently been certified by the API as SN-RC quality products (ILSAC GF-5).

1.4.2 Motor Oil Biodegradability

With the use of more bio-based materials in motor oils, along with the success of technologies like estolides, it is becoming important to understand if the environmental properties of the base oils are maintained after (1) being blended with additives and (2) being used in an engine.

To investigate this, motor oil samples were tested for biodegradability according to OECD 301B. The first formulation was 84% estolide with 16% additives, not yet used in an engine, and showed 68.1% biodegradation in 28 days. The same formulation was then used in an engine for 7,500 miles, tested on OECD 301B, and showed 74.4% biodegradation in 28 days. This result indicates that the additives do not appear to affect the biodegradability of the estolide base oil, nor does its use in an engine appear to affect the overall biodegradability of the motor oil.

In order to better understand the theory and logic behind these findings, Dr. Todd Stevens, a renowned expert in environmental microbiology and biogeochemistry, [19, 20, 21] was consulted. Dr. Stevens has worked in both routine biodegradation testing and research and development of novel biodegradation and bioremediation processes,[22] and is the proprietor of Stevens Ecology, a private laboratory for environmental analysis and R&D consulting.[23]

On the ability of additives to affect the biodegradability of a base oil, Dr. Stevens provided the following comments:

> Hypothetically, there are two ways that such additives could inhibit biodegradability of the base oil. First, they could be toxic or otherwise inhibitory to the microorganisms that carry out the biodegradation process. Second, they could be preferred substrates, such that biodegradation of the base oil is inhibited until biodegradation of the additives is completed. (This is known as "catabolite repression.") However, the mere fact that these additives may or may not be biodegradable has no bearing on whether or not the base oil will be biodegraded.

After testing the biodegradation of this formulation in his laboratory, Dr. Stevens stated, "Based on our experiments, we conclude that the presence of additives had no apparent effect on the biodegradability of the base oil."

Regarding the ability of a formulation to maintain its biodegradability after being used in an engine, Dr. Stevens commented:

> Certainly processes that make chemical alterations to a material can change the biodegradability of that material. The products of such reactions might have increased or decreased biodegradability, or might include some of both. Most processes that involve

heat and oxidation tend to increase biodegradability. Reactions that involve polymerization or aromatization can decrease biodegradability.

During use in an engine, motor oils are known to undergo two of the aforementioned processes: (1) heat/oxidation and (2) subsequent polymerizations of these heat/oxidation products. Therefore, because oxidation can lead to increased biodegradability, and polymerization can lead to decreased biodegradability, the true impact of these opposing processes on biodegradability is difficult to predict. However, based on the OECD 301B data generated by Dr. Stevens on fresh (68.1% in 28 days) and used (74.4% in 28 days) estolide motor oils, he concluded that, "The use of this oil in an engine did not inhibit, and may have slightly improved the biodegradability of the motor oil."[24]

1.5 Chemical Versatility of Estolides

From the perspective of chemical versatility, large variations of estolide products can exist, which make the family of compounds useful for a broad range of applications. For example, estolide products can be customized to enhance properties such as oxidative or hydrolytic stability, or be manipulated to improve characteristics like cold temperature flow (with some products achieving pour points as low as -54°C).[2,25] Estolide oligomerization can be controlled to make products with viscosities ranging from ISO VG 15 to ISO VG 2200, which allows products to be custom-tailored to fit just about any application.[26] In addition, the product can be functionalized with various moieties to yield compounds with additive-like properties, such as improved anti-wear or extreme pressure protection.[27,28] For these reasons, the estolide class of compounds has near limitless potential as a specialty chemical in the lubricants industry for years to come.

1.6 Conclusion

Many industry experts consider estolides to be the next generation of high-performance synthetic lubricants. Their potential for swift adoption in the marketplace has stemmed from a combination of strong performance and environmental characteristics, making estolides an essential tool for formulators of the future.

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