Synthetic Esters: Mother Nature's Second Choice™

Author: **Tyler Housel, CLS**
Member ACS, STLE, ILMA

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Synthetic Esters: Mother Nature's Second Choice™

Organic esters are one of the basic building blocks of life on Earth. All living things biochemically manipulate organic alcohols and fatty acids to form esters that suit the needs of the organism. Esters have always been a part of the food chain, and humans have worked with these natural and abundant esters for millennia to develop products such as wood varnish, sealing wax, axle grease and lamp oil.

Naturally occurring lipids are widely available and have many undeniable advantages including biodegradability, low cost, low flammability and they are non-toxic. Unfortunately, animal and vegetable oils cannot be used in most modern industrial applications because poor hydrolytic, oxidative and bio-stability leads to rancidity and degradation.

Industrial automation in the 20th century put additional stresses on process fluids and it became clear that natural oils were not up to the task. Chemists learned to intelligently design oils by rearranging and purifying natural lipids to suit their purpose.

Synthetic esters are manufactured by combining alcohols and carboxylic acids in an esterification reaction. There are dozens of commercially available alcohols and acids to choose from, and many feedstocks are derived from vegetable or animal sources. Ester chemistry allows the user to formulate lubricant basestocks to meet virtually any lubrication challenge. Although not quite natural, synthetic esters still retain the favorable health, toxicity and environmental benefits of the natural oils. When compared to other lubrication base oils, synthetic esters are clearly Mother Nature's Second Choice™.

Why Synthetic Esters?

Esters are naturally polar molecules which gives them an affinity for each other in the liquid state. This means they are less prone to evaporation than hydrocarbons, aromatics and ethers. At a given temperature and viscosity, synthetic esters are much less volatile than mineral oils, polyalphaolefins (PAO) and other less polar base oils.

www.inolex.com

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Another benefit of polarity is that the ester groups are attracted esters to metal surfaces where they form a molecular boundary layer which not only lubricates but also protects the metal from oxidation and corrosion.

All esters are polar; the other properties are determined by the type and ratio of organic alcohol and carboxylic acid ingredients. Therefore, the manufacturer designs a synthetic ester to provide the appropriate viscosity, volatility, thermal stability, pour point, flash point, biodegradability and even cost. To clarify this relationship, we divide synthetic esters into four subgroups: fatty acid esters, diesters, polyol esters and complex esters

Fatty Acid Esters

Fatty acid esters are manufactured from naturally occurring fatty acids that are commercially derived from animal or vegetable fats and oils. Based on renewable resources and also biodegradable, these esters are widely used in skin creams and other cosmetics and have an outstanding health and safety profile.

In industrial applications, synthetic fatty acid esters give a distinct performance advantage over natural triglyceride oils because we fix two weak links that occur in nature. Specifically, the triglyceride is deconstructed by separating the fatty acids from the glycerin. This fatty acid mixture is then purified to improve the character of the acid component. Finally, the acids are reconstituted with synthetic alcohols because glycerin is prone to oxidation and rancidity at elevated temperature. The resulting synthetic fatty acid ester has superior oxidative, hydrolytic and bio-stability and can be designed to meet the viscosity, volatility and other characteristics required for the application.

Diesters

Diesters are historically made from synthetic diacids and synthetic alcohols. As such, they are not based on renewable resources, but can still have an excellent health, safety and toxicity profile if aromatic diacids (phthalates) are avoided. In recent years, bio-based diester feedstocks have become available and it is likely that these will become more affordable in coming years.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148
215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Polyol Esters

Polyol esters have three or more ester groups so they give higher viscosity and lower in volatility than diesters. The polyol center is extremely stable at high temperature so polyol esters are preferred in hot operations where they give long life and resist varnish and deposit formation.

The acid component can be renewable or fully synthetic. Synthetic feedstocks optimize thermal stability and renewable acids are required if the oil must be readily biodegradable.

Complex Polyol Esters

Complex polyol esters are polymeric hybrids of polyol esters and diacids. By combining the two technologies, it is possible to achieve excellent thermal stability at moderate to very high viscosity. The polymeric character and multiple ester groups lead to a very high viscosity index, outstanding tack and exceptional boundary lubrication. Complex polyol esters can be manufactured with a large percentage of renewable carbons and many types are readily biodegradable.

Representative Synthetic Esters

It is possible to synthesize thousands of ester combinations from existing feedstocks, so we use simile to understand the toxicological and environmental properties. The ten compounds described herein all have industrial applications, and cover a range of molecular weights, volatilities and chemistries. It is reasonable to apply this information to similar synthetic esters by analogy.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Lexolube® Product	Category	Alcohol	Acid Component
IPP	Fatty acid ester	Isopropyl	Palmitic
IPO	Fatty acid ester	Isopropyl	Oleic
NBS	Fatty acid ester	n-Butyl	Stearic
EHP	Fatty acid ester	Ethyl hexyl	Palmitic
B-109	Fatty acid ester	Tridecyl	Stearic
2X-109	Diester	Tridecyl	Adipic
3N-310	Polyol ester	Trimethylol propane	C8-10
3G-310	Fatty acid polyol ester	Trimethylol propane	Oleic
POE series	Polyol ester	Dipentaerythritol	C5-10
CPE series	Complex polyol ester	Mixed polyol	Mixed

Basic Physical Properties

The first step in understanding synthetic esters is to determine the effect of the molecular size and structure. Esters used in the lubrication industry are not flammable under the DoT definition and generally have at least 19 carbons. Smaller esters are better described as solvents.

Viscosity and flash point increase quickly as the number of carbons in the ester increases. As expected, the Volatile Organic Content (VOC) decreases with carbon count, and is particularly sensitive to the number of carbons between 19 and 22. Air quality standards require low VOC because organic volatiles play a role in creating photochemical smog. Specific gravity is a measure of the ester density (number of ester groups divided by number of carbons) which also tends to increase as the molecule grows.

Viscosity, flash point and specific gravity were tested according to ASTM D-445, D-92 and D-1122 respectively. VOC was measured by ASTM E1868-10in accordance with SCAQMD Rule 1144. This is the new VOC standard required for metalworking fluids in Southern California.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148
215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Lexolube® Product	Number of Carbons	Viscosity @40°C	Flash Point	Specific Gravity	VOC - Rule 1144
IPP	19	5 cSt	165°C	0.85 at 25°C	38 g/L
IPO	21	5	175	0.85	24
NBS	22	6	195	0.85	7
EHP	24	9	220	0.86	1
B-109	31	17	230	0.86	5
2X-109	32	27	240	0.91	2
3N-310	33	19	250	0.94	<1
3G-310	60	49	320	0.91	<1
POE-68HT	52	68	290	0.99	<1
CPE-70	~70	68	290	0.98	<1

Toxicology, Health and Safety

Synthetic fatty acid esters such as IPP, NBS and EHP have been used in cosmetics for over 50 years and have an excellent toxicological and environmental profile. Many synthetic esters are approved by the FDA, CFIA, and other regulatory bodies for food processing lubricants where incidental contact with food products is possible. In summary, synthetic esters have an excellent health and safety profile.

The renewable content is the percentage of carbons in the final product that come from renewable (generally plant based) feed stocks. In the near future, additional bio-based feedstocks will be manufactured in commercial quantities and it is likely that fully renewable synthetic esters will be available.

Biodegradability is tested by the OECD 301B protocol. Greater than 70% degradation in 28 days means the product is readily biodegradable. Some esters were not tested directly, but were labeled readily biodegradable based on chemical analogs. Synthetic esters are designed to be more stable than animal or vegetable oils. They are metabolized (biodegraded) slowly and are non-toxic and increasingly bio-inert.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

LD 50 shows the dosage which causes death in 50% of a population of test animals (normally rats). In almost all cases, the LD 50 values for esters are listed as "greater than" meaning that most or all of the test population survived at the highest test concentration. It is uncommon to continue testing beyond 5 grams per Kg of body weight because it is unlikely that a person will accidentally ingest such a large amount of these compounds. The United Nations"Globally Harmonized System of Classification and Labeling of Chemicals (GHS), 2009" considers LD 50 values above 2 g/Kg to have a low acute toxicity hazard (Category 5), and above 5 g/Kg they have no hazard classification. In Chapter 3.1, page 110, the UN document states: "Recognizing the need to protect animal welfare, animal testing in Category 5 ranges is discouraged and should only be considered when there is a strong likelihood that results of such a test would have a direct relevance for protecting human health".

The American Chemistry Council Synthetic Esters Panel has published over 1000 pages of data on the toxicological, environmental and physical properties of synthetic esters over the past 10 years. The Panel grouped the esters based on structural similarity and determined that "read across" assessments were appropriate for expanding the data to cover analogous chemistries. This decision limits the testing required and has been applauded by animal rights activists.

The Environmental Working Group (EWG) maintains a safety database for cosmetic ingredients called the Skin Deep Cosmetics Database. This data is available online and contains entries for more than 79,000 products (as of early 2013). After considering available health, safety and environmental data, the EWG provides a grade from zero to ten. Higher numbers means the ingredient is more hazardous and consumers should seek safer alternatives. Many synthetic esters appear in the database because they are also used in cosmetics. With grades of 1 or lower, the synthetic esters are among the safest chemicals on the list.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Synthetic Ester	Renewable carbon	Biodegradability	LD50	EWG Grade (0-10 scale)
IPP	84%	Readily (>70%)	64 g/kg (6.4%)	0
IPO	86	Readily	Nd	0
NBS	82	Readily	>32	0-1
EHP	67	Readily	>5	0-1
B-109	58	Readily	Nd	0-1
2X-109	0	58.5%- Inherently	16	1
3N-310	82	65.5%- Inherently	>5	0
3G-310	90	Readily	Nd	-
POE-68HT	0	47.1%- Inherently	>5	0
CPE-70	50	Readily	>2	0

Performance Characteristics

Synthetic esters have been used in industrial lubricants for more than 50 years. They are excellent boundary lubricants and have outstanding lubricity, thermal stability and service life. Major markets for synthetic esters are metalworking fluids, textile lubricants, hydraulic fluids, compressor oils, automotive lubricants, gear and chain lubricants and grease. Although this paper focuses on the health and environmental benefits, it is important to remember that synthetic esters do not require a sacrifice in performance.

Conclusions

Synthetic esters have an outstanding environmental profile and are worker friendly. In fact, synthetic esters are widely used in cosmetics including skin care products. These products have been used in the lubricants industry for most of the 20th century because they are outstanding lubricants and perform well in many applications where other oils fail. There is no need to sacrifice performance to find a superior lubricant basestock with a favorable environmental and toxicological profile. If a vegetable oil doesn't meet your performance requirements, synthetic esters are *Mother Nature's Second Choice*™.

Inolex
2101 S. Swanson St.
Philadelphia, PA 19148

215 271 0800 office
215 271 2621 fax
lubeinfo@inolex.com email

Author: **Tyler Housel, CLS**
Member ACS, STLE, ILMA

Inolex Chemical Company
2101 South Swanson Street
Philadelphia, PA 19148

215-847-6333

thousel@inolex.com

Acknowledgements and References:

Inolex Chemical Company of Philadelphia, PA

- Funded this presentation and solely responsible for the content
- Funded analytical work on VOC
- Manufactured all synthetic esters tested
- Supplies Lexolube® synthetic esters
- www.inolex.com

American Chemistry Council

- Sponsored High Production Volume (HPV) Chemical Challenge Program
- Primary source for biodegradability and LD 50 data
- www.epa.gov

Environmental Working Group (EWG)

- Safety grade from SkinDeep Cosmetics Database
- www.ewg.com