VOC Assessment of Synthetic Ester Fluids

By Tyler Housel, CLS

Objective

This report is based on a presentation at the SCAQMD/ILMA Joint Symposium on Metalworking Fluids and VOC in March, 2012. The objective is to provide data on the volatility characteristics, health, safety and environmental profile and performance aspects of synthetic esters. This information can be applied to synthetic ester oils that are used as basestocks and additives to formulate metalworking fluids and other industrial lubricants.

The Evolution of Synthetic Esters in Lubricants

Natural fats and oils have been used as lubricants since the earliest days of civilization. Animal and vegetable oils cannot be used in modern industrial applications because of their poor hydrolytic and oxidative stability that leads to rancidity and degradation. Synthetic esters were developed in modern times to improve on these shortcomings.

Synthetic esters are manufactured by reacting alcohols and carboxylic acids in an esterification reaction. There are many commercially available alcohols and acids to choose from. They can be derived from animal, vegetable or fully synthetic sources. The chemistry is quite flexible and allows the user to formulate lubricant basestocks to meet virtually any lubrication challenge.

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 at a given temperature than a non-polar molecule such as a hydrocarbon mineral oil and therefore have lower volatility. Polarity attracts esters to metal surfaces where they form a molecular layer which not only lubricates but also protects the metal from oxidation and corrosion.

Beyond these general similarities, synthetic esters are broken into four subgroups: fatty acid esters, diesters, polyol esters and complex esters.

Fatty Acid Esters

Fatty acid esters are the most common synthetic esters used in metalworking fluids. They 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 chemistry allows us to fix two weak links that occur in nature. To do this, 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 and hydrolytic stability and can be designed to meet the viscosity and volatility profile and other characteristics required for the application.

Diesters

Diesters are 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. Diesters have two ester groups and are fully saturated so they are better than fatty acid esters at both high and low temperatures.

Polyol Esters

Polyol esters have three or more ester groups and this increases viscosity and lowers volatility further. 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. Synthetics optimize thermal stability and renewable acids are required if the oil must be readily biodegradable.

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Complex Polyol Esters

Complex polyol esters are polymeric hybrids of polyol esters and diacids which are combined to create an oil that is capable of reaching increasingly high viscosities. The polymeric character and multiple ester groups leads to a very high viscosity index, outstanding tack and exceptional boundary lubrication. These can be manufactured with a large percentage of renewable carbons and many types are readily biodegradable.

Ester Summary

For this investigation, we tested ten common synthetic esters representing each of the major categories. The esters all have industrial applications, and cover a range of molecular weights, volatilities and chemistries. They are listed below.

Synthetic Ester	Category	Alcohol	Acid component
IP 16	Fatty acid ester	Isopropyl	Palmitic
IP 18u	Fatty acid ester	Isopropyl	Oleic
NB 18	Fatty acid ester	n-Butyl	Stearic
EH 16	Fatty acid ester	Ethyl hexyl	Palmitic
TD 18	Fatty acid ester	Tridecyl	Stearic
Di TDA	Diester	Tridecyl	Adipic
TMP 8-10	Polyol ester	Trimethylol propane	C8-10
TMP 18u	Fatty acid polyol ester	Trimethylol propane	Oleic
DPE 5-10	Polyol ester	Dipentaerythritol	C5-10
68 CPE	Complex polyol ester	Mixed polyol	Mixed

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VOC and Other Physical Properties

Many of the presentations in this Symposium discuss the development and details of methodology for measuring VOC using the on the Loss-on-Drying by TGA (ASTM E1868-10) standard with additional requirements for SCAQMD Rule 1144. The results presented herein follow the Rule 1144 method. Viscosity, flash point and specific gravity of these esters were tested according to ASTM D-445, D-92 and D-1122 respectively.

The current VOC requirements under Rule 1144 vary according to the fluid category. The lowest limit is 50 grams per liter, and all of the esters tested were well below 50. As expected, there is strong evidence that VOC decreases as the number of carbons in the ester increases. Fewer carbons also lead to lower viscosity and lower flash point. The VOC seems particularly sensitive to the number of carbons between 19 and 22. Esters with 22 or more carbons give VOC values below 10 g/L and would not be expected to significantly contribute VOC in a formulated product.

Synthetic Ester	# of carbons	Viscosity @40°C	Flash Point	Specific Gravity	VOC- Rule 1144
IP 16	19	5 cSt	165°C	0.85 at 25°C	38 g/L
IP 18u	21	5	175	0.85	24
NB 18	22	6	195	0.85	7
EH 16	24	9	220	0.86	1
TD 18	31	17	230	0.86	5
Di TDA	32	27	240	0.91	2
TMP 8-10	33	19	250	0.94	<1
TMP 18u	60	49	320	0.91	<1
DPE 5-10	52	68	290	0.99	<1
68 CPE	~70	68	290	0.98	<1

Toxicology, Health and Safety

Synthetic fatty acid esters such as IP 16, NB 18 and EH 16 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 as appropriate for food processing lubricants where incidental contact with food products is possible. In summary, synthetic esters have an excellent health and safety profile.

In the table below, 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. A value 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.

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.

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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 69,000 products (as of early 2012). 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.

Synthetic Ester	Renewable carbon	Biodegradability	LD 50	EWG Grade (0-10 scale)
IP 16	84%	Readily (>70%)	64 g/kg (6.4%)	0
IP 18u	86	Readily	Nd	0
NB 18	82	Readily	>32	0-1
EH 16	67	85%- Readily	>5	0-1
TD 18	58	Readily	Nd	-
Di TDA	0	58.5%- Inherently	16	1
TMP 8-10	82	65.5%- Inherently	>5	-
TMP 18u	90	80.7%- Readily	Nd	-
DPE 5-10	0	47.1%- Inherently	>5	0
68 CPE	50	84.8%- Readily	>2	-

Performance Characteristics

Synthetic esters have been used in metalworking fluids and industrial lubricants for more than 50 years. They are recognized as 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.

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Only recently has their favorable health, safety and environmental characteristics been a factor in synthetic ester use in lubricants. This report was prepared to present new data on VOC measurements; however, it is important to remember that the use of synthetic esters does not require a sacrifice in performance. For those unfamiliar with the performance benefits, we conclude with a typical example of a semi-synthetic metalworking fluid.

Ingredient	Formula A (no ester)	Formula B (with ester)
Emulsifier/ Additive package	60%	60% (same)
Naphthenic oil (100SUS)	20	15
EH 16	0	2.5
460 CPE	0	2.5
Water	20	20
Dilution in water	20:1	20:1
Emulsion stability	Stable	Stable
ASTM D3233A failure load (Falex pin and vee)	3000 lbs	4000 lbs
Failure mode	Pin breaks	Wear
Appearance	Severe weld	Striations

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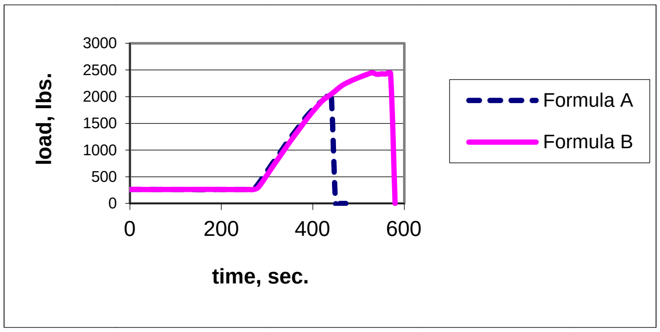
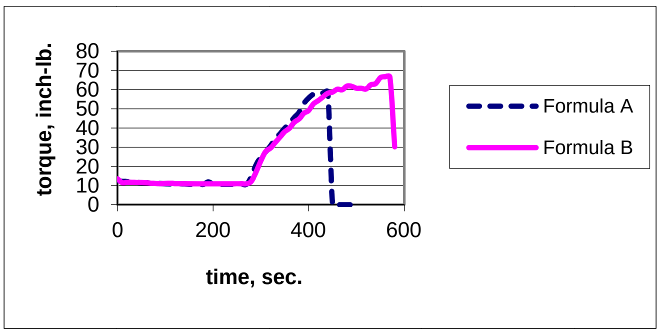
Wear data was generated using a Falex pin and vee machine and tested according to ASTM D3233A. The upper graph is gage load vs. time and the lower graph shows torque in the same experiment. There is a significant increase in load carrying ability of the concentrate with 5% total ester. Note that at a dilution of 20:1 in water, the actual amount of ester in the test fluid is only 0.25%.





Conclusions

Data generated with the SCAQMD Rule 1144 protocols shows that the VOC of synthetic esters range from 38 g/L to essentially zero. It appears that esters with 22 or more carbon atoms have a very low VOC and will not be expected to contribute much VOC in a metalworking fluid. Also, synthetic esters have an outstanding environmental profile and are worker friendly. In fact, synthetic esters are widely used in cosmetics including skin care products.

Synthetic esters 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 in the quest for a low VOC chemistry with a favorable environmental and toxicological profile.

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- 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.org