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 Professional paper

ESTERS, MULTIPURPOSE GROUP V - BASE FLUIDS, PROPERTIES AND APPLICATIONS

Abstract

Lube esters are currently the preferred basestocks to fulfill the requirements for renewable content. Most esters are readily bio-degradable according OECD 301 tests. They are compatible with most other common base stocks and deliver outstanding technical performance with selected additive packages.

Key words: synthetic oils, esters, application

Lubricant and ester history

Before the beginning of the first oil drilling, the growing demand and volume for lubricants were covered by natural oils and fats.

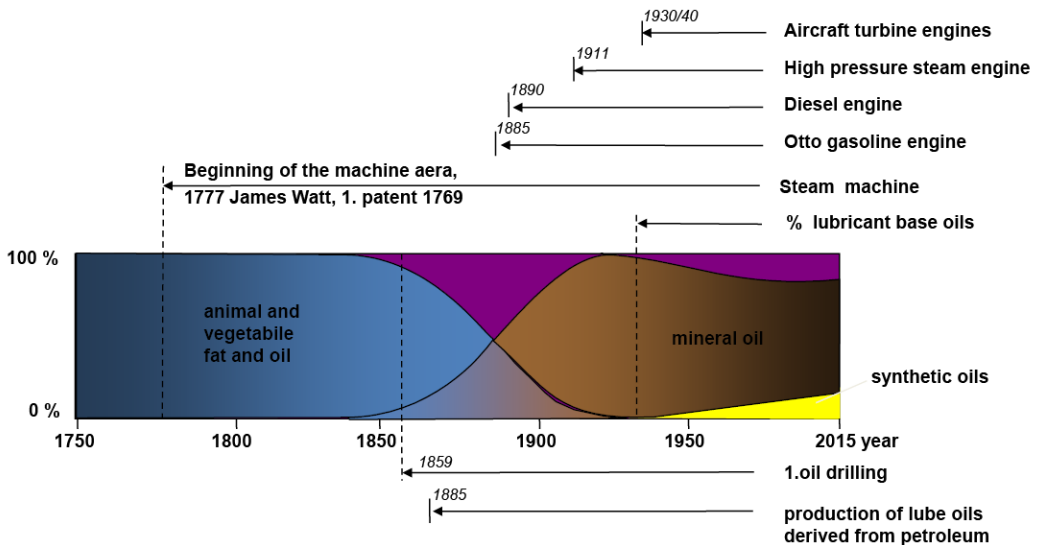


Figure 1: Lubricant history

From 1850's, more and more lubricants manufactured using mineral oil replaced renewable-based products – spurred by the increasing accessibility to fossil fuel. The first jet engines and subsequent space flights in the 1940's and 50's, added pressure in the marketplace with fossil-based lubricants struggling to meet demand – forming a critical turning point in synthetic lubricants.

Esters play a key role in the evolution process of synthetic lubricants. In modern history, lube esters had a rather dubious beginning as they were first used by Germany in World War II in jet engine turbine technology. The launch of the first jet turbine specification MIL- L-23699, in the 1950's, paved the way for dramatic industry advancements, and in the 70's, the first ester-based synthetic engine and gear oils for passenger cars were introduced to the marketplace. This led to longer drain intervals, longer engine life, and reduced maintenance costs.

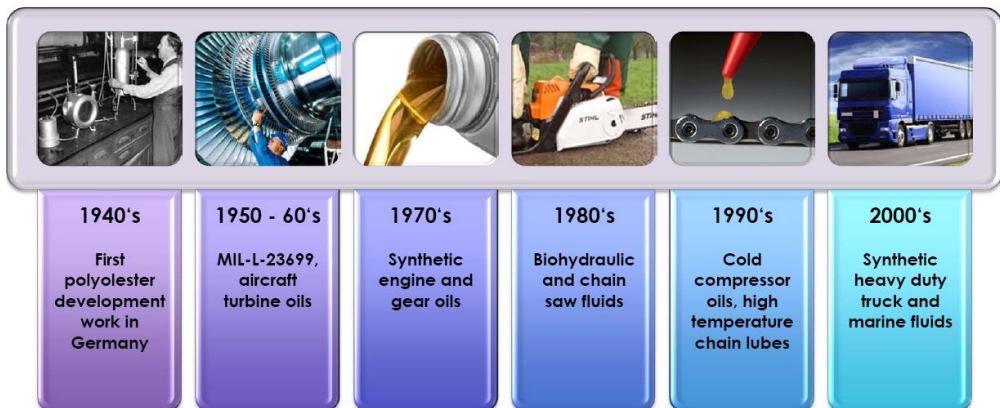


Figure 2: Modern history of lube esters

Increasing awareness on environmental issues led to more adoption of ester-based bio-hydraulics and mineral oil-free chain saw lubes in the 80's, followed by new worldwide regulations on the use of chlorinated hydrocarbon-free cold compressors coolants, in the 90's established. Chlorinated hydrocarbon had to be substituted by fluorinated hydrocarbons which were not compatible with standard mineral oil-based lubricant. New high polar polyolesters were solving this lubrication problem. Also in the 90's, the first high viscous complex esters were introduced to high temperature chain fluids in the food industry. The early 2000's saw ester-based heavy duty truck formulations increase the drain intervals drastically to over 1,000,000 miles. Also, there were new opportunities for esters in base fluids for bio-marine fluids and additives for chlorinated paraffinic-free metalworking fluids.

Ester for lubricants

Esters can be split into five groups: Mono, Di, Glycerol, Polyol, and Complex esters, all of which are made by the reaction of fatty acids with specific alcohols in the presence of a catalyst at temperatures of 180-240°C. This reaction is an equilibrium and controlled by the formation and removal of water, which explains why esters will always contain some remaining acid values.

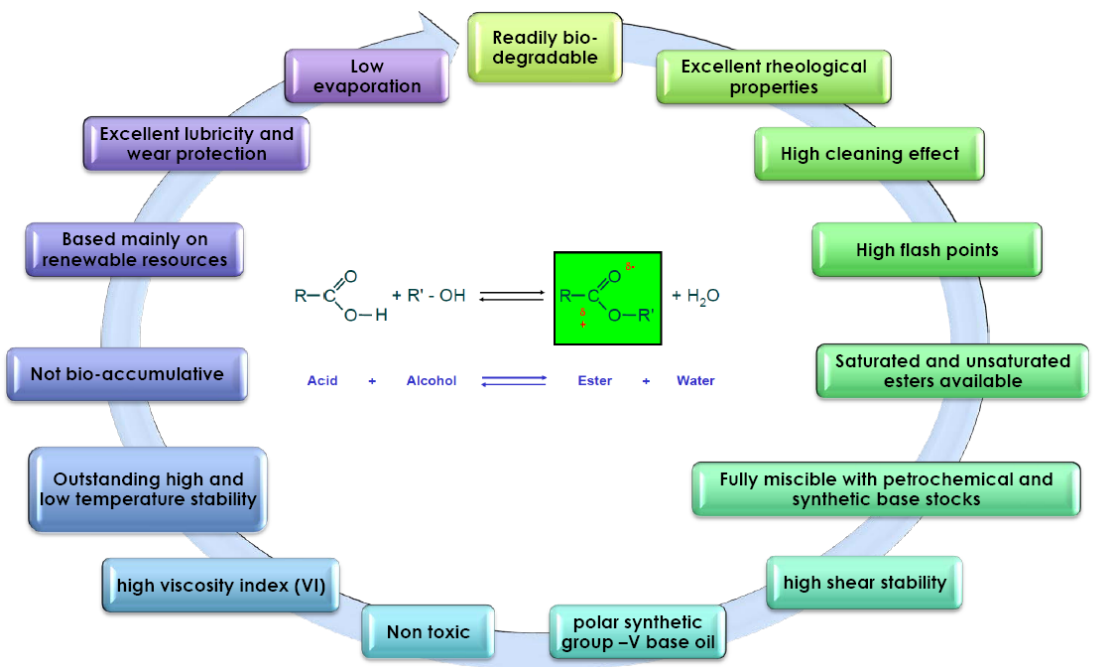


Figure 3: Properties and advantages of lube esters

Linear fatty acids from C-chain lengths of 8-18 carbons, and especially C18 unsaturated (oleic fatty acid), are the most preferred starting materials to be reacted with mono-alcohols (mostly branched) or polyols (e.g. trimethylpropane, pentaerythritol). For diesters and complex esters, dicarboxylic acids like adipic, sebacic, azelaic, and dimers are playing an important role. In the synthesis of esters, some basic design rules are useful. Branched starting materials will lower the viscosity index (VI) but result in excellent low temperature properties. Linear components give high VI's but poor pour points. Saturated fatty acids, branched or linear lead to high oxidation stability but in most cases to unfavourable setting points while unsaturated starting components cause poor oxidation stability with very good low temperature behaviour.

The effects can be demonstrated by the esterification of linear C18-fatty acid with linear and branched alcohols. A straight linear saturated ester like n-butylstearate with iodine value (IV) 1 and a pour point of +22°C shows an extremely high VI of 214. The branched iso-butylstearate version however gives a VI of 175 but a slightly better pour point of +19°C. The introduction of unsaturated oleic acid lifts the VI again to 219, bringing down the pour point to -20°C but reduces the oxidation stability dramatically. The same effects can be found with the higher viscous polyolesters. Polyolesters on the basis of only straight-chain fatty acids attain the kinematic viscosities at 40°C of around 100 mm²/s.

In case of higher viscosities, the so-called complex ester technology, polyols esterified with mono- and di- or tri-carboxylic fatty acids give access to higher tailor-made viscosity grades. Those high viscous polar base oils are very shear, low and the high temperature stability provides strong lubrication and film forming effect which are useful in the formulation of gear and neat oils.

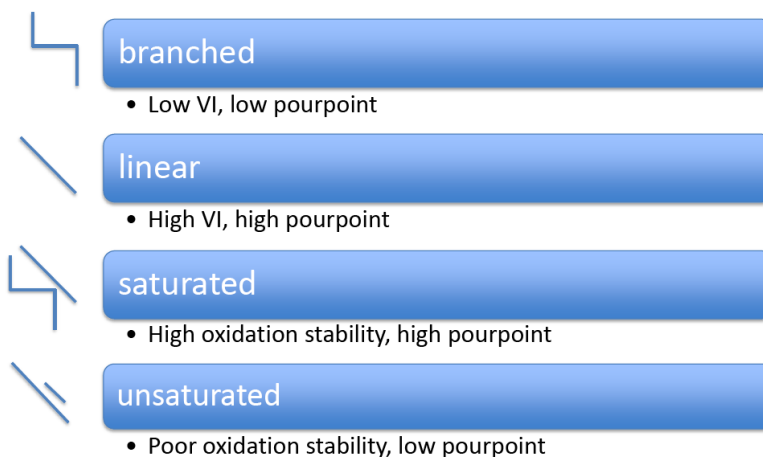


Figure 4: Basic ester design rules

Comparison of basestock types

Belonging to Group V, esters are based mostly on renewable resources and offer environmentally-responsible characteristics such as being readily bio-degradable (OECD 301 B min 60%), not bio-accumulative, non-toxic, and non-aquatic.

Because of those properties, esters are the preferred group of basestocks for all environmentally critical applications. Besides this, esters have excellent rheological behaviors, extremely high viscosity indices, low evaporation losses, and are fully miscible with mineral oils. They are available in all kind of ISO VG classes and can fulfill extreme low and high temperatures, and oxidation demands.

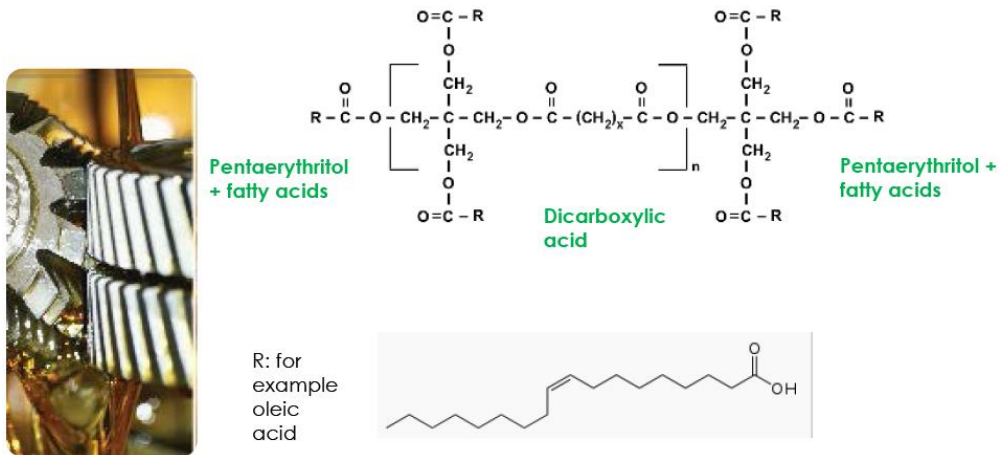


Figure 5: Example of a complex ester

C18- Esters	VI	Iodine value	Pourpoint	kin. Visc. at 40°C
n-Butylstearate	214	1	22°C	6,4 mm ² /s
iso-Butylstearate	175	1	19°C	6,8 mm ² /s
iso-Butyloleate	219	75	-20°C	6,0 m m ² /s
Neopentylglycol-distearate	200	1	25°C	24 mm ² /s
Neopentylglycol-dioleate	200	80	-30°C	24 mm ² /s
Trimethylolpropane-tristearate	180	1	25°C	46 mm ² /s
Trimethylolpropane-trioleate	180	85	-40°C	46 mm ² /s
Trimethylolpropane-complexester	180	88	-20°C	140 mm ² /s

Figure 6: C18 - Ester variations

If we compare the base stocks group I-IV and PAG from group V with ester oils of group V, we see significant differences in the oxidative, thermal and hydrolytic stability. Another weak point seems to be the elastomer compatibility.

	Solvency	Viscosity Index	Cold Temperatur Behaviour	Lubrication	Volatility	Oxidative Stability	Thermal Stability	Hydrolytic Stability	Elastomer Compatibility	Price
Group I	good	poor	poor	poor	poor – good	poor	good	very good	fair	Low
Group II	fair	fair	fair	poor	fair	good	good	very good	fair	Fair
Group III	poor	good	good	very poor	poor	very good	very good	very good	poor	Fair
Group IV : PAO	poor	very good	very good	fair	good	very good	very good	very good	poor	High
Group V : Ester	very good	good	very good	very good	good	poor – good	poor – good	poor – good	poor – fair	High
Group V : PAG	good	very good	good	very good	very good	fair	very good	very good	fair	High

Figure 7: Comparison of basestocks types

Lube esters of unsaturated fatty acids work at temperatures 60-120°C and those of saturated fatty acids work at temperatures >120°C and are available in all important viscosity classes. This demonstrates the oxidation tests (dry turbine oxidation-test (TOST), 100°C in the presence of copper and iron). Four Biohydraulic ISO VG 46 - ester-based (HEES) and mineral oil/ester blend (HEPR) formulations on saturated and unsaturated basis were compared. The unsaturated hydraulic oils did not pass more than 500 hours but the saturated ones passed more than 3000 hours.

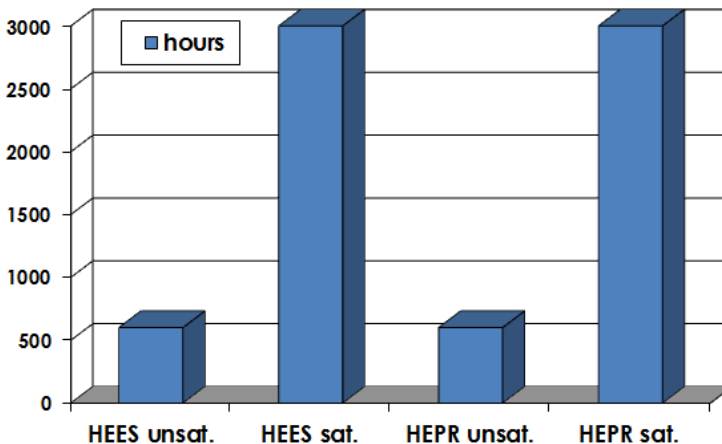


Figure 8: Dry TOST-test (100°C) results of ISO VG 46 HEES and HEPR (additized with 1.5 % R & O additive package)

In principle, esters can be split into fatty acids and alcohols in the presence of water. The hydrolytic stability is a function of the ester structure. This can be shown by using a simple test by dissolving 3 % potassiumhydroxide in pure esters and storing the blends in bottles at 80°C for 9 days. The hydrolytic effect is observed by measuring the increase of the acid value. The acid value started with 0 and was determined at each day over the storage phase. Linear glycerolesters, unsaturated or saturated, hydrolyse very quickly. Esters based on branched alcohols improves the stability dramatically and depends as well on the number of the functional alcohol groups. The graph below is demonstrating the results with oleic fatty acid esters (C18) based on glycerol (G), trimethylolpropane (TMP), neopentylglycol (NPG), ethylhexanol (EH) and pentaerythritol (PT).

Ester are excellent solvents because of their polar structure and tend to swell seals. That is why esters are used in combination with polyalphaolefins (PAO), which have a tendency to shrink seals. Specific PAO/ester blends can balance the seals compatibility of synthetic engine and gear oils.

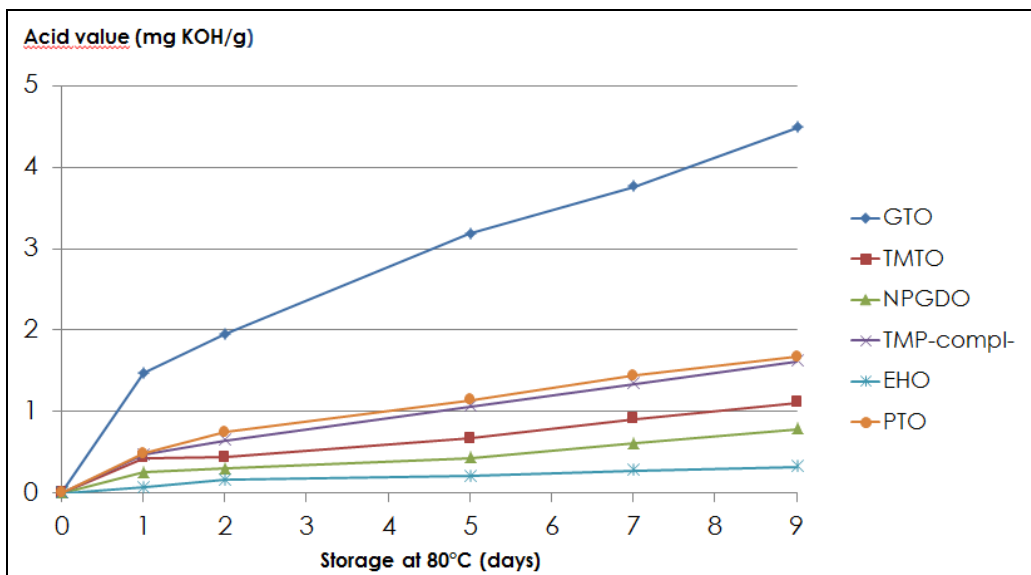


Figure 9: Hydrolytic stability of unsaturated esters (80°C with 3 % potassiumhydroxide)

Applications

The main purpose of monoesters are components for chlorine-free metalworking fluids. The unsaturated hydrolytic stable types are working as anti-wear additives e.g. in water-based systems for steel or aluminum processing and the saturated types for neat oils in conjunction with sulfur carriers.

Polyols and diesters with higher viscosity grades are performing in bio- and inflammable hydraulics, greases, engine, gear oil formulations. The high viscous complex esters are shear stable polymers made of polyols esterified with mono and dicarboxylic acids. These act as high performance anti-wear additives in neat oils, thickeners in wind turbine, gear and transmission fluids.

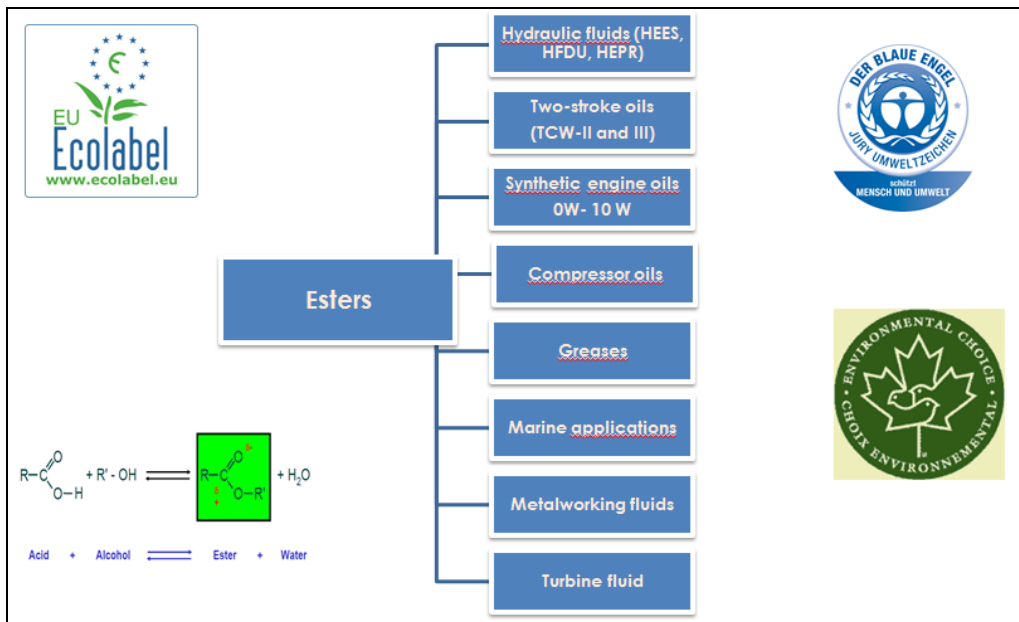


Figure 10: Ester applications

In 2013, a new application for esters in marine fluids became an industry standard in complying with the Vessel General Permit (VGP, published by USA Environmental Protection Agency). In the VGP regulation on oil and grease discharges, all ships navigating to US-harbors must use Environmentally Acceptable Lubricants (EAL) in all "oil to sea interface" or applications. Ester base stocks became the solution of choice in fulfilling the environmental demands of VGP. Esters are available in all viscosity grades, are miscible with conventional fluids and, therefore, are applicable for low and high performance marine lubes. Most oleochemical esters are VGP and EEL compliant (Lubricant Substance classification list – LUSC of the EU Eco label).

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