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Esters
The Most Versatile of Base Stock Technologies

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Choosing the right base stock technology is the starting point for any lubricant formulator as it is the base fluid that primarily determines the final properties of the lubricant itself. Whilst additives are a fundamental part of a well-designed lubricant even the best additives cannot turn a bad base fluid into a good base fluid, so choosing base fluids wisely is absolutely critical.

When deciding which base fluid or combination of base fluids to use the formulator will take into consideration many of the following factors and more:

- Application
- Viscosity at 40°C
- Viscosity at 100°C
- Viscosity at low temperature
- Viscosity at high temperature
- Viscosity index
- Oxidation / thermal stability
- Volatility
- Pour point
- Flash point
- Hydrolytic stability
- Compatibility with metals
- Compatibility with elastomer seals
- Friction / Traction properties
- Solvency
- Gas compatibility (e.g. R134a, hydrocarbon gases, ammonia etc)
- SAP value
- Biodegradability
- Renewability
- Aquatic toxicity
- Water solubility
- Oil / water solubility
- Incidental food contact applications
- Clean burn properties
- Price sensitivities
- Etc etc

The more properties that are identified as being essential to the final product will limit the range of base fluids which are suitable for a given application.

The API categorised crude oil derived base stocks based on sulphur content, saturates content and Viscosity Index in order to distinguish between different types of mineral base oils (Group I, Group II and Group III) and added two further categories; one for polyalphaolefins (Group IV) and one for everything else that didn't fall within the first four categories (Group V).

Group	Sulphur (% w/w)	Saturates	Viscosity Index
I	> 0.03	< 90	80 - 119
II	≤ 0.03	≥ 90	80 - 119
III	≤ 0.03	≥ 90	≥ 120
IV	polyalphaolefins		
V	All other stocks not included in Groups I, II, III and IV		

Table 1. *API classification of base stocks*

Esters fall into the Group V category along with other notable synthetic base fluids such as polyalkylene glycols, polyisobutylenes, silicone oils, phosphates esters, alkyl naphthalenes and others.

Esters as Group V Synthetic Base Fluids

There are essentially three types of esters available to the lubricant formulator:

1. natural esters
2. synthetic oleochemical esters
3. petrochemical esters

Natural esters were the source of the first lubricants ever used and they continue to be highly valued in applications such as metalworking fluids, metal rolling fluids, hydraulic fluids, greases and chain saw lubricants. Natural esters include vegetable crops such as rapeseed, canola oil, olive oil, coconut oil and palm oil and animal fats such as tallow and lard.

Of all the different types of mineral oil and synthetic fluids available to the formulator synthetic oleochemical esters and petrochemical ester are by far the most diverse and versatile, a

reflection of the diversity and availability of raw materials that can be used in their design.

Natural esters are categorised as triglycerides and can be represented schematically as follows:

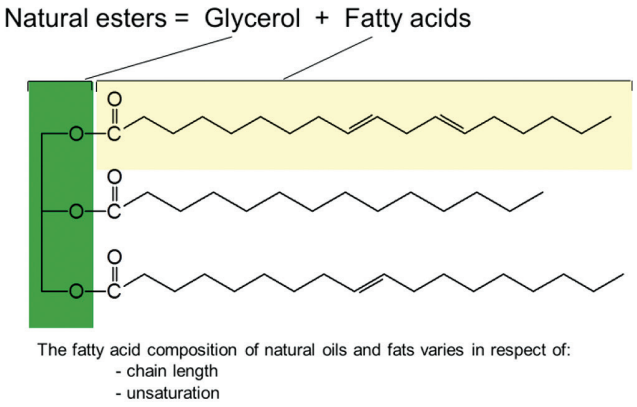


Figure 1. *Schematic representation of a natural ester*

The fatty acid composition is important as it is this part of the triglyceride which dictates most of the basic properties of the ester. Vegetable esters typically have kinematic viscosity at 40°C in the range of 32 – 46 mm^2/s and can vary from good oxidative stability to poor oxidative stability depending upon the degree of unsaturation in the fatty acid groups. For example, coconut and palm oils have a low degree of mono-unsaturation and poly-unsaturation and therefore have better oxidative stability properties than rapeseed oil.

The fatty acid part of vegetable and animal oils is a very important raw material in the manufacture of synthetic oleochemical esters. Fatty acids are produced by chemically splitting vegetable and animal oils into their constituent parts of glycerol and fatty acids using a hydrolysis process. The acids are then separated from glycerol and water, refined and chemically processed to produce raw materials which can be used in the manufacture of mono-esters, di-esters, polyol esters and polymeric esters.

Acids which can be produced through splitting, refining and additional chemical processing range from C8 – C22 mono-acids, C36 di-acids and C54 tri-acids, all very important building blocks in the manufacture of synthetic oleochemical esters.

Synthetic oleochemical esters are predominantly made by reacting mono- or poly- alcohols with one or more fatty acids, depending upon the required base fluid properties. Typical mono-alcohols would include C1 (methanol) to C18 alcohols (stearyl or isostearyl alcohol). Examples of poly alcohols include petrochemical derived neopentyl glycol, trimethyl propane, pentaerythritol, di-pentaerythritol and the naturally occurring glycerol.

Through appropriate raw material selection it is feasible to make esters with kinematic viscosity at 40°C from 2 to > 50,000 mm^2/s and from 1 to > 2000 mm^2/s at 100°C.

Petrochemical esters are derived from predominantly petrochemical produced alcohols and acids. Typically petrochemical esters would be considered to have a C renewability content of 0%. Petrochemical esters are widely available and used but tend to have a much narrower viscosity range than synthetic oleochemical esters, typically ranging from 5 mm^2/s up to 460mm^2/s at 40°C.

Key Basic Properties of Esters Compared to Other Base Stocks

Listed in table 2 are some of the basic properties that are desirable for base fluids and the relative strengths of different

	Group I	Group II	Group III	Group IV	Naphthenic	PAGs	Vegetable Esters	Petro-chemical Esters	Synthetic Oleo Esters
Viscosity Range @40°C (mm^2/s)	10 - 460	22 - 100	22 – 46	5 – 10000	10 - 400	10 - 165000	30 - 50	5 - 460	2 – 50,000
Viscosity Index	+	++	++	+++	-----	+++++	++++	++++	++++
Noack Volatility	+	++	+++	++++	++	++		+++++	+++++
Low Temp Performance	++	++	+++	+++++	+	++++	+	+++++	++++
Oxidation Stability	++	++	+++	++++	++	+++	-----	+++++	+ to ++++
Solvency / Additive Compatibility	++++	++	---	---	+++++	--	+++++	+++++	+++++
Biodegradability	-----	-----	-----	----	-----	-----	+++++	+++++	+++++
Renewability	-----	-----	-----	-----	-----	----	+++++	------	++++

Table 2. *Basic properties of a select range of base stocks*

types of base stocks, both mineral oil derived (including naphthenic oils) and a selection of synthetic base stocks (PAO, PAGs and Esters).

Each base stock type has its own unique set of characteristics which makes it the preferred choice in certain applications. In recent years there has been a decline in the availability of Group I but this has been more than compensated for by the increase in production of Group II and Group III base stocks (including GTL), as the demand for lower viscosity engine oils has increased.

Naphthenic oils find use in greases, metalworking fluids, transformer oils and process oils and PAOs in a wide range of high performance oils including but by no means limited to automotive transmission fluids, engine oils, industrial gear oils and incidental food contact lubricants. Polyalkylene glycols find their niches in fire resistant hydraulic fluids, metalworking and metal quenching fluids, industrial gear oils, incidental food contact lubricants and a range of other high performance industrial applications.

Esters are used in an enormous array of applications including engine oils, transmission fluids, refrigeration lubricants, aviation lubricants, air compressors, chain lubricants, incidental food contact applications, metalworking fluids, greases, hydraulic fluids, transformer fluids and many more.

Table 2 actually does not do justice to the variety of ester base fluids in commercial use today, nor does it explain how properties can be controlled through modest changes in the chemistry of the ester, some of which will be explained in the following sections.

Kinematic Viscosity at 40°C and Viscosity Index

Mineral oil derived base stocks are basically hydrocarbons and there are only so many hydrocarbon structures that can be refined or chemically synthesised which limits the variety and diversity of base fluids that can be produced. With regard to viscosity at 40^{O}C, this means that Group I base stocks are typically limited to the ISO range 10 – 460, Group II to ISO 22 – ISO 100 and Group III to ISO 22 – ISO 46. Naphthenic oils are limited to ISO 10 – 460.

Synthetic base stocks have a much wider viscosity range. PAOs can be produced with kinematic viscosities typically ranging from 5 – 10,000 mm^2/s at 40^{O}C, although in basic chemical composition terms PAO is a hydrocarbon of defined linearity, branching and molecular weight. Polyalkylene glycols (PAGs) have the broadest viscosity range of the synthetic base stocks considered here. PAGs can be produced in the viscosity range of 10 – 165,000 mm^2/s and of the all the product types shown PAGs are unique in that they are the only synthetic base stock type that can be chemically synthesised to be soluble in water, a characteristic that can be controlled through the ethylene oxide content in the product. By varying the type of oxides and the molecular weight of the molecules one can dictate whether the PAGs are water-soluble or oil-soluble, or indeed insoluble in both water and oil.

Vegetable and animal esters are very limited in their viscosity range (typically ISO 32 and 46), which is governed by the type of crop from which they are derived.

Synthetic oleochemical and petrochemical esters are the most diverse and flexible of all the base fluids, due to the fact that there is such a wide variety of raw materials to choose from and which can be combined in almost unlimited ways. This means that it is possible to produce many synthetic esters with the same viscosity properties at 40^{O}C (typically in the range of 2 – 50,000 mm^2/s) but with very different physical and chemical characteristics.

In terms of Viscosity Index (VI), much progress has been made in the development of Group II and Group III base oils compared to Group I base oils. The higher Viscosity Index of Group II and Group III base oils (120+) is a highly prized characteristic in the formulation of engine oils especially. Viscosity index for PAOs is higher again at around 130.

The chemistry of the ester dictates the Viscosity Index of ester base fluids. Aromatic esters such as the trimellitates typically have VIs in the region of 80, polyol esters made using short chain acids (for example C5 – C10 acids) are typically in the VI range 110 – 130 (similar to Group I, GroupII and Group III base stocks), diesters and polyol esters made using longer chain fatty acids can have VIs in the range 130 – 200 and polymeric esters can have VIs ranging from 150 to 300. Indeed, some of the very high viscosity polymeric esters can be used as VI booster additives.

Volatility

Volatility is a critical characteristic for automotive and industrial applications alike. Some applications call for high volatility, for example, aluminium cold rolling uses an annealing process to remove lubricant, whereas other applications call for very low levels of volatility, for example, engine oils and high temperature chain lubricants.

Volatility is a function of chemistry, molecular weight and molecular weight distribution.

Hydrocarbon base stocks and PAG base stocks are a mixture of different chemical compounds and / or oligomers. In terms of volatility characteristics, it is the lower molecular weight molecules that evaporate most easily and are essentially responsible for the temperature at which a specific base fluid will begin to evaporate and the amount of evaporation that takes place at a given temperature.

Many esters have a distinct advantage over other base stocks in that through the appropriate choice of raw materials it is possible to make esters having the same viscosity at a given temperature as other base stocks but with a very narrow molecular weight distribution. This means that esters have the lowest volatility properties of all the mineral oil derived and synthetic base stocks described in table 1.

Whilst progress is being made in the development of lower volatility Group II and Group III base stocks, figure 2 shows the relative Noack volatility performance characteristics of Group III and PAO base stocks and how they compare to the superior Noack volatility properties of ester base fluids.

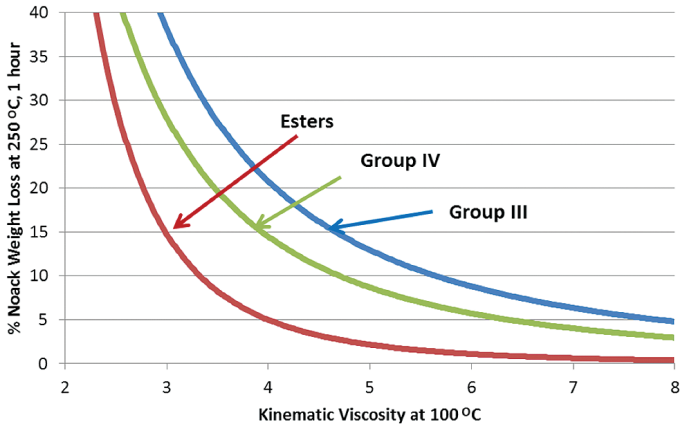


Figure 2. *Noack volatility properties of Group III, IV and esters vs kinematic viscosity at 100°C*

Low Temperature Performance

With regards to the hydrocarbon base stocks, PAOs have the advantage in that they have pour points (< - 60 °C) which are very much lower than equivalent ISO grade Group I, Group II or Group III base oils (-10 to -20 °C). Synthetic oleochemical esters on the other hand can be synthesised to have either high pour points / melting points (> 100°C) or very low pour points (< -60 °C), depending upon what is required in the end application.

For synthetic oleochemical and petrochemical esters, pour point characteristics can be influenced by the choice of raw materials, both alcohols and acids. Consider three commonly used C8/C10 esters based on glycerol, trimethylolpropane (TMP) and pentaerythritol (PE) and three TMP esters based on different C18 acids.

Low pour point esters are characterised by irregular structures which makes molecular packing within a fluid difficult or chaotic. Small, controllable changes in structure through branching, saturation / unsaturation and mixtures of fatty acids can be used to tune pour point characteristics, as can be seen in table 3.

Product	Pour Point
Glycerol C8/C10 triester	- 15°C
TMP C8/C10 triester	- 50°C
PE C8/C10 tetraester	- 3°C
TMP oleate	- 45°C
TMP stearate	+ 40°C
TMP isostearate	- 45°C

Table 3. *Pour point characteristics of C8/C10 esters and TMP C18 esters*

Whilst we generally consider low pour points to be a good thing, there are applications where a higher pour point is highly desirable, for example, some esters are used to provide lubrication and then temporary corrosion protection through the formation of a thin wax like film in the manufacture of sheet metal.

Low temperature performance doesn't just mean pour point properties but it also includes kinematic and dynamic viscosity properties at a range of low temperatures.

Low temperature viscosity properties are also a function of chemistry. As an example, Cold Cranking Simulator (CCS) dynamic viscosity measured at -35°C for Group II, Group III, Group IV and a selection of chemically different esters are shown in table 4.

If we consider hydrocarbon base oils with the same kinematic viscosity at 100°C then the Group II base fluid has the highest CCS viscosity, followed by Group III (1). Group III (2) is a more highly refined Group III base stock and as such has a lower viscosity at -35°C than Group III (1). Of the hydrocarbon base fluids PAO 4 has the lowest viscosity at -35°C (1374mPa.s)

Base Stock	KV @ 100 °C (mm²/s)	CCS @-35°C (mPa.s)
Group II	4	4927
Group III (1)	4.2	3200
Group III (2)	4.25	2668
Group IV (PAO)	4.1	1374
Polyol ester	4.4	2343
Di-ester	4.5	990
Di-ester	3.3	715
Mono-ester	3.3	550

Table 4. *CCS at -35°C for a selection of base stocks*

Now let's consider esters where the chemical structure is once again very important when fine tuning the low temperature flow properties of ester base oils. Two esters with similar viscosity at 100°C (approximately 4.4 and 4.5 mm²/s) display contrasting CCS viscosity at -35°C:

- the 4.4 mm²/s polyol ester has a high CCS viscosity (2343 mPa.s), somewhat lower than Group II and Group III base stocks but much higher than PAO 4.

- the 4.5 mm²/s diester of similar KV100 has a much lower CCS viscosity (990 mPa.s) than the polyol ester and indeed has the lowest CCS at -35°C of all the 4 – 4.5 mm²/s base stocks, including PAO 4.

The effect is not limited to 4 mm²/s polyol- and di-esters. Consider also two esters with a KV 100 of 3.3 mm²/s. Once again the influence of chemical structure can be seen on the low viscosity flow properties with the mono-ester having lower CCS viscosity (550mPa.s) than the di-ester (715 mPa.s).

As with all base stock selection, it is a combination of properties that are required and a balancing act usually needs to be performed. In the case of base fluid selection for an engine oil a combination of excellent low temperature flow properties and low Noack volatility are required and therefore both properties need to be considered when designing ester base fluids for engine oils.

Figure 3 shows the relationship between CCS at -35°C and Noack volatility and clearly demonstrates that esters have the best combination of CCS and Noack volatility properties when

compared to Group III and Group IV base fluids. This unique combination of properties makes esters a candidate base stock technology for future ultra low viscosity engine oils.

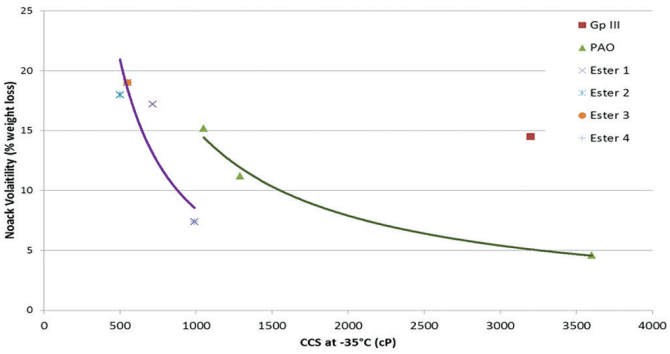


Figure 3. *Noack volatility vs CCS @ -35°C for a selection of base stocks*

Oxidation Stability

Oxidation stability is a highly desired feature for high temperature or long-life lubricants and is strongly influenced by the basic chemical composition of the base fluid, impurities and additive technology.

Thermal cracking and oxidation proceed via a free radical reaction and so if maximum oxidation resistance is required from an ester it would be designed so that it is based on a polyol alcohol reacted with fully saturated acids, or diacids or trimellitic acid reacted with fully saturated alcohols. The choice of alcohols or acids is in part dictated by the other properties that are required from the ester so some compromise in terms of thermal or oxidation stability may be required to ensure other key properties aren't compromised.

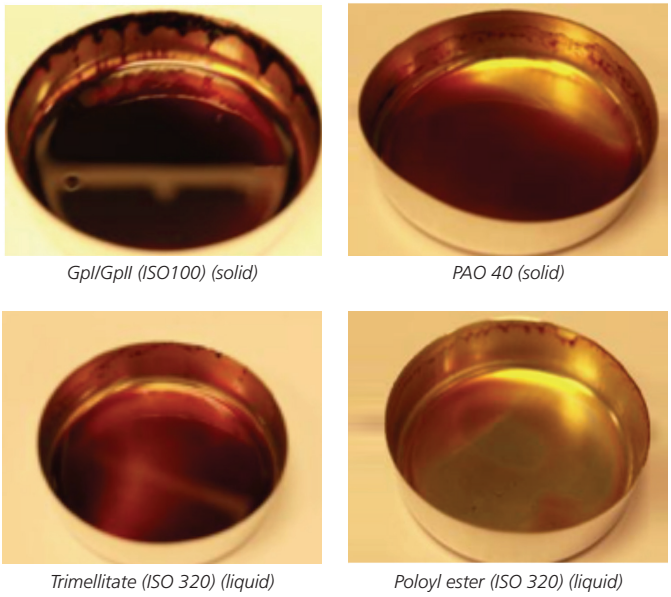
Table 5 shows the dry TOST (ASTM D943) oxidation stability properties for three different types of ester based environmentally acceptable hydraulic fluids (ISO46). Vegetable esters are the least oxidatively stable and therefore are limited to low temperature or short-life lubrication. Unsaturated oleochemical esters (for example oleate esters) have improved oxidation stability properties compared to vegetable esters but fully saturated oleochemical esters have the greatest resistance to oxidation and are the technology of choice for higher temperature or long-life lubricants.

Ester + Additive Pack	Time to increase TAN by 2.0mgKOH/g (hours)
Vegetable Oil	≤300
Unsaturated oleochemical ester	500 - 800
Saturated oleochemical ester	≥ 5000

Table 5. *Dry TOST test for esters*

Deposits and deposit control are also dependent upon thermal and oxidative stability characteristics of the base fluid and also on the solvency properties of the base fluid and hence its ability to dissolve deposits.

Figure 4 demonstrates the appearance and form of several types of base stocks when subjected to high thermal stress. In this example a thin film of lubricant is placed into an aluminium pan, which is then placed in a forced draft oven at 260°C for a period of 8 hours.



GpI/GpII (ISO100) (solid) *PAO 40 (solid)*

Trimellitate (ISO 320) (liquid) *Poloyl ester (ISO 320) (liquid)*

Figure 4. *Deposit forming tendencies of different base stocks*

Group I / Group II blends and PAO 40 form hard resinous deposits as they begin to thermally breakdown, whereas specially designed oxidation resistant esters are less prone to polymerisation and remain liquid for much longer than hydrocarbon base fluids.

Renewability and Biodegradability

Some applications require the use of products with high renewability content and in those situations natural esters and synthetic oleochemical esters are the products of choice. Natural esters would be classified as being 100% renewable and synthetic oleochemical esters would typically have a renewability content in the range 70 – 100%.

Biodegradability and renewability when combined together are the two properties which allow esters to be completely differentiated from all other base stock types. Whilst some progress is being made on developing new low viscosity hydrocarbon base fluids with high renewability content, they cannot compare to esters which can range in viscosity up to and including ISO 1000.

Biodegradability and renewability need not be mutually inclusive, it is perfectly feasible to make esters from petrochemical feedstocks (0% renewable) which are biodegradable and to make esters from renewable or sustainable based feedstocks (with or without the use of some petrochemcial feedstocks) which are very resistant to biodegradation. Building in resistance to biodegradation can be very beneficial, especially in environments where biodegradation leads to a severe deterioration in lubricant performance, for example, in metalworking fluids.

In recent years the introduction and compliance to the European Eco-label in particular has lead to significant growth in the demand for lubricants which are both biodegradable and high in C renewability content.

For environmentally acceptable lubricants, esters must also have low toxicity towards aquatic organisms and be non-bioaccumulating but these are essentially a given for esters whereas biodegradability and renewability content are controllable and are used to design-in all the other properties of the ester base fluid, such as oxidation stability and low temperature performance.

Ester Base Fluid Properties and Applications

As mentioned at the very beginning, the formulator has a broad range of base fluids from which to choose and it is essential that the correct base fluid is selected for a given application, whether that is a mineral oil derived hydrocarbon base fluid or a synthetic base fluid. It should be remembered that esters are not a simple group of compounds, there are literally hundreds of different types of esters in use around the world in a whole range of applications.

In this short article a small but very important selection of key physical properties have been described and there are many more which are also critical for different applications. Figure 5 attempts to draw some links between different physical properties and their importance in some key applications but even this schematic fails to do justice to the breadth of properties and applications in which esters find use.

Esters certainly have the greatest flexibility of the different types of base fluids available today and they can be tuned to give specific physical and chemical properties. Given the wide range of acids and alcohols available and the possibility to combine them in unique ways there is almost certainly an ester that is already commercially available or that can be designed to help meet the challenges of the lubricants industry today and in the future.

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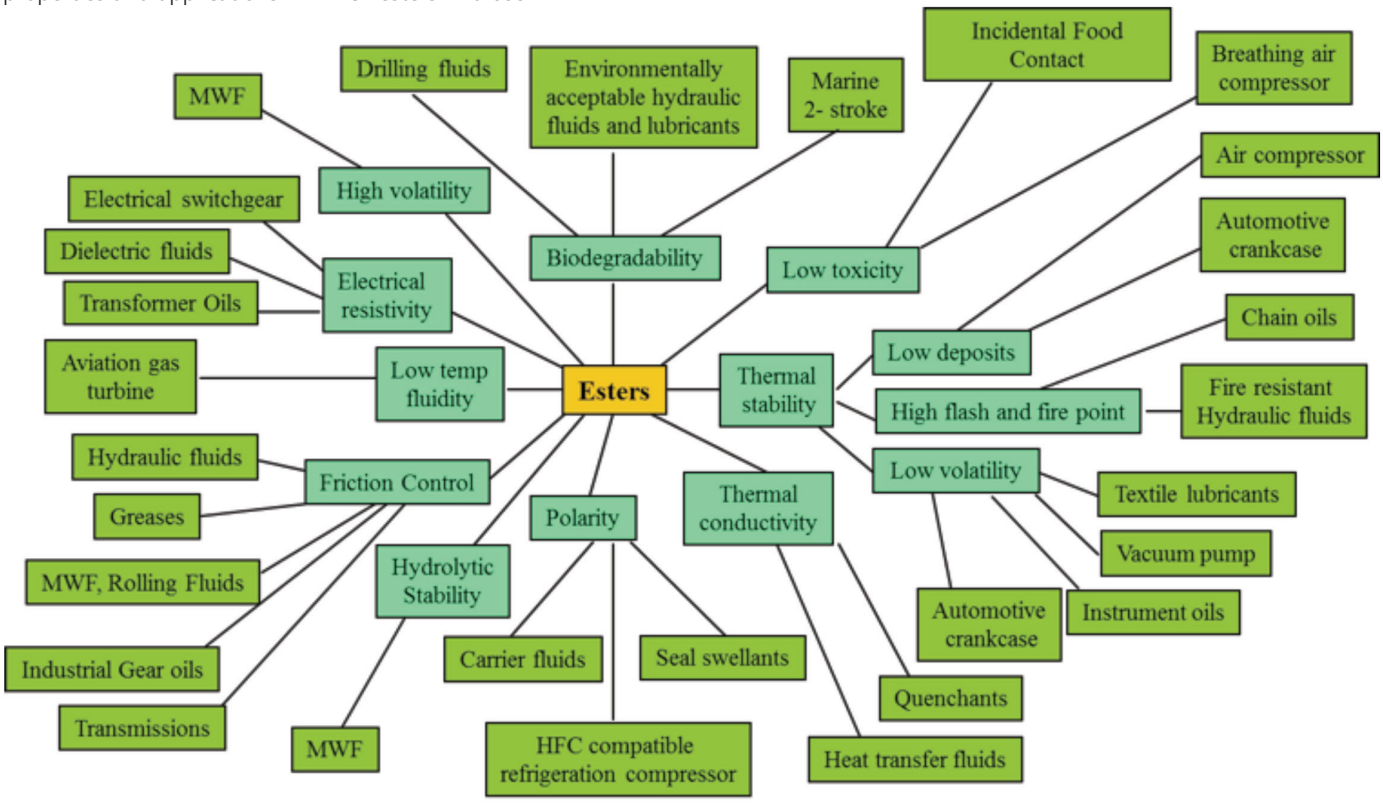

Figure 5. *Schematic of feature and applications for esters base fluids*