

## Estolides - The innovative alternative of ester base oils

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### Introduction

Synthetic esters have been used as base fluids or additives for lubricants for decades. The initial driving force behind this evolution were worries about the finite nature of crude oil reserves. But thoughts about toxicity and biodegradability also began to play a significant role. Sustainability is an aspect of ever greater importance. Following nature's example, circular material cycles using renewable materials are to be implemented as far as possible. A zero balance in CO<sub>2</sub> emissions is one of the important factors here.

The form of these sustainability factors is, to a large extent, determined by the base fluids of the lubricants. Mineral oils are still predominantly in use today but increasingly being replaced by synthetic esters.

Esters stand out when compared to mineral oils due to a number of advantages. On account of the ester group's polarity, they exhibit a high affinity to metallic surfaces. This results in good lubricating properties. In addition, they have lower volatility than mineral oils along with a high viscosity index, which means the viscosity is less dependent on the temperature. By choosing different polyols, using various fatty acids and esterification with dicarboxylic acids, it is possible to vary properties such as viscosity and viscous behaviour, stability and cold-temperature behaviour over a wide range. However, not all properties can be optimised simultaneously since many are diametrically opposed in their behaviour. For example, improved resistance to hydrolysis inevitably results in reduced biodegradability (Stolz, et al., 2019).

For specific applications it would be desirable to have esters with more degrees-of-freedom of modification, since this enables further optimisation of the products. The estolides provide a highly promising approach for this matter.

### The substance class of estolides

Estolides are oligomeric esters based on a special fatty acid with an additional functional group. They cover a wide range of viscosity and, by virtue of their adaptable molecule, can have product properties that vary within a spectrum of above-average width.

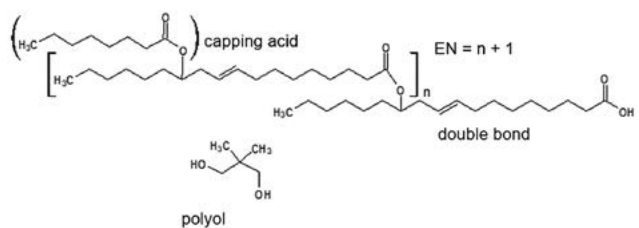


Figure 1: Basic structure of an estolide

Figure 1 shows the basic structure of an estolide. Here, a hydroxy-fatty acid forms the basis of the estolide. This can form oligomers at first by esterification with itself. The extent of oligomerisation is expressed as estolide number (EN). The hydroxy acids used may come from natural sources such as ricinoleic acid, for example. This is available as such or in its hydrogenated form. Alternatively, a hydroxy acid may be obtained from unsaturated fatty acids using mineral acids as a catalyst. The oligomerisation reaction is interrupted by a capping fatty acid which, in turn, by skilful selection, offers the ability to influence the product properties.

The resulting estolide still has a free acid group on the starting fatty acid which can be further esterified with alcohols. Linear or branched alcohols, both saturated and unsaturated, can be used here, for example. In this way, it is possible to produce estolides with a lower viscosity. Another alternative is to use polyols with a neopentyl structure, which results in very good cold-temperature behaviour and both good oxidative and thermal stability.

Parameter	Modification	Primary effect
EN	Increase in molecular weight and molecule size	Viscosity Cold-temperature behaviour Oxidation stability Lubricating effect
Capping fatty acid	Chain length, Double bonds, Linearity	Cold-temperature behaviour Oxidation stability
Hydroxy-fatty acid	Double bonds, Chain length, Steric arrangement	Cold-temperature behaviour
Polyol	Steric arrangement, Molecular weight, Number of hydroxy groups	Viscosity Low-temperature behaviour Lubricating effect

Table 1: Modifications of the estolide ester and their effect

Table 1 shows the properties of the estolide with regard to various relevant parameters for the lubricants industry in direct comparison to a saturated and an unsaturated complex ester from the same viscosity class (ISO VG 320). It is clear that the complex esters achieve a good to very good performance while the strengths of the saturated and unsaturated variants lie in different areas.

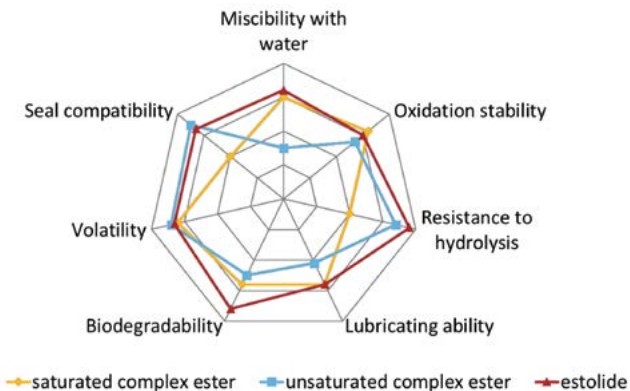


Figure 2: General comparison of estolides versus complex esters

The following explanations are intended to show that the estolides can go beyond the previous restrictions and, through the combination of the strengths of both complex esters, come close to an ideal type of ester.

### Oxidation stability

Lubricants based on esters can be impaired at high temperatures due to oxidation and/or thermal decomposition processes and are thereby severely limited in their lubricating properties and effects. Decomposition breaks the lubricant down into volatile low molecular mass components. The consequences are unwanted variations in viscosity, loss of oil and excessive vapour formation due to evaporation of these volatile components. This also results in a loss of lubricating effect. The lubricants also lose their lubricating effect due to polymerisation and the products that arise from this.

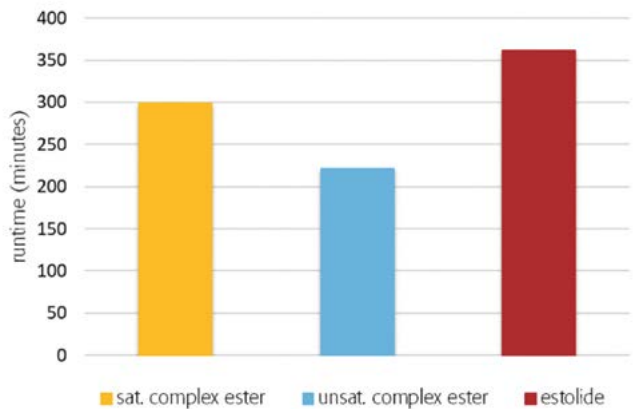


Figure 3: Results of oxidation stability according to ASTM 2272

Figure 3 shows the oxidation stability of the estolide compared to complex esters. In each case 1% of an additive package was used. As expected, the results show that the double bonds of the unsaturated complex ester favour radical oxidation. Hence the saturated complex ester performs far better than the unsaturated variant with regard to oxidation stability. Although the estolide molecule also contains double bonds, it exhibits better values not just in comparison to the unsaturated complex ester. In a

direct performance comparison with the saturated variant too, the estolide is convincing with a higher stability. Since the molecular structure of the estolide somewhat rules out stabilisation of the double bonds due to effects like mesomerism, the better values can be presumed to be due primarily to a steric effect.

The oxidation at the double bond proceeds initially via the formation of peroxy (ROO.) radicals (Stolz, et al., 2019). However, these are adjacent to the space-consuming estolide bond. The double bonds of an unsaturated capping acid might, in this case, have a negative impact (Cermak, et al., 2003).

## Resistance to hydrolysis

In recent years, esters have increasingly been used in lubricating preparations in which resistance to hydrolysis is deemed a crucial selection criterion. A good example of this is their use in the production of lubricating grease.

With the known ester compounds, the ester may be split into its fatty acid and alcohol components during in-situ saponification in the presence of water. The outcome of this is incomplete formation of the lubricating grease's structure and thus a significant reduction in the quality of the end product is noticeable. As illustrated in Figure 4, the alkaline saponification is irreversible.

For applications in the lubricants industry too, the presence of water can be troublesome and lead to hydrolysis of the Base Oils. Constituents such as acids and bases or metals such as copper, iron or nickel act catalytically and promote this unwanted effect.

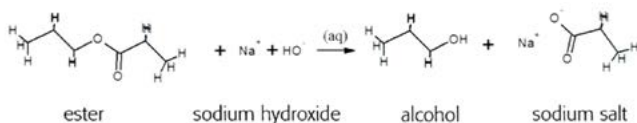


Figure 4: Saponification reaction

Figure 5 contrasts the resistance to hydrolysis of a saturated and an unsaturated complex ester and that

of an estolide. It is evident that the ester bond of a short-chain saturated complex ester is far more prone to hydrolysis than that of an unsaturated ester. But the estolide exhibits the best values here too with persuasively good resistance to hydrolysis.

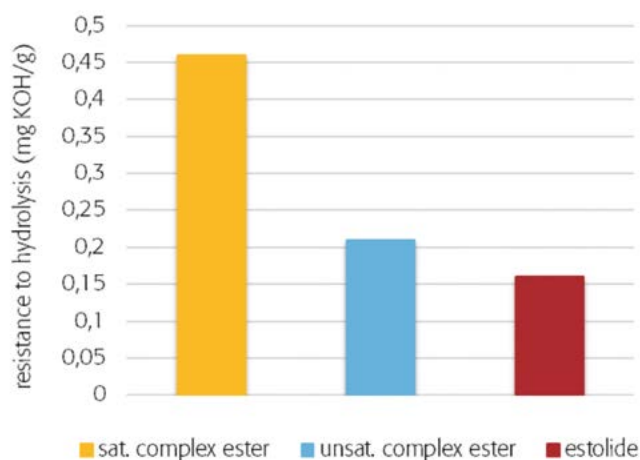


Figure 5: Results of resistance to hydrolysis according to ASTM D2619

The good resistance to hydrolysis of an unsaturated complex ester has already been reported previously (Stolz, et al., 2019). Unlike complex esters though, the molecular structure of the estolide has a significant number of secondary ester bonds that are far more resistant to hydrolysis due to direct branching on the ester group (Leslie R. Rudnick, 1999). This theory is also supported by other papers written on the subject (Cermak, et al., 2001).

## Wear properties

Additives are an indispensable part of the high performance lubricants that are required in the industry today. Only by adding these synthetic agents can the end product be given the desired properties tailored precisely to the specific purpose of use.

To minimise wear, extreme pressure (EP) additives are added to the lubricant and these release chemical compounds at the high temperatures that arise. The released substances react with the metal surface under the conditions that prevail to form layers which

are sheared off under the high pressure. Wear of the metal surfaces is delayed in this way. An unwanted side effect of the use of EP additives though can be an increase in long-term wear since metal is lost from the surface of materials due to the resulting metal bond. This negative side effect can be reduced by using a suitable Base Oil: The use of a Base Oil with its own very good wear properties can reduce the amount of EP additive needed without affecting the wear properties of the end product.

Figure 6 shows the characteristic wear values of an unsaturated complex ester, a saturated complex ester and an estolide measured according to DIN 51350-3.

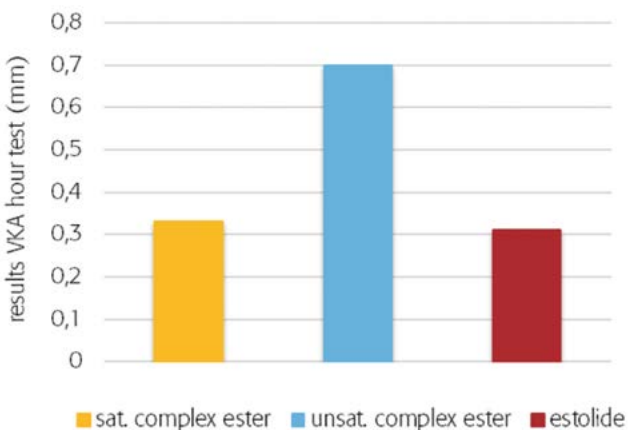


Figure 6: Results of the characteristic wear values according to DIN 51350-3

The saturated complex ester exhibits better values than the unsaturated one due to the shorter aliphatic chains of the fatty acids. The good resistance to oxidation of this ester is also of significance in the long test runs. The additional polarity of the double bond of the unsaturated variant cannot compensate for this.

The tested estolide exhibited slightly better values in this case as well. This result is consistent with research work on the wear properties of karanja oil and the estolides extracted from it (Vetticad, et al., 2016). The authors attribute the improved wear properties to the hydrodynamic boundary film at the contact surfaces.

## Evaporation loss

The evaporation loss of a lubricant is caused by highly volatile components but also by the thermal decomposition resulting in formation of short-chain components. The evaporation loss is measured using the Noack method at 250°C for a period of one hour under a constant flow of air. Engine oils for which the test was originally designed recorded a loss certainly in the double-digit percentage range.

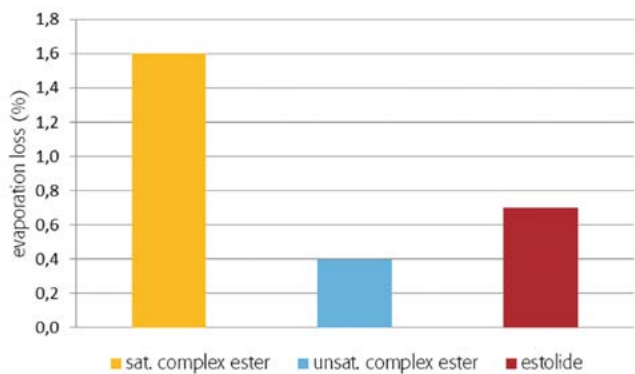


Figure 7: Results of evaporation loss according to the Noack method

As Figure 7 shows the ester compounds generally exhibit lower values. The unsaturated complex ester performs far better than the saturated one. This result is based, inter alia, on the far higher flash point of the unsaturated variants. This may be due to the higher polarity because of the double bonds but also the higher molecular mass may correspondingly affect the residual amount of free monocarboxylic acid. This might also be the reason why the estolide value comes out slightly higher than that of the unsaturated complex ester. Despite this, the values for the estolide still lie well below those measured for linear ethylhexyl estolides by Cermak et al. (Cermak, et al., 2007).

## Seal compatibility

Elastomers are used as seals in fluid technology systems. An elastomer refers to any substance that has the ability to return to its original size and shape following deformation. External influences though

can alter the behaviour of elastomers and therefore also have an effect on seals. These influences include pressure, temperature and exposure to solar radiation, for example, but also contact with the lubricant itself. Contact with the lubricant may result in lubricant constituents lodging in the seal or the dislodging of sealing material components (Vidović, 2014). Seals swell or shrink accordingly when this happens.

The results shown in figure 8 were obtained for acrylonitrile butadiene rubber (NBR1), which is regarded as moderately compatible with ester oils. The swelling behaviour of the ester is influenced by the polarity, the molecule size and steric effects but also by the accompanying substances.

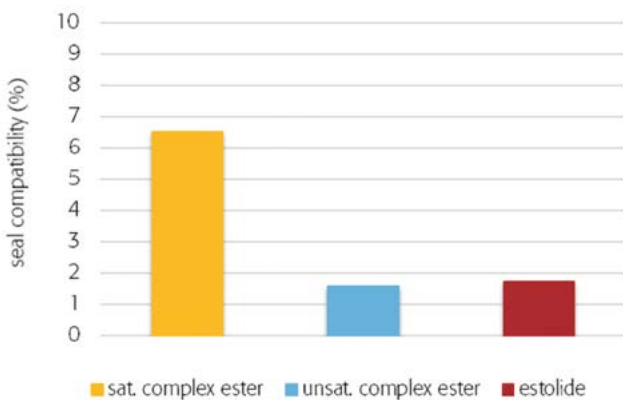


Figure 8: Results of seal compatibility according to DIN ISO 6072

Saturated short-chain esters only perform little beneficial here and for low ISO-VG classes often lie above the critical level of 10% swelling. The behaviour of the unsaturated esters is far better due to their long-chain monocarboxylic acids.

In a direct comparison the estolide is almost on a par with the unsaturated complex ester, even though it has a saturated component due to the capping fatty acid. However, this is situated in the immediate vicinity of the base fatty acid where the influence is able to develop less strongly.

## Biodegradability

Biodegradable lubricants are becoming even more important since the emission of substances into the environment cannot be completely avoided in a number of applications. This applies not only in the case of loss lubrication. For example, in agriculture, forestry or the building industry, significant amounts of lubricant can get into the environment due to leaks and other defects. The maritime ecosystems are particularly sensitive. This is why there are now a number of laws, regulations and bodies such as the Vessel General Permit (VGP), EU Ecolabel and Oslo and Paris Conventions (OSPAR) which prescribe the use of biodegradable lubricants.

An important role in biodegradability is played by the molecule size and polarity but also by the resistance to hydrolysis of products. Thus the biodegradability of the ester oils decreases with increasing ISO VG class. As can be gathered from Figure 9 the biodegradability of the unsaturated complex ester is slightly lower than that of the saturated variant due to the improved resistance to hydrolysis. All the more astonishing is the estolide's very good biodegradability with similarly good resistance to hydrolysis and a high ISO VG class. This can be partly explained by the emulsion properties of the estolide. Besides the aforementioned factors, an important role is undoubtedly played by other effects such as transportability across biological membranes.

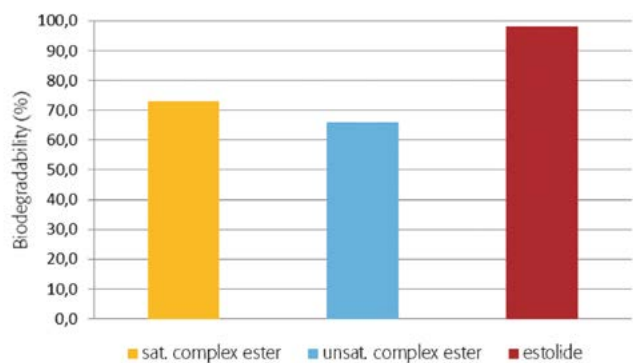


Figure 9: Results of biodegradability (28 days)



## Demulsibility

The demulsibility of an oil describes its ability to separate from water after having formed an emulsion with it. In some applications such as hydraulic oils, good demulsibility is one of the requirements that the base oil must fulfil. For applications such as cooling lubricants or marine- sector lubricants, a moderate to slight demulsibility is required.

The demulsifying properties of a base oil depend primarily on the polar and apolar groups that are present as well as on their division. Steric effects such as the shielding by space-consuming groups play a role too. Moreover, with the estolides the capping fatty acids used and the alcohol have a strong influence.

The results in Figure 10 reflect the fraction of the water-, oil- and emulsion phase in ml after thoroughly mixing 40 ml each of base oil and water. Similar to the saturated complex ester, the estolide still distinctly separates out water but forms hardly any free oil.

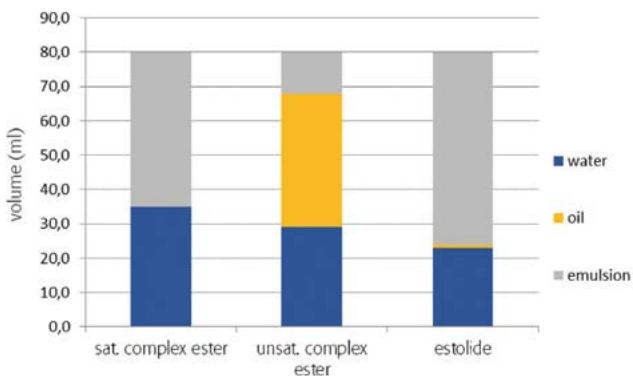


Figure 10: Results of demulsibility

## Summary

The performance data show the outstanding results of the estolide, which unites the advantages of both the saturated and unsaturated complex esters in one product. Thus, estolides are able to effortlessly fulfil the diverse demands on base oils for lubricants and are particularly suitable for high performance applications. By virtue of their adaptable molecule they not only cover a broad spectrum of viscosity but

can also be varied widely in their product properties. The high stability, low friction coefficient and high resistance to wear make estolides the obvious choice for use in lubricating grease applications where resistance to hydrolysis and oxidation are indispensable.

Despite the already outstanding properties of the estolide, the focus of future work will be to improve parameters such as the demulsibility without affecting the otherwise very positive properties a lot. The molecular structure of the estolide offers sufficient scope to achieve this.

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