

The iodine value as a measure of the stability of ester base oils

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Introduction

The use of synthetic esters as base liquids is due to the fact that these fluids are liquid even at low temperatures. For some applications pour points of less than -60°C are specified, requirements of values below -40°C are quite common. These properties can only be achieved through the use of:

- saturated short-chain fatty acids (chain length $\leq \text{C}10$)
- branched chain fatty acids
- unsaturated fatty acids.

In this case, the use of unsaturated fatty acids, however, is often rejected from the outset by general requirements, such as, for example, an iodine value below 5 mgJ2/100 g . The background behind this requirement is in many cases the assumption that only esters with a low iodine value offer sufficient stability. This statement is a wide generalisation and, in addition, completely neglects the fact that stability implies very different behaviour of the base oils. Thus, it is necessary to differentiate between

- thermal stability
- oxidation stability
- hydrolytic stability.

Even if the different forms of stability are naturally partly dependent on each other, there are clear differences. As an example, it can be mentioned at this point, that an ester with outstanding hydrolytic stability does not necessarily have a very good oxidation stability.

In addition, this raises difficulties of assessing the different measurement procedures in terms of their significance for the above-mentioned properties. The object of this article is to differentiate between these aspects of the stability of synthetic esters and to produce a reference to the measurement methods. Of course, there are other considerations on the stability of esters, such as the work or shear stability. This, however, is outside the scope of this article.

Stability of synthetic esters

Thermal stability

Most applications of lubricants are in a higher temperature range and this presupposes that the base oils used are stable under the given conditions. In general ester compounds show good thermal stability, comparable with that of mineral oil or in some cases even better. The ester bond itself is significantly more stable than a C-C bond.

Nevertheless, at temperatures above 300°C a pyrolysis of the ester takes place, through which decomposition is triggered by a decline in an olefin and a carboxylic acid. Ester compounds with a β-hydrogen atom in the polyol are significantly more vulnerable and respond as shown in the equation in Figure 1.

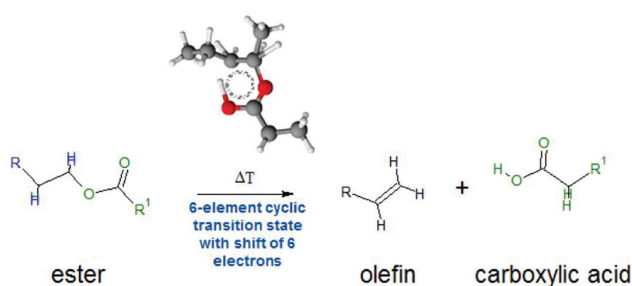


Figure 1. The thermal decomposition reaction process.

The reaction proceeds over a six-element cyclic transition state. The reaction starts with the decomposition of the β-hydrogen atom by the carbonyl oxygen atom. This breaks the oxygen-carbon bond of the alkoxy group. In this conversion, three pairs of electrons are displaced, similar to the Diels-Alder reaction. According to Bredt's rule there are no double bonds formed to bridge head atoms. If the formation of a conjugated system is possible by the elimination then this is preferable. Otherwise, the Hofmann rule is respected (elimination in the direction of the least substituted carbon atom). This reaction occurs, for example, in the case of natural triglycerides, such as sunflower oil.

If the β-hydrogen atom is replaced by alkyl groups, as is the case in the polyol esters, the pyrolysis occurs due to free radicals. A corresponding representation is shown in Figure 2. This type of reaction requires a higher energy supply and only takes places at higher temperatures. Esters based on pentaerythritol have the highest stability, followed by trimethylolpropane and neopentane glycol. Through the formation of free radicals this reaction can be easily prevented with antioxidants.

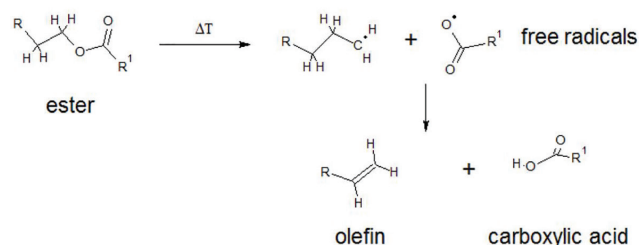


Figure 2. Thermal ester decomposition of free radicals.

Oxidation stability

The properties of the hydrocarbon chain play a decisive role when considering the oxidation stability of esters. This applies to the arrangement of the various CH-groups, but also the number and distribution of unsaturated bonds.

The influence of unsaturated fatty acids was examined in detail in the autoxidation of lipids in the food sector. The mechanisms shown in Figure 3 were postulated for the progress of this reaction. The alkyl radicals necessary to start the chain can be produced by temperature effects, shear forces, UV-radiation and other influences. The radical intermediate stages formed, especially the peroxy-radical (ROO.), have good stability and can only abstract particularly activated H-atoms of the ally groups (Belitz, et al, 2013).

Type of grease	Dissociation-energy (kJ/mol)	Relative reaction-speed
Stearic acid	414	1
Oleic acid	334	100
Linoleic acid	289	1200
Linolenic acid	167	2500

Table 1. Oxidation of fatty acids depending on the iodine value (Frankel, 1998).

This step is slow and is, therefore, the speed limiting step in the chain reaction. Thus, the reaction rate increases with the number of double bonds in a fatty acid molecule at an exponential rate (see Table 1). A special position, however, is occupied by linolenic acid, since here the particularly reactive 1.4 Penta-DienSystem is transferred to a stable conjugated DienSystem.

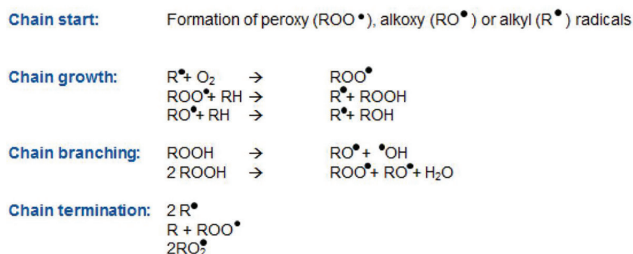


Figure 3. Radical oxidation.

The order of -CH₃ > CH₂ > CH applies for the stability of the individual chain links of saturated fatty acids (Leslie R. Rudnick, 1999). The -CH₃ group is 15 times more stable than a -CH₂ group. Consequently short-chain fatty acids have better stability. Branched-chain fatty acids should also show worse stability, which is, however, often hidden by steric effects. Of interest, however, is how the individual secondary carbon atoms of the aliphatic chain differ. This has been considered by P. Sniegowski in detail in the model of the neopentyl-hexanoates (see Figure 4) (Sniegowski, 1977).

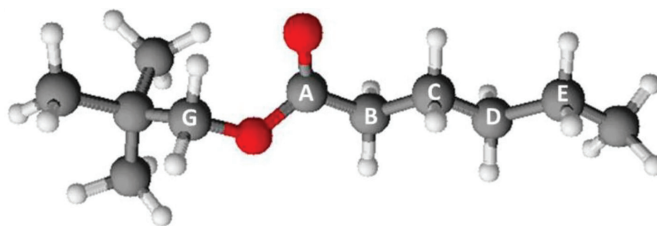


Figure 4. Methylene groups of the neopentyl-hexanoats.

Whether the α-C atom of the alcohol group had a different reactivity was also investigated. Some authors suggest a 4.5 fold higher affinity to the formation of the RO₂-radical (V.N.Bakunin, 1992). Sniegowski could now show that the methyl group has a significantly higher stability than the methylene group. At the same time, the secondary carbon group shows a much lower tendency to the formation of radicals in the α-position. This applies both to the acyl and alcohol component. The author thinks that the electron affinity of the carbonyl oxygen is responsible for this.

Hydrolytic stability

Unlike mineral oils, esters have a polar group, the ester group. This causes a variety of positive properties, such as, for example, the affinity to metal surfaces, high viscosity indices and, last but not least, good biodegradability. At the same time, however, this functional group is susceptible to hydrolysis under certain process conditions.

The hydrolysis of the ester is running rather slowly. Lubricant esters, which have a content of a few hundred ppm water are stable under normal storage conditions, but they do not have an increase in the acid number. This only occurs under the influence of catalysts. In general, a distinction is made between an acid and a basic catalysed ester hydrolysis. Also, metals act catalytically on the hydrolysis. The reaction speed of the hydrolysis, as seems likely, is affected by the temperature.

There are 8 different mechanisms for the ester hydrolysis (Smith, et al, 2007). These are divided into acidic and alkaline catalysis, the attack on the alkyl or acyl carbon and a mono- or bimolecular mechanism. The base catalysed ester decomposition progresses as shown in the reaction diagram in Figure 5. Unlike during acid catalysis no free acid is formed but the corresponding salt, which causes a not reversible reaction. The catalytic converter, the basic connection, enters the reaction as a stoichiometric component and is consumed. This process plays a role primarily in greases.

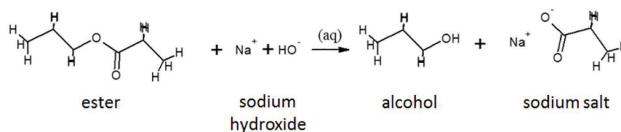


Figure 5. Saponification reaction.

Of greater significance is the acid-catalysed ester decomposition according to the AAC2-mechanism (A = acid, AC = acyl decomposition 2 = bimolecular mechanism).

This is characterised by acyl decomposition and a tetrahedral intermediate state. Two molecules of water are required in the intermediate step, one molecule that acts as a proton donor and one as a nucleophile.

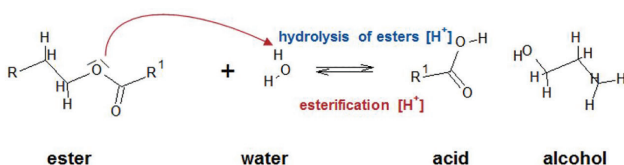


Figure 6. Acid ester decomposition.

The net reaction is shown in Figure 6. The reaction rate depends on the concentration of the reactants, ester and water, as well as on the catalytic converter. The temperature relationship follows the Arrhenius equation. Water is only soluble in esters to a limited extent, which restricts the ester decomposition. However, the acid formed works autocatalytically.

In practice, the hydrolysis of the ester is less problematic than the theoretical considerations suggest. By means of appropriate measures, the hydrolytic stability can be further improved.

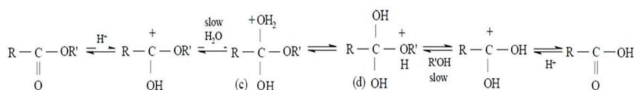


Figure 7. The reaction process of the acid ester decomposition.

Thus, a low acid number as well as the freedom of catalyst residues from the esterification and the hydrolysis work in opposite directions.

A conjugated π -electron system has a positive effect on the hydrolysis stability as it does in aromatic esters, for example, benzoic acid. Through this the C=O bond resonance is stabilised and reacts at a much slower pace for the tetrahedral transition state (Euranto, 1969). Steric effects also lead to a significant stabilisation of the ester bond, since the bond angles of the esters can be compressed from 120° to 109° in the tetrahedral

transition state. If there are large-scale structures in the vicinity of the ester group, the formation of this transition state becomes more difficult. This is the case, for example, with iso acids. This measure is all the more effective, the closer the branching is to the ester bond. However, a branched alcohol is therefore less effective (Leslie R. Rudnick, 1999).

Test methods

RPVOT (ASTM D-2272)

The RPVOT (Rotating Pressure Vessel Oxidation Test) was designed for the fast determination of the resistance to oxidation and ageing of lubricants. About 50 g of test substance and 5 g of distilled water are weighed in a reaction vessel. A previously polished copper or iron coil in the oil-water mixture is used as a catalyst. The reaction vessel is screwed tightly into a pressure-tight stainless steel container and connected to a pressure gauge. It is now filled with pure oxygen up to a pressure of 620 kPa. The apparatus is then rotated (60 to 100 rpm) and heated to 150°C in an oil bath. There is initially a pressure rise due to the extension of the media. Over a given time the oxygen reacts with the test medium and the result is a pressure drop proportional to the amount of oxygen consumed. The time it takes the pressure to fall by 175 kPa under the maximum is measured. Oxidation-resistant lubricants, therefore, exhibit a longer time interval. The reproducibility is around 22%.

Beverage Bottle Test (ASTM D-2619 /DIN 51348)

The hydrolytic stability of lubricants can be measured with the beverage bottle test. For this purpose, 75ml of the ester oil and 25ml of distilled water are put into a pressure-resistant bottle together with a copper strip as a catalyst. The bottles were clamped in a holder, placed in an oven at 93°C and rotated at 5 rpm around their longitudinal axis. After 48 hours, the increase in the acid number of the organic phase, the acid number of the aqueous phase, as well as the weight and the condition of the copper plate (as specified in ASTM D130) is evaluated.

DSC

One of the most efficient methods for investigating the thermal stability of esters is the Differential Scanning Calorimetry (in short: DSC). The principle of the method provides a heat flow differential measurement between the sample and an inert reference. Both samples are placed in a furnace which has a selectable heating rate and brought to specified temperature. If an endothermic or exothermic reaction takes place in the sample, this reduces or increases the heat flow between the furnace and the sample. This leads to a temperature difference to the comparison sample. A HP-DSC, which worked isobarically with 100 bar nitrogen, was used for investigations as part of this work. In this way oxidation, but also faults due to evaporation of low molecular components, are avoided.

If there is thermal decomposition of ester oils there are endothermic reactions. The evaluation of the onset and the peaks of the response curve allow statements about the thermal stability.

Test results

Various model substances were tested in order to investigate the stability of saturated and unsaturated esters. Various polyols were used, as well as substances networked with dimeric acid. From the trimethylol propane a triester of a commercial oleic fatty acid and a triester of caprylic-caproic acid (50:50) were used. Because there are significant differences in viscosity in both variants, a partly networked ester was manufactured with adipic acid and C8-C10. This, as well as the trimethylol propane trioleate, has a viscosity of 46 m² s⁻¹.

Oxidation stability

Figure 8 below shows the results of the RPVOT test graphically. If one looks at the results of the ISO VG 46 esters, the saturated esters, as was to be expected, have a significantly better oxidation stability. The reason for this is that the unsaturated fatty acids promote the bonding of ROO. radicals.

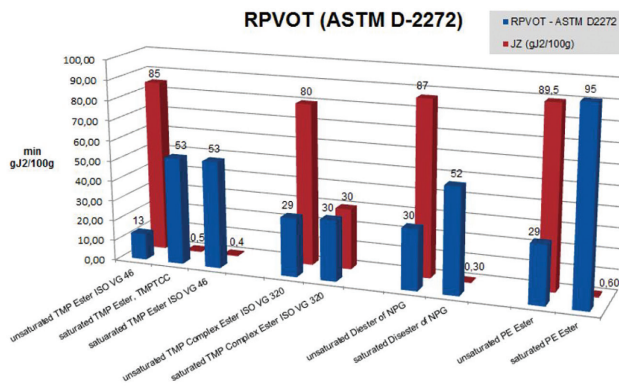


Figure 8. Results of the RPVOT measurements.

On the other hand, the effect is significantly lower in the complex esters of the ISO VG 320. The unsaturated complex esters reach values, which also lie in the area of saturated esters. This difference can be attributed to the steric hindrance, as well as to the low iodine value contribution of the mono-carboxylic acids.

The pure base liquids - mineral oils, polyalphaolefins (PAO) and polyalkylene glycols (PAG) included - generally have values, which are considerably lower than the requirements of the formulated lubricants. In the RPVOT, for example, usually over 200 hours are required for ester based hydraulic oils and for turbine oils more than 600 hours. The additives are crucial, since there is no base oil as such that fulfils these conditions. If unsaturated fatty acids are used special attention must be given to the additive package.

Hydrolytic stability

The results of the beverage bottle test are shown in Figure 9. These show that the unsaturated esters - contrary to popular opinion - generally prove to be hydrolytically more stable. The reason for this is primarily the steric hindrance due to the larger scale structure of the oleic acid. This reasoning is supported by the fact that the penta esters within the polyol test series had the highest stability.

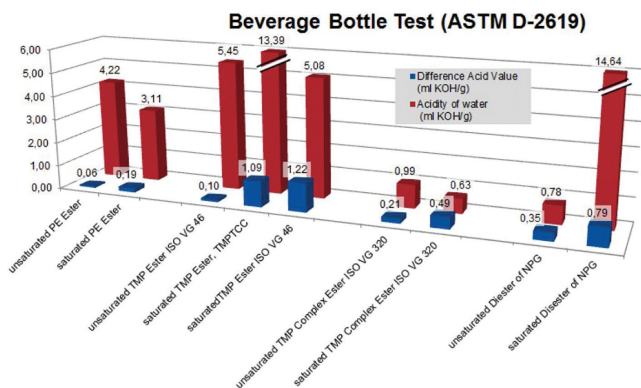


Figure 9. Results of the beverage bottle tests.

As expected, the results of the series of tests show that the hydrolytic stability of pentaerythritol is greater than that of trimethylol propane, which, in turn, is greater than that of neopentyl glycol.

According to the test results very hydrolytic stable products can also be produced with complex esters which screen the ester bond even more effectively. Furthermore, the partially aromatic structures of the dicarboxylic acids used have structures that lead to an additional resonance stabilisation. This property plays an important role especially in the production of lubricating greases.

Thermal stability

Figure 10 shows the results of the high-pressure DSC measurement. The graphs, on which Figure 10 is based, have a significant exothermic peak at approx. 180°C up to 200°C in the range greater than -30 J/g. An explanation for this reaction could not be found. Since this occurs in both, saturated and unsaturated variants, participation of the double bond can be excluded. The energy tint of the peak is too high for a secondary reaction with any existing free fatty acid. In a standard DSC under normal pressure, this behaviour does not occur.

A clear reaction peak can be seen for all esters at approx. 440°C which could not be completely

recorded due to the maximum measuring temperature. Therefore the “onset” was evaluated. As can be seen in the Figure 10, this will enter into force for all investigated products at approximately the same temperature, regardless of the presence of unsaturated groups or the molecular weight. It is, therefore, concluded that there is a pyrolysis with subsequent evaporation.

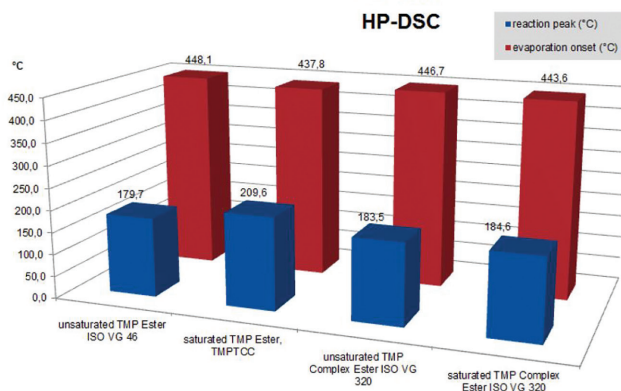


Figure 10. Results of the HP DSC under N2 [100 bar].

Summary

The suitability of an ester as the base fluid is decided by a wide range of properties, mainly those listed in Figure 11. The selection of raw materials or the modification of the manufacturing process, can have a big impact on these properties. However, it is not possible to improve all the criteria at the same time. In the case of the iodine value of the fatty acids considered here, the reduction leads to improved thermal and oxidative stability. At the same time, however, the esters have a significantly worse cold behaviour, as well as a poorer hydrolytic stability. The esters must be carefully matched to the respective application. General statements, such as saturated esters are more stable, are not, in general, correct.

Performance comparison of saturated and unsaturated esters

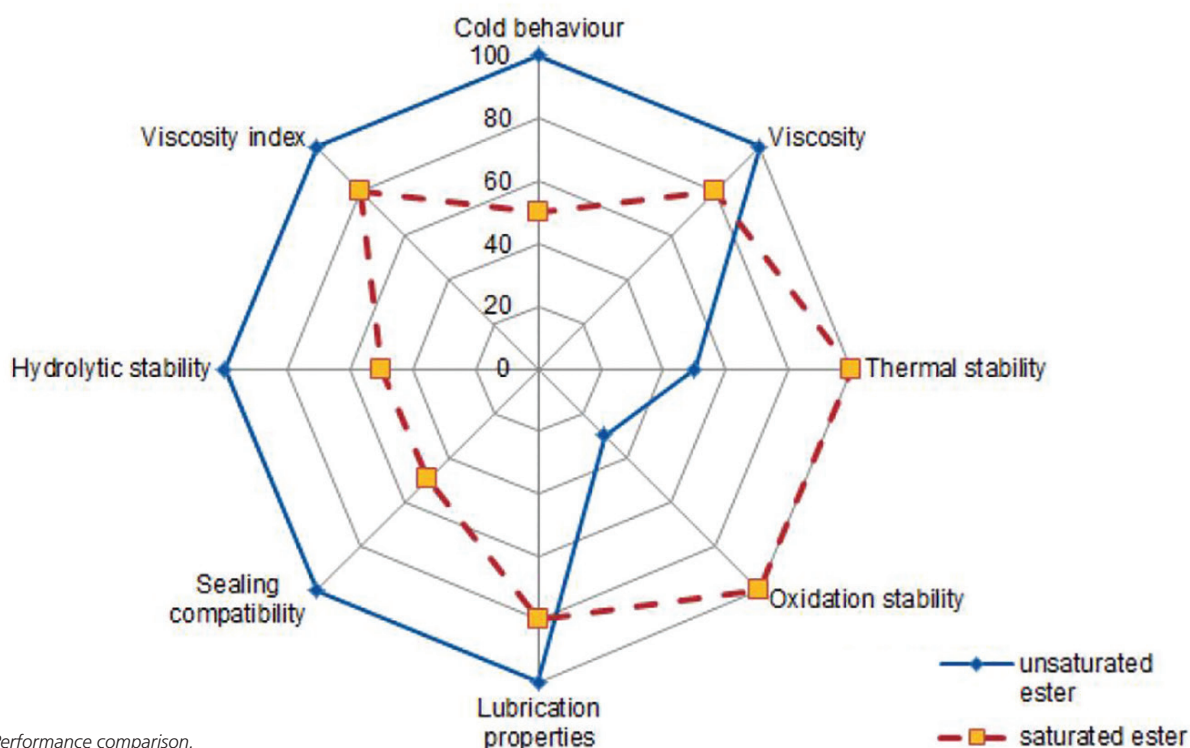


Figure 11. Performance comparison.

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