

## **ESTERS IN SYNTHETIC LUBRICANTS**

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In the simplest terms, esters can be defined as the reaction products of acids and alcohols. Thousands of different kinds of esters are commercially produced for a broad range of applications. Within the realm of synthetic lubrication, a relatively small but still substantial family of esters have been found to be very useful in severe environment applications. This paper shall provide a general overview of the more common esters used in synthetic lubricants and discuss their important benefits and utilities.

Esters have been used successfully in lubrication for more than 60 years and are the preferred stock in many severe applications where their benefits solve problems or bring value. For example, esters have been used exclusively in jet engine lubricants worldwide for over 50 years due to their unique combination of low temperature flowability with clean high temperature operation. Esters are also the preferred stock in the new synthetic refrigeration lubricants used with CFC replacement refrigerants. Here the combination of branching and polarity make the esters miscible with the HFC refrigerants and improves both low and high temperature performance characteristics. In automotive applications, the first qualified synthetic crankcase motor oils were based entirely on ester formulations and these products were quite successful when properly formulated. Esters have given way to PAOs in this application due to PAOs lower cost and their formulating similarities to mineral oil. Nevertheless, esters are often used in combination with PAOs in full synthetic motor oils in order to balance the effect on seals, solubilize additives, reduce volatility, and improve energy efficiency through higher lubricity. The percentage of ester used can vary anywhere from 5 to 25% depending upon the desired properties and the type of ester employed.

The new frontier for esters is the industrial marketplace where the number of products, applications, and operating conditions is enormous. In many cases, the very same equipment which operates satisfactorily on mineral oil in one plant could benefit greatly from the use of an ester lubricant in another plant where the equipment is operated under more severe conditions. This is a marketplace where old problems or new challenges can arise at any time or any location. The high performance properties and custom design versatility of esters is ideally suited to solve these problems. Ester lubricants have already captured certain niches in the industrial market such as reciprocating air compressors and high temperature industrial oven chain lubricants. When one focuses on temperature extremes and their telltale signs such as smoking and deposits, the potential applications for the problem solving ester lubricants are virtually endless.

**Ester Chemistry**

In many ways esters are very similar to the more commonly known and used synthetic hydrocarbons or PAOs. Like PAOs, esters are synthesized from relatively pure and simple starting materials to produce predetermined molecular structures designed specifically for high performance lubrication. Both types of synthetic basestocks are primarily branched hydrocarbons which are thermally stable, have high viscosity indices, and lack the undesirable and unstable impurities found in conventional petroleum based oils. The primary structural difference between esters and PAOs is the presence of oxygen in the hydrocarbon molecules in the form of multiple ester linkages (COOR) which impart polarity to the molecules. This polarity affects the way esters behave as lubricants in the following ways:

1) **Volatility:** The polarity of the ester molecules causes them to be attracted to one another and this intermolecular attraction requires more energy (heat) for the esters to transfer from a liquid to a gaseous state. Therefore, at a given molecular weight or viscosity, the esters will exhibit a lower vapor pressure which translates into a higher flash point and a lower rate of evaporation for the lubricant. Generally speaking, the more ester linkages in a specific ester, the higher its flash point and the lower its volatility.

2) **Lubricity:** Polarity also causes the ester molecules to be attracted to positively charged metal surfaces. As a result, the molecules tend to line up on the metal surface creating a film which requires additional energy (load) to wipe them off. The result is a stronger film which translates into higher lubricity and lower energy consumption in lubricant applications.

3) **Detergency/Dispersency:** The polar nature of esters also makes them good solvents and dispersants. This allows the esters to solubilize or disperse oil degradation by-products which might otherwise be deposited as varnish or sludge, and translates into cleaner operation and improved additive solubility in the final lubricant.

4) **Biodegradability:** While stable against oxidative and thermal breakdown, the ester linkage provides a vulnerable site for microbes to begin their work of biodegrading the ester molecule. This translates into very high biodegradability rates for ester lubricants and allows more environmentally friendly products to be formulated.

Another important difference between esters and PAOs is the incredible versatility in the design of ester molecules due to the high number of commercially available acids and alcohols from which to choose. For example, if one is seeking a 6 cSt synthetic basestock, the choices available with PAOs are a straight cut 6 cSt or a “dumbbell” blend of a lighter and heavier PAO. In either case, the properties of the resulting basestock are essentially the same. With esters, literally dozens of 6 cSt products can be designed each with a different chemical structure selected for the specific desired property. This allows the “ester engineer” to custom design the structure of the ester molecules to an optimized set of properties determined by the end customer or application. The performance properties

that can be varied in ester design include viscosity, viscosity index, volatility, high temperature coking tendencies, biodegradability, lubricity, hydrolytic stability, additive solubility, and seal compatibility.

As with any product, there are also downsides to esters. The most common concern when formulating with ester basestocks is compatibility with the elastomer material used in the seals. All esters will tend to swell and soften most elastomer seals however, the degree to which they do so can be controlled through proper selection. When seal swell is desirable, such as in balancing the seal shrinkage and hardening characteristics of PAOs, more polar esters should be used such as those with lower molecular weight and/or higher number of ester linkages. When used as the exclusive basestock, the ester should be designed for compatibility with seals or the seals should be changed to those types which are more compatible with esters.

Another potential disadvantage with esters is their ability to react with water or hydrolyze under certain conditions. Generally this hydrolysis reaction requires the presence of water and heat with a relatively strong acid or base to catalyze the reaction. Since esters are usually used in very high temperature applications, high amounts of water are usually not present and hydrolysis is rarely a problem in actual use. Where the application environment may lead to hydrolysis, the ester structure can be altered to greatly improve its hydrolytic stability and additives can be selected to minimize any effects.

The following is a discussion of the structures and features of the more common ester families used in synthetic lubrication.

### **Diesters**

Diesters were the original ester structures introduced to synthetic lubricants during the second World War. These products are made by reacting monohydric alcohols with dibasic acids creating a molecule which may be linear, branched, or aromatic and with two ester groups. Diesters which are often abbreviated DBE (dibasic acid esters) are named after the type of dibasic acid used and are often abbreviated with letters. For example, a diester made by reacting isodecyl alcohol with adipic acid would be known as an "adipate" type diester and would be abbreviated "DIDA" (Diisodecyl Adipate).

Listed below are the more common families of diesters used in synthetic lubricants, and the alcohols most commonly employed.

Adipates are the most widely used diesters due to their low relative cost and good balance of properties. They generally range from about 2.3 to 5.3 cSt at 100°C and exhibit pour points below -60°C. The viscosity indices of adipates usually run from about 130 to 150 and their oxidative stability, like most of the diesters, are comparable to PAOs. The primary difference between adipate diesters and PAOs is the presence of two ester

linkages and the associated polarity benefits outlined previously. The most common use of adipate diesters is in combination with PAOs in numerous applications such as screw compressor oils, gear and transmission oils, automotive crankcase oils, and hydraulic fluids. Adipates are also used as the sole basestock where biodegradability is desired or high temperature cleanliness is critical such as in textile lubricants and oven chain oils.

Azelates, Sebacates, and Dodecanedioates are similar to adipates except that in each case the carbon chain length (backbone) of the dibasic acid is longer. This “backbone stretching” significantly increases viscosity index and improves the lubricity characteristics of the ester while retaining all the desirable properties of the adipates. The only downside to these types of diesters is price which tends to run about 50 – 100+% higher than adipates at the wholesale level. This group of linear DBEs are mainly used in older military specifications and where the lubricity factor becomes an important parameter.

Phthalates are aromatic diesters and this ring structure greatly reduces the viscosity index (usually well below 100) and eliminates most of the biodegradability benefit. In all other respects, phthalates behave similar to other diesters and are about 20 – 30% lower in cost. Phthalates are used extensively in air compressor lubricants (especially the reciprocating type) where low viscosity index is the norm and low cost clean operation is desirable.

Dimerates are made by combining two oleic acids which creates a large branched dibasic acid from which interesting diesters are made. Dimerates exhibit high viscosity and high viscosity indices while retaining excellent low temperature flow. Compared to adipates, dimerates are higher in price (30 – 40%), have marginal biodegradability, and are not as clean in high temperature operations. Their lubricity is good and they are often used in synthetic gear oils and 2-cycle oils.

The alcohols used to make diesters will also affect the properties of the finished esters and thus are important factors in the design process. For example, three of the common alcohols used to make diesters each contain eight carbons, and when reacted with adipic acid, all create a dioctyl adipate. However, the properties are entirely different. The n-octyl adipate would have the highest viscosity and the highest viscosity index (about 50% higher than the 2-ethylhexyl adipate) but would exhibit a relatively high freeze point making their use in low temperature applications virtually impossible. By branching the octyl alcohol, the other two DOAs exhibit no freeze point tendencies and have pour points well below -60°C. The iso-octyl adipate offers the best balance of properties combining a high viscosity index with a wide temperature range. The 2-ethylhexyl adipate has a VI about 45 units lower and a somewhat higher volatility. These examples demonstrate the importance of combining the right alcohols with the right acids when designing diester structures and allows the ester engineer a great deal of flexibility in his work. In addition, the alcohols may be reacted alone or blended with other alcohols to form coesters with their own unique properties.

## Polyol Esters

The term “polyol esters” is short for neopentyl polyol esters which are made by reacting monobasic acids with polyhedric alcohols having a neopentyl structure. The unique feature of the structure of polyol ester molecules is the fact that there are no hydrogens on the beta-carbon. Since this “beta-hydrogen” is the first site of thermal attack on diesters, eliminating this site substantially elevates the thermal stability of polyol esters and allows them to be used at much higher temperatures. In addition, polyol esters usually have more ester groups than the diesters and this added polarity further reduces volatility and enhances the lubricity characteristics while retaining all the other desirable properties inherent with diesters. This makes polyol esters ideally suited for the higher temperature applications where the performance of diesters and PAOs begin to fade.

Like diesters, many different acids and alcohols are available for manufacturing polyol esters and indeed an even greater number of permutations are possible due to the multiple ester linkages. Unlike diesters, polyol esters (POEs) are named after the alcohol instead of the acid and the acids are often represented by their carbon chain length. For example, a polyol ester made by reacting a mixture of nC8 and nC10 fatty acids with trimethylolpropane alcohol would be referred to as a “TMP” ester and represented as TMP C8C10. The following is a list of the more common types of polyol esters:

Neopentyl Glycols (NPGs) – 2 Hydroxyls

Trimethylolpropanes (TMPs) – 3 Hydroxyls

Pentaerythritols (PEs) – 4 Hydroxyls

DiPentaerythritols (DiPEs) – 6 Hydroxyls

Each of the alcohols shown above have no beta-hydrogens and differ primarily in the number of hydroxyl groups they contain for reaction with the fatty acids. The difference in ester properties as they relate to the alcohols are primarily those related to molecular weight such as viscosity, pour point, flash point, and volatility. The versatility in designing these fluids is primarily related to the selection and mix of the acids esterified onto the alcohols.

The normal or linear acids all contribute similar performance properties with the physicals being influenced by their carbon chain length or molecular weight. For example, lighter acids such as C5 may be desirable for reducing low temperature viscosity on the higher alcohols, or the same purpose can be achieved by esterifying longer acids (C10) onto the shorter alcohols. While the properties of the normal acids are mainly related to the chain length, there are some more subtle differences among them which can allow the formulator to vary such properties as thermal stability and lubricity.

Branched acids add a new dimension since the length, location, and number of branches all impact the performance of the final ester. For example, a branch incorporated near the

acid group may help to hinder hydrolysis while multiple branches may be useful for building viscosity, improving low temperature flow, and enhancing thermal stability and cleanliness. The versatility of this family is best understood when one considers that multiple acids are usually co-esterified with the polyol alcohol allowing the ester engineer to control multiple properties in a single ester. Indeed single acids are rarely used in polyol esters because of the enhanced properties that can be obtained through co-esterification.

Polyol esters can extend the high temperature operating range of a lubricant by as much as 50 – 100°C due to their superior stability and low volatility. They are also renowned for their film strength and increased lubricity which is useful in reducing energy consumption in many applications. The only downside of polyol esters compared to diesters is their higher price tag, generally 20 – 70+% higher on a wholesale basis.

The major application for polyol esters is jet engine lubricants where they have been used exclusively for more than 40 years. In this application, the oil is expected to flow at –65°C, pump readily at –40°C, and withstand sump temperature over 200°C with drain intervals measured in years. Only polyol esters have been found to satisfy this demanding application and incorporating even small amounts of diesters or PAOs will cause the lubricant to fail vital specifications. Polyol esters are also the ester of choice for blending with PAOs in passenger car motor oils. This change from lower cost diesters to polyols was driven primarily by the need for reduced fuel consumption and lower volatility in modern specifications. They are sometimes used in 2-cycle oils as well for the same reasons. In industrial markets polyol esters are used extensively in synthetic refrigeration lubricants due to their miscibility with non-chlorine refrigerants. They are also widely used in very high temperature operations such as industrial oven chains, tenter frames, stationary turbine engines, high temperature grease, fire resistant transformer coolants, fire resistant hydraulic fluids, and textile lubricants.

In general, polyol esters represent the highest performance level available for high temperature applications at a reasonable price. Although they cost more than many other types of synthetics, the benefits often combine to make this chemistry the most cost effective in severe environment applications. The primary benefits include extended life, higher temperature operation, reduced maintenance and downtime, lower energy consumption, reduced smoke and disposal, and biodegradability.

### **Other esters**

While diesters and polyol esters represent the most widely used ester families in synthetic lubrication, two other families are worth mentioning. These are monoesters and trimellitates.

Monoesters are made by reacting monohydric alcohols with monobasic fatty acids creating

a molecule with a single ester linkage and linear or branched alkyl groups. These products are generally very low in viscosity (usually under 2 cSt at 100°C) and exhibit extremely low pour points and high VIs. The presence of the ester linkage imparts polarity which helps to offset the high volatility expected with such small molecules. Hence, when compared to a hydrocarbon of equal molecular weight, a monoester will have a significantly higher flash point giving it a broader temperature range in use. Monoesters are used primarily for extremely cold applications such as in Arctic hydraulic oils and deep sea drilling. They can also be used in formulating automotive aftermarket additives to improve cold starting.

Trimellitates are aromatic triesters which are similar to the phthalates described under diesters but with a third ester linkage. By taking on three alcohols, the trimellitates are significantly more viscous than the linear adipates or phthalates. Viscosities range from about 9 to 20 cSt at 100°C. Like phthalates, trimellitates have a low viscosity index and poor biodegradability with a price range between adipates and polyols. Trimellitates are generally used where high viscosity is needed as in gear lubricants, chain lubricants, and grease.

### **Summary**

Esters are a broad and diverse family of synthetic lubricant basestocks which can be custom designed to meet specific physical and performance properties. The inherent polarity of esters improves their performance in lubrication by reducing volatility, increasing lubricity, providing cleaner operation, and making the products biodegradable. A wide range of available raw materials allow an ester designer the ability to optimize a product over a wide range of variables in order to maximize the performance and value to the client. They may be used alone in very high temperature applications for optimum performance or blended with PAOs or other synthetic basestocks where their complementary properties improve the balance of the finished lubricant. Esters have been used in synthetic lubricants for more than 60 years and continue to grow as the drive for efficiency make operating environments more severe. Because of the complexity involved in the designing, selecting, and blending of an ester basestock, the choice of the optimum ester should be left to a qualified ester engineer who can better balance the desired properties.