3 Esters

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3.1 INTRODUCTION AND HISTORICAL DEVELOPMENT

The ester functional group provides a versatile means of assembling complex organic structures from simple acid and alcohol building blocks. Ester products are ubiquitous in both synthetic and natural product chemistry. This chapter focuses on synthetic organic ester basefluids, that is, viscous, water-immiscible liquids, containing only C, H, and O, manufactured by esterification processes, and used as major components of formulations intended to reduce friction and wear in machinery.

Other chapters in this book cover inorganic esters containing phosphorus (Neutral Phosphate Esters), carbonate esters (Diakyl Carbonates), naturally occurring esters produced by physical processing of plant or animal tissues (Natural Oils as Lubricants), and materials manufactured by addition polymerization of olefinic ester monomers (Polymer Esters) or unsaturated acids (Estolides). The use of amphiphilic esters (polyalkylene glycol esters and partial esters) at lower concentrations as surfactants in aqueous emulsion formulations is also covered (Metalworking Fluids) and their use as lubricity additives in nonaqueous formulations is reviewed elsewhere [1].

The use of esters as lubricants is as old as human technology because natural fats and oils, which are predominantly triesters of glycerol with linear fatty acids, have been used to lubricate sliding contacts from the chariots of ancient Egypt [2] to the steam engines of the Industrial Revolution [3]. However, modern synthetic ester basefluids date from the mid-twentieth century, when the application requirements of the rapidly evolving military technology during World War II began to exploit the potential of petrochemical raw materials as building blocks for optimized lubricants.

Some of the groundwork had been laid by the requirement for low volatility, low melting fluids for use as plasticizers for flexible polymers, particularly with the adoption of polyvinylchloride (PVC) for electrical insulation. A wide range of materials, including esters based on aromatic and aliphatic diacids, were screened and commercialized as PVC plasticizers during the 1920s and 1930s [4] and some had already found use in specialized lubricant applications, including vacuum pump and instrument oils by the late 1930s [5].

During the 1930s, limited availability of suitable mineral oil basestocks in Germany directed attention to large-scale production of synthetic lubricants from chemical feedstocks. The increasing performance demands of aircraft engine technology also led to a need for lubricant basefluids with stability and operating temperature ranges, which could not be achieved with the mineral oils of the time [5,6].

An extensive research program was instigated, led by Dr. Hermann Zorn at the Leuna works of I.G. Farben, and a wide range of synthetic basefluid (SBF) chemistries were investigated [7]. Additional impetus was provided by the German experience in Russia during the winter of 1941–1942, where mineral oil-based lubricants gelled in the extreme cold, immobilizing motorized transport. Diester basefluids, as well as synthetic hydrocarbons based on Fischer-Tropsch chemistry, were found to have much better low-temperature flow properties, and these became the main focus of German synthetic lubricant technology development in the latter years of the war [8].

Approximately 3500 different ester structures were synthesized and characterized during this program. Diesters based on adipic or methyladipic acids and C6–C12 oxoalcohols were selected for scale-up and were manufactured by I.G. Farben at production rates of up to 100 barrels per day (i.e., an annualized rate of approximately 6.5 ktes pa). The products were mainly used as minor components (10%–25%) of blends with mineral oils or synthetic hydrocarbons, in high-performance applications including aircraft engine and hydraulic oils and low-temperature railroad oils [8].

Prior to the war, workers at the Deutsche Fettsäure-Werke GmbH in Witten (DFW) had also synthesized esters by reaction of the neopentyl polyols trimethylolmethane or pentarythritol (PE) with short chain (C6–C12) natural fatty acids and shown that these polyol esters had superior properties to the castor oil triglycerides then used in aviation lubricants. Although not developed as extensively as diester fluids by the German war effort, DFW recognized the potential of these polyol esters, both as high-stability basefluids in their own right and as blend components to optimize the properties of synthetic hydrocarbon oils [8].

A more limited research program had also been underway in the United States led by W. A. Zisman at the U.S. Naval Research Laboratory, focusing on diester chemistries [5,6,9]. The subsequent Cold War ensured continued military interest and an active research program into synthetic ester basefluid and additive technology was maintained, building on the results of the German program [10,11].

The further development of ester lubricants was initially closely linked to that of the aviation gas turbine, which could not be adequately lubricated with mineral oil due to extreme temperature requirements. Although many alternative chemistries were evaluated and some found limited application (see Trends toward Synthetic Fluids and Lubricants in Aerospace), first diester [6] and then polyol ester [11,12] basefluids became the standard for military applications. The market grew further as gas turbine engines were introduced in civil aviation, where requirements were originally set based on published military specifications and similar basefluid and formulation technology was therefore required.
With their capability proven against the exacting standards of the aviation industry, the use of synthetic ester basefluids has now become widespread in many other lubricant applications. In automotive engine and gear oils, the major use of ester base fluids has been as components of blends with synthetic hydrocarbons (see Polyalphaolefins; Gas to Liquids), or highly refined (API Group III) mineral oils (see Chemically Modified Mineral Oils), where the ester component is used to modify the solvency, seal swell, and lubricity characteristics of the hydrocarbon. Originally developed for use in extreme low-temperature environments [5], such mixed SBFs have become increasingly widely used in top tier conventional passenger car and heavy duty diesel formulations, driven by ever more stringent targets for fuel economy and extended fill since the 1970s (see Automotive Crankcase Oils).

In some cases, requirements for synthetic ester basefluid have been created directly by environmental legislation. For example, the Montreal Convention of 1987 mandated the phase out of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerant gases. The replacement hydrofluorocarbon (HFC) gases are incompatible with mineral oil base fluids due to their higher polarity. Neopentyl ester base fluids were found to be suitable and the demand for polyol ester HFC-compatible refrigeration compressor lubricants has grown strongly since the early 1990s as the gas changes have been implemented across the various sectors of the refrigeration industry (see Refrigeration Lubes).

Another major growth area for synthetic esters over the last two decades has been in environmentally acceptable hydraulic fluids. The use of biodegradable fluids is increasingly required by legislation where mobile hydraulic equipment is used in environmentally sensitive areas. Because the ester group provides a site for initial microbial attack, ester base fluids can be designed to have acceptable biodegradability while having better oxidative stability and low-temperature flow characteristics than straight vegetable oils (see Environmentally Friendly Hydraulic Fluids).

Synthetic ester base fluids are now found across the range of lubricant applications, including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils, and grease formulations, wherever the ability to tailor properties by molecular design, or the inherent properties of the ester group, offer a sufficient performance advantage to justify the additional cost over mineral oils.

3.2 CHEMISTRY

3.2.1 Ester Structure

The structure of the ester functional group is shown in Figure 3.1, which also illustrates how it is formed by chemical reaction of carboxylic acid and alcohol raw materials, with removal of water. The relative simplicity of the reaction chemistry, and the ready availability of a wide range of monofunctional and polyfunctional acid and alcohol building blocks, mean that complex molecules can be constructed cost-effectively using ester linking groups with better control of the molecular structure than is currently possible with hydrocarbon chemistry [13].

The raw materials used for ester lubricants generally carry relatively large hydrocarbon substituent groups and the properties of ester lubricant base fluids are largely influenced by the number and structure of these hydrocarbon groups [10,14]. However, the presence of the ester group modifies the properties relative to those of an analogous hydrocarbon. In particular, the ester group carries a permanent dipole moment of approximately 1.7 Debye units due to unsymmetrical distribution of electron density in the carbon–oxygen bonds, and ester base fluids are therefore more polar than hydrocarbons. Ester polarity varies with the number and spacing of ester groups in the structure.

Structure–property relationships for ester base fluids are discussed in more detail later.

3.2.2 Raw Materials

3.2.2.1 General

Because the esterification process does not modify the hydrocarbon backbone of the acid and alcohol raw materials, the ability to construct a particular ester structure obviously depends on availability of the required building blocks. Although almost every conceivable acid or alcohol has been or can be prepared in the laboratory, only a limited range are available commercially at suitable scale and cost to be of interest as raw materials for ester lubricants.

Synthetic lubricant base fluids represent a small fraction of the overall chemical industry. For raw materials to be available at commercially viable costing it is generally necessary that they be manufactured at very large scale for primary use in larger volume market sectors such as polymers, coatings, or surfactants.

The chemical industry has undergone substantial restructuring and globalization since the original development of ester base fluids. While many new products have been introduced, overall the diversity of the viable raw material range has reduced over time as the larger chemical sectors have consolidated their usage around preferred materials and smaller scale processes have become uneconomic. For example, neither the methyldipic acids nor the “Leuna alcohols” which were the major raw materials used in the original German 1940s diester lubricants are readily commercially available in the twenty-first century.
The following sections summarize the major raw materials currently used in ester lubricant basefluids.

### 3.2.2.2 Renewability

Raw materials used for esters can be based either on petrochemical or renewable sources. Increasing environmental awareness particularly in Europe and North America has created a demand for fluids with reduced environmental impacts [15,16]. Over the same period, overcapacity and reduction in subsidies for food production have prompted efforts by agricultural producer groups to seek nonfood applications for their crops. Lubricant applications appeared an obvious industrial outlet for natural fats and oils, and consequently much effort has been directed to investigating and promoting opportunities for their use [17,18].

This work has largely resulted in the rediscovery of the performance limitations of natural oils, which had led to their substitution by mineral basefluids for most lubricant applications during the early twentieth century; poor oxidative stability, high pour points, and limited viscosity range [19,20]. Furthermore, recent years have seen a recovery in farm gate prices for traditional food uses, as well as development of large-scale capacity for conversion of both oilseed and grain crops into fuels. As the potential market for fuels is approximately 10 times greater than that for organic materials, it will be readily able to absorb any future overcapacity. Accordingly, producer interest in promoting renewable raw materials for materials applications such as lubricants has diminished, although the momentum imparted to government and academic research programs may take longer to dissipate.

However, it has been sufficiently influential that some standards for environmentally acceptable fluids include a requirement that a proportion of the carbon content of the fluid should be derived from renewable sources, as well as stipulating minimum standards for biodegradability, ecotoxicity, and application performance [21,22].

Fortunately, although natural triglycerides are unsuitable for most high-performance lubricant applications, they can serve as sources of renewable raw materials for synthetic esters through hydrolysis to the constituent fatty acids, which can then be purified and derivatized as required. A significant proportion of acid and alcohol raw materials used for synthetic ester basefluids are of renewable origin, and this is indicated in the following sections.

Synthetic esters therefore represent an overlap between the synthetic and bio-based lubricant product categories, since they can be designed to be readily biodegradable and to incorporate renewable raw materials. However, they are not normally derived exclusively from renewables and indeed many of their useful properties depend on the use of raw materials that are (currently) derived from petrochemical sources [23].

In general, cost-effective manufacture of such renewable oleochemical raw materials requires a low-cost source, which is not suitable for use in food or feed. Typical sources include tallow from slaughterhouse waste, acid oils from deodorization of food-grade vegetable oils, and the “top and bottom” fractions from lauric oil fatty acids, which are unsuitable for surfactant production. The composition and availability of such sources varies, so extensive processing is required to produce derivatives of consistent quality. Furthermore, oleochemical processing also generally gives rise to coproducts for which economic applications must also be found. For example, separation of oleic acid from tallow for use in ester lubricants coproduces glycerol and stearic acid. These considerations will limit the available range of renewable-derived raw materials for the foreseeable future.

### 3.2.2.3 Acids

#### 3.2.2.3.1 Monoacids

The carbon number and functionality of acid and alcohol raw materials are of key importance because they will determine the molecular weight of the product and the relative concentration of ester groups and therefore the viscosity and polarity of the ester product.

Linear saturated carboxylic acids used in lubricant basefluids generally have carbon numbers in the range C\(_8\)–C\(_{12}\). Shorter chain acids are not used because of their relatively high corrosivity and offensive odor if released by degradation processes during use. Longer linear alkyl chains result in products with unacceptable low-temperature flow properties. Disruption of the linear alkyl chains by unsaturation or branching allows the use of higher carbon numbers.

Available monocarboxylic acids include the linear natural fatty acids, which contain even numbers of carbon atoms in the range C\(_8\)–C\(_{22}\). These may be used either as mixtures in the naturally occurring ratio (e.g., tallow fatty acids, cocomo fatty acids) or fractionated into narrower cuts or single chain lengths. The most widely used for manufacture of lubricant basefluids are C\(_8\)–C\(_{10}\) and oleic acid (monounsaturated C\(_{18}\) acid). Although petrochemical routes have been used, these are currently only commercially available from renewable sources [24]. Because these acids arise as components of a natural raw material in fixed ratio, their pricing and availability depends on the supply-demand balance for each of the components. Pricing for the C\(_8\)–C\(_{10}\) fraction has been highly volatile over the last years, which has led to some substitution by linear C\(_9\) and some reformulation to alternative technologies.

Shorter chain linear C-odd (C\(_3\)–C\(_5\)) monocarboxylic acids are manufactured from petrochemical raw materials by carbonylation/oxidation. These processes give rise to smaller quantities of branched isomers, which may remain in the product as minor components or be separated for sale as coproducts. For example, conversion of C\(_3\) olefin 1-butene to C\(_4\) acid gives the linear C\(_4\) valeric acid as major product, with minor amounts of branched isovaleric isomers as coproducts. Linear C\(_5\) and C\(_6\) acids are also available from renewable raw materials. The renewable routes do not generate branched coproducts but do involve side reactions leading to linear acids of different carbon numbers [24,25]. In some cases, this
different impurity profile between petrochemical and renewable materials can impact the properties of derivative esters. Fully branched C₈ and C₉ short chain acids are available from petrochemical processing, in each case as single isomers (2-ethylhexanoic and 3,5,5-trimethylhexanoic acids, respectively) [25]. Mixed isomer branched C₈ acid (isooctanoic acid), which was used as a raw material for biodegradable polyol esters, is no longer commercially available following the closure of Exxon’s manufacturing plant in Harnes, France, during 2004. C₁₀ 2-propylheptanoic acid [108] and higher carbon number α-branched “Guerbet” acids are available in principle and can be used similarly to 2-ethylhexanoic, but have not yet found high-volume application.

Acids having the α,α-dibranched structure (“neo acids”) are available but generally not suitable for use as ester raw materials because steric hindrance results in very low reactivity.

Longer chain branched C₁₈ isostearic acid is available from renewable raw materials as coproduct from the manufacture of dimer and trimer acids [24]. Degree of branching and level of residual unsaturation in isostearic acids depend on the source, and products from different suppliers are generally not interchangeable.

3.2.2.3.2  Di- and Polyfunctional Acids
Linear aliphatic diacids in the range C₄–C₁₂ are produced in large volume for manufacture of polyamides and are suitable for production of diesters. The most widely available are C₆ adipic, C₉ azelaic, C₁₀ sebacic, and C₁₂ dodecanedioic. Currently, C₈ and C₁₂ are petrochemical-derived, whereas the C₉ and C₁₀ diacids are renewable-derived [26].

C₁₀ dimer and C₃₄ trimer acids are branched mixed isomer materials manufactured from renewable polyunsaturated fatty acids. Dimer and trimer acids have very complex product distributions, including some residual unsaturation and formation of both alicyclic and aromatic ring structures. The composition of dimer and trimer acids and therefore the properties of their derivatives, depends significantly according to the raw material origin and degree of processing [24,26].

A range of aromatic diacids and polyacids are also readily available due to their high volume use in polymers, coatings, and plasticizers. The most widely used in lubricants are the unsymmetrical 1,2-difunctional phthalic and 1,2,4-trifunctional trimellitic acids. Tetrafunctional pyromellitic acid has also been used. All are marketed as the corresponding anhydrides [27]. Esters of terephthalic acid, particularly bis(2-ethylhexyl) terephthalate (DOTP), have longstanding use in plasticizer applications where volumes have increased significantly between different producers. Both C-odd and fully branched monoalcohols are available from both petrochemical and renewable raw materials. Both routes generate a carbon number distribution from C₈ upward, which can be fractionated into tighter cuts or single chain products; the C₈–C₁₀ fraction is preferred for lubricants. These alcohols can be dimerized to monobranched Guerbet alcohols, with useful carbon numbers in the range C₁₆–C₂₀ [28]. As with the analogous acid, pricing for the C₈–C₁₀ alcohol fraction has been volatile over recent years leading to some substitution by linear C₈, which had previously only been available as a component of C₉–C₁₁ mixed linear/branched surfactant alcohol grades.

C-odd surfactant alcohols are typically sold to a carbon number range rather than as single chain length, and are normally predominantly linear but with significant branched content.

Single isomer, fully branched monoalcohols include C₈ (2-ethylhexanol), C₉ (3,5,5-trimethylhexanol), and C₁₀ (2-propylheptanol). Mixed isomer branched alcohols derived from polymerized C₃ and/or C₄ olefins are also available with carbon numbers ranging from approximately C₉–C₁₃. Compositions of these mixed isomer materials may vary significantly between different producers. Both C-odd and fully branched monoalcohols are based on petrochemical raw materials [28,29].

3.2.2.4.2  Di- and Polyfunctional Alcohols
The polyols most commonly used in lubricant esters are the “neopentyl polyols,” which have primary alcohol methylol groups attached to a quaternary carbon atom, due to the superior thermal stability of esters based on this structure. All of the neopentyl polyols have historically been derived from petrochemical raw materials, but fully or partially bio-based grades are now commercially available.

Neopentyl polyols are available with functionality from two to six. The most widely used are neopentyl glycol (NPG, difunctional), trimethylolpropane (TMP, trifunctional), and pentaerythritol (PE, tetrafunctional) [30].

Hexafunctional dipentaerythritol (DiPE) is a minor coproduct in the production of PE. PE may be sold as the production mix technical PE (Tech PE), containing approximately 10% DiPE, or purified to monopentaerythritol (Mono PE), and DiPE. Esters based on Tech PE have higher viscosity and lower pour point than corresponding Mono PE esters, and Tech PE is therefore preferred for some applications.
Trifunctional trimethylol ethane (TME) was used in the original German DFW polyol esters, but TMP has been more widely used since it has been more available and less costly. Esters of TMP have slightly higher viscosity and lower pour point, though slightly inferior oxidative stability to TME analogues [31].

Many other diols, including ethylene glycol, propylene glycol, and their oligomers, are readily available and have more limited use as ester raw materials. Higher polymers of ethylene oxide and/or propylene oxide (see Polyalkylene Glycols) can be esterified to PEG or PAG esters, but these materials are typically amphiphilic and used in surfactant, rather than basefluid, applications. Diesters of longer chain glycols such as hexane diol with monoacids have been evaluated, but properties were generally inferior to those of analogues assembled using the corresponding difunctional acid and monoacohol [32].

Polysols other than neopentyl glycols are used to some extent, particularly the bio-based trifunctional glycerol and hexafunctional sorbitol. (Petrochemical routes to glycerol exist, but the present market is essentially all renewable due to coproduction in the manufacture of fatty acid methyl esters for biodiesel.) Glycerol can be reacted with desirable fatty acid fractions (e.g., short chain C6–C10 or monounsaturated oleic acid) to give synthetic triglycerides having much better stability and low-temperature characteristics than natural oils, though inferior to TMP analogues. Sorbitol undergoes side reactions under typical esterification conditions, which partially convert the original hexitol to tetrafunctional sorbitan and di-functional isosorbide, leading to very complex reaction mixtures [33]. Partially esterified sorbitol derivatives are widely used as surfactants. Alternatively, sorbitol can be fully converted to isosorbide and esterified to diesters which have been promoted for plasticizer applications and may find some use in lubricants [110]. Glycerol and sorbitol both contain secondary alcohol groups and their ester derivatives therefore have relatively low thermal stability, limiting their suitability for high-temperature applications.

### 3.2.3 Ester Types

Table 3.1 shows how the different ester basefluid structures are classified according to the combinations of mono- and polyfunctional acid and alcohol raw materials used.

Ester basefluids are frequently based on mixed raw materials with a distribution of chain lengths or isomer structures, either because the raw materials are only available as mixtures, or because pure components are intentionally blended prior to reaction to produce a mixed feed. Where mixed monoalcohol and/or monoaacid raw material feeds are used in manufacture of a monoester, the composition of the resulting monoester mix is identical to that which would be obtained if the individual raw materials were reacted separately and blended after reaction. However, when mixed monofunctional feeds are used in manufacture of a diester or polyol ester, cross products are formed, in which residues from the different monofunctional raw materials are combined in the same ester product molecule. Such mixed-feed reaction products therefore have a higher structural diversity than blends of the same raw materials esterified separately and blended post-reaction [34].

#### 3.2.3.1 Monoesters

Monoesters result from reaction of monofunctional acid (e.g., oleic, isostearic) with monofunctional alcohol. They contain only one ester group and only two hydrocarbon residues. They are therefore the lowest molecular weight and typically lowest viscosity/highest volatility ester product group. Table 3.2 illustrates how the physical properties of monoesters of an acid raw material, in this case oleic acid, can be systematically varied by selection of the alcohol raw material.

Monoleate esters are typically used in metalworking applications.

#### 3.2.3.2 Diesters

Diesters result from reaction of di- or polyacid with (normally branched) monofunctional alcohol. Because of the wider range of diacid structures available, diesters are normally subdivided into three distinct groups.

Diesters based on short chain (C6–C12) linear diacids with plasticizer alcohols (Figure 3.2) are relatively low-viscosity,

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Viscosity at 100°C (cSt)</th>
<th>VI</th>
<th>Pour Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>4.5</td>
<td>1.8</td>
<td>–</td>
<td>–12</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>5.3</td>
<td>2.0</td>
<td>221</td>
<td>–21</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>6.0</td>
<td>2.2</td>
<td>219</td>
<td>–50</td>
</tr>
<tr>
<td>2-Ethyl hexyl</td>
<td>8.0</td>
<td>2.8</td>
<td>238</td>
<td>–35</td>
</tr>
<tr>
<td>Iso-octyl</td>
<td>9.1</td>
<td>2.9</td>
<td>192</td>
<td>–29</td>
</tr>
<tr>
<td>Decyl</td>
<td>10.2</td>
<td>3.4</td>
<td>246</td>
<td>–3</td>
</tr>
<tr>
<td>Glycerol mono-oleate</td>
<td>100</td>
<td>10.4</td>
<td>83</td>
<td>0</td>
</tr>
</tbody>
</table>

**TABLE 3.1**

The Major Ester Basefluid Structural Types

<table>
<thead>
<tr>
<th>Monoalcohol</th>
<th>Monoester</th>
<th>Di- or Polyacid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di- or polyol</td>
<td>Polyolet</td>
<td>Complex ester</td>
</tr>
</tbody>
</table>

**TABLE 3.2**

Typical Physical Properties of Mono-Oleates

FIGURE 3.2 Chemical structure of diesters of short chain linear diacids.
high-polarity materials with typically very good VIs and pour points. Examples of commercially available short chain diesters are given in Table 3.3 showing how their properties can be varied by selection of acid and alcohol carbon number and degree of branching. Derivatives of C₃₆ dimer acids have significantly higher viscosity and lower polarity due to the higher carbon number acid raw material. Because of residual unsaturation and branching on the diacid backbone, thermal and oxidative stability is lower than for short chain diesters. The alcohol carbon number makes proportionally less difference to the product molecular weight, so selection of alcohol raw material makes less difference to final product molecular weight, as shown in Table 3.4. The alcohol most widely used is 2-ethylhexanol. Dimer acids from different sources vary widely in structure, depending on the degree of unsaturation of the fatty acid raw material and the process conditions. Lubricant dimerate esters are normally based on technical grades of dimer acid which contain relatively high levels of trifunctional trimer acid and some residual unsaturation.

Derivatives of aromatic acids or anhydrides have distinct properties because of the presence of the aromatic ring, which is more rigid and more polarizable than linear aliphatic chains. Accordingly, aromatic esters have different solvency characteristics, higher viscosity, and lower VI than linear aliphatic esters of the same alcohol raw materials. (The entire group is generally described as diesters, although obviously derivatives of trimellitic anhydride are in fact triesters.) Structures of typical aromatic esters are shown in Figure 3.3. Properties of the aromatic esters are shown in Table 3.5, illustrating how viscosity depends both on the alcohol raw material and the acid functionality that determines how many alcohol groups are included in each ester molecule.

3.2.3.3 Neopentyl Polyol Esters

Reaction of a polyfunctional alcohol with monofunctional acid(s) produces a polyol ester (Figure 3.4).

Physical properties of a range of single-component neopentyl polyol esters are given in Table 3.6, showing that viscosity and other properties can be varied over a very wide range by appropriate selection of the acid raw material(s) and the polyol functionality. In practice, the majority of commercial polyol ester fluids are based on mixed acid raw materials, and

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Viscosity at 100°C (cSt)</th>
<th>Viscosity Index</th>
<th>Pour Point (°C)</th>
<th>Noack at 250°C/1hr (% loss)</th>
<th>CEC-L-33-A-93% Biodeg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Ethyl hexyl</td>
<td>91.1</td>
<td>12.7</td>
<td>136</td>
<td>−50</td>
<td>0.8</td>
<td>49</td>
</tr>
<tr>
<td>2-Ethyl hexyl (C36 hydrogenated)</td>
<td>92.0</td>
<td>12.7</td>
<td>135</td>
<td>−41</td>
<td>0.2</td>
<td>24</td>
</tr>
<tr>
<td>C9/C11</td>
<td>94.9</td>
<td>14.0</td>
<td>151</td>
<td>−15</td>
<td>1.1</td>
<td>78</td>
</tr>
<tr>
<td>iso-tridecyl</td>
<td>140.0</td>
<td>17.0</td>
<td>132</td>
<td>−27</td>
<td>0.6</td>
<td>30</td>
</tr>
</tbody>
</table>
therefore contain a statistical distribution of mixed ester products. The higher structural diversity of mixed polyol esters generally gives improved low-temperature fluidity, whereas other parameters such as viscosity vary in the same way as a blend of the pure single component esters. Neopentyl polyol esters have superior thermal stability compared to diesters. Solvency characteristics are also somewhat different because the ester groups are rigidly oriented at the center of the molecule.

### 3.2.3.4 Complex Esters

The ester types described earlier contain relatively well-defined molecular structures, with molecular weight range depending only on the carbon number distribution in the raw materials. However, if polyfunctional acids and polyfunctional alcohols are reacted together, the resulting complex ester product has an oligomeric polyester backbone with a statistical distribution of molecular weights. Lubricant basefluid complex esters are normally manufactured using one monofunctional raw material of either type in addition to the polyfunctional reactants, to act as end capper to convert unreacted acid or hydroxyl functionality.

Final product average molecular weight is controlled by the ratio of polyfunctional acid and alcohol reactants. Exclusively difunctional reactants give linear backbone structures and relatively narrow molecular weight distribution, whereas inclusion of tri- or tetrafunctional reactants gives branched backbones with broader distributions [35].

Complex ester chemistry therefore represents a route to products having very high viscosity while retaining good biodegradability due to the ester links in the backbone. Furthermore, because of their polymeric nature, complex esters are subject to less stringent new substance notification requirements in major regulated territories, including the EU and the United States. This reduces both the time and cost of new product introduction and therefore favors innovation in this area. However, because of the distribution of molecular weights, complex esters typically have higher volatility and poorer material compatibility (elastomer compatibility, miscibility with other basefluid types, and interference with functional additives) than simple esters of the same viscosity.

Oligomeric polyesters related to complex esters can also be produced by condensation homopolymerisation of hydroxy-acid monomers containing both acid and alcohol groups, e.g., ricinoleic or 12-hydroxystearic acids derived from castor oil. In this case, the polyfunctional acid and alcohol groups are necessarily present in 1:1 ratio and a defined ratio of at least one nonvolatile monofunctional endcapper is required to control molecular weight. For basefluid applications, it is normally necessary to minimize both unreacted acid and alcohol

### TABLE 3.5

**Typical Physical Properties of Aromatic Esters**

<table>
<thead>
<tr>
<th>Ester</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Viscosity at 100°C (cSt)</th>
<th>Viscosity Index</th>
<th>Pour Point °C</th>
<th>Noack 250°C/1 h (% loss)</th>
<th>OECD 301 Biodegradability % (28 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(2-ethylhexyl) phthalate</td>
<td>26.4</td>
<td>4.2</td>
<td>21</td>
<td>−43</td>
<td>19</td>
<td>82</td>
</tr>
<tr>
<td>Di-isononyl phthalate</td>
<td>38.5</td>
<td>5.3</td>
<td>50</td>
<td>−44</td>
<td>12</td>
<td>81</td>
</tr>
<tr>
<td>Bis(2-propylheptyl) phthalate</td>
<td>37</td>
<td>5.1</td>
<td>40</td>
<td>−48</td>
<td>11</td>
<td>80–90</td>
</tr>
<tr>
<td>Di-isodecyl phthalate</td>
<td>45.5</td>
<td>5.8</td>
<td>49</td>
<td>−47</td>
<td>9</td>
<td>67</td>
</tr>
<tr>
<td>Di-isotridecyl phthalate (1)</td>
<td>80.5</td>
<td>8.2</td>
<td>46</td>
<td>−43</td>
<td>3</td>
<td>71</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) terephthalate</td>
<td>29</td>
<td>4.5</td>
<td>87</td>
<td>−45</td>
<td>10</td>
<td>73–78</td>
</tr>
<tr>
<td>Tris (octyl, decyl) trimellitate</td>
<td>52</td>
<td>8.1</td>
<td>126</td>
<td>−45(2)</td>
<td>0.4</td>
<td>21–45</td>
</tr>
<tr>
<td>Tris (2-ethylhexyl) trimellitate</td>
<td>90</td>
<td>9.7</td>
<td>82</td>
<td>−36</td>
<td>1.6</td>
<td>20</td>
</tr>
<tr>
<td>Tri-isodecyl trimellitate</td>
<td>145</td>
<td>13</td>
<td>79</td>
<td>−30</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Tri-isotridecyl trimellitate(1)</td>
<td>305</td>
<td>20.5</td>
<td>76</td>
<td>−9</td>
<td>1.6</td>
<td>–</td>
</tr>
<tr>
<td>Tetakis (2-ethylhexyl) pyromellitate</td>
<td>172</td>
<td>16.3</td>
<td>98</td>
<td>−27</td>
<td>0.4</td>
<td>0–10</td>
</tr>
</tbody>
</table>

1. Derived from tridecanol based on propylene tetramer.
2. Freezes at ca 0°C on prolonged storage.
groups, which requires use of both alcohol and acid endcaps. The resulting product distribution therefore contains some monoester derived from reaction between endcappers. Complex esters based on hydroxyacids have found limited use as basefluids but have established application as polymeric surfactant hydrophobes [111]. An alternative route based on unsaturated fatty acids, using addition of carboxylic acids to olefins instead of esterification, has recently been developed [112] and is described in a separate chapter (Estolides). The estolide ester group forms part of the polymer backbone, so these products are more closely related to complex esters than to Polymeric Esters where the ester group is part of a pendant chain. The backbone chain length between ester groups is more variable for estolides manufactured by addition to olefin than for poly 12-hydroxystearates and the olefin-addition estolides therefore have better low-temperature fluidity. Whichever manufacturing route is used, the estolide ester group is equivalent to an ester of a secondary hydroxyl group and therefore has inherently lower thermal stability, but higher hydrolytic stability, than the primary hydroxyl ester groups present in most other ester SBFs.

### 3.2.3.5 Other Esters

The previous sections describe the main classes of esters intended for use as lubricant basefluids. In all of these, the reactive and H-bonding acid and alcohol groups are essentially fully converted to ester, substituent groups are hydrocarbons, and no other functional groups are present. However, it will be apparent that the flexibility of esterification chemistry also allows assembly of many other chemical structures with additional functionality and reactivity, some of which find application as lubricant and fuel additives.

Significant examples include:

- Partially esterified polyol esters with residual hydroxyl functionality used as friction modifiers [1].
- Complex esters with unreacted acid or alcohol functionality used as tribo-polymerizing antiwear additives [36].
- Amphiphilic PEG or PAG esters containing polyol segments based on polar polymers of ethylene oxide and/or propylene oxide used as soluble oils and emulsifiers [37,38].

### 3.2.4 Synthesis and Production

#### 3.2.4.1 Manufacturing Process

There are typically four distinct stages to manufacture of ester lubricant basefluids:

1. Esterification
2. Stripping of excess reactants
3. Neutralization
4. Filtration

The basic chemical reaction for the esterification process is shown in Figure 3.1. Esterification is an equilibrium process, and formation of the ester group is carried out by mixing the acid and alcohol raw material while removing the water of reaction in order to drive the equilibrium to the right-hand side. Ester lubricant basefluids are normally manufactured batchwise, using a stirred reaction vessel equipped with heating, cooling, and overheads capable of condensing and separating water of reaction from volatile organic reactants by fractionation or decantation [13].

To facilitate removal of water and accelerate reaction, esterification processes are normally carried out at a temperature of at least 100°C, and since the products have good thermal stability, higher temperatures up to about 250°C are commonly used. Esterification catalysts may be used; these include strong mineral acids such as sulfuric or p-toluene sulfonic acids for use at lower temperatures and Lewis acid catalysts such as tin and titanium alcoholates at higher temperatures. Azeotroping agents may also be used to assist in removal of water [13].

For diester products, the monoalcohol reactants normally have significant volatility, and a 10%–20% molar excess of monoalcohol is frequently used to drive the equilibrium.
At the end of reaction, excess volatile reactant is removed by stripping under reduced pressure and recycled to subsequent batches.

Similarly, for polyol esters, excess monoacid reactant may be used and stripped at the end of reaction. Because the excess acid serves to catalyze the reaction, polyol esters are frequently manufactured without use of additional catalyst.

The esterification and stripping process will typically give a conversion of acid groups of >99% in the crude reaction product. However, because very low acid values are generally required for lubricant basefluids, further reduction of acid concentration is frequently necessary. This can be achieved by treatment of the crude reaction product by addition of a base such as sodium carbonate or calcium hydroxide, which converts residual acid to carboxylate soaps that can be removed by water washing and/or filtration.

Adsorbents such as bleaching earths, activated aluminas, or activated carbons may be added prior to filtration to control color and concentration of specific impurities such as catalyst residues. Final product purification is normally carried out by cake filtration using a suitable filter aid in a press-type filter, followed by polishing filtration to the required standard of particulate cleanliness using bag or cartridge filters.

### 3.3.4.2 Specifications

As for all lubricant basefluids, ester fluid specifications typically include pour point and flash point, which will normally define the useful application temperature range, as well as a viscosity range at one or more relevant temperatures. Other parameters specifically relevant to the ester structure, or to downstream application requirements may also be included. For example, ester specifications often include Acid Value and Hydroxyl Value, which indicate degree of conversion of the raw materials. Esters having a defined chemical composition may also be specified by nominal chemical purity.

Trace impurities such as catalyst residues can significantly affect thermal, oxidative, and hydrolytic stability as well as other application parameters including demulsibility, air release, and foaming. The precise relationships are not always well understood, so these issues may be addressed either by specifying maximum levels for identified impurities such as heavy metals or ash content, or by specifying application test performance criteria.

Application performance of ester basefluids is therefore dependent on processing parameters and upstream raw material quality as well as on their nominal composition. Table 3.7 lists typical specification parameters, indicating their dependence on each of these controlling factors.

### 3.3 PROPERTIES AND PERFORMANCE CHARACTERISTICS

#### 3.3.1 Structure–Property Relationships

Structure–property relationships for ester basefluids are broadly similar to those that have been established for mineral oils and synthetic hydrocarbons [32].
Esters

However, a key advantage of ester basefluids is that this understanding can be exploited more effectively to optimize product properties because their compositions can be controlled to give more uniform molecular structures. This degree of control is generally not possible with mineral oil basestocks that consist of complex mixtures of naturally occurring hydrocarbons, nor with synthetic fluids manufactured by polymerization processes (e.g., polyalphaolefins, polyalkylene glycols, polybutenes, Fischer–Tropsch gas to liquid isomerates), that give a distribution of molecular weights.

A corollary to this is that the physical properties (viscosities, density, etc.) associated with a defined ester structure will, in principle, be fixed and invariant rather than varying within a controllable range as with a mineral oil distillation fraction. In practice, some variation in properties is generally found due to batch-to-batch variation in raw material composition. If properties are required that do not match those of any single ester structure, then they can normally be achieved by use of mixed raw materials (Section 3.2.2), or by blending finished products.

3.3.1 Viscosity
Viscosity generally increases with increased molecular weight and with reduced molecular flexibility. Ester molecular weight can be increased by either increasing the carbon number of the raw materials, or by increasing raw material functionality (more ester groups per molecule). Flexibility is reduced by introducing branching, particularly quaternary branching and ring structures [14,32].

![Figure 3.5](image_url) The effect of chain length on the viscosity of linear acid polyol esters.

Figure 3.5 shows the effect of molecular weight by illustrating the change in viscosity at 100°C with acid chain length for a range of polyol esters. Table 3.8 demonstrates the variation in viscosity due to degree of chain branching for PE esters of C8 and C9 acids.

The effect of branching can also be seen from the data in Table 3.9, which compare the physical properties of trimellitate esters of isodecane from different sources. Isodecane is manufactured by carbonylation of C12 olefin, which can be derived from C2, C3, or C4 raw materials, each giving a characteristic isomer distribution. It is apparent that these nominally identical trimellitate esters have viscosities that are sufficiently different that they do not fall within the same ISO viscosity grade and are therefore not interchangeable materials.

3.3.1.2 Volatility
Volatility generally decreases with increasing molecular weight but increases with reduced flexibility (branching and cyclics) since this prevents close packing and reduces the strength of intermolecular dispersion forces at high temperature [14,32].

Lubricant basefluids are typically specified in terms of flashpoint or Noack volatility. For fluids containing a range of structures, both parameters are dominated by the behavior of the most volatile component present. As a result, the flashpoint of a fluid containing a mixture of structures will be lower than that of a single-component fluid having the same average molecular weight. Furthermore, under high-temperature service conditions where some of the fluid is volatilized,

<table>
<thead>
<tr>
<th>Specification parameter</th>
<th>Nominal composition</th>
<th>Raw material</th>
<th>Reaction</th>
<th>Post-processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyl value</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodine value</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Physical properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity index</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low-temperature fluidity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pour point</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cloud point</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-temperature stability</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flash point</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fire point</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleanliness</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Particle count</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Filterability</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Demulsibility</td>
<td></td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3.8 The Effect of Branching on Viscosity

<table>
<thead>
<tr>
<th>Pentaerythritol Tetraester</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Viscosity at 100°C (cSt)</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear C8</td>
<td>25.5</td>
<td>5.5</td>
<td>141</td>
</tr>
<tr>
<td>branched C8</td>
<td>44</td>
<td>6.23</td>
<td>83</td>
</tr>
<tr>
<td>(2-ethylhexanoic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>linear C9</td>
<td>31.5</td>
<td>6.1</td>
<td>149</td>
</tr>
<tr>
<td>branched C9</td>
<td>111</td>
<td>11.3</td>
<td>86</td>
</tr>
</tbody>
</table>
TABLE 3.9
The Change in Physical Properties of a Trimellitate Using Different Sources of Isotridecanol

<table>
<thead>
<tr>
<th>Isotridecanol type</th>
<th>Viscosity at 40°C (cSt)</th>
<th>Viscosity at 100°C (cSt)</th>
<th>VI</th>
<th>Flashpoint (°C)</th>
<th>Pour Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene tetramer</td>
<td>315</td>
<td>19.9</td>
<td>67</td>
<td>298</td>
<td>−7</td>
</tr>
<tr>
<td>n-butene trimer</td>
<td>189</td>
<td>16.7</td>
<td>93</td>
<td>268</td>
<td>−17</td>
</tr>
<tr>
<td>Isobutene trimer</td>
<td>366</td>
<td>21.6</td>
<td>65</td>
<td>296</td>
<td>−23</td>
</tr>
<tr>
<td>Mixed C3/C4</td>
<td>320</td>
<td>20.8</td>
<td>73</td>
<td>234</td>
<td>−7</td>
</tr>
</tbody>
</table>

TABLE 3.10
Pour Points for a Range of Polyol Esters

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Acid</th>
<th>Longest CH₂ Chain</th>
<th>Symmetry</th>
<th>Pour Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMP</td>
<td>Stearic</td>
<td>16</td>
<td>Low</td>
<td>+45</td>
</tr>
<tr>
<td>TMP</td>
<td>Oleic</td>
<td>7</td>
<td>Low</td>
<td>−51</td>
</tr>
<tr>
<td>TMP</td>
<td>Oleic/mixed</td>
<td>7</td>
<td>Very low</td>
<td>−56</td>
</tr>
<tr>
<td>TMP</td>
<td>Isoleatare</td>
<td>9 (approx.)</td>
<td>Low</td>
<td>−30</td>
</tr>
<tr>
<td>PE</td>
<td>Oleic</td>
<td>7</td>
<td>High</td>
<td>−24</td>
</tr>
<tr>
<td>NPG</td>
<td>Oleic</td>
<td>7</td>
<td>High</td>
<td>−21</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Oleic</td>
<td>7</td>
<td>Mid</td>
<td>−16</td>
</tr>
</tbody>
</table>

For the TMP series, the data show that although the saturated stearate ester is a solid at room temperature, introducing unsaturation (oleate) or branching (isostearate) reduces pour point to acceptably low values. Within the oleate series, increasing symmetry by changing from trifunctional TMP to even-numbered difunctional (NPG) or tetrafunctional (PE) leads to an increase in pour point. Data for glycerol trioleate are included for comparison, showing that the triglyceride structure (selected by nature to pack into regular lipid membrane bilayers) has a much higher pour point than the synthetic TMP trioleate.

There is therefore an inevitable trade-off between viscosity index (VI) and pour point. This can be resolved to some extent by increasing structural diversity, but as noted earlier, this has a detrimental effect on volatility.

Even with the structural control possible for synthetic esters, it is not possible to simultaneously optimize all performance parameters. There is no single ideal lubricant structure, only an optimum compromise that is unique to each intended application.

3.3.1.4 Lubricity
The factors affecting lubricity (i.e., coefficient of friction and wear rate) depend on the lubrication regime.

3.3.1.4.1 Hydrodynamic Lubrication
Under hydrodynamic lubrication conditions, bearing surfaces are separated by a relatively thick fluid-film, there is no wear, and the friction coefficient depends only on the fluid kinematic viscosity at the operating conditions (temperature, pressure, and shear). Hydrodynamic lubrication is therefore only dependent on the physical properties of the lubricant basefluid rather than its chemical composition. However, selection of a synthetic lubricant can be necessary in order to provide the best physical properties [40].

To optimize energy efficiency, it is generally desirable to select a lubricant with the lowest viscosity sufficient to ensure full fluid-film lubrication at maximum expected operating temperature, combined with a high VI in order to minimize viscosity, and therefore viscous drag, at lower temperature operation.

Exact requirements will depend on specific application, but it is obvious from the structure–property relationships outlined earlier that there will be a practical limit to the lowest viscosity achievable before high volatility becomes a limiting factor. Use of single component high VI ester will
normally represent a significantly more efficient viscosity/volatility trade-off than will be achievable with mixed structure basefluids.

In practice, lubricant formulators normally also use polymeric VI improvers, rather than relying on basefluid VI alone. This brings both advantages and disadvantages; the non-Newtonian rheology (reversible shear thinning) behavior of polymer solutions may reduce hydrodynamic friction, but mechanical degradation (irreversible shear thinning) and oxidative degradation of polymers can lead to deposit formation and change of rheology during lubricant lifetime. Where VI improvers are used in basefluids with significant ester content, their rheological properties will be modified because of differential solvation by the more polar fluid. Polymer/basefluid interactions are very complex and require case-by-case optimization.

3.3.1.4.2 Elastohydrodynamic Lubrication

As the lubrication regime passes from hydrodynamic into elastohydrodynamic lubrication (EHL), the thickness of the fluid-film reduces and may approach molecular dimensions. At the same time, the pressure in the contact zone increases dramatically. The rheology and even the composition of this thin high-pressure lubricant film depend on the pressure–viscosity coefficient of the basefluid and on the surface affinity of the various components of a formulation and are generally very different from those of the bulk lubricant. Lubricity under EHL conditions is also much more dependent on the materials of construction and surface finish of the contacting surfaces. The key lubricity parameters are the EHL friction coefficient and the maximum load that can be supported. A higher EHL film viscosity, that is, higher P–V coefficient, will typically give a higher friction coefficient, but a stronger film [40].

Pressure–viscosity coefficients typically have an inverse relationship to VI (i.e., high VI normally implies low P–V coefficient). Because current commercial synthetic esters are generally designed to have higher VI than mineral oils, they have relatively lower P–V coefficients. The P–V coefficient of a lubricant is increased by increasing degree of branching and number of cyclic structures, presence of aromaticity, and increasing length of side chains branches [32].

Values for P–V coefficient at 40°C have been reported [41–44] for TMP ester (8.4–9.8 GPa⁻¹), PE esters (7.5–12.2 GPa⁻¹), phthalates (13.6 GPa⁻¹), and diesters (6.6–7.6 GPa⁻¹). Note, however, that P–V coefficients vary with temperature as shown in the results in Table 3.11.

Furthermore, in real life lubricant formulations where multiple components are present, the more polar components are concentrated in the layers adjacent to the polar metal surface. This effect is well known as the basis of action of friction modifier additives, but has also been observed in blends of polar and nonpolar basefluids, for example, PAO/ester under EHL conditions [45]. Because the thickness of the EHL film may be as low as a few tens of molecules, this effect can significantly alter the composition and rheology of the EHL film compared to that of the bulk composition. P–V coefficients of pure basefluids are therefore not necessarily related to their EHL behavior. Conversely, P–V coefficients that have been determined indirectly by measurement of film thickness under EHL conditions may be significantly dependent on presence of low-concentration components.

Because of this complexity, it is very difficult to theoretically predict and rationalize EHL behavior, but the effects described can be exploited practically by lubricant formulators to control lubricity in EHL contacts. For example, recent work suggests that when a small amount of a high-viscosity polar ester is added to a low-viscosity nonpolar basefluid (PAO), the ester will preferentially stick to the surface. When the two metal surfaces are far apart, the bulk viscosity is controlled by the PAO. When the surfaces come closer together, the PAO is squeezed out of the contact zone. The polar ester sticks to the surface and stays in the contact area. As the ester has high viscosity, the bulk viscosity of the oil will increase as the surfaces come closer together. Finally, a point will be reached where only the more viscous polar ester remains [45]. Such an effect can be very beneficial as it will increase the strength of the EHL film and may allow reduction in dose rate of antirust additives.

3.3.1.4.3 Mixed Film

Mixed film lubrication, as the term implies, is actually a combination of boundary and hydrodynamic or EHL regimes. In the mixed lubrication regime, the contact characteristics are determined by varying combinations of fluid-film and boundary lubrication effects. Some asperity contact may occur and interaction takes place between mono- and multilayer boundary lubricating films while a partial fluid-film lubrication action develops in the bulk of the space between the metal surfaces. It follows that both the physical properties of the lubricant (per EHL) and the chemical properties of the lubricant (per boundary) are important [46].

3.3.1.4.4 Boundary Lubrication

Under boundary conditions, there is asperity contact between the surfaces. The load is mainly carried through these solid contacts, the major contribution to the frictional force is the energy required for deformation of contacting asperities, and boundary friction coefficients generally show little dependence on lubricant viscosity. However, lubricant basefluids or additives can modify the boundary friction and wear.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure–Viscosity Coefficient GPa⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>40°C</td>
<td>30.2 12.2</td>
</tr>
<tr>
<td>60°C</td>
<td>26.1 14.9</td>
</tr>
<tr>
<td>80°C</td>
<td>15.2 12.8</td>
</tr>
<tr>
<td>100°C</td>
<td>19.3 14.9</td>
</tr>
<tr>
<td>120°C</td>
<td>16.6 13.9</td>
</tr>
</tbody>
</table>

TABLE 3.11
Pressure–Viscosity Coefficients for a Variety of Lubricants

Lubricant: PAO/ester (8.4–9.8 GPa⁻¹), PE esters (7.5–12.2 GPa⁻¹), phthalates (13.6 GPa⁻¹), and diesters (6.6–7.6 GPa⁻¹).
properties. In particular, components that form a coherent chemisorbed or physisorbed layer that deforms more readily than the underlying metal surface will reduce the boundary friction coefficients. If this film is strong and thick enough to prevent metal–metal contact, it will also reduce wear.

Lubricants having a high polarity or affinity for metal oxide surfaces, such as esters, have a greater tendency to form such adsorbed layers than less polar fluids, such as mineral oils or synthetic hydrocarbons, and therefore have lower boundary friction coefficients. Esters containing predominantly linear alkyl substituents can form a more coherently packed adsorbed film, and consequently show lower boundary friction coefficients, than those with branched alkyl substituents. This principle can be extended to the use of components with longer linear alkyl chains and polar head-groups (acid, amide, or partial ester), which are widely used as friction-modifying additives in a range of lubrication applications, particularly in low-polarity basefluids such as hydrocarbons [1,46]. In some cases, the lower friction coefficients observed with ester basefluids may in fact be due to the formation of trace levels of their carboxylic acid raw materials by thermolysis of the ester bonds under the very high local flash temperature conditions of asperity contact. Carboxylic acids have higher polarity than the ester group because they can act as hydrogen bond donors, or even form surface-bound metal carboxylate soaps, and are therefore preferentially adsorbed even at very low concentrations [47,48].

However, although ester basefluids can reduce wear by increasing strength of an EHL film and reduce boundary friction by formation of a low surface energy adsorbed layer, they do not inherently contribute to the formation of the type of thicker film formed by antiwear additives such as ZDDP. In fact, high polarity ester basefluids may interfere with the action of antiwear additives either by excluding the antiwear additive from the immediate metal surface, or by solvating the initial products of antiwear additive decomposition such that they do not form a stable film [49].

Under very severe extreme pressure conditions, asperity contact inevitably results in metal–metal contact that can remove the protective metal oxide surface layer leading to welding between exposed metal surfaces. Under these conditions, scuffing wear can be minimized by the presence of components that lead to rapid reformation of a protective nonmetallic layer or metal oxide, sulfide, or equivalent. The oxygen content of ester lubricants can help minimize scuffing wear by serving as an available reservoir of oxygen for rapid oxide formation [46,47].

### 3.3.1.5 Polarity and Material Compatibility

The dipole moment of the ester functional group results in dipole–dipole and dipole-induced dipole interactions between ester basefluid molecules and other components. These forces are stronger and more localized than the dispersion forces that act between aliphatic hydrocarbons [50]. This has a direct impact on application performance in a number of ways.

Esters are good solvents for polar additives and for the polar initial products of thermal decomposition of lubricant components that lead to deposit and varnish formation. For most ester basefluid structures, the polarity is only slightly higher than that of mineral oil and such esters have excellent compatibility with most common types of lubricant basefluids. Ester basefluids can therefore be blended with the very nonpolar synthetic hydrocarbon basefluids or Gp III and III+ basefluids, to increase solubility of VI improver, detergent, and friction modifier additives that would otherwise be insoluble. In particular, esters may be used as the basefluid in additive packages, where the polar components are present at much higher concentrations. Furthermore, esters can be used in machinery that previously used mineral oil, PAO, PIBs, and most PAGs without significant cross-contamination problems.

However, for ester fluids with a high concentration of ester groups and high molecular weight, for example, complex esters derived from low carbon number raw materials, the polarity of the ester itself may be so high that it becomes immiscible with low polarity hydrocarbon basefluids at lower temperatures.

As noted earlier, polar esters may be preferentially adsorbed on contacting metal surfaces and modify mixed and boundary lubricty. However, they can also interact with other engineering components, in particular elastomeric polymers used in seals and gaskets. Elastomeric polymers have relatively open cross-linked structures and basefluid components may be absorbed into the polymer network, causing it to swell and soften. This effect can either be desirable to ensure effective sealing or undesirable if it leads to degradation of mechanical properties through chemical reaction of the polymer network or loss of low molecular weight polymer components. Thus, esters are frequently used as seal swell agents in synthetic hydrocarbon formulations to prevent elastomer shrinkage, but care is required to ensure elastomer compatibility where esters are used at high concentration.

Table 3.12 gives an overview of typical ester compatibility with commonly used elastomers and other engineering materials. It is important to note that the processing of the elastomer can have a major impact on its performance. As esters can be efficient solvents, they have the potential to extract any substances used during the manufacture of the elastomer. Elastomers from different suppliers can have significant difference in terms of the degree of cross-linking, fillers, and process residuals. Compatibility will also depend on the specific ester type and the contact conditions. Therefore, any information on ester compatibility with elastomers in general should be confirmed by appropriate tests on the specific materials of interest.

Finally, because of the stronger intermolecular bonding, ester basefluids typically have lower volatility than equivalent hydrocarbons, although the magnitude of this effect is small compared to the volatility reduction due to narrower molecular weight distribution.

The magnitudes of all of these polarity effects depend on the number of ester groups per molecule and the size of the molecules, as well as on how the ester groups are distributed, and the structures surrounding them. These effects of solvency, polymer compatibility, and fluid miscibility are of great
practical interest in many other areas of technology, and many attempts have been made to improve the theoretical understanding by quantitative group contribution methods [50]. However, the majority of these general approaches are either too oversimplified or too complex for practical application.

A widely used measure of ester lubricant polarity is the nonpolarity index or NPI, defined as [49]:

\[
\text{Nonpolarity index (NPI)} = \frac{\text{Total no. of atoms} \times \text{RMM}}{\text{No. of carboxylate groups} \times 100}
\]

where

- RMM is the relative molecular mass.

NPI of esters was originally developed to predict interactions of esters with polar system components, for example, elastomer swell and interference with the activity of polar antiwear additives. NPI is a measure of nonpolarity, so a high value implies a relatively low polarity [49]. High NPI esters have relatively low interactions with polar elastomers and antiwear additives.

However, because the NPI metric conflates two independent parameters, namely ester polarity and molecular weight, into a single value, it only correlates with experimental measurements when the effects of these two parameters are acting in the same direction. For prediction of compatibility of esters with nonpolar components, such as solubility in low polarity basefluids, it is not applicable.

### 3.3.2 Stability

#### 3.3.2.1 Thermal and Oxidative Stability

Because thermal and oxidative stress are normally encountered simultaneously in lubricant applications and their practical effects are difficult to separate, they are normally discussed together, but they are in fact distinct processes that can operate independently.

The ester group itself is highly resistant to oxidation, and slightly increases the oxidative stability of the adjacent carbon atoms [31,51]. The initial oxidation chemistry of ester basefluids is therefore primarily that of the substituent hydrocarbon groups. In principle, during the later stages of oxidative decomposition, hydroxyl and carboxyl functional groups formed by oxidation may undergo transesterification reactions with the ester groups originally present to form degradation products, which would not be formed so readily from hydrocarbons [52–54]. However, in practice, such extensive degradation would not occur during the normal lubricant lifetime.

The detailed processes involved in hydrocarbon oxidation have been intensively studied and are relatively well understood [55,56]. The chemistry will not be described in detail here, except to note that the initial attack on each molecule is by free radical abstraction of a hydrogen atom. The rate of this process depends on the stability of the free radical thus formed. The order of stability of C–H bonds in the structures likely to be encountered in lubricant basefluids is as follows (Ar = benzene ring):

#### 3.3.2.2 Chemical Stability

The chemical stability of esters is determined largely by the substitution pattern on the adjacent aromatic rings. Table 3.12 presents a summary of ester basefluid compatibility data.

<table>
<thead>
<tr>
<th>Suitable</th>
<th>Marginal</th>
<th>Unsuitable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastomers</td>
<td>Nitrile rubber (Buna-N, NBR)</td>
<td>Nitrile rubber (Buna-N, NBR)</td>
</tr>
<tr>
<td>Only if nitrile exceeds 36%</td>
<td>With nitrile content below 30%</td>
<td></td>
</tr>
<tr>
<td>Fluorosilicone rubber</td>
<td>Polyurethane</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>Fluorocarbon (Viton, Teflon)</td>
<td>Ethyl propylene terpolymer (EPDM)</td>
<td>Styrene–butadiene rubber (SBR)</td>
</tr>
<tr>
<td>Polyester (Hytrel)</td>
<td>Polycarbonate rubber</td>
<td>Butyl rubber</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>Ethylene–propylene copolymer (EPR)</td>
<td>Chlorosulfonated polyethylene (very marginal?)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polychloroprene (Neoprene) (very marginal?)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethylene/ acrylic (EAE)</td>
</tr>
<tr>
<td>Paints</td>
<td>Polysulfide (Thiokol)</td>
<td>Acrylic</td>
</tr>
<tr>
<td>Epoxy</td>
<td>Oil-resistant alkyds</td>
<td>Household latex</td>
</tr>
<tr>
<td>Baked phenolic</td>
<td>Phenolic</td>
<td>Polyvinyl chloride (PVC)</td>
</tr>
<tr>
<td>Two component</td>
<td>Single component</td>
<td></td>
</tr>
<tr>
<td>Urethane</td>
<td>Urethane</td>
<td>Varnish</td>
</tr>
<tr>
<td>Moisture-cured urethane</td>
<td>Industrial latex</td>
<td>Lacquer</td>
</tr>
<tr>
<td>Plastics</td>
<td>Polyurethane</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>Nylon</td>
<td>Polyethylene</td>
<td>Polyvinyl chloride (PVC)</td>
</tr>
<tr>
<td>Fluorocarbon</td>
<td>Polypropylene</td>
<td>Styrene (ABS)</td>
</tr>
<tr>
<td>Polyoxyethylene</td>
<td>Polysulfone</td>
<td>Styrene acrylonitrile (SAN)</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Acrylic (Lacite, Plexiglas) (very marginal?)</td>
<td>Polysulfones</td>
</tr>
<tr>
<td>Acetyl</td>
<td>Polyethylene oxide (Noryl)</td>
<td>Acrylic (Lexan) (very marginal?)</td>
</tr>
<tr>
<td>Polyamides</td>
<td>Phenylene oxide (Noryl)</td>
<td>Polyphenylene oxide</td>
</tr>
<tr>
<td>Metals</td>
<td>Cadmium</td>
<td>Lead</td>
</tr>
<tr>
<td>Steel and alloys</td>
<td>Zinc</td>
<td></td>
</tr>
<tr>
<td>Aluminum and alloys</td>
<td>Magnesium</td>
<td></td>
</tr>
</tbody>
</table>
60 Synthetics, Mineral Oils, and Bio-Based Lubricants

The relative stability of the molecule with respect to initial oxidative attack depends on the number of each of these bond types in the molecule and their steric accessibility. This leads to the following “rules of thumb” for oxidative stability of ester basefluids:

- Linear and quaternary branched esters are more stable than tertiary branched.
- Short chains are more stable than long.
- For polyol esters, the order of stability is PE > DiPE > TMP > NPG.
- Esters with olefinic unsaturation, for example, oleates, have lower oxidative stability.
- Esters containing olefinic polyunsaturation (conjugated or methylene-interrupted), for example, most vegetable oils, have very low oxidative stability [57,58].

Because the fundamental oxidation processes are essentially identical, conventional lubricant antioxidants have similar effectiveness in ester basefluids as in mineral oils or synthetic hydrocarbons. Note that comparisons of oxidation stability between fluids should only be carried out in the presence of equivalent and realistically high levels of antioxidants, since lightly processed mineral oil and vegetable oils may already contain trace (but variable) levels of naturally occurring free radical inhibitors whereas synthetic fluids do not [59–61].

Residual unreacted alcohol groups have been shown to have some antioxidant activity in ester basefluids due to side reactions, which decompose free radicals [62]. However, the effect does not become significant except at concentrations sufficient to increase the polarity of the fluid to a level that affects compatibility with other formulation components.

When thermal stability is measured in the absence of oxidative stress or catalysts, the ester linkage is normally the first site of thermolysis [11,12,63]. For esters with hydrogen atoms attached to the β carbon of the alcohol residue, the predominant decomposition pathway is β elimination to form carboxylic acid and olefin. The rate of this process is insignificant at most lubricant operating temperatures but becomes detectable at temperatures >275°C. For esters without β hydrogens, particularly the neopentyl polyl esters, this pathway is not possible and decomposition is by a free radical route at significantly higher temperatures (>315°C) [64,65]. These pathways are illustrated in Figure 3.6.

In contact with untreated ferrous metal, the decomposition temperatures of polyol esters are significantly reduced and decomposition is detected at temperatures as low as 200°C. However, in the presence of phosphate esters, such as tricresylphosphate (TCP), the metal surface is passivated and does not catalyze decomposition [66]. For this reason, neopentyl polyl esters used in high-temperature applications such as aviation gas turbine lubricants are normally additized with TCP.

Although separate thermal and oxidative degradation processes can be identified for ester basefluids under ideal conditions, in practical lubricant applications both processes occur simultaneously and interact in complex ways. Both oxidation and thermolysis of esters lead eventually to formation of carboxylic acid groups, which increase the acid value of the oil. Increased acid value can accelerate both processes and can also result in corrosion. Corrosion leads to increase in dissolved metals, which further catalyze both oxidation and thermolysis. Alternatively, oxidation processes may result in deposition of lacquers or varnishes on metal surfaces that inhibit further corrosion and surface-catalyzed fluid decomposition processes [67,68].

Metal catalysis has two roles in ester oxidation: it promotes the degradation of ester molecules by accelerating hydroperoxide decomposition and it affects condensation of oxidation products to form sludge and varnish. The rate of catalytic activity on oxidation rate in decreasing order of activity was found to be the following: low-carbon steel > stainless steel > lead > aluminum > brass > copper. The rate of catalytic activity on the deposit formation in decreasing order of activity was found to be the following: low-carbon steel > stainless steel > aluminum > brass > copper > lead [68].

Thus, practical optimization of thermal and oxidative stability of a formulated ester lubricant requires more than just basefluid structure optimization. Additives, including antioxidants (e.g., phenolics and amines), which act as free radical scavengers, antiwear additives (e.g., phosphites can act as hydroperoxide scavengers), metal passivators (e.g., phosphates), and metal deactivators (e.g., thiadiazoles), can act independently or synergistically to stabilize the formulation [55,61]. Decomposition products of these additives, however, particularly strong acids, may in turn have a detrimental effect on stability of the ester.

However, other things being equal, use of an ester basefluid designed and specified for inherently high thermal and
TABLE 3.13
Panel Coker Results on a Variety of Lubricants
Addivated with 1% Aminic Antioxidant (275°C for 22 h in Air)

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Visual Demerit Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral oil</td>
<td>3.95</td>
</tr>
<tr>
<td>PAO 6</td>
<td>&gt;4.00</td>
</tr>
<tr>
<td>Standard diester</td>
<td>2.50</td>
</tr>
<tr>
<td>Standard phthalate</td>
<td>1.07</td>
</tr>
<tr>
<td>Standard trimellitate</td>
<td>0.50</td>
</tr>
<tr>
<td>Optimized trimellitate</td>
<td>0.04</td>
</tr>
<tr>
<td>Standard TMP polyol ester</td>
<td>0.57</td>
</tr>
<tr>
<td>Optimized TMP polyol ester</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Visual rating system
>2.0 Thick carbonaceous deposits.
2.0–0.5 Low levels of deposits.
<0.5 Virtually no deposits.

oxidative stability can significantly improve lubricant performance. This is illustrated by the Panel Coker test results shown in Table 3.13. In the Panel Coker test, a lubricant formulation is dripped onto a heated steel plate at 275°C for 22 h in air. The lubricant is collected at the bottom of the plate and recirculated for repeated application to the steel plate. At the end of the test, the deposits are visually analyzed and given a demerit rating. Several lubricants addivated with 1% aminic antioxidant have been evaluated [107] (Table 3.13).

The results clearly show the effects described earlier. Aromatic phthalates give superior results to aliphatic diesters and polyol esters give superior performance to diesters. Use of highly oxidatively stable substituents such as 3,5,5-trimethylhexyl derivatives allows further optimization of oxidative stability within each ester category. The effect of residual metals (catalysts, neutralizing agents, etc.) can be seen in Table 3.14. It is clear that even small levels of certain contaminants can make a huge difference to the deposit-forming tendency of an ester. This reemphasizes the need for a tight specification.

3.3.2.2 Hydrolytic Stability
As noted earlier, the esterification reaction is reversible (Figure 3.1) and the ester products can in principle undergo hydrolysis, that is, reaction with water to regenerate the starting materials. In practice, this is rarely a problem in nonaqueous lubricant applications because at ambient temperatures the reaction rate constant is low and at elevated temperatures the residual concentration of water dissolved in the lubricant and available for reaction is low. However, an understanding of the fundamental processes involved in ester hydrolysis may be useful to prevent any potential problems developing.

Hydrolysis occurs via an acid-catalyzed mechanism and the reaction rate is proportional to the concentration of water and the concentration of acid. A hydrogen ion adds to the carboxyl oxygen of the ester linkage, converting it transiently to a carbonium ion, which rapidly adds water to form a positively charged tetrahedral intermediate. This tetrahedral intermediate then separates into carboxylic acid and alcohol, regenerating a proton that can then catalyze further reaction. The reaction is therefore autocatalytic. The more acid that forms, the faster the breakdown, which in turn creates more acid. However, water is consumed in the reaction, which can only progress if more water is available [69,70].

There are therefore two fundamental ways to control the rate of ester hydrolysis: reduce the water concentration or reduce the acid concentration. Other trace components such as residues of transition metal esterification catalysts may also act as catalysts and must be controlled, but unlike the acid, their effect is not autocatalytic [71].

The rate of hydrolysis can in principle also be limited by restricting temperature, although this is not practically possible for most lubricant applications.

Different ester structures have different inherent rates of hydrolysis. Aromatic esters and esters with branching at the 2 position of the acid group hydrolyze more slowly.

The extent of hydrolysis can be measured by monitoring the acid value of the fluid. Figure 3.7 shows the progress of hydrolysis for polyol esters in a sealed system, modeling the behavior of hermetically sealed refrigeration compressor lubricants. As water is consumed, the acid value of the polyol ester increases. When the water is completely consumed, the acid value reaches a plateau. The results illustrate that the final degree of “de-esterification” or hydrolysis is directly related to the amount of water present.

Use of a more hydrolytically stable structure reduces the rate of hydrolysis but does not change the final acid value (Figure 3.8).

In most cases, however, it is not possible to prevent water ingress during lubricant service life. Therefore, where hydrolytic stability is a concern, it should be controlled by a tight initial acid value specification and limiting the use of additives that may themselves hydrolyze more rapidly to produce acid by-products (e.g., phosphate esters).

There is also a theoretical possibility of interesterification or transesterification between different ester groups. As with simple hydrolysis, these processes are normally too slow to be significant, but can be catalyzed by some additives or contaminants. Transesterification may also occur if a fluid is subjected to thermal cycling where partial hydrolysis is followed by re-esterification at higher temperature. In blended basefluids this would result in change of composition due to
3.3.2.3 Shear Stability

Ester basefluids show similar shear stability to hydrocarbons of similar viscosity profiles. Materials of relatively low viscosity intended for use as basefluids show Newtonian rheology, with no dynamic shear thinning effects at shear rates likely to be encountered in service and no permanent shear thinning.

Blends containing higher viscosity materials such as high molecular weight complex esters may exhibit dynamic shear thinning. Mechanical degradation of long polymer chains leading to permanent shear thinning may become significant under very high shear conditions for materials with molecular weights above about 10,000 amu [47].

3.3.3 Safety, Health, and Environmental Properties

3.3.3.1 Biodegradability

The biochemistry of microbial attack on esters is well known in general outline and has been reviewed in detail [72–76]. The initial step is normally hydrolysis of an ester group, either abiotically or catalyzed by microbial lipase enzymes. The initial hydrolysis products have higher water solubility than the ester and are therefore more bio-available, so hydrolysis of the remaining ester groups occurs more rapidly, releasing the original acid and alcohol raw materials for biodegradation by microbial oxidation.

The biodegradability of ester basefluids is therefore primarily determined by the relative hydrolytic stability of the ester groups, and the biodegradability of the acid and alcohol raw materials [77,78].

Many different biodegradability test protocols have been developed to simulate different real world environmental conditions. Older literature (including previous editions of this work) often refers to initial biodegradability in fresh water determined by the CEC L-33-A-95 protocol, based on quantification of solvent-extractable non-polar components. This method is no longer used because it required halogenated solvents for extraction. A replacement (CEC L-103-12) has been developed [114]. However, most current specification criteria refer to Ready Biodegradability assessed by OECD 301 or equivalent methods which measure biodegradation by oxygen uptake or CO2 formation over 29 days [115]. Since the hydrolysis reactions increase polarity but do not involve oxygen uptake or CO2 formation, they contribute to initial biodegradability, but are not detected by ready biodegradability tests. Biodegradability values by CEC L-33-A-95 are therefore typically higher than values measured by OECD 301.

Esters of predominantly linear raw materials are generally readily biodegradable, particularly those derived from unmodified natural fatty acids. Esters with hydrolytically stable ester groups (particularly esters of aromatic and 2-alkyl substituted acids) or branched hydrocarbon chains have much lower biodegradability. Some typical values for biodegradability are shown in Table 3.15. However, it
TABLE 3.15
Biodegradabilities of Various Ester Lubricant Groups

<table>
<thead>
<tr>
<th>Ester Type</th>
<th>Monoesters</th>
<th>Diesters</th>
<th>Phthalates</th>
<th>Dimerates</th>
<th>Triestilates</th>
<th>Linear polyols</th>
<th>Branched polyols</th>
<th>Complex polyols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodegradability EC-L-33-A-95 (21 Days)</td>
<td>70–100</td>
<td>70–100</td>
<td>40–100</td>
<td>20–80</td>
<td>20–80</td>
<td>80–100</td>
<td>20–50</td>
<td>0–90</td>
</tr>
<tr>
<td>Biodegradability OECD 301B (28 Days)</td>
<td>30–95</td>
<td>10–80</td>
<td>5–70</td>
<td>10–50</td>
<td>0–40</td>
<td>50–99</td>
<td>5–40</td>
<td>10–90</td>
</tr>
</tbody>
</table>

should be noted that biodegradability tests are characterized by high variability. Significantly different results may be obtained for identical materials. For example, results ranging from 56–80% have been reported for the diester fluid diisotridecyl adipate. Ready biodegradability data are normally included in supplier literature and safety data sheets for ester lubricants.

3.3.3.2 Toxicty and Ecotoxicity

Esters used as lubricant basefluids generally have low acute toxicity by ingestion, skin absorption, or inhalation of airborne mist. However, concerns exist over possible long-term effects of some phthalate esters. Phthalates have been intensively studied due to their high volume use as plasticizers in consumer products. This has led to legislation restricting applications of some phthalates, including bis(2-ethylhexyl) phthalate (DOP) which was historically the most widely used PVC plasticizer. The materials of concern were not widely used in lubricant applications and have been largely substituted by other aromatic esters.

Lubricating oils can act as solvents for natural fats present in the skin and prolonged skin contact can result in physical damage due to defatting and potential for contact dermatitis. Because of their higher polarity, esters are generally better solvents than mineral oils of similar viscosity and can give rise to such effects more rapidly. Use of appropriate personal protective equipment is therefore particularly important when working with ester fluids.

3.3.3.3 Recycling and Reuse

Uncontrolled lubricant emissions to the environment due to losses in service and illegal disposal of used oils have been significantly reduced and globally approximately 50% of lubricant basefluids are now recovered. The majority of this material is used as fuel oil replacement in heating or power generation [16], but an increasing proportion is recycled for reuse as lubricant basefluid (see Re-refined Base Oils). However, because the application benefits of esters depend on their chemical structure, beneficial re-use in lubricant applications is only possible where materials can be strictly segregated. When esters are diluted in larger volumes of mineral oil, as in recovered automotive engine oils, the ester content becomes a low-value trace component, which may be removed as part of the heavy ends waste stream during reprocessing. End of life fate of ester basefluids therefore depends on the application. However, the large majority of used ester basefluids are currently eventually disposed of by combustion. Esters have slightly lower calorific value than mineral oil but otherwise have similar combustion characteristics.

3.3.3.4 Renewability

Some specifications for biolubricant applications include a requirement for a minimum bio-based or renewable content. This is calculated on the basis of the number fraction of carbon atoms in the product which were derived from renewable rather than petrochemical sources, not on the weight fraction of raw materials used. As noted above, some ester raw materials are commercially available based on either renewable or petrochemical sources and may be used interchangeably. For esters based on such raw materials, suppliers normally quote minimum and maximum values for renewable carbon content. The actual renewable content of a specific sample of ester lubricant can be verified by radiocarbon analysis (e.g., ASTM D6866 - 16 or equivalent).

3.4 APPLICATION AREAS

3.4.1 ENGINE OILS

Engine oils are the highest volume lubricant application for mineral oils and synthetic hydrocarbons, but relatively less significant for esters. Application requirements for automotive engine oils are reviewed in detail elsewhere in this book (Crankcase Lubricants). The long-term drivers for the automotive lubricant market are cost of ownership, reliability, and compliance with legislative standards for fuel economy and emissions (Automotive Trends). These application performance drivers translate into the following requirements for lubricant formulation properties [79–81]:

- Low viscosity at low temperatures for short-trip fuel economy, with acceptably low volatility even at increasing engine operating temperatures.
- Increased oxidation stability to increase lubricant lifetime and service intervals.
- Reductions in sulfated ash, phosphorus, and sulfur (SAPS) to ensure exhaust catalyst durability and compliance with emissions regulations.
- Improved wear protection, even with reduced levels of traditional antiwear additives and lower fluid viscosity.
- Retention of boundary friction modifier activity throughout the lubricant lifetime.
- Lower deposit formation, particularly carbonaceous cylinder deposits which may contribute to Low Speed Pre-Ignition (LSPI).
From the discussion of structure–property relationships in the previous sections, it is apparent that synthetic ester technology has the potential to deliver optimized viscosity/volatility performance, inherently high VIs, good solvency for oxidation products, and excellent frictional properties. Esters have therefore always attracted interest as potential engine oil basefluids and formulations have been developed based on straight ester fluids [116] and even on vegetable oils (Vegetable-Oil-Based Internal Combustion Engine Oil). However, the required application properties of engine oils cannot be delivered by basefluid properties alone; engine oils are complex formulations which rely on a range of additives (see Crankcase Lubricants). Additive technology has developed incrementally over many decades with mineral oils dominating the market. Conventional additive packages have therefore been designed for activity in mineral oils and are not optimized for performance in higher polarity ester fluids. Fully ester-based engine oil formulations have therefore not found application except in niche areas such as racing oils.

Current synthetic engine oils are based on PAOs, GTL basestocks, or Gp III+ oils as the main basestocks. These highly aliphatic hydrocarbons have lower polarity than Gp I and Gp II fluids and perform differently in terms of additive compatibility, oxidation product solubility, and elastomer swell. Low levels of ester basefluids are therefore typically added to give a blended basefluid with optimized polarity. Products of this type have been established in the marketplace since the 1960s [62,82]. Initial formulations were based on PAOs with a small amount of a phthalate (to act as a seal swellant). These formulations were followed by PAO/adipate ester blends where the diester was used at between 5% and 20%. Here, the ester acted as a seal swellant, an additive solubilizer, and made an important contribution to the desired deposit/volatility targets. A typical 5W/40 engine oil formulation of this type is shown in Table 3.16. Short chain TMP esters were preferred over diesters due to their superior thermal stability [81]. However, pricing of the short chain C₈-C₁₀ acid raw materials has been volatile over recent years which has disincentivized use of the TMP esters.

Current formulations typically use ester dose rates of <10%. At these low levels the properties of the ester make a relatively low contribution to the viscosity of the formulation. The polarity and solvency characteristics of the ester are therefore of more relevance than its viscosity and VI. Effectively the ester behaves more as a functional additive than a basefluid component. However, because of the large size of the automotive engine oil market and the increasingly high penetration of synthetics, this sector remains a large and growing application area for ester fluids.

### 3.4.2 Automotive Gear

The automotive gear oil market is subject to the same overall industry drivers as crankcase oils [83], with the additional feature that new technologies with distinct lubrication requirements, such as automatic dual clutch (DCT) and continuously variable transmissions (CVT), are increasingly important (see Transmissions and Transmission Fluids, Automotive Gear Lubricants).

The expectation for fill-for-life gear lubrication and demands for improved fuel economy leading to smaller, lighter transmission systems with reduced lubricant charge demand optimized thermal, oxidative, and shear stability to cope with higher stresses for longer lifetimes. Fuel economy and user expectations for smooth shifting demand optimized lubricity.

The main advantages of esters in this sector are their relatively high VIs, and low-temperature flow properties. This allows synthetic gear oils to operate over a much wider temperature range than conventional oils. Also the good shear stability of ester-based oils gives major performance advantages.

Synthetic manual transmission fluids, like synthetic crankcase oils, are typically based on PAO blended with ester as a minor component for polarity modification [84]. A typical ester-based 75W gear oil can be found in Table 3.17. Fluids for automatic DCT systems are generally similar to manual transmission fluids with adjustments to optimize anti-shudder performance.

Fluids for toroidal CVT systems require very high EHL friction. This implies fluids having very high P–V coefficients so that the lubricant transiently solidifies in the EHL contact, enabling it to transmit traction forces. The structural requirements for such traction fluids are well understood, but hydrocarbons with appropriate structures are difficult to manufacture. Ester-based fluids have therefore been extensively investigated [85]. However, although their synthesis is more straightforward, the high flexibility of the ester linkage limits the maximum traction coefficient, and hydrocarbon technology has become the most widely adopted (see Cyclohydrocarbons) although esters are still of interest as minor basefluid components for rheology optimization [86,87].

### TABLE 3.16

**Typical Synthetic Passenger Car Motor Oil Formulation**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester basestock</td>
<td>5–20</td>
<td>Diesters or TMP polyol esters</td>
</tr>
<tr>
<td>Friction modifier</td>
<td>0–3</td>
<td>Amide/ester organic FM MO-based inorganic FM</td>
</tr>
<tr>
<td>Hydrocarbon oil</td>
<td>40–70</td>
<td>PAO, hydrocracked, alkyl naphthalene</td>
</tr>
<tr>
<td>VI improver</td>
<td>8–15</td>
<td></td>
</tr>
<tr>
<td>Additive pack</td>
<td>10–20</td>
<td>Antiwear, detergent inhibition pack, etc.</td>
</tr>
</tbody>
</table>

### TABLE 3.17

**Typical Synthetic Gear Oil Formulation (e.g., 75 W)**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester</td>
<td>5–30</td>
<td>Diesters polyols</td>
</tr>
<tr>
<td>PAO</td>
<td>60–85</td>
<td>Blends of PAO 4, 6, 40, and 100</td>
</tr>
<tr>
<td>Additive pack</td>
<td>7–13</td>
<td></td>
</tr>
</tbody>
</table>
3.4.3 Two Stroke

Ester lubricants offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixtures. The good solvency characteristics result in lower deposits and less engine fouling. The lower volatility and boundary friction allow use of lower viscosity oils, removing the requirement for high-viscosity mineral oils (brightstock) and allowing leaner burn ratios. In turn, this significantly reduces exhaust fume (smoke) due to unburnt or partially combusted lubricant [88]. The excellent solubility of esters also allows them to be used without solvents (which are usually added to conventional two-stroke oil to help miscibility with the fuel and low-temperature fluidity). A typical ester-based formulation can be seen in Table 3.18.

The leaner burn ratios result in reduced oil emissions, which is a benefit in environmentally sensitive applications such as marine outboard engines and chainsaw motors. The high biodegradabilities of esters, low ecotoxicity, and clean-burn characteristics of ester formulations make them excellent candidates for “environmental considerate” labeling such as Blue Angel in Germany. Dimerate esters have been widely used [89]. However, despite their high renewable content, dimerate esters have relatively poor biodegradability. Therefore, where biodegradability is an important factor, NPG or TMP-based polyols have replaced dimersates [90]. Biodegradable polyol ester formulations (>70% OECD 301B) for use in chain saw and Jet Ski applications are in commercial use.

Low-temperature performance is important in some applications, such as engines used to power snowmobile-type vehicles. Therefore, esters with low pour points of down to −56°C are very suitable for these applications.

3.4.4 Aviation Turbine Oils

The bulk of aviation lubricant demand is for gas turbine (jet engine) lubricants (see Gas Turbine Oils). Aviation turbine oils require an extraordinarily wide fluid temperature range because of the combination of high engine operating temperatures and very low ambient temperature during high altitude flight. The oil must be stable and involatile enough to provide adequate lubrication and cooling during operation, while remaining fluid at very low temperatures in order to allow in-flight “re-lighting” in the event of temporary engine failure. Mineral oils were found to be unsuitable although special naphthenic oils were used for some military applications in the former USSR. Esters rapidly became the preferred basefluid for both civil and military aviation elsewhere [5]. Efforts continued to identify even higher performing fluids and a very wide range of alternative SBFs have been evaluated. Some have found limited military use (see Polyphenyl Ethers) [117] but esters have remained the most widely used fluid type, delivering performance adequate for applications including civil supersonic transport (SST) between 1969 and 2003 [118].

The first generation of oils (Type I) were diesters, typically based on bis(2-ethylhexyl) sebacate, but these have been replaced in most applications by more thermally stable polyol esters. Diesters are still used in less demanding applications such as small private aircraft or turbo-prop engines [91].

Since gas turbine engines were originally developed for military aircraft, lubricants were first controlled by U.S. military specifications MIL-L-7808 (3 & 4 cSt oils) and MIL-L-23699 (5 cSt oils). (Now MIL-PRF-7808L, MIL-PRF-23699G [119]). 5 cSt oils were preferred for civil aviation turbines and MIL-PRF-23699 became the default specification in the civil aviation industry. Subsequently, it was recognized that it was not appropriate for the U.S. military to manage material accreditations for a global civil application. Responsibility for civil aviation specifications was been transferred to SAE (Society of Automotive Engineers) and a civil specification developed as SAE-AS5780 [120].

SAE-AS5780 is closely based on MIL-PRF-23699 and industry literature still refers to both specifications. MIL-PRF-23699 recognizes three sub-types of 5 cSt oils; standard (STD), high thermal stability (HTS), and corrosion inhibited (C/I). SAE-AS5780 recognizes two classes, Standard Performance Class (SPC) and High Performance Class (HPC). SAE, SPC, and HPC requirements are very similar to requirements for MIL, STD, and HTS, respectively, although there are minor updates. (Civil aviation does not generally require C/I performance. C/I conformance was generally achieved through formulation rather than basefluid modification.)

AS5780 SPC products currently represent the large majority of the aviation turbine lubricant market, although other grades are produced at significant volume for military aviation, spin-off industrial applications (e.g., aero-derivative turbines), and minor civil aviation applications such as auxiliary power unit oils. AS-5780 HPC class is defined as “Lubricant intended for more demanding service in which engine operating conditions and/or service durations require higher thermal capability.”

For both SPC and HPC fluids, the specification is based around test requirements which are divided into:

- Physical Properties
- Chemical Properties
- Stability Properties
- Deposition Properties
- Tribological Properties

Physical and tribological property requirements for HPC lubricants are identical to those for SPC. Chemical property
requirements are almost identical, but permit slightly more rapid swelling of fluorocarbon elastomers by the HPC fluids. The distinction between SPC and HPC fluids is primarily associated with stability at very high temperatures as measured by change in fluid viscosity, increase in acid number, and formation of solid sludge or deposits.

The specifications define physical properties and application performance, but do not dictate chemical composition. Section 3 of SAE-AS5780 requires only that the basefluid be based on polyol ester, plus some restrictions on permitted additives. In particular, the standard allows for sale of products having different chemical compositions under the same marketing brand name, as long as each different formulation has been independently qualified.

There are many different combinations of POE raw materials which can be used to achieve the required physical properties. The range of raw materials with preferred cost or availability has changed over time, leading to commercialization of different product chemistries. Most 5 cSt fluids are based on PE esters of mixed short chain acids with carbon numbers in the range \( C_7 - C_{10} \) \([121]\) but there is some use of TMP esters of linear \( C_7 - C_{10} \) \([122]\). Aviation POE basefluids were originally developed based on tech PE, having a composition close to the crude reaction product. The DiPE and other higher polyol components increase product viscosity. The higher structural diversity also inhibits solidification, so tech PE esters have higher viscosity (and VI) and lower pour points, than the equivalent mono PE products. Consequently, aviation POEs could not easily be reformulated onto straight mono PE and producers have continued to make use of tech PE, although tech PE has increasingly become a niche product which is no longer lower cost than pure mono PE.

Because they have the same physical property requirements, HPC fluids are based on the same general types of ester basefluids as SPC fluids. However, the products and manufacturing process are varied using one or more of three basic approaches to improve oxidative stability; POE structure optimization, elimination of unstable impurities, and optimizing use of additives.

The different acid raw materials used in POE manufacture vary in inherent oxidative stability depending on their structure. POE stability can be improved by restricting the raw materials used to only the most stable acids. For linear acids, stability decreases with increasing chain length. Most branched acids have lower stability, but one particular branched acid, 3,5,5-trimethylhexanoic acid (also known as isononanoic acid, iC9) has particularly high stability. Inclusion of some iC9 acid in a formulation therefore tends to improve oxidative stability \([92]\). Also, the branched structure makes a higher contribution to viscosity, which allows a reduction in the average carbon number of the overall fatty acid mix. This further improves stability, although at the expense of some decrease in VI and lubricity and relatively higher volatility. Use of a mixture of purified mono PE and purified DiPE gives better thermal stability than tech PE.

Polyol ester turbine oils are always additized with approximately 1–2% of an aromatic phosphate ester, normally tricresyl phosphate (TCP) to passivate metal surfaces and prevent catalytic decomposition and also provide some antiwear activity. There has been concern that use of TCP in combination with fluids based on TMP esters could lead to formation of TMP phosphate (TMP-P) which is neurotoxic \([93]\), SPC fluids are generally formulated with a mixture of alkylated diphenylamine and phenyl \( \alpha \)-naphthylamine antioxidants for high-temperature stability. Minor amounts of other additives including corrosion inhibitors and antifoams may also be present.

Reclamation of polyol ester aviation lubricants to original specification standards has been demonstrated \([78]\) but is not currently practiced.

### 3.4.5 Hydraulic Fluids

Hydraulic fluids are used primarily to transmit power but are also required to provide adequate lubrication to moving parts, e.g., motors and actuators in the hydraulic circuit. In principle, the only heat source is from frictional and viscous losses, so service temperatures and thermal stresses on the lubricant are generally lower than for engine oils. The large majority of hydraulic fluids are formulated with MO basefluids, with viscosity in the range ISO 22 to ISO 68, depending on the expected operating temperature. The reason for selection of esters or other SBF or natural triglycerides in hydraulics are most often due to the potential impact of leaks from the high-pressure sections. In mobile equipment, these represent environmental pollution and biodegradability may be a legal requirement. In factory systems, high pressure oil leaks may form oil mists which are a flammability hazard and high flash and fire points may be required. These sectors therefore represent the major uses of esters in hydraulics. Esters and other SBFs may also be preferred for hydraulic systems operating in extremely low ambient temperatures, where MOs having sufficiently low viscosity would have unacceptably low flash point \([Y2]\).

#### 3.4.5.1 Biodegradable Hydraulic Fluids

Biodegradable hydraulic fluids have been a major growth area for esters over recent decades (see Environmentally Friendly Hydraulic Fluids). The major application is in mobile hydraulic equipment used in environmentally sensitive areas, for example, in forestry and water-course maintenance. Such equipment pumps hydraulic fluid at high pressure through flexible hoses and any damage to the hoses results in loss of fluid to the environment.

As noted earlier, some labelling schemes also require that the lubricant should have a minimum renewability content (i.e., to use natural-based feedstocks). Table 3.19 compares the biodegradability versus renewable content for a range of lubricants \([94]\). It can be clearly seen that esters allow for the development of high-biodegradability, renewable, and high-performance hydraulic fluids.

There are three market segments for biohydraulics, defined by type of equipment and operating temperature. For low severity, high loss equipment operating up to 60°C, mainly farming equipment, vegetable oils may be used. For medium severity, medium loss applications up to 100°C, mainly in
forestry operations, synthetic esters with a high content of renewable raw materials, for example, TMP oleates are used. High severity applications, particularly in the construction industry, may require fluids capable of extended lifetimes at operating temperatures in excess of 100°C. Development of biodegradable fluids with the necessary high oxidative and thermal stability has been a major challenge for the industry. It is also essential for hydraulic fluids intended for outdoor use in mobile equipment to possess satisfactory pumpability at the prevailing ambient temperatures during the initial period of operation with cold fluid. All types of hydraulic fluids increase in viscosity and eventually solidify as temperature decreases.

An understanding of structure–property relationships has been used to develop two distinct approaches to higher performing biodegradable hydraulic fluids. The first route is to improve TMP oleate type products by modifying the fatty acid raw material composition so as to increase the degree of saturation, reduce the average alkyl chain length, and decrease molecular symmetry. Using this approach, it has been possible to design products containing 85% renewable raw materials, but with oxidative stability and low-temperature fluidity greatly superior to standard TMP oleate products. Figure 3.9 compares the change in viscosity with time during storage at −30°C for standard TMP oleate and new-generation product [16,94].

The alternative route is to redesign the molecular structure more fundamentally, using neopentyl polyol alcohols and saturated acids to optimize thermo-oxidative stability and biodegradability. This approach significantly reduces the renewable raw material content but has led to development of products combining ready biodegradability with thermo-oxidative stability, superior to that of mineral oil-based formulations [16]. In terms of hydrolytic and oxidative stability, the basefluids show the following trend (decreasing order of stability): saturated polyols > diesters > modified TMP oleates > TMP oleates > high oleic sunflower oil > rapeseed.

Table 3.20 gives a typical formulation for an ester-based biohydraulic fluid. The ester selected will be dependent on the trade-off between cost, renewability, oxidative stability, biodegradability, and low-temperature pumpability.

### 3.4.5.2 Fire Resistant

Ester-based fire-resistant hydraulic oils are classified as HFUD fluids [91]. They compete in this market sector with natural triglycerides and with phosphate esters (HFDR fluids) (see Fire-Resistant Hydraulic Fluids, Neutral Phosphate Esters). Ester HFUD fluids are normally based on long chain polyol esters such as TMP oleates, similar to those used in medium severity biodegradable hydraulic oils [131,132].

Fire resistance of ester HFUDs is due only to their low volatility and thermal stability, whereas the phosphorus content of phosphate esters further lowers their heat of combustion, and formation of phosphorus oxide combustion products inhibits flame spread. Phosphate esters therefore have superior inherent fire resistance. However, phosphate esters generally have inferior VI and pour point, lower thermal stability, and are more aggressive to seals and coatings than triglycerides and polyol esters. Hybrid fluids based on blends of organic and phosphate esters have been evaluated [133] but most applications require the performance characteristics of one type or the other. To enable polyol esters to pass certain fire-resistance tests, for example, the factory spray test, 0.5–2% of a VI improver-type polymeric additive may be added. This additive helps modify the spray pattern of the fluid pumped through the nozzle by increasing the droplet size. Larger droplets of lubricant are much more difficult to ignite. A typical HFUD fluid formulation can be seen in Table 3.21. [131]

### TABLE 3.20

**Typical Ester-Based Biodegradable Hydraulic Fluid**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester basestock</td>
<td>&gt;95</td>
<td>TMP oleate ester or modified TMP oleates or diesters or polyols or complex polyols</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>1–2</td>
<td>Phenolic + aminic</td>
</tr>
<tr>
<td>Metal deactivator</td>
<td>0.2–0.5</td>
<td>Metal-free</td>
</tr>
<tr>
<td>Antisewear</td>
<td>0.4–1.0</td>
<td>Metal-free</td>
</tr>
<tr>
<td>Antifoam</td>
<td>&lt;50 ppm</td>
<td>Metal-free, usually non-silicone</td>
</tr>
</tbody>
</table>

### FIGURE 3.9

Low-temperature storage stability of standard TMP oleate vs modified.

### TABLE 3.19

**Comparison of Lubricant Biodegradability and Renewability**

<table>
<thead>
<tr>
<th>% OECD 301B Biodegradability</th>
<th>% Renewability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable oil 70–100</td>
<td>100</td>
</tr>
<tr>
<td>Mineral oil 20–40</td>
<td>0</td>
</tr>
<tr>
<td>PAO</td>
<td>20–60</td>
</tr>
<tr>
<td>Alkyl benzene 5–20</td>
<td>0</td>
</tr>
<tr>
<td>Diesters 40–80</td>
<td>0–80</td>
</tr>
<tr>
<td>Aromatic ester 5–70</td>
<td>0</td>
</tr>
<tr>
<td>Polyl ester 20–99</td>
<td>0–85</td>
</tr>
<tr>
<td>Complex ester 20–90</td>
<td>0–100</td>
</tr>
<tr>
<td>Polyglycerol 10–70</td>
<td>0</td>
</tr>
<tr>
<td>Complex polyols</td>
<td>0</td>
</tr>
<tr>
<td>Diesters 40–80</td>
<td>0–80</td>
</tr>
<tr>
<td>Alkyl benzene 5–20</td>
<td>0</td>
</tr>
<tr>
<td>Aromatic ester 5–70</td>
<td>0</td>
</tr>
<tr>
<td>Polyl ester 20–99</td>
<td>0–85</td>
</tr>
<tr>
<td>Complex ester 20–90</td>
<td>0–100</td>
</tr>
<tr>
<td>Polyglycerol 10–70</td>
<td>0</td>
</tr>
<tr>
<td>Complex polyols</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 3.21
Typical Ester-Based HFDU Fluid

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester basestock</td>
<td>&gt;96</td>
<td>NPG, TMP, PE polyol ester (e.g., TMP oleate)</td>
</tr>
<tr>
<td>VI improver</td>
<td>1–2</td>
<td>Droplet modifier</td>
</tr>
<tr>
<td>Additive pack</td>
<td>1–2</td>
<td>Antiwear, antioxidant, anticorrosion, etc.</td>
</tr>
</tbody>
</table>

TABLE 3.22
Typical Ester-Based Air Compressor Formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester basestock</td>
<td>5–98</td>
<td>Diester or aromatic esters or polyol esters</td>
</tr>
<tr>
<td>Other basestock</td>
<td>0–93</td>
<td>PAO or PAG</td>
</tr>
<tr>
<td>Additive</td>
<td>1–5</td>
<td>Antioxidant, antiwear, anticorrosion, antifoam</td>
</tr>
</tbody>
</table>

3.4.6 Air Compressor

The main advantages of esters in air compressor systems are their high stability, good solvency, and low volatility, which have important safety implications as well as offering potential for lower total cost operation and cleaner downstream gas for sensitive applications such as breathing air.

Air compressor oils are required to act as lubricants, coolants, and oil seals at moving parts. For safety reasons, it is critically important to minimize formation of carbonaceous deposits around the outlet/discharge valves, where high temperature, high system pressure, and high partial pressure of O₂ present a real risk of fire and explosion [95]. Ester oils can be designed for extremely high oxidative stability, and their solvency characteristics further reduce deposition of sludge and varnish.

Selection of high oxidative stability basefluids has a secondary benefit to the user in terms of extended drain intervals (by as much as 8- to 10-fold) and improved energy efficiency, as well as other associated cost savings, such as less frequent replacements of oil filters and air/oil separators [96].

The low volatility of esters compared to mineral oils of the same viscosity also results in reduced carryover of lubricant into the gas. These properties, coupled with their higher flash and autoignition temperatures, and low order of toxicity for vapor inhalation and ingestion, make them considerably safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradability can also lessen their environmental impact [97].

Because of their high solvency, aromatic esters and particularly trimellitate esters are widely used in air compressors. Mixed diester/polyalkylene glycol systems can also be used, exploiting the clean-burn characteristics of the PAG [98]. Because of the high polarity of these systems, care is required in the specification of elastomeric sealing materials: the use of Viton is usually recommended.

A typical ester-based air compressor formulation can be seen in Table 3.22.

3.4.7 Refrigeration Compressor

A major growth sector for synthetic ester basefluids during the last two decades has been as HFC-compatible refrigeration compressor lubricants. Refrigeration compressor lubricants present a range of unique performance requirements.

They generally operate in a sealed refrigeration circuit, having no exposure to atmospheric oxygen. However, many systems, particularly domestic appliances, are sealed-for-life and expected to operate for 10–20 years. Domestic appliance compressors are typically driven by an internal electric motor. Some of the compressor lubricant is inevitably circulated with the working fluid through the hot and cold sections of the circuit and must therefore have good miscibility with the working fluid and good low-temperature fluidity in order to ensure adequate oil return. The working fluid condenses at delivery pressure to a low-viscosity liquid which dilutes the lubricant. Therefore, in addition to providing adequate lubrication, the compressor lubricant must have outstanding thermal stability and long-term compatibility with other system materials including the working fluid, electrical insulation, elastomers etc. (see Refrigeration Lubricants, Compressors, and Pumps, Natural and Process Compressors).

Polyol esters were long known to be suitable for use as refrigeration compressor lubricants [123], having lower tendency to foam formation at low temperature than napthenic mineral oils. However, they were not widely used prior to the phase out of chlorofluorocarbon (CFC) refrigerant gases. The hydrofluorocarbon (HFC) refrigerants which replaced CFCs in many applications because of their lower Ozone Depletion Potential (ODP), also have a much higher polarity and traditional refrigeration lubricants based on napthenic mineral oils were found to have inadequate miscibility. Polyol esters have become the most widely used basefluid for use with most HFC gases in stationary applications, with polyvinyl ethers (PVEs) as the only real alternative [124]. Mobile air-conditioning systems are typically mechanically driven and therefore do not require high dielectric strength and low conductivity in the lubricant. End-capped PAGs are more commonly used in these systems (see Polyalkylene Glycols) [99].

A very wide range of compressor types including reciprocating, rotary, and screw compressors having widely different lubricant requirements are used in refrigeration systems. Together with the possibility for lubricant dilution by refrigerant gas, this requires a correspondingly broad range of fluid viscosities. POE refrigeration lubricants are commercially available in viscosity grades from ISO 7 to ISO 320.

Low-viscosity oils (<ISO 10) are based on NPG polyols; high-viscosity oils (>ISO 150) are based on DiPE polyols or complex esters. Intermediate viscosity products are based on pure PE polyols themselves or blended with NPG or DiPE.
Esters have not been widely used because of concerns over potential reaction with phosphate ester additives under fire conditions [92]. The acids used are generally mixed C₅–C₈ linear or C₈–C₁₀ branched, with ester product compositions tailored to ensure optimum compatibility with the gas [125].

Because the fluid has no contact with atmosphere, high levels of antioxidant additives are not required, although low levels of phenolic antioxidant are normally used to ensure stability in storage. Aromatic phosphate esters are often used as antiwear agents. Refrigeration lubricants are manufactured to very low moisture content to prevent ice formation in cold sections, so hydrolytic stability is not a problem. However, some manufacturers use epoxide acid catcher additives as a precautionary measure to control any increase in acid value. Gas bubbles in the fluid have a noise-damping effect and foam control agents are sometimes added to control compressor noise. A typical ester-based formulation can be seen in Table 3.23.

The refrigeration compressor lubricant market continues to evolve as regulatory attention has switched to minimizing Global Warming Potential (GWP) as well as ODP. This is likely to involve progressive phase out of R134a and blends over the coming years. Where the replacement gases are also HFCs, for example R32 replacing R410A in air-conditioning, it is likely that POEs will remain the preferred basefluid [126].

Esters may also be used as compressor lubricants in other non-air applications, such as gas transmission and chemical plant process gas systems, wherever their compatibility (polarity, solvency, and reactivity) with the compressant is better than that of mineral oils or other synthetics.

### 3.4.8 High-Temperature Chain Oils

Many manufacturing products today require extreme heat, either in the manufacturing, finishing, curing, or drying process. Application areas such as textile factories, car plants, and pottery/glass kilns use roller chains, stenter chains, and sliding chains (see High-Temperature Chain Oils). Lubricants for these chains see temperatures above 150°C, and sometimes as high as 1000°C. Esters are required that have high oxidative stabilities, low volatilities, and excellent clean-burn properties. A typical ester-based chain oil formulation can be seen in Table 3.24.

Dimerates tend to be used in cost-effective formulations. For higher temperatures, trimellitates and PE/diPE polyol esters tend to be favored [100]. Trimellitates tend to have a poorer stability than POEs but decompose to leave a soft (easy to remove) deposit. Polyol esters decompose at higher temperature but can leave behind a harder deposit (varnish). Often blends of trimellitates and polyols are used to obtain the correct balance.

VI improvers are often used as tackifiers/thickeners. For very oxidative stable formulations, high-viscosity polymeric esters have been used as a tackifier.

### 3.4.9 Metalworking Fluids

Metalworking fluids represent a highly diverse and fragmented sector including high- and low-temperature rolling oils, coolants for cutting and drilling operations, and lubricants for stamping and forming operations (see Metalworking Fluids) as well as quenching oils used for controlled cooling of castings [127]. The contact conditions normally involve intentional deformation of the metal and generation of new metal surface and are therefore very different from the rolling and sliding contacts found in the majority of other applications. Esters can be used either as additives (typically used at a treat-rate of 5%–15%) or as the base oil. The primary reason for using an ester as additive is to reduce the friction between tool and work piece, with the specific aims of improving surface finish and/or extending tool life. Their use as base oils is usually the result of some additional requirement, such as higher lubricity, minimizing misting, or a desire for a controllable level of biodegradability [134]. The use of esters is set to increase as machining techniques develop and as greater consideration is given to the environmental and health aspects of metalworking formulations.

A wide range of esters are used in neat oils, including monoesters (e.g., methyl oleate or isopropyl palmitate), dies- ters (e.g., propylene glycol diolate), and polyol esters (e.g., TMP triolate).

In water-miscible fluids, the most commonly used esters are isopropyl oleate, iso-butyl stearate, neopentylglycol diolate, and a number of TMP derivatives. A common feature of the esters used in water-miscible formulations is their greater resistance to hydrolysis as compared to methyl esters.

Natural oils and fats, such as coconut and palm oils, and synthetic esters, for example, esters of NPG, TMP, and PE, are widely used in many rolling formulations [135]. Complex

### TABLE 3.23

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester</td>
<td>&gt;95</td>
<td>Polyol ester (e.g., NPG, PE, DiPE)</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0–1000 ppm</td>
<td>Storage stabilizer</td>
</tr>
<tr>
<td>Antimicrobial</td>
<td>0–5</td>
<td>To reduce wear</td>
</tr>
<tr>
<td>Foaming agent</td>
<td>0–1000 ppm</td>
<td>To reduce noise</td>
</tr>
</tbody>
</table>

### TABLE 3.24

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester</td>
<td>&gt;75</td>
<td>Dimerate</td>
</tr>
<tr>
<td>Tackifier/thickeren</td>
<td>2–20</td>
<td>VI improver (PIB, PMMA) polymeric esters</td>
</tr>
<tr>
<td>Additive pack</td>
<td>2–8</td>
<td>Antioxidant, antiwear, anticorrosion</td>
</tr>
</tbody>
</table>
Esters have been evaluated for minimum quantity lubrication in cutting oils, [101] and may find application in formulations developed to substitute for medium chain chlorinated paraffins [135], either alone or in combination with EP additives, such as phosphate esters and sulfurized esters or olefins.

### 3.4.10 Greases

Esters are commonly used as basestocks for greases when one or more of the following properties are required:

- Low-temperature flow (e.g., aircraft wheel bearings)
- High-temperature applications
- Biodegradability
- Low toxicity (e.g., food-use applications)

A range of ester types (diesters, phthalates, trimellitates, pyromellitates, and polyols) are used in this application (see Synthetic Greases). Esters can be used in combination with traditional carboxylate soap gellant technology, although there is a possibility of some ester saponification occurring, which may modify the properties. Ester basefluids are more commonly used in combination with nonstandard thickener technologies such as polyureas [102].

### 3.4.11 Drilling Muds

Ester-based organic compounds are one type of SBF added to drilling muds used during offshore oil-drilling operations. Since 1990, the oil and gas extraction industry developed SBFs with synthetic and nonsynthetic oil-like materials as the basefluid to provide the drilling performance characteristics of traditional oil-based fluids (OBFs) based on diesel and mineral oil. Drilling fluids are needed to cool and lubricate the drill bit and to help bring rock cuttings to the surface.

Ester-based drilling fluids have the following advantages over OBFs:

- Faster and deeper drilling
- Greater worker safety through lower toxicity
- Elimination of polynuclear aromatic hydrocarbons (PAHs)
- Excellent biodegradability and lower bioaccumulation potential
- Potentially less drilling waste volume
- Reduced drilling costs

Government and industry research found that several synthetic-based fluids used in mud formulations exhibited similar biodegradation profiles to mineral oils offering no apparent benefits. As a result, the UK government decided to reduce the discharge of a number of synthetic fluids. Esters were not subjected to the same reduction program because of their rapid biodegradation [103] and continue to find application [128]. A typical ester-based drilling formulation can be seen in Table 3.25.

### 3.4.12 Transformer/Dielectric Fluids

Electrically insulating dielectric fluids are used to provide cooling in high power transformers. Operating temperatures are generally relatively low, but very long service lifetimes (10–20 years) are expected. As with hydraulic fluids, the majority of the market is mineral oil based, but there is a large sub-segment where fire resistance is necessary. Historically, polychlorinated biphenyls (PCBs) were used in this application and a market developed for other SBFs including esters when use of PCBs was prohibited. Short chain pentaerythritol esters were found to be suitable and have taken and maintained a significant market share [104,105]. The ester fluids used are PE esters of mixed short chain fatty acids, similar to those used in aviation turbine oils. In addition to fire resistance, secondary benefits of polyol esters include higher water solubility, which extends the lifetime of cellulose-based solid insulator components, and biodegradability in the event of spillage. The products are typically stabilized with low levels of phenolic antioxidant and corrosion inhibitor additives.

A long-standing industry standard specification for synthetic ester dielectric fluids specifies use of pentaerythritol esters [129] and includes requirements for viscosity, pour point, and flash point which effectively constrain the range of suitable acid raw materials to mixed linear/branched C7–C10 acids. As for appliance refrigeration lubricants, application-specific performance requirements for transformer fluids include very high electrical resistivity and dielectric strength (breakdown voltage) and low dielectric dissipation factor. These parameters are mainly controlled by impurities rather than bulk composition and require low acid and hydroxyl value as well as high levels of fluid cleanliness since particulate contamination can provide a pathway for arcing. Dissipation factor can be impacted by traces of other ester lubricant basefluid types, so control of batch to batch cross-contamination is critically important where ester dielectric fluids are manufactured on multi-product plants. Dielectric fluids are normally supplied degassed and are vacuum-treated to remove dissolved gases before packing.

More recently, highly purified natural triglycerides similar to those used in HETG hydraulics have also been found

**TABLE 3.25**

**Typical Ester-Based Drilling Lubricant Formulation**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Dose Rate</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester</td>
<td>20–30</td>
<td>Fatty ester</td>
</tr>
<tr>
<td>Water</td>
<td>10–20</td>
<td></td>
</tr>
<tr>
<td>Calcium chloride brine</td>
<td>3–8</td>
<td>Alkalinity</td>
</tr>
<tr>
<td>Viscosifier</td>
<td>0.5–3</td>
<td></td>
</tr>
<tr>
<td>Primary emulsifier</td>
<td>0.5–3</td>
<td></td>
</tr>
<tr>
<td>Secondary emulsifiers/wetting agent</td>
<td>0.25–1</td>
<td></td>
</tr>
<tr>
<td>Fluid loss control</td>
<td>0.25–1</td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>0.5–2</td>
<td>Alkalinity</td>
</tr>
<tr>
<td>Weighting agent</td>
<td>40–60</td>
<td>e.g., barite or clay</td>
</tr>
</tbody>
</table>
Esters to be suitable as fire-resistant and biodegradable transformer fluids [130] and these products now represent a higher overall volume than the longer established synthetics. However, their lower oxidative stability and relatively high pour points mean that they are mainly used in sealed transformers, taking market share from MO rather than synthetic esters.

3.5 MARKETING AND ECONOMICS

3.5.1 MANUFACTURERS

A list of companies who both produce and market synthetic ester basefluids, the relevant trade names, and main product types (diesters, short chain polyol esters, oleochemicals) are given in Table 3.26. Table 3.26 does not include companies who produce esters for internal use only.

Significant changes in recent years include the following:

Nyco increased ester capacity at Tournai, Belgium, in 2012 and commissioned a plant manufacturing antioxidant additives optimized for performance with ester fluids in 2016.

Industria Quimica Lasem were acquired by Nisshin OilliO Group in 2011, and continue to offer a range of ester basefluids under the Docoil tradename.

Olein closed their ester plant in Sandefjord, Norway, during 2014, with products transferred to other assets in Europe and Asia.

Italmatch acquired Union Derivan (Undesa) in 2013. The group is mainly focussed on Polymer Esters and additive chemistries, but also offer some diester (Ketjenlube) and oleate (Dapralube) basefluids.

KLK Oleo commissioned new ester capacity for a range including lubricant basefluids at their site in Klang, Malaysia, during 2017.

Oxea have commissioned a new specialty ester plant in Nanjing, China, for a product range including polyol esters which will be marketed in refrigeration compressor applications by Lubrizol.

Lanxess acquired Chemtura in 2017. The Hatco division including the Hatcol product range is now part of Lanxess lubricant additives business unit.

Emery Oleo (formerly the upstream raw materials business of Cognis) have introduced a lubricant ester product range based on their captive natural fatty acid and dimer acid raw materials, branded as Dehylub. Esterification capacity has been developed or upgraded at their production sites in Cincinnati, OH, Loxstedt, Germany, and Telok, Malaysia.

Calumet announced doubling of ester capacity at their Louisiana, MO, plant in 2015. The former Hercolute products have been rebadged as Calester. In 2018, Calumet acquired Biosynthetic Technologies including intellectual property rights to estolide technology and will transfer production activities to the MO site.

**TABLE 3.26**

<table>
<thead>
<tr>
<th>Company (Former Business Names)</th>
<th>Tradenames (Former Tradenames)</th>
<th>Manufacturing Region</th>
<th>Main Product Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adeka Corporation</td>
<td>Adeka™</td>
<td>Asia</td>
<td>Polyol Ester</td>
</tr>
<tr>
<td>BASF (Cognis)</td>
<td>Synative™ ES, Glissofluid™</td>
<td>Asia, Europe, Americas</td>
<td>Polyol Esters, Diesters</td>
</tr>
<tr>
<td>Cargill</td>
<td>Envirotemp</td>
<td>Americas</td>
<td>Polyol Esters, Diesters, Oleochemical</td>
</tr>
<tr>
<td>Croda (Uniqema)</td>
<td>Prolube™, Perfad™</td>
<td>Europe, Americas, Asia</td>
<td>Polyol Esters, Diesters, Oleochemical</td>
</tr>
<tr>
<td>EmeryOleo (Cognis)</td>
<td>DeHyLub™</td>
<td>Americas, Europe</td>
<td>Polyol Esters, Diesters</td>
</tr>
<tr>
<td>ExxonMobil</td>
<td>Esterex™</td>
<td>Americas</td>
<td>Polyol Esters</td>
</tr>
<tr>
<td>Hercules (now Calumet Speciality Products)</td>
<td>Calester™ (Hercolute™)</td>
<td>Europe, Americas, Asia</td>
<td>Polyol Esters, Diesters, Oleochemical</td>
</tr>
</tbody>
</table>

### Notes
- The list in Table 3.26 does not include companies who produce esters for internal use only.
- Significant changes in recent years include the following:
  - Nyco increased ester capacity at Tournai, Belgium, in 2012.
  - Industria Quimica Lasem were acquired by Nisshin OilliO Group in 2011.
  - Oleon closed their ester plant in Sandefjord, Norway, during 2014.
  - Italmatch acquired Union Derivan (Undesa) in 2013.
  - KLK Oleo commissioned new ester capacity for a range including lubricant basefluids at their site in Klang, Malaysia, during 2017.
  - Oxea have commissioned a new specialty ester plant in Nanjing, China.
  - Emery Oleo (formerly the upstream raw materials business of Cognis) have introduced a lubricant ester product range based on their captive natural fatty acid and dimer acid raw materials.
Zschimmer & Schwartz acquired the Inolex Lexolube ester business in 2017. Production will be transferred to Milledgeville, GA.

Canadian plasticizer producer PolyOne have entered the lubricant market with a range of diester fluids under the Synprime tradename.

ExxonMobil closed the former Mobil ester plant in Edison, NJ, and transferred production to assets in TX.

### 3.5.2 Markets

The overall size of the ester lubricant market is very difficult to define, both in terms of producer capacity and market sales volume.

The majority of ester basefluid products are manufactured on multipurpose production assets by producers who also manufacture for other application areas (e.g., surfactants, coatings, plasticizers, biofuels, and fuel additives). Production rates may be significantly different for different ester products manufactured on the same assets, so actual capacity will depend on product mix. Declared plant capacity is therefore not a good guide, even where it is available, complete, and correct.

Similarly, many of the materials marketed as ester lubricant basefluids also have major applications in other market segments, although typically with different specification requirements. Some lubricant formulators may manufacture their own basefluids internally. Estimates for total production volumes of specific substances therefore do not necessarily relate to lubricant consumption.

Published market estimates for total lubricant volume typically do not differentiate between specific basefluid types and are inconsistent over whether some major functional fluid applications (e.g., transformer oils, hydraulic oils) are included or not. Some sources may include solid wax ester lubricants used as polymer processing additives.

Approximate annual volume and growth rate for the product types and market sectors discussed in this chapter are shown in Table 3.27. (These values are author estimates drawn from a range of sources.)

### 3.6 Outlook

The history of synthetic ester lubricants has been characterized by an initial phase of very rapid product discovery and development when essentially all of the materials currently in use were first developed and commercialized, followed by a much slower process of progressive spread of the technology across all areas of the lubricant industry, with some major increases in demand triggered by legislative changes.

Overall, this pattern looks likely to continue for the foreseeable future. The range of potential raw materials offered by the petrochemical and traditional oleochemical industry is mature and stabilized by established high levels of demand. Raw material innovation is therefore likely to continue to focus on optimizing production economics for current products rather than introducing new substances.

At the esterification level, although there is still scope for innovation through combining the available raw material slate in different ways, the broad range of existing materials and high costs of global notification for new substances will tend to direct attention toward optimizing specifications and finding new applications for existing products.

However, for the lubricant formulator and end user, market requirements to optimize lubricity, durability, and environmental acceptability of lubricant formulations will continue to drive progressive replacement of mineral oil formulations with higher performing synthetics. Because of their extreme structural flexibility and environmental performance, esters are expected to take an increasing share of this increasing overall demand for synthetics in all lubricant sectors. Some specific areas expected to see further demand are listed in the following.

In the major volume areas of automotive crankcase and gear oils, there will be increasing competition from electric vehicle technology. The threat of large scale substitution will make OEMs and formulators more reluctant to invest in long-term R&D directed to radical changes in internal combustion engine technology. However, internal combustion engines will retain the large majority of the market for at least the next decade and will continue to be subject to increasing legislative pressure on fuel economy and emissions standards, as well as economic drivers to increase lifetime and service intervals. This will continue the current trends to incremental substitution of traditional MO-based formulations by higher performing synthetics and semi-synthetics based on PAO, Group III+, and GTL fluids and will drive further demand for esters as polarity modifiers. In industrial sectors, demand for polyol esters for HFC-compatible refrigeration lubricants will initially level off as the industrial refrigeration sector completes the switchover. The overall refrigeration lubricant market will continue to grow as economic growth in Asia drives air-conditioning demand. However, market volume for esters or other SBFs will continue to depend on legislation relating to the refrigerant gases and in particular the adoption of fluorinated refrigerants having low GWP. Meanwhile biodegradable lubricants will be increasingly widely specified for potentially dispersible industrial applications in shipping and mobile hydraulic. The high level of current interest in natural and bio-based lubricants will result in opportunities for synthetic esters as higher performing alternatives to natural oils.

Sustained development and growth of synthetic ester basefluid chemistry can therefore be expected to continue over the coming decade.

<table>
<thead>
<tr>
<th>Region</th>
<th>Annual Volume (ktes)</th>
<th>Annual Growth Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMEA</td>
<td>150</td>
<td>3</td>
</tr>
<tr>
<td>Americas</td>
<td>135</td>
<td>5</td>
</tr>
<tr>
<td>Asia</td>
<td>85</td>
<td>5</td>
</tr>
</tbody>
</table>
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