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Turbine Engine Lubricant and Additive Degradation Mechanisms

David W. Johnson

Abstract

Modern ester based synthetic lubricants have been used in various formulations with anti-oxidants, phosphorus based anti-wear additives and other additives for many years. The physical and chemical properties of both the basestock and additives are known to change through use. Basestocks are normally thought to degrade through various mechanisms, while additive can either degrade or are used as they react when they complete the function that they are added for. In this chapter, the composition of modern turbine engine lubricants and the mechanisms by which the lubricants degrade over time will be examined. Potential changes in bearing materials being evaluated for future engines and the effects of possible new ionic liquids based additives will be discussed as they relate to currently used additives. Also included will be a discussion of effects of degradation on the lubricant properties, how the changes affect turbine engines and how the changes can impact human health. These new materials introduce a number of new possible degradation schemes that must be evaluated before the materials enter wide-spread use.

Keywords: lubrication, additives, oxidation, hydrolysis, decomposition, nanoparticles, phosphates, toxicity

1. Introduction

Lubrication is essential in applications where moving parts are involved. Aircraft propulsion systems involve large numbers of moving parts, many of which move at high speeds under severe temperatures and stresses. Turbine engine lubricants perform essential functions in reducing wear, reducing friction and dissipating heat from the engine. Modern engines are designed to operate at higher temperatures and shear rates, placing increased demands on the lubricants and additives. Typical turbine engine lubricants consist of a basestock which is a mixture of synthetic esters and a series of additives that modify the properties of the basestock. Additives are included to reduce oxidation of the basestock, reduce wear of the metal bearings or modify properties of the lubricant [1].

All lubricants, when subjected to high temperatures undergo degradation, which changes both the physical and chemical properties of the material. Physical property changes can include increases or decreases in viscosity, changes in boiling point or freezing point among others. Chemical properties that can change include corrosion of metals, formation of polymers and oxidation of the base stock. In addition to the basestock lubricants contain a range of additives that modify the properties of the basestock. Degradation of the additives reduces their effectiveness and can

result in the failure of the engine. In turbine engine applications, additive depletion is an important diagnostic of lubricant health.

In addition to lubricant degradation being important to engine health there are significant implications to human health. On the vast majority of commercial aircraft, the air used to pressurize the cabin is drawn from the engine just after the compressor section. Lubricant degradation products have been shown to pass from the engine into the cabin on seal failure with severe health effects. Of perhaps greater significance is the normal low level leakage of lubricants and degradation products into the cabin under normal flight conditions. It is known that all seals leak some and some of the leaked material can be transmitted into the passenger cabin as both vapors and nano-droplets. The chronic toxicity of these materials is of great concern [2].

In this chapter, the composition of typical turbine engine lubricants will be presented in Section 2. The decomposition mechanisms of the basestock are presented in Section 3, followed by the additive degradation mechanism in Section 4. Finally, in Section 5 synergistic and antisnergistic interactions of lubricants and additives are examined. Changes in bearing systems and the incorporation of ionic liquids and nanoparticles will be included and finally in Section 6, some of the consequences of lubricant degradation will be examined.

2. Composition of turbine engine lubricants

Turbine engine lubricants have changed dramatically over the years in response to the increasing stresses applied to the lubricant. In particular higher shear stress, higher operating temperatures and lower storage temperatures have made changes in both basestocks and additive packages necessary. Natural petroleum based oils could not meet the temperature demands which made the selection of synthetic materials, modified with a number of additives necessary for this application [3]. In order to meet the demands for modern aircraft, lubricants based on synthetic esters were developed and have been refined many times, both in terms of the basestocks and the additive packages to meet the current specifications.

2.1 Basestock composition

The composition of lubricant basestocks for turbine engines is somewhat variable as long as they can meet the performance requirements set forth in the standards SAE5780 for commercial aircraft and either MIL-PRF 23699 [4] or MIL-PRF 7808 [5] for military aircraft. One of the requirements is to be compatible with all of the previously approved lubricants in a given specification to avoid the inevitable mixing. Esters have been used since the 1940 as synthetic basestocks that have desirable thermal properties, however no single ester meets all requirements. Modern lubricant basestocks use a mixture of a number of esters in order to tailor the properties of the lubricant to the desired properties. These specifications have resulted in the use of certain common ester basestocks. Ester basestocks for turbine engines are all ester based using polyols and common carboxylic acids. Some of the common alcohols used are shown in **Figure 1**.

The polyols shown have been selected because they are highly hindered and also lack hydrogen atoms in the β position. Previous studies have shown that increases thermal and hydrolytic stability results when there is no hydrogen atom present on the β carbon atom. The carboxylic acids used to make the esters are a combination of linear and branched acids with a blend being frequently used to arrive at the desired viscosity. Normally 5 cs (SAE5780 and MIL-PRF 23699) basestocks

use pentaerythritol and dipentaerythritol for the alcohols and C5-C10 linear and branched acids. Lower viscosity lubricants (Mil-PRF 7808) are based on neopentyl glycol and trimethylolpropane as the alcohol and C5-C12 linear carboxylic acids. The incorporation of branched acids in lubricants has a significant effect on the thermal stability and physical properties of the lubricant. Some of the different acids are shown in **Figure 2**.

2.2 Common additives

Lubricants with ester basestocks require a series of additives in order to lubricate under the conditions observed in turbine engines. Typical additive packages include antioxidants, typically an aromatic amine, an anti-wear additive, typically a phosphate ester and possibly an antifoaming additive and a viscosity index modifier. The structures of various additives are shown in **Figure 3**.

Most additives degrade as a part of their mechanism of action, which means that their concentration is constantly decreasing. Many of them also degrade through other mechanisms as well. In general, when the additives have degraded beyond a certain point, either they must be replenished or the lubricant must be changed.

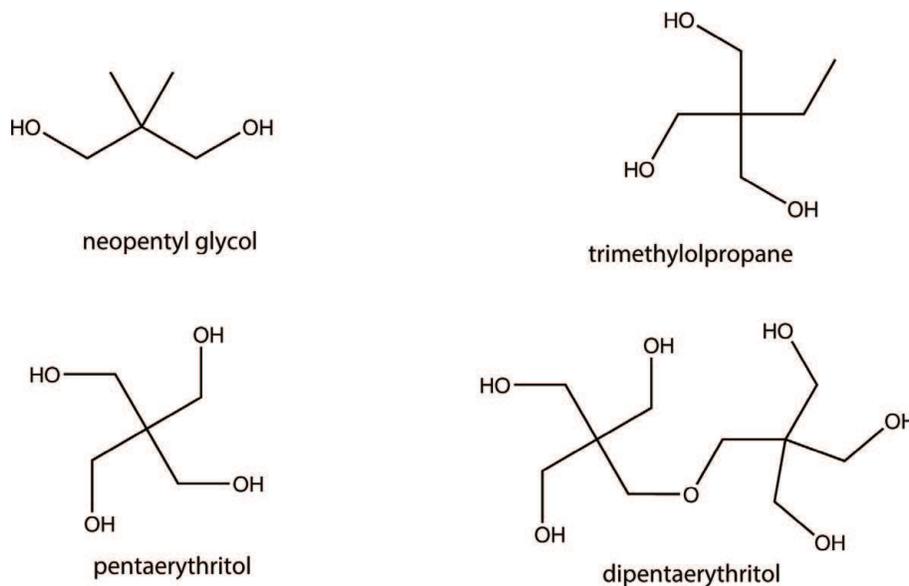


Figure 1.
Common polyols used to make ester-based lubricant basestocks.

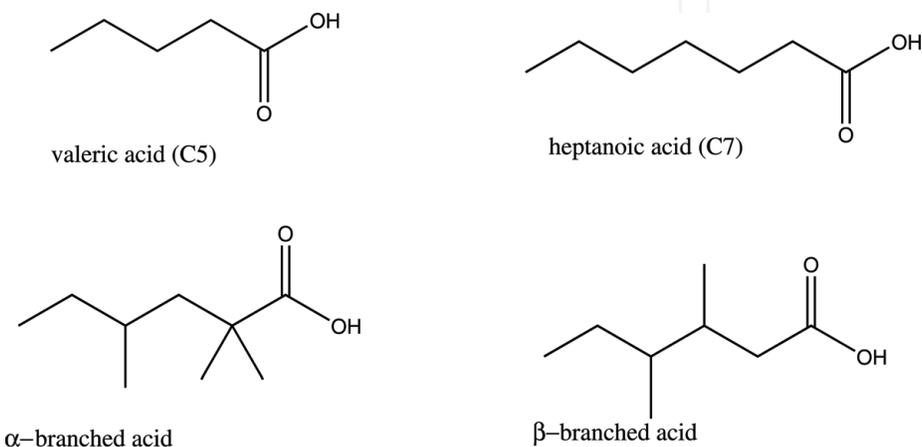


Figure 2.
Some of the acids used in the preparation of synthetic lubricants.

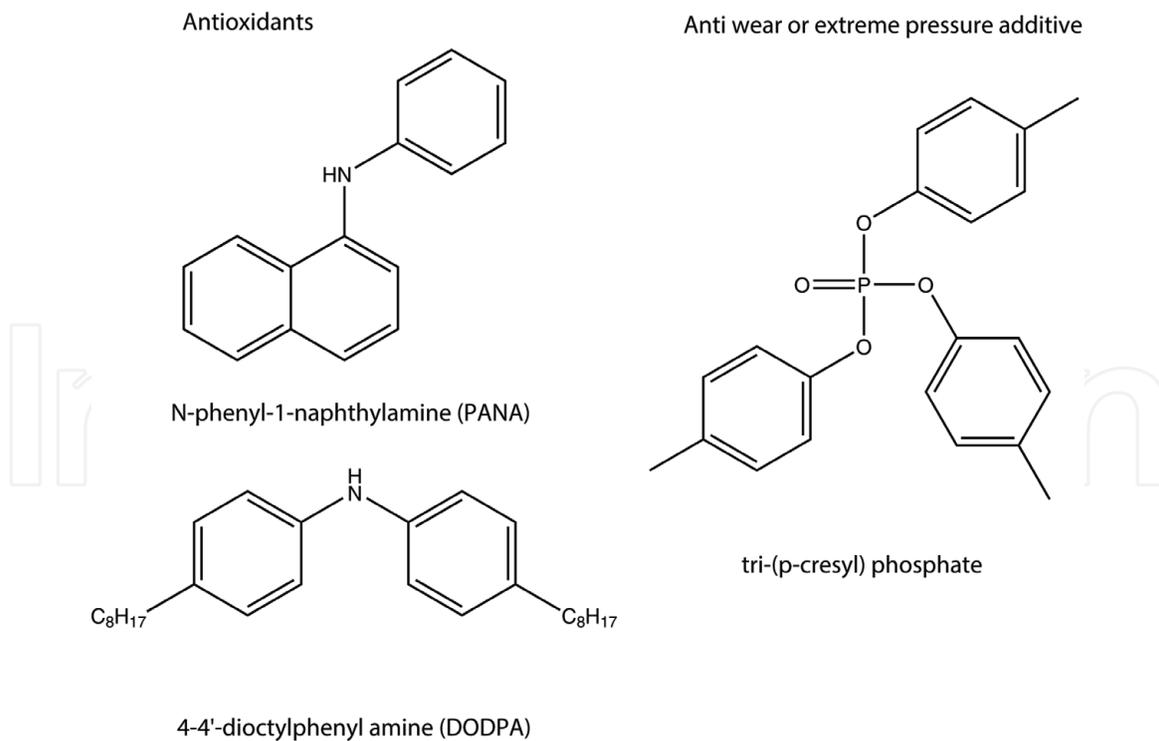


Figure 3.
Structures of some lubricant additives used for turbine engines.

Fortunately, most turbine engines lose some lubricant under normal operating conditions and the oil lost is replenished on a regular basis. These procedures maintain the additive packages at acceptable levels.

3. Lubricant basestock degradation mechanisms

Conventional lubricants are petroleum based and consist of hydrocarbons including a huge number of isomers. The primary degradation mechanism for hydrocarbons is oxidation, which leads to the formation of alcohols and carboxylic acids. Synthetic lubricants typically by oxidation to carboxylic acids, aldehydes and ketones under extreme conditions, and degrade by hydrolysis, due to the presence of water and in some cases by transesterification with phosphate ester additives. In addition to the degradation of the basestock due to oxygen, the role of bearing surfaces where extremely high temperatures and pressures; along with the presence of metals and surface treatments such as metal carbides must be considered. In addition, lubricant esters can act synergistically with certain additives [6] and can react differently in the present of metals and or metal carbides.

3.1 Hydrolysis

The hydrolysis of the ester basestock is the reaction of the basestock with water to form an alcohol and a carboxylic acid. This reaction is catalyzed by acids or bases, which are frequently present within the lubricant and does require water. The water can come from various sources, including contamination of the lubricant and the exposure of the lubricant to the environment. Water is soluble in typical ester basestocks to a level of about 500 ppm, meaning that water is readily available in the lubrication systems for turbine engines. The mechanism for the hydrolysis of esters is shown in **Figure 3**.

Hydrolysis of esters can occur through either an acid or base catalyzed mechanism, with significant differences in the mechanism. The acid catalyzed mechanism [7] begins with the protonation of the carbonyl oxygen atom, followed by a water molecule attacking the carbonyl carbon atom of the ester. The carbonyl carbon normally has a partial positive charge which is increased by the protonation of the oxygen atom yielding the hemiacetal shown in **Figure 4**. One of the water can be transferred to the alcohol oxygen atom and then the alcohol is lost completing the hydrolysis.

The base catalyzed mechanism [8] involves a water molecule attacking the carbonyl carbon atom, followed by transfer of a proton to the carbonyl oxygen atom. The base the assist with the transfer of the proton from the carbonyl oxygen atom the oxygen atom of the alcohol as the alcohol leaves forming the carboxylic acid.

The two hydrolysis mechanisms require that water be able to attack the carbonyl group of the ester. The use of hindered alcohols such as the various neopentyl alcohols (**Figure 1**) reduces the ability of the water to approach the carbonyl carbon atom. The use of branched chain acids further reduces the ability of water to attack the carbonyl, resulting in an increase in the hydrolytic stability of the ester [9].

3.2 Oxidation

Ester based lubricants are all subject to high temperature oxidation which has the most detrimental effect on their properties. Early work examined changes in the bulk composition of ester based lubricants showing the formation of a wide range of acids. The lighter carboxylic acids were attributed to oxidation of the acid chains. Other products were attributed to oxidation of the alcohol [10]. Later work proposed an explanation for oxidation that is based on a radical chain mechanism.

Oxidation occurs through a complex radical chain mechanism which is common to a wide range of organic materials. The initial stages of the oxidation involve the formation of an alkyl peroxy radical by reaction with oxygen. The reaction is propagated by the attack of an alkyl peroxy radical on a methylene group of the ester. The α position of the acid, has been shown to be significantly more reactive than other methylene groups in the carboxylic acid [11]. This reaction is significantly hindered in the polyol esters, especially when branched chain acids with branches at C-2 are included. A more recent study, using isotope labelling techniques has shown that the initial site of oxidation is at C-1 of the alcohol, cleaving the carbon–oxygen

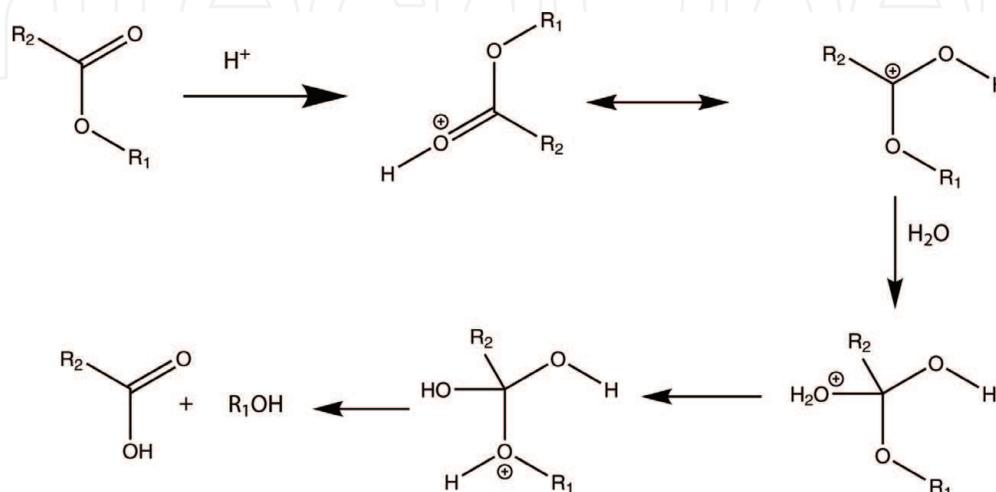


Figure 4.
Mechanism for the acid catalyzed hydrolysis of esters.

bond between the first carbon of the alcohol and the ester oxygen, followed by further oxidation at that carbon to form the organic acid [12]. After the initial attack, the reaction can progress to form anhydrides which continue to react to form aldehydes, acids and eventually high molecular weight compounds which can form sludge in the engine. The mechanism of the initial stages of the oxidation of the esters is shown in **Figure 5**.

3.3 Elimination reactions

Ester based lubricants have been observed to decompose. One possible reaction of esters is an elimination reaction in which an alkene and a carboxylic acid are the products. The mechanism for this reaction involves the loss of a proton on the β carbon atom leading to the formation of a double bond and the elimination of the carboxylate anion. The mechanism for the β elimination reaction is shown in **Figure 6**.

The use of alcohols without hydrogen atoms at the β carbon atom eliminates this mechanism, but under operating conditions of turbine engines, high temperature and metal catalyzed elimination reactions are possible. For this reason, modern ester based lubricants are based on neopentyl polyols, where elimination is blocked due to the lack of hydrogen atoms at the β position. Significant work has been conducted on optimizing the properties of the lubricant for use in turbine engines [13, 14].

3.4 Role of bearing materials as catalysts

Lubricant basestocks, in addition to being subjected to high temperatures and pressures, are also in contact with bearing surfaces which contain a combination of metals, metal oxides and surface carbides. Under normal circumstances, ferrous

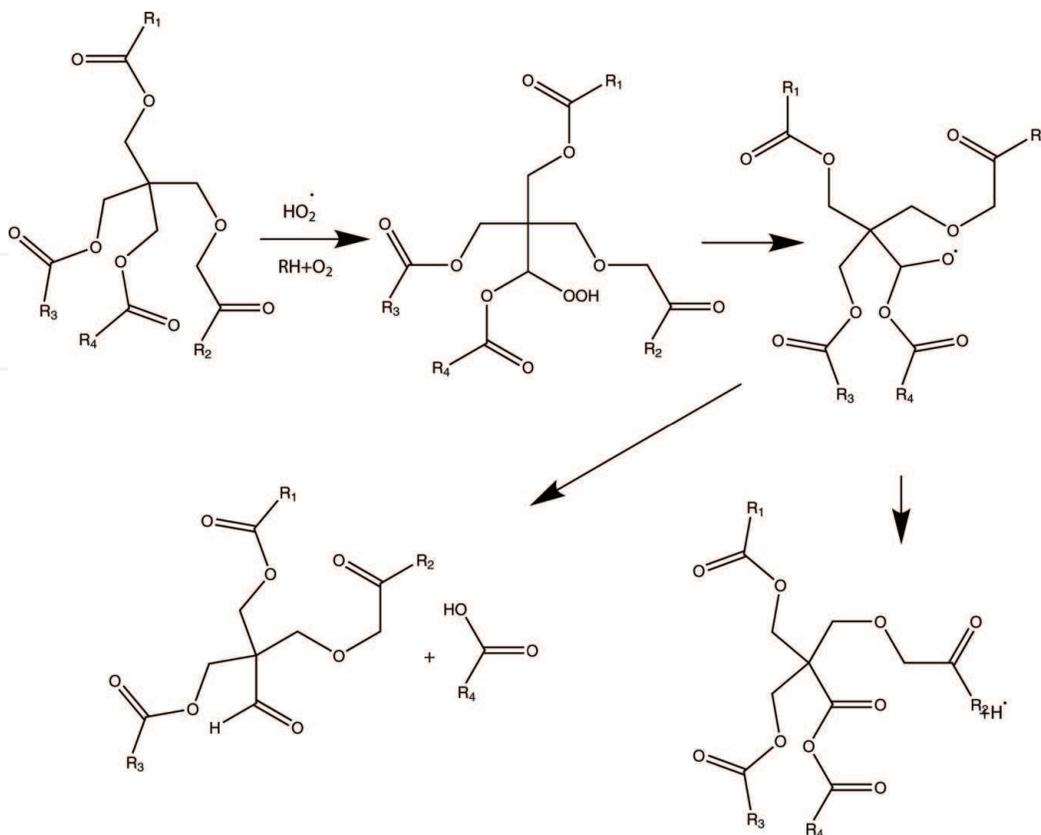


Figure 5.
A part of the mechanism for the oxidation of neopentyl polyols.

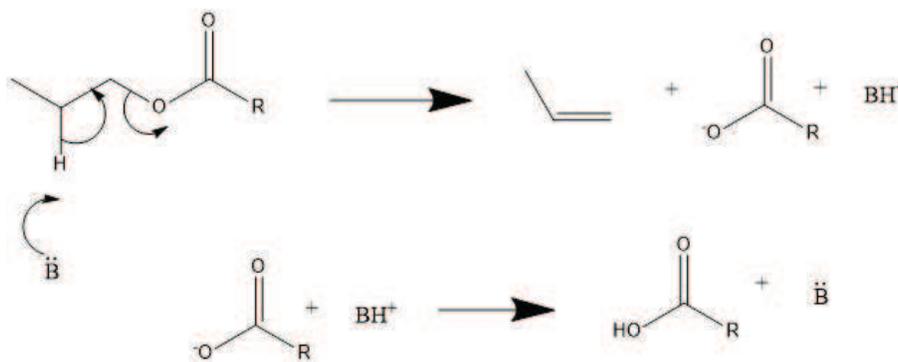


Figure 6.
Mechanism for the β elimination reaction.

metal are known to increase the rate of thermal degradation of polyol ester based lubricants, especially at temperatures above 220°C. The mechanism for this reaction, however is not completely understood [15]. The incorporation of phosphate esters is known to reduce the catalytic effect of ferrous metals, probably due to the formation of a phosphate film on the surface of the metal (see Section 4.1.2) [16].

4. Lubricant additive degradation

Lubricant additives are in many ways designed to degrade as they serve their purpose in the formulated lubricant. As the lubricant is lost in service primarily due to leakage, new lubricant is added which act to replenish the additives used. Lubricant loss is typically estimated at as much as one quart per hour depending on the engine [17]. It is possible to use the amount of remaining additives to determine the need for engine service or lubricant replacement. One example of an instrument for the analysis of remaining antioxidant as an engine diagnostic is RULER [18].

4.1 Phosphate esters

Phosphate esters are normally required as an extreme pressure or anti-wear additive. The phosphate esters react with the metal surface to form a lubricious polymeric coating. The coating protects the bearing under conditions of start-up, inadequate flow or extreme shear, where the coating wears away, but is continuously reformed from unreacted phosphate ester in the lubricant. The mechanism of action of the additive causes its degradation over time [19].

4.1.1 Hydrolysis

Hydrolysis of phosphate esters is the reaction of the triester with water to form a diester and an aromatic alcohol. The diester can further react under the same conditions to form the monoester and eventually phosphoric acid. Two classes of mechanisms have been proposed for the hydrolysis in aqueous solution, dissociative mechanisms that proceed through a PO_3^- anion and associative mechanisms then proceed through a penta coordinate phosphorous intermediate [20]. The likely mechanism in the non-polar lubricant medium where the attacking species is a water molecule is most likely through the associative mechanism, which does not require formation of a PO_3^- ion. The mechanism of the reaction is based on the addition of water to the phosphorus atom, followed by loss of a proton and elimination of the alcohol (phenol) [21]. The mechanism is shown schematically in **Figure 7**.

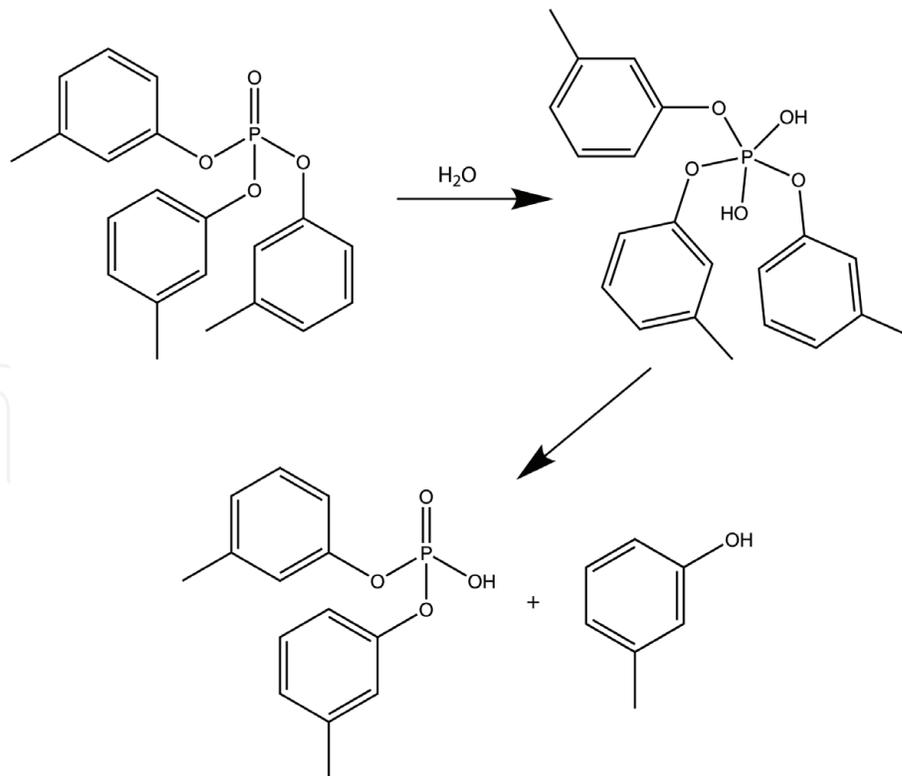


Figure 7.
Mechanism for the hydrolysis of phosphate esters in polyol ester-based lubricants.

Hydrolysis is an important degradation mechanism because it forms a range of phosphate partial esters, some of which do not form a lubricious coating on the bearing and contribute to the acids contained in the lubricant.

4.1.2 Polymerization at metal surface

Phosphate esters are used as anti-wear of extreme pressure lubricants and work by reactions with the bearing surface to form a polymeric coating that is durable and lubricious [22]. The reaction normally occurs at the oxidized metal surface and results in the formation of an initial layer of graphite, followed by a layer of an iron rich, iron polyphosphate [23]. After the initial coating is formed the film can increase in thickness as iron diffuses to the surface [24]. The coating continuously wears away during use and is reformed as iron diffuses through the coating. The nature of the polymeric lubricious film is shown in **Figure 8**.

The mechanism for the formation of a polyphosphate polymer begins with the bonding of the phosphate ester (typically tricresylphosphate) to the oxidized iron surface, displacing cresol. The initial steps of the mechanism that leads to the formation of a coating is shown in **Figure 9**.

The bound phosphate reacts further with other bound phosphate esters displacing additional cresol leading to the formation of a polymeric coating strongly bound to the metal surface. Typically, on the surface of the metal some of the partially reacted phosphate remains. X-ray photoelectron spectroscopy results show a surface composition corresponding to approximately one cresol remaining per phosphorus atom on the surface as is shown in **Figure 8**.

Under extreme pressure conditions, the outer layers are removed from the surface and are lost as polymeric phosphorus containing nanoparticles which are not reconverted to the triaryl phosphate in the lubricant. It should be noted that this mechanism explains how the phosphate esters act as an anti-wear additive but it also

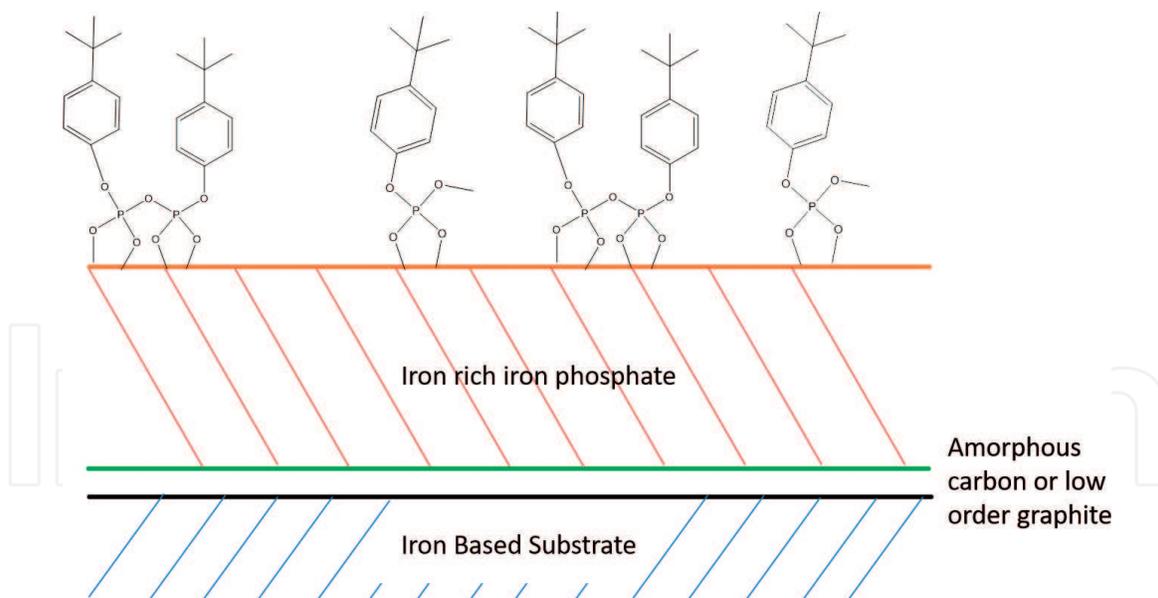


Figure 8.
Schematic representation of the iron phosphate film.

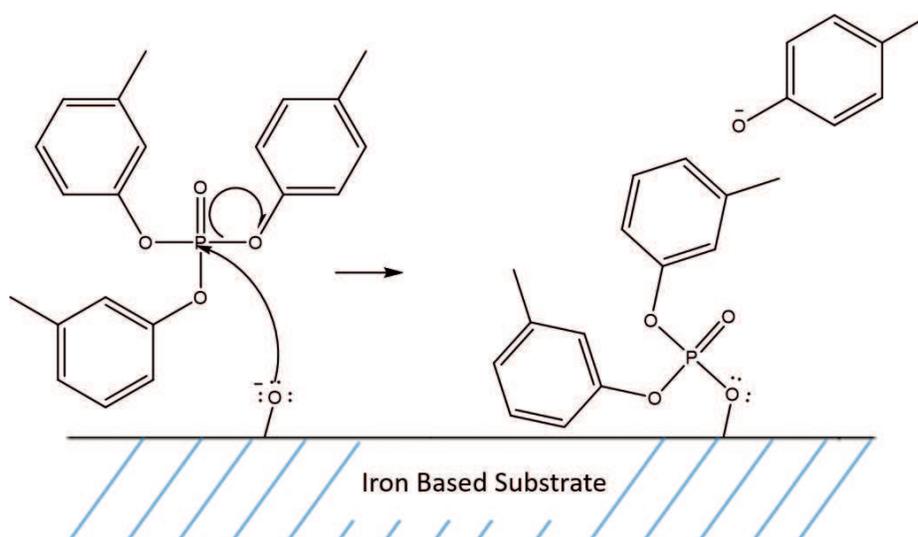


Figure 9.
Mechanism of phosphate film formation and structure of phosphate film.

leads to the degradation of the phosphate esters. The formation of nanoparticles through the wear of the coating formed at the bearing surface leads to a darkening of the oil color, but many of these particles are removed by filtration or eventually settle in the oil sump.

4.1.3 *Trans esterification lubricant esters*

The last of the reactions of phosphate esters is the reaction between phosphate esters and lubricant esters to form aryl esters and alkyl phosphate esters. This is a reaction that can occur in either a single step or could initially form the acid which can further react to form another ester. The single step process is shown in **Figure 10**.

This reaction can be of particular concern since the alkyl phosphate formed can undergo transesterification intramolecularly to form the product shown in **Figure 11** which is structurally similar to the known neurotoxin which would be formed by a similar reaction with trimethylolpropane [25, 26].

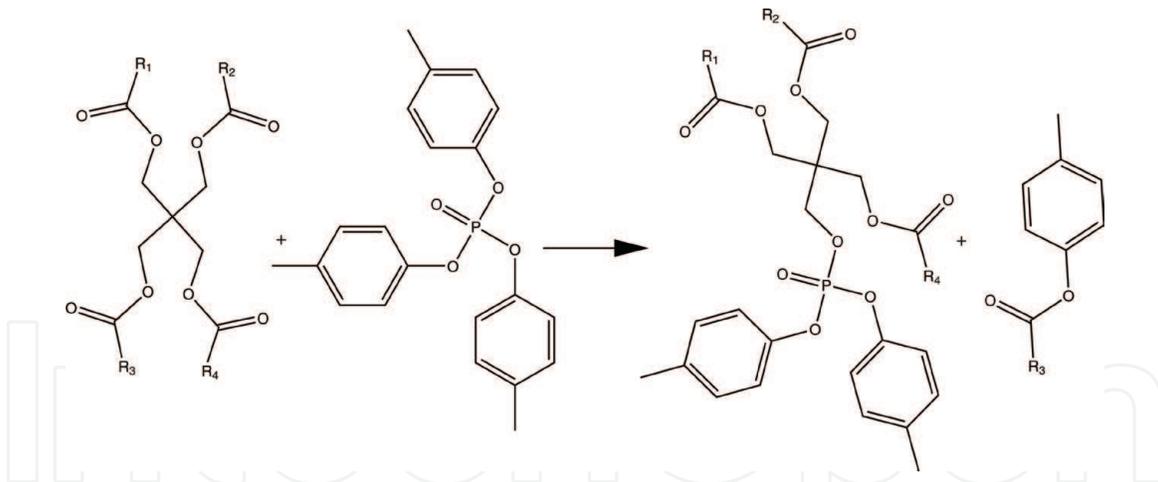


Figure 10.
Transesterification of a phosphate ester with a lubricant ester to form an alkyl phosphate and an aryl ester.

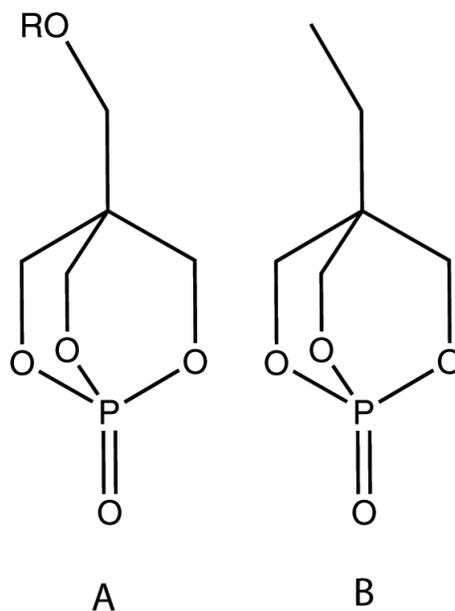


Figure 11.
Final product of the transesterification of pentaerythritol ester (A) and the known neurotoxin formed from trimethylol propane (B).

The structure shown in **Figure 11(A)** assumes the final acid group has been hydrolyzed. Either this compound or the corresponding ester might be assumed to have a toxicity comparable or greater than the compound shown in **Figure 11(B)**.

4.1.4 Addition to pendant groups

A final reaction that occurs with phosphate ester additives is addition reactions on the pendant aromatic rings. In this reaction, the carbon–oxygen bond in a phosphate ester is broken at the metal surface. The leaving group remains at the metal surface until it is added to another molecule of phosphate ester [27]. The mechanism for the formation of addition products is shown in **Figure 12**.

These addition reactions result in higher molecular weight species that might in part be responsible for the formation of the layer of carbon, initially described as a carbide layer [28], but later determined to be either amorphous carbon or low order graphite [29], immediately adjacent to the iron surface. This layer is consistently observed in Auger spectroscopy as is shown in **Figure 13**.

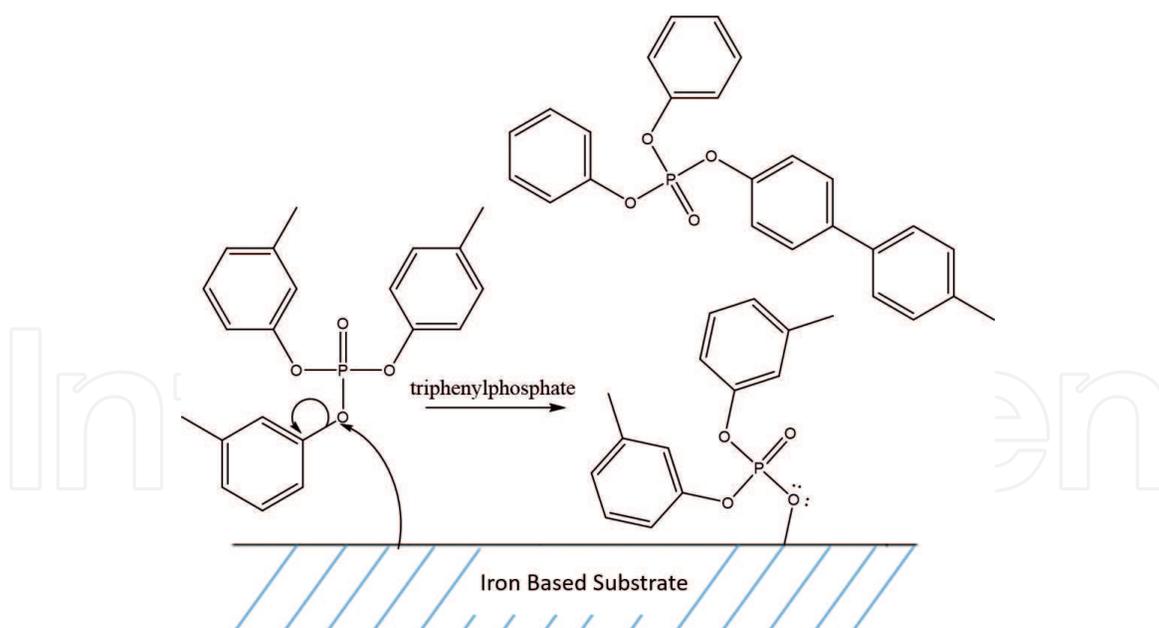


Figure 12.
Reaction of phosphate esters with reduced metal surfaces showing the addition of a tolyl group to triphenyl phosphate.

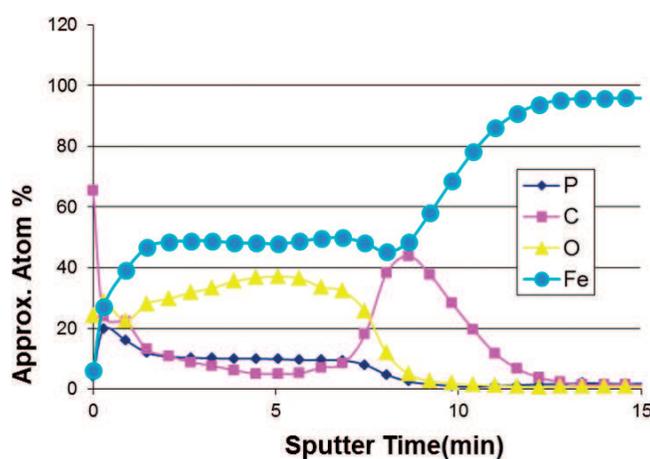


Figure 13.
Auger depth profile of a film formed by the deposition of BTPP onto an iron foil at 425°C under nitrogen (sputter rate 1.5 nm/min).

4.2 Antioxidants

Synthetic lubricants are oxidative degraded via a radical chain mechanism at high temperatures. Molecular oxygen abstracts a hydrogen atom forming a free radical. The radical reacts with the basestock abstracting hydrogen atoms or other groups, adding that fragment and creating a new radical and in general increasing the size of the molecule. The chain mechanism continues until the growing chain encounters another radical, resulting in chain termination. Antioxidants are typically added to the lubricant formulation to reduce the rate of lubricant decomposition by reacting with radicals formed in the initiation step of lubricant oxidation.

Anti-oxidant additives can act in two different ways. First, they can react with oxygen to form a stable species reducing the possibility of the chain initiation step in the mechanism. Second, the antioxidant can react with radicals formed, forming a more stable species and acting as a chain termination step [30]. Among the most common types of antioxidants used in lubricants are hindered phenols and aromatic amines.

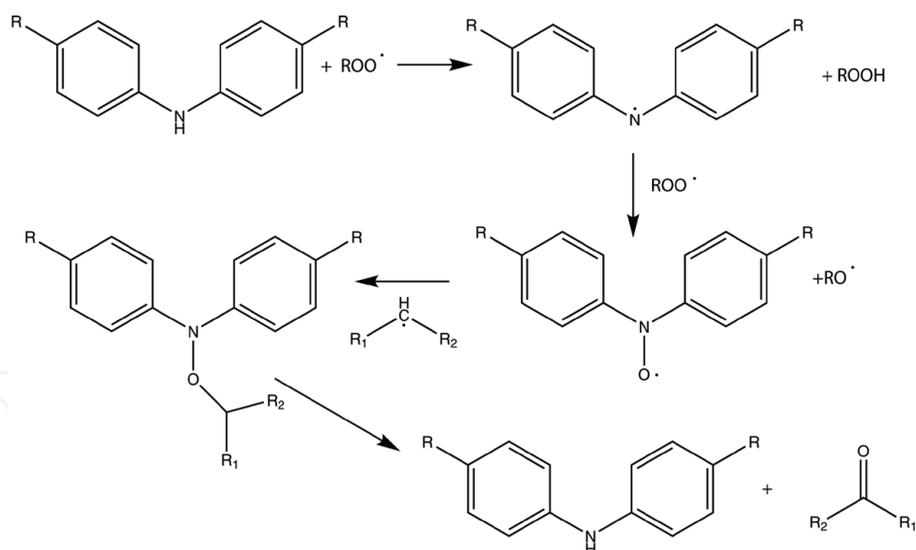


Figure 14.
High temperature mechanism for the antioxidant activity of alkylated diphenyl amine antioxidants.

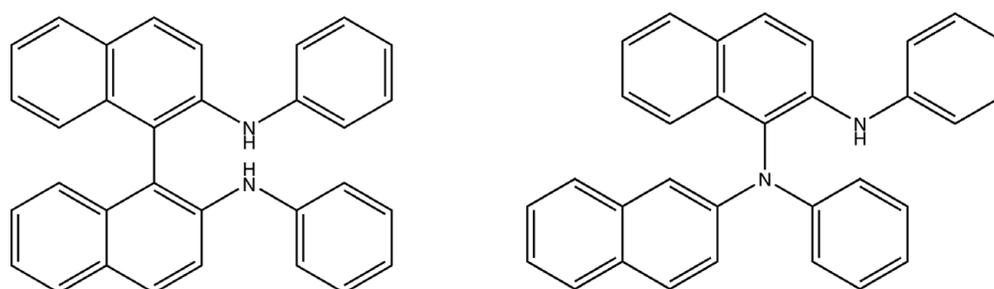


Figure 15.
Products of the reaction of PANA as an antioxidant in lubricants.

Aerospace lubricants typically rely on the hindered aryl amines N-phenyl-1-naphthylamine (PANA) and p-diocetyldiphenyl amine (DODPA) (structures shown in **Figure 3**) as antioxidants because they have the potential to react with a greater number of hydroperoxy radicals [31]. There are two very common mechanisms in which aryl amines act as antioxidants, a low temperature ($<120^{\circ}\text{C}$) and a high temperature mechanism ($>120^{\circ}\text{C}$). A common feature of the mechanisms is the reaction of the amine to form radicals. These reactions form aminoxy radicals to form N-alkoxyamines which appear to be the actual antioxidant species [32]. The high temperature mechanism through which aryl amines act as antioxidants is shown in **Figure 14**.

Other mechanisms that have been reported examined the possibility that the diphenyl amine radical formed in the first step in **Figure 14** could disproportionate and then react with itself to form more complex species that eventually lead to poly conjugated systems upon reaction with additional hydroperoxy radicals. The reaction of N-phenyl-1-naphthylamine proceeds somewhat differently due to the susceptibility of the α hydrogen of the naphthyl ring to radical attack leading to the formation of dimers and higher polymers as in **Figure 15** [33] or the formation of quinone imines and naphthoquinones [34].

5. Synergistic reactions between lubricants, additives and bearing materials

The reactions of the individual components are not always sufficient to predict the chemistry of a formulated lubricant. Some reactions are inhibited by the

additives, but may be accelerated by combinations of additives and surface chemistries. Rolling contact fatigue testing with M-50 bearings, for example indicated that PANA and DODPA added to a lubricant along with tricresyl phosphate resulted in an increase in wear over systems where the PANA and DODPA were absent [35]. An explanation might include the antioxidants reduce the oxidation of the metal surface which interferes with the binding of the phosphate ester to the surface [36]. Another system where results are unpredictable is when advanced bearing materials are used with polyolesters and phosphate esters. These observations demonstrate the importance of considering all of the components in the lubrication system instead of the individual reactivities of the various components.

6. Incorporation of advanced bearing steels, ionic liquid additives and nanoparticle based additives

6.1 Advanced bearing steels and ceramic bearings

The need for more efficient and more powerful jet engines for military and commercial applications has caused a need for lighter, more durable bearing materials. Harder metal alloys and ceramic bearings are approaches to serve these needs. Changes in bearing materials, however may not be completely compatible with current lubricant basestocks and additive packages.

Many advanced bearing materials are made from carburized stainless steels. The materials begin with a stainless steel which can be formed into the desired shape. The part is then heat treated in the presence of a carbon source resulting in the formation of surface carbides [37]. The surface carbides increase the hardness of the surface significantly. Phosphate esters have been shown to interact with the stainless steels in the absence of carburization [38], but in the presence of all three components, metal carbides, phosphate esters and polyol esters the decomposition is much more rapid [39]. When carburized bearings were tested with polyol ester based lubricants formulated with phosphate esters, an increase in fatigue life and wear performance was observed [40].

Ceramic bearings have good potential for high temperature use in turbine engines. Unlubricated ceramic bearings performed poorly, however when an appropriate lubricant was added they performed better [41]. Typical lubricant additives, however did not perform well under conditions typically seen in steel bearings. At very high temperatures, a film was formed but it did not decrease friction or increase bearing life [42]. To form a lubricious anti-wear coating, the ceramics were pretreated to introduce a thin film of iron which allowed the phosphates to form an anti-wear coating [43].

6.2 Ionic liquid additives

Ionic liquids have been considered as potential replacements for both basestocks and additives. As a potential replacement for the basestock, increased costs make them inappropriate for use in turbine engines [44]. A number of ionic liquids are under investigation for use as anti-wear or extreme pressure additives. These additives contain phosphorus in either the cation, as a phosphonium ion or the anion as a tri-alkyl phosphate. Ionic liquids that incorporate the phosphorus in the phosphate anion have been shown to be the most effective [45]. Ionic liquids containing tri-alkyl phosphates interact strongly with metal surfaces through mechanisms also seen in the tri-aryl phosphates [46] discussed in Section 3.1. Ionic liquids with phosphonium cations with a non-phosphate anion have shown superior performance under high load [47]. Ionic liquids have the advantage of reduced volatility, which is

important in some applications. Ionic liquid based anti-wear additives show some of the same interferences with antioxidants that are observed with triaryl phosphates, performing better in oils where the additives have been depleted [48].

6.3 Nanoparticle based lubricant additives

Nanomaterials and nanoparticles have been studied for use as additives in liquid lubricants. Some of the initial problems that have been discovered are the dispersion of the nanoparticles and the stability of the dispersion. Capping metal nanoparticles with a monolayer of non-polar organic molecules have resulted in nanoparticles that are oil soluble [49]. A wide range of nanoparticles have been studied and several have shown promise for use in liquid lubricants. Chemical composition was found to be important in anti-wear performance, where morphology and size of the particles were more important in friction reduction. Nanoparticles with layered structures were among the better morphologies [50]. Nanomaterials as lubricant additives appear to have a bright future in lubrication, although none are in current use in aerospace liquid lubricants.

7. Consequences of lubricant degradation

Lubricant degradation has a significant effect on the properties of the lubricant which can have significant consequences in aerospace. Degradation results in an increase in the chemical reactivity of the oil through the formation of acid and bases, changes in viscosity and changes in thermal conductivity. All of these can result in reduced life of the engine and also decreased operational efficiency. It is important that all of these effects be minimized for safe air travel.

There is an additional safety concern associated with lubricants and their degradation products present in most commercial and military aircraft. Air used to pressurize the cabin is drawn from the engine through a bleed air nozzle. While under normal operation, the air is thought to be safe, seal leakage results in traces of lubricant directed into the cabin. In cases of seal failure, high concentrations of lubricants, additive and degradation products enter the cabin. Smoke events are caused by seal failures, as well as other causes. Fume events occur in 2.1 of every 10,000 flights [51] and oil fumes are noted in 1% of all flights. The health related concerns are indicated by the 30% of fume events where crew impairment has been recorded even though there is recognized under reporting of impairment [52].

Aerotoxic syndrome has been described as an occupational illness along with epidemiological evidence [53]. Possible toxicological mechanism leading to aerotoxic syndrome has been described by Howard et al. [54]. A possible cause for Aerotoxic syndrome is based on repeated low dose exposure to organo-phosphorus compounds derived from phosphate esters [55]. High doses of organophosphates are known to cause organophosphate induced peripheral neuropathy (OPIDN) [56], however the doses encountered here are much lower, suggesting other chronic mechanisms [57]. The toxicity evidence indicates the need for clean air requirements for aircraft using bleed air for cabin pressurization [58].

8. Conclusion

The common mechanisms that degrade lubricant basestocks and additives have been discussed in the sections above. The degradation of the basestock is considered to be of greatest concern for the general health of the engine. The degradation of

the additives is a large part of how they work. Considerable effort has been put into finding additives that react appropriately, and are of limited volatility and thermally stable. They are included as part of the lubricant to degrade, and as long as they are not depleted completely they will function in that capacity.

Through molecular design of the esters used in the basestock, the importance of some of the mechanisms have been reduced. Modern esters used in the basestock are based on polyols that do not base hydrogen atoms in the β position making β elimination impossible by this mechanism. Hydrolysis is of significant concern, since it both produces acids and alters the physical properties (viscosity, and pour point in particular) of the lubricant. Oxidation also has the potential to produce acids and change the physical properties of the lubricant. The addition of better and better antioxidants has reduced the importance of this mechanism. It also should be noted that the acids produced by either oxidation or hydrolysis are carboxylic acids which are much less corrosive than the mineral acids frequently formed by the oxidation of sulfur and nitrogen compounds found in mineral oils.

Lubricants are under development that will continue to increase the operating temperature without significant degradation of their properties. Molecular design has been used to slow the various basestock degradation mechanisms through the choice of the acids used to form polyol esters can block both oxidation and hydrolysis. The knowledge of these mechanisms has made preparation of high performance lubricants a reality.

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