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## Lubricants for Turbine Engines

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#### Abstract

The lubricant systems used in turbine engine applications are discussed with respect to the particular problems associated with aircraft applications. After initially describing the relevant specifications, the typical basestocks are described along with some common degradation schemes. The additive systems, including antioxidants, anti-foaming agents, and anti-wear additives needed to achieve the typical specifications, are described along with their mechanism of action and degradation mechanisms. The methods used for the monitoring of lubricant health, including in-line and offline methods, are also discussed. Finally, future changes in specifications, basestocks, and additives are discussed with respect to new, high-performance bearing materials.

**Keywords:** synthetic lubricants, anti-oxidants, phosphate esters, condition monitoring, tribology, lubricant additives

#### 1. Introduction

Lubrication is critical in any application where moving parts are involved. Aircraft involve large numbers of different types of moving parts, many of which are associated with the propulsion system. The objectives of lubrication are primarily to improve energy efficiency by reducing friction and to improve component lifetime by reducing wear of the moving parts. An added benefit of an efficient lubrication system is a reduction in the engine operating temperature because of the heat dissipation through the lubricant system [1].

Turbine engine lubrication is an extremely demanding application for lubricants for several important reasons, as follows:

• Reliability due to the consequences of failure. Aircraft applications are the only applications where it is not possible to stop immediately and investigate a lubricant failure indication.

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- High operating cost associated with added weight, making backup and redundant systems highly undesirable. This requirement leads to small volumes of lubricant and results in high heat dissipation requirements and high operating temperatures.
- Wide range of temperatures, pressures, and speeds that the lubricant is exposed to under normal operating and storage conditions.

The combination of these requirements eliminates the possibility of an ideal natural lubricant or synthetic lubricant meeting all of the requirements. As speeds and temperatures increased, automotive lubricants initially used in aircraft were replaced by specialty lubricants for aircraft engines. As the propulsion systems changed from conventional engines to turbine engines, lubricants based on mineral oils were inadequate and a new class of lubricants was needed [2].

In the years after World War II, turbine engines were developed and began to dominate both military and commercial aircraft propulsion. Turbine engines require the lubricant to be stable and fluid over a wide range of temperatures. Ground starting temperature may be as low as -54°C and temperature as high as 300°C may be observed at times in the operating engine. Over time, a number of different lubricants were developed with very different chemistries and compatibilities. Many different locations had lubricants that were developed to suit the local conditions and needs. With a number of incompatible fluids, the global nature of aircraft use, and the grave consequences of mistakes, a need for standardization became apparent. To address this problem, a system of lubricant specifications has been developed for turbine engine lubricants.

### 2. Early basestocks

The earliest lubricants used in turbine engines were highly refined mineral oils. Mineral oils, however, lack the high temperature stability to withstand the high temperatures found in different points of the engine. Severe oxidation of the light mineral oils results in significant increases in the viscosity of the oil. The problems of severe oxidation and degradation highlighted the need for a new class of oils, which lead to the development of a class of synthetic aviation turbine oils [3].

The search for a new class of synthetic aviation lubricants led to the examination of organic esters as basestocks. Over 3500 different esters were examined for lubricant use between 1937 and 1944. A number of candidates had some of the required properties, including thermal stability, pour point, or boiling point, but none met all of the requirements. It should be possible based on the number of di-acids and alcohols available to achieve the desired viscosity and other properties with a pure compound; however, to achieve the wide liquid range required for Air Force needs, the blending of multiple esters was thought to be preferable to a single compound. The U.S. pour point of  $-40^{\circ}$ C and high temperature requirement for a 3 cS fluid could be met by the reaction of simple mono-alcohols with dibasic carboxylic acids. The earliest commercial lubricant based on organic esters involved branched alcohols such as 2-ethylhexyl alcohol and adipic acid, azelic acid, and sebacic acid (**Figure 1**).



Figure 1. Structures of common components of lubricant esters.

Higher viscosity requirements of the British could be met using longer-chain acids and alcohols, but the low temperature requirements could not be met by these combinations. The solution was to use a slightly more viscous blend of the 3cS fluid with a viscosity improver, typically a polyglycol.

Two fundamentally different and incompatible lubricants were both unacceptable and major potential hazards. The use of the wrong lubricant was considered unacceptable even for emergency use. In the 1960s, an intermediate viscosity oil was developed with a viscosity of 5.5 cS at 99°C that could replace both of the fluids, especially for future engines. This fluid also was adopted by the U.S. Navy for use in its aircraft. The advent of supersonic aircraft led to a need for even higher oil temperatures and improved stability.

Hydrolysis is a characteristic reaction of esters in the presence of water. Hydrolysis can be avoided through the use of longer-chain and branched alcohols. The primary route for the degradation of the esters used in the lubricants described above is through an elimination reaction initiated by the loss of the hydrogen atom on the  $\beta$  carbon to the carboxylate (**Figure 2**).



**Figure 2.** Mechanism for  $\beta$ -elimination.

The  $\beta$ -elimination results in the decomposition of the ester to alkenes, carboxylic acids. Although the mechanism involves a base, it is simply an acceptor for the proton and could be a variety of species present in the lubricant. Because  $\beta$ -elimination requires a hydrogen atom on the  $\beta$  carbon atom, the elimination of hydrogen atoms at that position resulted in a series of more thermally stable lubricants.

#### 3. Current basestocks

As turbine engine technology developed and the desire for supersonic flight became the norm for the military, higher bearing load and bearing temperatures were needed. These developments required more stable lubricant basestocks. Because  $\beta$ -elimination reactions were one mode of degradation, alcohols that lacked hydrogen atoms at the  $\beta$  position were desired. Some common alcohols that fit the bill are the neopentyl polyols. These highly hindered alcohols react with acids of various chain lengths to form esters under acid catalyzed conditions, providing the lubricant esters in good yields. Current lubricants are based on the neopentyl polyols such as neopentyl glycol, pentaerythiol, and dipentaerythritol (**Figure 3**).



Figure 3. Structure of some esters commonly used in aircraft lubricants.

The esters used in the current aircraft lubricants use a mixture of carboxylic acids with between 5 and 9 carbon atoms, typically and may involve either linear acids or branched acids. Many common lubricants are based on a mixture of valeric acid, iso-valeric acid, heptanoic acid, nonanoic acid, and 3,5,5-trimethylhexanoic acid. The lubricants are prepared either from the acid-catalyzed esterification of the polyol with a mixture of the desired acids or it may involve the trans-esterification of a fatty acid methyl ester (FAME) with the polyol. The reaction can occur in a random manner, or can be controlled to occur stepwise, allowing more sterically hindered acids to react first and then complete the esterification with the less hindered acid [5]. The latter method allows esters to be prepared from biologically derived oils, such as vegetable oil [6]. The composition of the mixture of acids can be used to adjust the physical properties, including the viscosity and viscosity index of the resulting basestock [7]. The fact that a mixture is used also results in a wider liquid range for the resulting lubricant.

In general, esters based on the neopentyl polyols have excellent thermal stability and can perform well as lubricants. If, however, lower-quality reactants are used to prepare the ester, a substantially more reactive lubricant is obtained. Certainly, impurities in the alcohols that contain  $\beta$ -hydrogen atoms would significantly alter the high temperature stability. Other possible impurities include significant quantities of excess acid, which would increase the corrosivity of the oil; water, which has a significant solubility in the oil, can result in hydrolysis; and higher molecular weight polyols, such as dipentaerythritol or tripentaerythritol, can have a negative effect on the low temperature properties of the mixture.

The two grades of MIL-PRF-7808 that are available differ substantially in composition as is needed to obtain the difference in viscosity. The grade 3 lubricant because of the low temperature requirement has a higher content of low molecular weight acids and neopentylglycol as the dominant polyol. The total ion chromatogram from the gas chromatography-mass spectrometry (GC-MS) evaluation of a 3cS MIL-PRF-7808K grade 3 lubricant is shown in **Figure 4**.



Figure 4. A portion of the total ion chromatogram of a MIL-PRF-7808K grade 3 lubricant.

In an effort to obtain superior high temperature properties to the MIL-PRF-7808K grade 3 and still retain better low temperature properties than is available with MIL-PRF-23699, MIL-PRF-7808K grade 4 was developed. The grade 4 oil used a different mixture of acids and

alcohols to achieve a good compromise in properties. The total ion chromatogram from the GC-MS evaluation of a 4cS MIL-PRF-7808K grade 4 lubricant is shown in **Figure 5**.



Figure 5. A portion of the total ion chromatogram of a MIL-PRF-7808K grade 4 lubricant.

This lubricant contains primarily the pentaerythritol esters of valeric acid, heptanoic acid, octanoic acid, and 3,3-dimetylheptanoic acid. Also observed between 20 and 23 min retention time are four peaks that correspond to isomers of the tri-cresyl phosphate additive. The large number of different esters helps with the wide liquid range desired, whereas the higher molecular weights lead to an increase in viscosity from 3 to 4 cS.

A further increase in molecular weight is desirable for MIL-PRF-23699 lubricants, which have a still better thermal stability and viscosity. The change in molecular weight can be seen in the distribution of esters in **Figure 6**.



Figure 6. Total ion chromatogram of an MIL-PRF-23699 HTS lubricant showing the retention times where the esters elute.

The analysis of the acid composition of this lubricant indicates that at least six different acids are present in the mixture. The ability of multiple manufacturers to use somewhat different acid and alcohol blends yet achieve the same properties and have a compatible lubricant is thought to be a huge advantage.

Lubricant degradation at high temperatures is a significant problem. Degradation can result in an increase in acid number, an increase in viscosity, or an increase in the reactivity of the lubricant. For hindered esters where the  $\beta$ -elimination (discussed earlier) is blocked, there are

several possible reactions, including hydrolysis of the ester, trans-esterification of the ester with another ester, and oxidation of the ester.

The hydrolysis of esters is a well-known reaction that involves as the initial step the attack of either a water molecule of a hydroxide ion at the carbonyl carbon. The use of highly hindered esters reduces the rate of acid- and base-catalyzed hydrolysis by blocking easy access to the carbonyl carbon of the ester. The rate of hydrolysis can be reduced if water is excluded from the oil; however, it is soluble to a concentration of approximately 0.5% in these lubricants. Hydrolysis typically results in the presence of acids (increased acid number) and partial esters, where the polyol has one or more hydroxyl groups present.

The process of trans-esterification can be best seen as changes in the acids attached to a given molecule. This process has long been known because, if a lubricant is prepared containing two initial esters with the same alcohol and different acids [i.e.  $PE(nC_5)_4$  and  $PE(nC_7)_4$ ], after a period of time, the acids are scrambled and  $PE(nC_5)_3(nC_7)$ , etc., are found in the mixture. This process does not normally result in a serious change in the properties of the lubricant and is actually thought to be beneficial by increasing the number of different components. However, if transesterification occurs with a phosphate ester from an additive, changes of reactivity are possible (**Figure 7**).



Figure 7. Reaction of a lubricant ester with phosphate esters by trans-esterification.

Possibly the most detrimental reaction to the properties of polyolester-based lubricants is hightemperature oxidation. The initial stages of the oxidation involve the attack of an alkyl peroxy radical on a methylene group of the ester. The position  $\alpha$  to the carbonyl has been shown to be significantly more reactive than other methylene groups in the molecule [8]. 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 that can form a sludge in the engine (**Figure 8**) [9].



Figure 8. Thermal oxidation of PE ester at high temperature to give either anhydrides or an aldehyde and an acid.

The production of either an anhydride or an aldehyde is undesirable because they are reactive and have a tendency to polymerize, creating high molecular weight species. These reactions are eliminated in the presence of either BHT or an amine antioxidant until those concentrations are depleted.

### 4. Important lubricant properties

The development of a lubricant specification requires an examination of what properties are important and what methods will be used to demonstrate that the specification has been met. Many of the common properties, including the method used for the determination of the property, are shown below.

**Viscosity (ASTM D 445)** — Determines the thickness of the lubricant film that coats the bearing. Viscosity is measured at several temperatures and helps determine the maximum operating temperature of the engine. Changes in viscosity are observed as a lubricant degrades and these changes are a measure of lubricant health.

**Pour Point (ASTM D 97)**—The temperature at which a liquid becomes semi-solid or loses its flow characteristics. This property is related to the ability to service or start an engine in cold climates.

**Flash Point (ASTM D 92)**—The lowest temperature at which vapors of a fluid will ignite. Measuring a flash point requires an ignition source. At the flash point, the vapor may cease to burn when the ignition source is removed. This parameter is used as a way to control flammability, although understanding flammability requires a knowledge of many other parameters.

**Total Acid Number (ASTM D 664)**—A titration-based determination of the amount of acids contained in oil. Acids in the oil may cause corrosion of the bearings and valve guides. In esterbased lubricants, the acid number can indicate exposure of the lubricant to water, resulting in the hydrolysis of the oil. It can also indicate incomplete reaction when the oil was prepared. As the lubricant is used, the acid number of the used oil is also be an indicator of lubricant degradation.

**Lubricant Compatibility (FED-STD-791, Method 3403)**—A determination of hot aging miscibility of the candidate oil with other oils that might be encountered when the engine is in service. This test is necessary due to differences in the additive packages that various manufacturers use to achieve the required performance standard.

**Elastomer Compatibility [Def Staf 05-50 (Part 61) Method 22]**—A test used to determine the swell and deterioration of seal materials when soaked in oil for an extended time. Some high-stability basestocks and additive packages can cause the deterioration of certain seal materials over time.

**Oxidation and Corrosion Stability (ASTM D 4636)**—This test examines the bulk oil stability and the impact of breakdown products on certain representative metallic materials.

**Thermal Stability and Corrosivity (FED-STD-791, Method 3411)**—A quality control test for identifying contamination from non-aviation ester-based products.

**Deposit Control**—This test involves a full-scale heated bearing test rig. The test is run for 100 h, and the oil condition is evaluated and the cleanliness of the bearing is evaluated for the formation of deposits.

**Load-Carrying Capacity or Boundary Film Lubricating Ability (FED-STD-791, Method 6509)**—This property is measured with a Ryder Gear Test.

**Foaming Tendency**—Can be measured by either a static (ASTM D 892) or a dynamic method (Fed-STD-791, Method 3214). Oil can foam when subjected to the shear forces in the engine. Foaming is frequently due to impurities of various silicone compounds.

Sediment or Particulate Contamination (FED-STD-791, Method 310 or 3013)—This test measures the amount of suspended or dissolved solids in the oil. The low maximum ash content of MIL-PRF-23699 precludes the use of metal containing lubricant additives.

**Hydrolytic Stability [Def Stan 05-50 (Part 61) Method 6]**—Evaluates the storage stability and the stability of the oil in capped lubrication systems. Hydrolysis is a degradation reaction of the oil with water to regenerate the original alcohol and acids used to prepare the ester.

**Evaporation Loss (AST D 972)**—This test determines the amount of volatile components in the lubricant. A low evaporation loss means that too much oil will not be consumed during operation.

**Shear Stability (ASTM D 2603)** — Shear stability means that the lubricant will not lose viscosity due to the mechanical forces encountered in the operating engine.

**Corrosion Inhibition (SAE ARP 4240)** — Determined by ball corrosion testing, this attribute is only required for MIL-PRF-23699 oils of C/I class. Oils of the C/I class are primarily used in marine applications.

**Storage Stability Tests**—This test ensures that all of the lubricants remain miscible during extended storage periods of up to 3 years.

Acid Assay (FED-STD-791, Method 3500) — In this method, the component acids used in the preparation of the ester are measured. This is needed to ensure that different batches of the lubricant are similar to the original qualified lubricant.

**Trace Metals** — The trace metal content of new oils is controlled to provide a good baseline for the spectrographic oil analysis program.

**Spectrographic Oil Analysis Program (SOAP)**— The concentration of several wear metals (Fe, Ag, Cr, Al, Mg, Ti, Mo, and V) are measured regularly by atomic emission either using a rotating carbon electrode or by inductively coupled plasma (ICP-OES). As an engine is used, the concentrations of wear metals increase. If the normal wear pattern of the engine is known, changes in the metal concentrations that are not consistent with the pattern can be an indicator of impending problems. Excessive wear metals in the oil are an indication that some type of maintenance is needed and the metals present may provide an indication of the area of concern.

### 5. Lubricant specifications

Lubricant compatibility as a global problem requires standardization; however, the decision was made to not require a single supplier or a single highly specified composition. This would eliminate competition and would stop the development of better compositions. Instead, a series of detailed specifications were adopted for lubricants based on sets of properties. In the end, commercial jet aircraft lubricants are primarily governed by standard SAE-5780. Military jet aircraft generally fall under two standards based on different low temperature requirements. U.S. Air Force (USAF) aircraft typically use the MIL-PRF-7808 [10] specification because of the need for pumpability at lower temperatures. Naval aviation uses MIL-PRF-23699 [11], which has better high temperature properties. In most areas, MIL-PRF-23699 and SAE-5780 specifications are quite similar and many currently available products meet both of these specifications. These specifications undergo regular review and revision. In addition, MIL-PRF-7808L is now available in two grades with different viscosities: grade 3, a 3 cS viscosity fluid, and grade 4, a 4 cS viscosity fluid. The two grades require changes in the basestock composition, although similar chemistries are used. MIL-PRF-23699 is available in three types: standard, corrosion inhibiting (CI), and high thermal stability (HTS). The three MIL-PRF-23699 types differ primarily in the additive package used. A summary of the different lubricants is given in Table 1.

Specification	Grade or type	Viscosity	Common use					
		(cS at 100°C)						
MIL-PRF-7808L	Grade 3	3	Best low temperature properties					
MIL-PRF-7808L	Grade 4	4	Improved high temperature properties but higher pour point					
MIL-PRF-23699		5	Good viscosity index-not suitable for very cold climates					
MIL-PRF-23699	CI	5	Includes CI-for use in maritime environments					
MIL-PRF-23699	HTS	5	Best high temperature stability					
Table 1. Common lubricant specifications used in aircraft engines.								

Some of the specifications for each of the lubricants are included in **Table 2**.

Specification	MIL-PRF-7808L	MIL-PRF-7808L	MIL-PRF-23699	MIL-PRF-23699 CI	MIL-PRF-23699 HTS			
	grade 3	grade 4						
Viscosity (cS)	3.0 min	1.1 min	4.90–5.40	4.90–5.40	4.90–5.40			
205°C	11.5 min	4.0 min	23.0 min	23.0 min	23.0 min			
100°C	$1.7 \times 10^4 \text{ max}$	17.0 min	13,000 max	13,000 max	13,000 max			
40°C		$2.0 \times 10^4 \text{ max}$						
-40°C								
-51°C								
Flash point (°C)	210 min	210 min	246	246	246			
Evaporative loss (%)	30 max	15 max	10 max	10 max	10 max			
Foaming (static)	100 max	100 max	25 max	25 max	25 max			
Volume (ml)	60 max	60 max	60 max	60 max	60 max			
Collapse time (s)								
Deposition test	1.5 max	0.7 max	218°C	218°C	218°C			
Rating	20 max	20 max	15 max	15 max	15 max			
TAN change	100 max	100 max	120 max	120 max	60 max			
(mg KOH/g)	100 max	100 max						
Viscosity at 40°C %								
Change Oil								
consumption (ml)								
Lead corrosion (g/m <sup>2</sup> )	9.3 max	9.3 max						
Corrosion test	232°C	232°C	±2.0	±2.0	±2.0			
Silver (g/m <sup>2</sup> )	±4.5 max	±4.5 max						
Bronze (g/m <sup>2</sup> )	±4.5 max	±4.5 max						

**Table 2.** A summary of selected performance specifications for MIL-PRF-7808L [10] and MIL-PRF-23699 [11]lubricants.

### 6. Lubricant additives

Additives are a part of all lubricant systems because they can impart properties to the overall lubricant that the basestock does not possess. They can also allow longer lubricant lifetimes by eliminating certain modes of basestock decomposition. For example, when a lubricant is used, it is exposed to temperatures much higher than the bulk oil temperature for short periods of time, in the presence of oxygen. Additives can reduce the decomposition of the basestock by scavenging free radicals formed in the initial stages of the reaction. Aircraft lubricants typically contain the following groups of additives:

- Boundary lubrication additives (anti-wear, lubricity, and extreme pressure)
- Antioxidants
- Anti-corrosion additives
- Anti-foaming additives
- Metal deactivators
- Viscosity index improvers

The choices of additives are frequently limited based on the thermal stability of the additive, needs for long lifetimes, and tendencies of the additives to form deposits [12]. The mechanisms of action associated with each of the types of additive are described in the following sections.

#### 6.1. Antioxidants

One of the primary decomposition reactions of lubricants is oxidation primarily by atmospheric oxygen. In lubricants derived from crude oil, there are normally enough naturally occurring sulfur compounds to inhibit oxidation for a period of time. Synthetic lubricants and some highly refined natural lubricants, however, must have additives to reduce or eliminate oxidation in the presence of oxygen. Oxidation of lubricants typically leads to an increase in viscosity and the formation of sludge and is the primary limit to the maximum bulk oil temperature.

Most classes of natural and synthetic lubricants are oxidatively degraded via a radical chain mechanism. In this mechanism, molecular oxygen attracts a hydrogen atom creating a free radical. The radical formed reacts with other lubricant molecules attracting hydrogen atoms or other groups, generally increasing the size of the molecule. The chain continues until it encounters another radical, resulting in chain termination.

Antioxidant additives can act in two different ways. First, they can react with oxygen to form a stable species. Second, the antioxidant can react with radicals formed, acting as a chain termination step. Among the most common antioxidants are hindered phenols and aromatic amines. The structure of these compounds is shown in **Figure 9**.



Figure 9. Structures of some common antioxidants.

As higher-temperature lubricants are being developed, these antioxidants are not sufficiently stable, which has led to the introduction of some high molecular weight polymeric antioxidants. Although the structures of these systems are proprietary, they solve similar problems and may involve similar chemistry.

All of the antioxidants above react to quench radical chain reactions. Because the amine antioxidants are common in aircraft lubricants, their mechanism will be discussed in more detail. It is commonly thought that the hindered amines are rapidly oxidized to the aminoxy radical. This radical reacts with alkyl radicals, trapping them to form N-alkoxy amines, which react with peroxyl radicals to give products and regenerate the aminoxy radical [13]. The oxidation of BHT has also been thoroughly studied. The initial oxidation by a radical removes a hydrogen atom forming a phenoxy radical that then reacts to form a quinoid, which is relatively stable.

#### 6.2. Anti-corrosion additives

A corrosion inhibitor is a compound that decreases the rate of corrosion of a material, typically a metal or metal alloy. Corrosion inhibitors are of greater importance in the MIL-PRF-23699 CI lubricants primarily because of their intended use in more corrosive environments. Typically, with iron-based alloys (steel), corrosion occurs due to the presence of oxygen in contact with the steel, which results in the formation of rust. Corrosion inhibitors act by forming a passive layer on the surface of the alloy that protects the surface from further oxidation. Metal surfaces are typically covered with a layer of oxides and hydroxides formed when the metal is placed in contact with air. In some metals, such as aluminum, the oxide layer protects the surface from further oxidation (passivation). In iron-based alloys, however, the oxide layer is porous and further protection is needed.

Typical rust inhibitors include metal sulfonates and metal carboxylates. These additives act because they have an ionic head group that can bind to the metal oxide surface and a non-polar tail that forms a protective coating over the metal. These additives, however, are not ash less and may not qualify for the MIL-PRF-23699 CI standard. A product that avoids this problem consists of a mixture of an amine, carboxylic acid esters, and a phosphate ester. The mixture itself is proprietary; however, the MDS does at least give an approximate composition.

#### 6.3. Anti-foaming additives

Foam is formed when air is trapped in a liquid forming bubbles. It is frequently observed when a stream of liquid re-enters the bulk liquid, such as when fuel is added to a fuel tank. Foams can result in reduced capacity and reduced pumping efficiency and prevent lubricants from effectively flowing. In aircraft applications, lubricants should form minimal amounts of foam and the foam formed should rapidly collapse. Typically, lubricant foaming is caused by contamination with high molecular weight silicone greases, which form foams that do not easily collapse. Foams collapse when the air bubbles merge forming larger bubbles that rise and the bubbles pop releasing the air at the surface [14].

Anti-foaming additives are all surface active agents that are insoluble in the lubricant. They typically are of low viscosity, which allows them to spread over the surface of the oil. Many also contain some solid particles dispersed in the additive. When a foam forms, the bubbles have structures similar to lipid bilayers called lamella. The anti-foaming additive locates itself at the air-liquid interface, maximizing the surface area of the foam bubbles. Smaller bubbles merge and the larger bubbles move toward the surface, causing the foam to collapse.

Aircraft lubricant foam control additives are typically moderate molecular weight silicone oils. It have been observed that silicone oils can act in many ways, causing foam in some cases and eliminating the foam in others depending on molecular weights and structures. The current anti-foaming additives have been shown to successfully eliminate foaming in the lubrication system.

#### 6.4. Boundary lubrication additives

In aircraft applications, a lubricant must be effective in different lubrication regimes, including the fluid film lubrication regimes (hydrodynamic lubrication and elasto-hydrodynamic lubrication) and boundary lubrication. Hydrodynamic lubrication, where the two bearing surfaces are separated by a complete film of the lubricant, is generally desirable. As the shear stress on the bearing increases, the lubricant properties are not adequate and the film is no longer of sufficient thickness. Elasto-hydrodynamic lubrication occurs between rolling bodies [15]. These systems operate under stresses where a fluid film would not be expected to be maintained. The high pressure, however, causes a temporary increase in the viscosity of the lubricant in the contact area and a fluid film is maintained. Boundary lubrication involves direct contact between the surfaces of the bearings. Boundary lubrication is generally undesirable but is also unavoidable especially during start-up and shutdown. Boundary lubrication additives are required to reduce friction between and wear of the engine components until lubricant flow is adequate to maintain fluid film lubrication.

A number of boundary lubrication additives have been developed for various purposes and the vast majority are based on phosphorus or sulfur compounds. For aircraft applications, sulfur compounds are generally less desirable because of the lack of stability and the formation of strong acids on oxidation. Phosphorus compounds can include phosphate esters, thiophosphate esters, and metal thiophosphates. Metal thiophosphates and thiophosphate esters contain sulfur, and the metal dithiophosphates are more likely to form metal containing ash on decomposition. For aircraft applications, phosphate esters and, in particular, triaryl phosphates are the additives of choice.

Triaryl phosphates are characterized by three aromatic rings attached to the phosphorus through oxygen linkages. The most common commercial additives are tricresyl phosphate and butylated triphenyl phosphate. The structures of these compounds are shown in **Figure 10**.



Figure 10. Structures of some common tri-aryl phosphate esters.

Phosphate esters are known to react at the surface of metals to form a coating that is both durable and lubricious. Phosphate esters have been shown to react with oxides or hydroxides on the metal surface to form a multilayer coating that is chemically bound to the surface. As the coating wears away, iron diffuses to the surface and more of the coating forms. The mechanism for coating formation begins with the oxide surface of the iron. A surface oxide displaces one of the alkyl groups from the phosphate ester giving a bound phosphate di-ester. Further reaction occurs to form iron polyphosphate, which has, at the surface, bound aryl groups (**Figure 11**) [16].

If a metal bearing is operated under conditions where little oxygen is present, there still appears to be a reaction to give a similar film. The principle difference in the film formation mechanism is to break a C-O bond to the aromatic ring, leaving a bound metal phosphate. The product of this reaction has been shown to add to another aromatic ring forming higher molecular weight phosphate esters. Under these circumstances, a coating of similar structure is still formed [17].

Advanced bearings under development have a very different surface chemistry. These bearings will be made from carburized or nitrided stainless steels. After machining of the bearing, it is heat treated in the presence of a carbon or nitrogen source. The resulting surfaces have little oxide or hydroxide present but a surface dominated by carbides or nitrides. It is unknown if phosphate ester additives will form a lubricious film on these surfaces. The non-heat-treated steels have been shown to react; however, heat-treated steals are currently under study [18]. The interaction of antioxidants, esters, and phosphate esters in the presence of various carbides has been shown to increase reactivity [19].





#### 6.5. Metal atom deactivators

Metal ion deactivators are incorporated into lubricants to react with metal ions typically formed from the action of naturally occurring acids on the metallic parts of the lubrication system. The metal ions are of concern because of their catalytic effects, principally the tendency of copper ions to form a gummy copper mercaptide gel.

In aviation lubricants, the primary metal ion deactivator is benzotriazole. It is thought that benzotriazole reacts with metal atoms at the surface and in solution. On the surface, benzotriazole forms a passive layer that prevents further reaction at the metal surface. Dissolved metal ions react with the benzotriazole to form a complex, which reduces the reactivity of the soluble metal ion. An added benefit of benzotriazole as an additive is that it also acts as an antioxidant [20].

### 7. Future developments

In the quest for higher-performance turbine engines, a number of changes are under development. Possibly the most significant is the development of harder and more corrosionresistant metal alloys such as Pyrowear and CSS22, among others, hard coatings such as TiC, and low-density silicone nitride–bearing materials. These materials are designed for high load carrying and higher temperature, which leads to challenges in lubricant stability. Harder and more stable coatings will allow for higher temperatures and loads adding stress to the lubricant system. It may be necessary to develop new basestocks that have wider liquid ranges and greater thermal stability.

More importantly, all of these new bearing materials have radically different surface chemistry than traditional steel-based bearings. The additive packages, particularly boundary lubrication additives, are dependent on the presence of an oxide or hydroxide surface coating to react with. The new bearing materials have a surface chemistry dominated by the presence of carbides or nitrides. The data are uncertain as to the level of surface coverage and the reactivity of the phosphate esters with these new surfaces.

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