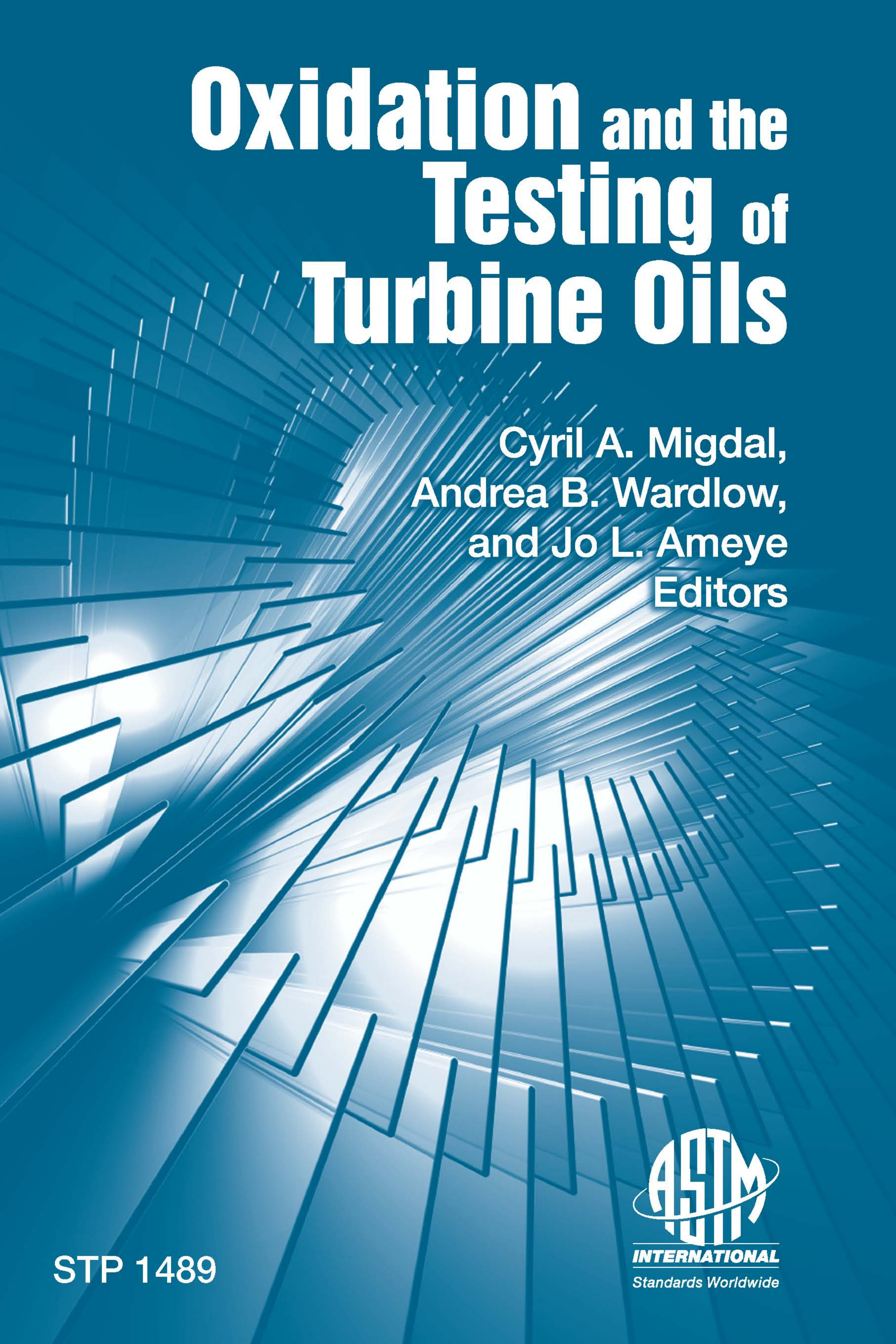

Oxidation and the Testing of Turbine Oils

Cyril A. Migdal,
Andrea B. Wardlow,
and Jo L. Ameye
Editors

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Foreword

This publication, *Oxidation and the Testing of Turbine Oils*, contains papers presented at the symposium of the same name held in Norfolk, Virginia , on December 5, 2005. The symposium was sponsored by ASTM Committee D2 on Petroleum Products and Lubricants and its Subcommittees D02.09 on Oxidation and D02.C0 on Turbine Oils. The symposium co-chairman were Cyril A. Migdal, Chemtura Corporation, Middlebury, Connecticut and Andrea B. Wardlow, ExxonMobil Research & Engineering, Paulsboro, New Jersey.

Contents

Overview

This publication is a compilation of the papers delivered at the Symposium on Oxidation and the Testing of Turbine Oils, held in Norfolk, Virginia, on December 5, 2005. The symposium was sponsored by ASTM Committee D2 on Petroleum Products and Lubricants and its Subcommittees D02.09 on Oxidation and D02.C0 on Turbine Oils.

This Symposium brought together original equipment manufacturers, end users, lubricant producers, lubricant additive suppliers, test equipment manufacturers, and standard test method developers in a forum to hear about industry trends to gain an understanding of the suffering points, evolving lubricant /antioxidant additive technologies, and changing equipment designs and operating conditions, with a focus on how these factors impact oxidation. As a standardization organization, the knowledge gained from this symposium is being used to develop new and improved oxidation tests for turbine oils to service and support each facet of the lubricant and turbine industry represented at the symposium.

Subcommittees D02.09 and D02.C0 have wrestled with the question: Are the current bench tests, ASTM D943 TOST, ASTM D4310 Sludge Tendency and ASTM D2272 RPVOT adequate predicative tools for measuring oxidative degradation? Can we do better? Based the excellent turn out for the symposium, it is clear that the answer to this question is yes, we can do better.

To put the state of the art into perspective the original ASTM D943 method issued in 1947. The longest life oil in the original D943 round robin lasted less than 4000 hrs. Turbine Oils available in the marketplace today exhibit TOST lives of greater than 10,000 hrs; far exceeding the original scope of the D943 test. Many of these long life oils challenge the scope of the other available oxidation test as well. Thus the industry is left with using tools that are eligible for retirement to distinguish the quality and durability of new and in-service turbine oils.

This publication has been assembled to provide you with knowledge about industry trends, novel oxidation tests and modifications of existing tests for further consideration. Today Subcommittee D02.09 is taking the first step toward bridging the gap between available standardized oxidation stability testing tools and the state-of-the-art lubricants, which are characterized by them. Several new test methods are under development specifically targeted to evaluate varnish formation plaguing gas turbines, particularly units operating in peak or cyclic service and to evaluate long life steam turbine oils manufactured with highly refined and synthetic base stocks.

This publication is made possible by the dedication and hard work of the authors and the support of their employers; the reviewers who volunteer to read the papers and provide feedback; and the ASTM staff who grease the wheels.

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Oxidation Fundamentals and Its Application to Turbine Oil Testing

ABSTRACT: The current turbine oil oxidation bench tests have been in place for many years. Recently, however, the basestocks used to formulate these lubricants have changed significantly. Traditional basestocks, containing high levels of aromatics and sulfur, have been substantially displaced by more highly refined basestocks, which have very low levels of aromatics and almost no sulfur. Over time it has become clear that the oxidation performance of the different basestock classes is quite different. One key question, however, remains unanswered, "What modifications are required in current bench tests to adequately mimic oxidation processes in modern turbine lubricants?" In order to adequately address this critical question, the fundamentals of lubricant oxidation and stabilization will be discussed. Data will be presented on the oxidation of different basestocks under varying conditions of temperature, metal catalysts and antioxidant type, using model bulk oil oxidation tests. The data highlights the fundamental oxidation mechanisms that can occur in turbine oil systems and new test methods are proposed.

KEYWORDS: oxidation, stabilization, deposits, sludge, antioxidant, turbine oil, basestock, metal catalysts, bench tests, ASTM D 943, ASTM D 2272, CM-A (ASTM D 2070)

Introduction

Recent years have seen a growing demand for extended life steam, gas, and combined cycle turbine oils. This has been partly due to the introduction of more highly refined basestocks exhibiting improved oxidation resistance. However, many marketing claims for these long-life lubricants have been based on extended ASTM D 943 Life Turbine Oil Stability Tests. To a lesser extent claims for extended length ASTM D 2272 Rotating Pressure Vessel Oxidation Tests have been used. One concern in the technical community is that these extended length claims are based on performance tests that were originally developed for conventional solvent refined basestocks. Chemically, the newer hydrocracked and iso-dewaxed basestocks are quite different from the traditional solvent refined materials. These chemical differences have been well documented [1–4]. Most noteworthy is the significant reduction in aromatics and sulfur as a result of the new refining processes. In some basestocks the level of aromatics and sulfur can be quite low. These chemical changes significantly impact the finished turbine oils performance in oxidation bench tests. One question that still remains unanswered relates to the adequacy of current test methods for evaluating the oxidation resistance of turbine oils formulated with these new basestocks.

To properly address these concerns, and suggest testing alternatives for the future, it is critical to have a detailed understanding of the mechanism of lubricant oxidation and stabilization. It is equally important to understand how the chemistry of the various basestock types impacts overall oxidation stability. The purpose of this paper is to provide this overview. The first part of the paper details the mechanism of a lubricants oxidation and how antioxidant additives function to stabilize the lubricant. Consideration will be given to temperature effects, metal contamination effects, and the effect of lubricant chemical composition (i.e., the effects of lubricant-based aromatics and sulfur). The second part of the paper provides the results of an oxidation study performed using two new model bulk oil oxidation tests. The study includes oxidation results collected at a range of temperatures, catalyst types, test lengths, and basestock types. The results suggest possible alternative test methods that should be considered as improvements over the current tests.

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Part I—Mechanism of Lubricant Oxidation and Stabilization

A number of excellent publications are available covering the mechanism of hydrocarbon oxidation and antioxidant function [5–10]. This brief review will discuss these mechanisms from the standpoint of Turbine Oil Oxidation, with an understanding of the chemical and physical changes that occur in turbine oils during the oxidation process. It should be pointed out that lubricant oxidation and stabilization is a complicated process with many varied mechanistic interpretations depending on lubricant molecular structure, oxidation conditions, and stabilization system. This review is designed to provide the basics.

Lubricant Oxidation

Metal Catalyzed Chain Initiation

Almost all conditions of lubrication involve contamination by various metals. The metals of most concern in a turbine are copper and iron. These metals play a critical role in the chain initiation process of lubricant oxidation. Two types of initiation reactions have been proposed (Reactions 1 and 2).

$$\mathrm{RH} + \mathrm{O_2} \rightarrow \mathrm{R}\cdot + \mathrm{HOO}\cdot \tag{1}$$

$$2\mathrm{RH} + \mathrm{O_2} \rightarrow 2\mathrm{R}\cdot + \mathrm{H_2O_2} \tag{2}$$

these reactions are generally very slow at room temperature but proceed at a moderate rate above 100°C. The ease with which hydrocarbon molecules undergo Reactions 1 and 2 follow the bond dissociation energies for the respective hydrocarbon types (kcal/mole): benzylic (85) > allylic (89) > tertiary (92) > secondary (95) > primary (98) > phenyl (112) [11]. Thus, aromatics are the most easily oxidized via hydrogen abstraction in the benzylic position (α-paraffinic or naphthenic hydrogen relative to the aromatic ring).

A second class of initiation reactions occurs at a much lower temperature and is catalyzed by the presence of iron or copper contaminants. These are the hydroperoxide decomposition initiation reactions and are illustrated below (Reactions 3 and 4).

$$\mathrm{Fe^{3+}} + \mathrm{ROOH} \rightarrow \mathrm{Fe^{2+}} + \mathrm{ROO}\cdot + \mathrm{H^+} \tag{3a}$$

$$\mathrm{Fe^{2+}} + \mathrm{ROOH} \rightarrow \mathrm{Fe^{3+}} + \mathrm{RO}\cdot + \mathrm{HO^-} \tag{3b}$$

$$\mathrm{Cu^{2+}} + \mathrm{ROOH} \rightarrow \mathrm{Cu^+} + \mathrm{ROO}\cdot + \mathrm{H^+} \tag{4a}$$

$$\mathrm{Cu^+} + \mathrm{ROOH} \rightarrow \mathrm{Cu^{2+}} + \mathrm{RO}\cdot + \mathrm{HO^-} \tag{4b}$$

As hydroperoxide levels increase due to oxidation, the hydroperoxide decomposition initiation reactions start to predominate. Metal catalyzed oxidation and its inhibition have been extensively reviewed [12].

Chain Propagation and Branching

The chain propagation step generally involves the reaction of a substrate to produce additional radicals that "propagate" the oxidation sequence. The first propagation step involves the rapid reaction of alkyl radicals (R·) with dissolved oxygen ($\mathrm{O_2}$) in the lubricant to produce peroxy radicals (ROO·) (Reaction 5). These peroxy radicals subsequently react with additional hydrocarbon molecules to produce hydroperoxides (ROOH) and additional alkyl radicals (Reaction 6).

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot \tag{5}$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot \tag{6}$$

Thus Reaction 6 illustrates the formation of hydroperoxides that take part in the metal catalyzed initiation reactions. A variety of chain branching steps are possible based on the lubricant type and system temperature. Some of these are shown in Reactions 7 through 9.

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot \tag{7}$$

$$\mathrm{RO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R}\cdot \tag{8}$$

$$\mathrm{HO}\cdot + \mathrm{RH} \rightarrow \mathrm{H_2O} + \mathrm{R}\cdot \tag{9}$$

Many other initiation, propagation, and chain branching reactions have been proposed and excellent reviews are available that cover these mechanisms and the kinetics of autoxidation [13,14].

Formation of Aldehydes and Ketones

Two unique reactions in the chain branching sequence are the formation of aldehydes and ketones. These are unique chemical species in the oxidation process because their subsequent reactions lead to the formation of oligomers, polymers, and eventually sludge and deposits. There are a number of oxidation pathways that lead to the formation of these species. Two of the more accepted mechanisms are shown in Reactions 10 and 11.

Reaction 10 involves a chain scission step that results in the formation of an alkyl radical and two lower molecular weight hydrocarbon fragments. This reaction affects the physical properties of the lubricant in three ways; (1) the viscosity will decrease, (2) the volatility will increase, and (3) the polarity will increase. The alkyl radicals produced are available to react with oxygen in a propagation step as shown in Reaction 5.

Reaction 11 is representative of a chain termination reaction that consumes two peroxy radicals and generates an alcohol and carbonyl compound. This pathway can only be followed if the peroxy radicals contain an extractable α-hydrogen atom. In this mechanism the polarity of the hydrocarbon will increase but the molecular weight will be substantially unaffected.

$$\mathrm{RR'HCO}\cdot \rightarrow \mathrm{RCH{=}O} + \mathrm{R'}\cdot \tag{10a}$$

$$\mathrm{RR'R''CO}\cdot \rightarrow \mathrm{RR'C{=}O} + \mathrm{R''}\cdot \tag{10b}$$

$$2\mathrm{RR'CHOO}\cdot \rightarrow \mathrm{R'RC{=}O} + \mathrm{RCHOHR'} + \mathrm{O_2} \tag{11}$$

Formation of Alcohols and Water

Reaction 11 provides one example of alcohol formation during the oxidation process. Alternatively, an alkoxy radical (RO·) or hydroxy radical (HO·) can abstract a hydrogen from another hydrocarbon molecule to produce, respectively, alcohols and water (Reaction 8 and 9).

Formation of Carboxylic Acids

As oxidation progresses acid levels start to increase. This is primarily due to the formation of carboxylic acids. This increase in lubricant acidity results in further oxidation caused by the prooxidant effect of the carboxylic acids. Carboxylic acids are formed by oxidation of aldehydes and ketones. The mechanism for this oxidation varies based on the type of lubricant derived aldehydes and ketones. Figure 1 provides a typical mechanism for these oxidations. Note that oxidation of ketones proceeds by initial abstraction of an α-hydrogen, while oxidation of aldehydes proceeds by initial abstraction of an aldehydic hydrogen. Ketones, in general, are oxidized more slowly than aldehydes. The ketone oxidation can proceed through a nonradical rearrangement that results in two lower molecular weight organic fragments [15]. Thus, another example is illustrated where lubricant oxidation results in a decrease of hydrocarbon molecular weight. The aldehyde oxidation can proceed through an intermediate peroxy-acid that undergoes molecular decomposition to form the carboxylic acid [16].

Condensation Reactions

Thus far examples have been provided where lubricant oxidation results in a decrease in viscosity, an increase in volatility, and an increase in polarity. However, most lubricants subjected to oxidation tests or used in the field generally undergo an increase in viscosity as oxidation proceeds. This contradiction

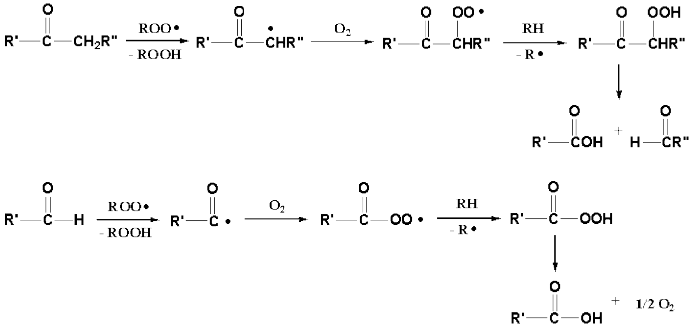


FIG. 1—*Oxidation of aldehydes and ketones to carboxylic acids.*

between mechanism and practice can be explained by the condensation reactions that start playing a significant role as the levels of aldehydes and ketones become appreciable. These reactions are best known as Aldol Condensations and are illustrated in Fig. 2 for the reaction of ketones [17].

These reactions can progress leading to the formation of oligomers and low molecular weight polymers. This results in a significant increase in the apparent viscosity of the lubricant. Thus, the reduction in lubricant molecular weight caused by chain scission reactions that form aldehydes, ketones, and carboxylic acids, is counteracted by the increase in lubricant molecular weight caused by condensation reactions. In the early stages of lubricant oxidation, it may be possible to observe a small viscosity drop caused by chain scission. However, as the overall oxidation progresses the affects of the condensation reactions begin to overwhelm the affects of the chain scission reactions. This results in an overall increase in lubricant viscosity that continues as the number and frequency of condensation reactions increases. Severe oxidation conditions can usually result in a lubricant that solidifies and shows significant weight loss due to volatilization.

Sludge and Deposit Formation

The condensation products described above are high molecular weight polar oligomer molecules. These materials have a finite solubility in the unoxidized portion of the lubricant. Condensation products containing a high concentration of aromatic groups (R' and R''=Aryl in Fig. 2) will be chemically quite different from the paraffinic and naphthenic oil molecules that make up the major components of the lubricant. Eventually the chemical changes in these oligomers will cause them to be insoluble in the unoxidized portion of the oil. At this point the oligomers will separate from the system resulting in the formation of sludge and deposits. Sludge is usually characterized as insolubles in the bulk oil, while deposits are formed on metal surfaces. Deposit formation is further promoted by the attraction of polar oligomers to hot polar metal surfaces.

Many materials in the lubricant can promote the formation of sludge and deposits. The increased kinetic rate of aromatic group oxidation usually leads to an increase in sludge and deposits. Metal con-

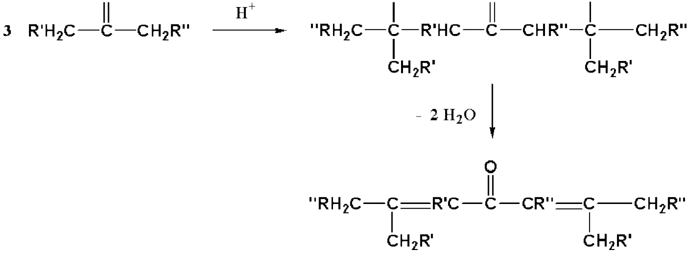


FIG. 2—*Condensation of ketones during lubricant oxidation.*

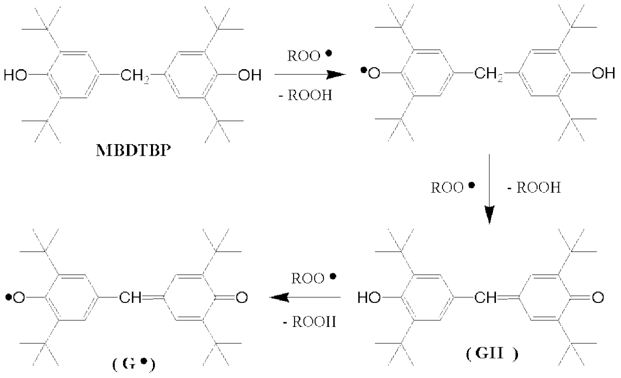


FIG. 3—*Mechanism of 4,4′-methylenebis(2,6-di-tert-butylphenol) function.*

taminants (copper and iron), baseoil sulfur, additive sulfur and arylamines can also promote the formation of sludge and deposits. This is especially true in lubricants containing a high level of aromatic structures. The next section will describe the effects of additives in more detail.

Lubricant Stabilization

Lubricant stabilization mechanisms involve the use of antioxidants. Two types of antioxidants are generally employed based on the type of stabilization effect they provide. Primary antioxidants function to scavenge alkyl peroxy and alkoxy radicals before they can react with oil molecules in the propagation reactions. This process eliminates the possibility for Reaction 6 to take place. The most common types of primary antioxidants are hindered phenolics and arylamines. Secondary antioxidants function to decompose the unstable alkyl hydroperoxides to the more stable alcohol form. In doing so Initiation Reactions 3 and 4, and Propagation Reactions 7, 8, and 9 are prevented. The most common types of secondary antioxidants are phosphorus and sulfur compounds. The mechanism of antioxidant function is very much dependent on the type of antioxidant being employed and the chemical composition of the lubricant. Consideration of oxidation temperature, metal contamination, and chemical composition of the lubricant basestock should all be considered when selecting an antioxidant system. Also, certain combinations of antioxidants exhibit a stabilization synergy that cannot be achieved when using the antioxidants individually. This synergy is also dependent on temperature, metal contamination, and basestock composition.

Some examples of antioxidant stabilization mechanisms are provided below.

Primary Antioxidants: Hindered Phenolics and Arylamines

One of the most effective hindered phenolic antioxidant stabilizers used in lubricants is 4,4′-methylenebis(2,6-di-tert-butylphenol) (MBDTBP). It's chemical structure and mechanism of function is shown in Fig. 3. The molecules effectiveness is attributed to the presence of tert-butyl groups in the ortho position relative to the reactive hydroxyl group. Under oxidative conditions the MBDTBP molecule "scavenges" an alkyl peroxy radical to produce an alkyl hydroperoxide. The MBDTBP molecule is transformed to a phenoxy radical which is significantly more stable than the alkyl peroxy radical it destroys. The formation of an alkyl hydroperoxide terminates the propagation step in the oxidation process.

The MBDTBP molecule is capable of scavenging three alkyl hydroperoxide molecules before forming the galvinoxyl radical (G·). In the presence of oxygen galvinoxyl will react further resulting in cleavage of the MBDTBP structure and formation of 2,6-di-tert-butyl-benzoquinone (2,6-BQ) and 3,5-di-tert-butyl-4-hydroxybenzaldehyde (3,5-BA) [18]. This process is illustrated in Fig. 4. The benzaldehyde product is an effective antioxidant as well and will scavenge an additional alkyl peroxy radical. However, the oxidation of galvinoxyl results in the formation of an alkyl radical. So overall, the MBDTBP molecule can destroy three radicals.

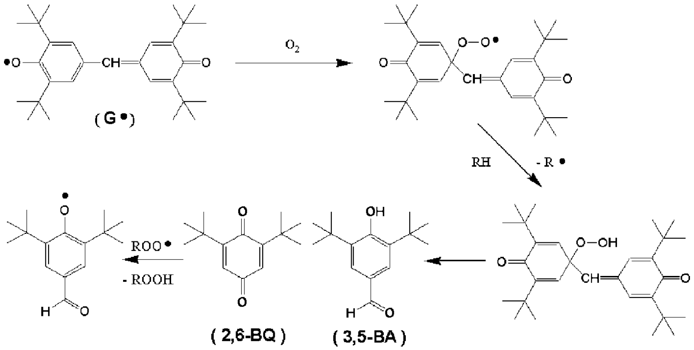


FIG. 4—*Mechanism of galvinoxyl decomposition.*

Most of the alkylated diphenylamine antioxidants available commercially are mixtures of mono- and di-alkylated diphenylamines. Alkylation is predominantly in the para-position relative to the amine group. An example of a para-substituted and di-alkylated diphenylamine is illustrated as NH in Fig. 5. The mechanism of alkylated diphenylamine function is complex involving both a catalytic cycle where the starting amine is regenerated, and a decomposition step where the nitroxyl radical (NO·) is destroyed along with the ability of the amine to regenerate. The nitroxyl radical is formed by reaction of two alkyl peroxy radicals with the alkylated diphenylamine NH. The first step in this process generates an alkyl hydroperoxide while the second step generates an alkoxy radical.

The nitroxyl radical can undergo one of two possible fates. Under high temperature oxidation conditions it can react with an alkyl radical to form an alkoxyamine derivative (NOR). This pathway is illustrated in Fig. 5. This derivative can thermally degrade to regenerate the alkylated diphenylamine and form a ketone [19]. Alternatively, under low temperature oxidation conditions, the nitroxyl radical can react with two alkyl peroxy radicals and one alkoxy radical to form lower molecular weight benzoquinone (BQ) and nitroso amine (NA) degradation products [20]. This pathway is illustrated in Fig. 6. These BQ and NA fragments have no antioxidant activity and destroy the catalytic cycle. The propensity to react through either the high temperature or low temperature paths is dependent on temperature, degree of oxidation (concentration of peroxy versus alkyl radicals or concentration of oxygen), and the chemical nature of the alkylated diphenylamine itself. Electron Paramagnetic Resonance (EPR) studies support the preference for the catalytic cycle at elevated temperatures [21].

If oxidation conditions are favorable, the catalytic cycle can destroy a large number of alkyl and alkyl peroxy radicals before nitroxyl amine degradation occurs. There are reports of stoichiometric efficiencies for alkylated diphenylamine degradation of radicals in excess of 40 radicals per molecule.

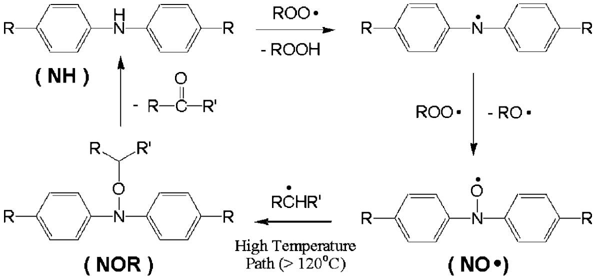


FIG. 5—*Mechanism of alkylated diphenylamine function.*

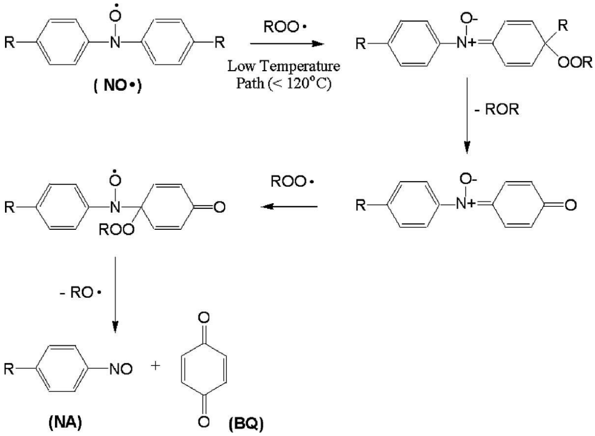


FIG. 6—*Mechanism of alkylated diphenylamine nitroxyl radical decomposition.*

Secondary Antioxidants: Phosphorus and Sulfur Compounds

Secondary antioxidants function by decomposing alkyl hydroperoxides to less reactive alcohols. The most effective chemistries that perform this function are sulfur and phosphorus compounds. Examples of sulfur compounds include sulfides, disulfides, polysulfides, phenothiazines, dithiocarbamates, thiadiazoles, and thiarams. Phosphorus compounds include alkyl and aryl phosphites and phosphonates. Examples of chemistries containing both sulfur and phosphorus include metal dithiophosphates, phosphorothioates, and thiophospates.

The mechanism of secondary antioxidant function is illustrated in Fig. 7 for an alkyl sulfide. Similar mechanisms have been proposed for alkyl disulfides and thiodipropionates [22,23]. The first step usually involves decomposition of an alkyl hydroperoxide to form an alcohol. In this process the sulfide (S) is converted to a sulfoxide (SO). At elevated temperatures the sulfoxide can undergo a series of decomposition steps leading to the formation of sulfenic (SOH) and sulfinic (SO_2H) acids. Under certain conditions sulfates (SO_3H) and sulfur dioxide (SO_2) can form. These latter species are known to be effective decomposers of alkyl hydroperoxides. Thus, two distinct mechanisms for the antioxidancy of sulfur can occur. The first is a stoichiometric process that converts one alkyl hydroperoxide to an alcohol. The second is a catalytic process where sulfur acids and sulfur dioxide decompose many alkyl hydroperoxides. This latter mechanism is quite complicated since the intermediate sulfenic and sulfinic acids can also react with alkyl peroxy radicals to form alkyl hydroperoxides. The sulfenic acids can also form sulfuric acid, which is a powerful catalyst for degradation and polymerization of the lubricant.

Complicating the mechanism of sulfur antioxidancy even further is the fact that certain sulfur chemistries are corrosive. Certain base oils also contain high levels of sulfur that provide antioxidancy but can also promote degradation, polymerization, and sludge formation. It has also been shown that specific combinations and concentrations of basestock sulfur and aromatics can enhance the oxidative stability of a given basestock [24]. These factors make selecting a sulfur compound for use as an antioxidant a considerable challenge.

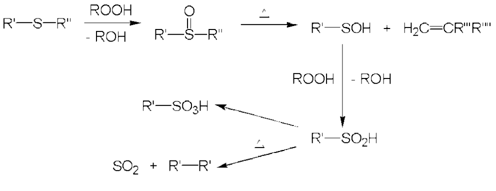


FIG. 7—*Mechanism of sulfide function.*

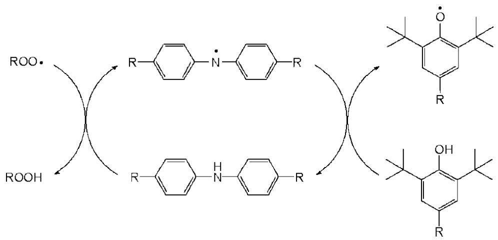


FIG. 8—*Mechanism of synergism between phenolics and alkylated diphenylamines.*

Antioxidant Synergy

Synergy is defined as the action between two discrete materials such that the total combined effect or response is greater than the sum of the effects or responses taken individually. Three types of antioxidant synergy are relevant in lubricants.

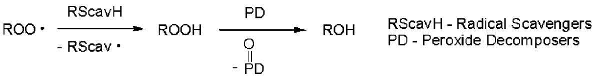
Homosynergism occurs when two antioxidants acting by the same mechanism interact, generally in a single electron transfer cascade. The best example of this in lubricants is the synergy between hindered phenolics and alkylated diphenylamines. This is illustrated in Fig. 8. The alkylated diphenylamine reacts with an alkyl peroxy radical to form the more stable alkyl hydroperoxide. In this process the amine is converted to an aminyl radical. This reaction is favored over alkyl peroxy radical reaction with the hindered phenolic because the alkylated diphenylamine is much more reactive. However, the resulting aminyl radical is less stable compared to the hindered phenoxy radical. Therefore, the hindered phenolic reacts with the aminyl radical to regenerate the alkylated diphenylamine. This results in the hindered phenolic being converted to the stable phenoxy radical. The overall effect consumes the hindered phenolic antioxidant in order to regenerate the more reactive alkylated diphenylamine. The cycle is driven by the higher reactivity of the alkylated diphenylamine compared to the hindered phenolic, and the greater stability of the phenoxy radical compared to the aminyl radical. This synergism can also occur when two hindered phenolics of varying reactivities and stabilities are present.

Heterosynergism occurs when two antioxidants act by a different mechanism and hence complement each other. The best example of this in lubricants is the synergy between radical scavengers and peroxide decomposers. This is illustrated in Fig. 9. The radical scavenger (hindered phenolic or alkylated diphenylamine) reacts with an alkyl peroxy radical to form an alkyl hydroperoxide. While this terminates the propagation step, complete stabilization is not achieved because the reactive hydroperoxide can thermally cleave to form alkoxy and hydroxy radicals that are effective in the chain branching sequence. However, the peroxide decomposer (sulfur or phosphorus compounds) can convert the alkyl hydroperoxide to the stable alcohol, thus preventing the chain branching step from occurring.

Based on the above discussion, a third type of synergism can be envisioned. This would involve antioxidants that combine the homosynergism and heterosynergism features. Examples of this would include sulfurized phenolics and alkylated phenothiazines. This is generally referred to as autosynergism and has been reviewed extensively by Scott [25].

Mechanism of Sludge and Deposit Formation Promoted by Antioxidants

As earlier discussed, sludge and deposit formation usually results from the build up of high molecular weight condensation products that have limited solubility in the lubricant. Since the aromatic compounds in the oil are more prone to participation in condensation reactions, their presence tends to further promote sludge and deposits.



$$\mathrm{ROO}\bullet \xrightarrow[-\,\mathrm{RScav}\,\bullet]{\mathrm{RScavH}} \mathrm{ROOH} \xrightarrow[\substack{\mathrm{O}\\ \|\\ -\,\mathrm{PD}}]{\mathrm{PD}} \mathrm{ROH}$$

FIG. 9—*Mechanism of synergism between radical scavengers and peroxide decomposers.*

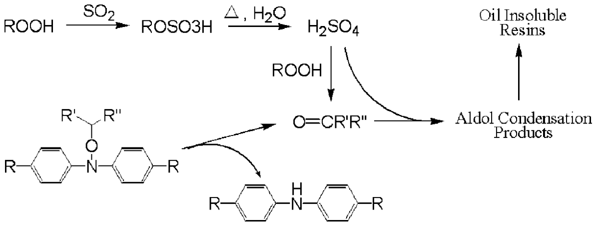


FIG. 10—*Deposit formation promoted by sulfur and diphenylamine antioxidants.*

Ideally, any materials that can catalyze these condensation reactions, or promote the formation of the active carbonyl compounds necessary for the condensation reactions, are likely to promote sludge and deposit formation. Based on the mechanisms proposed in Figs. 5 and 7, it's apparent that sulfur compounds and alkylated diphenylamines, while excellent antioxidants, can also promote sludge and deposits. The sulfur compounds do this by forming sulfur acid species that catalyze the condensation reactions. The alkylated diphenylamines do this by generating carbonyl compounds. This concept is illustrated in Fig. 10. Note, when R′ or R″ are aromatic, or when the alkyl hydroperoxide ROOH is benzylic, the tendency to form carbonyl compounds increases. This is due to the ease with which benzylic hydrogens (hydrogens in the α-position relative to the aromatic ring) are abstracted to form alkyl radicals.

This scheme suggests that the ability to control sludge and deposits is directly related to the presence of sulfur (basestock derived or additive derived), diarylamine antioxidants, and basestock aromatics. Of course, the type of sulfur species, arylamines, and aromatics also play a critical role. For example, more reactive or acidic sulfur compounds are likely to promote greater sludge formation compared to less reactive or neutral sulfur compounds. It has also been reported that the proper selection of arylamine and phenolic antioxidant combinations can significantly reduce sludge formation, even in basestocks containing a considerable amount of aromatics and sulfur [26].

Conclusions

From a mechanistic standpoint it's clear the following should be considered when developing turbine oils with high oxidation stability.

(1) Select a basestock with as little sulfur and aromatics as possible.
(2) Use sulfur containing additives and arylamines sparingly to suppress sludge and deposit formation.
(3) Minimize, as practical as possible, metal contamination.
(4) Capitalize on homosynergism and heterosynergism effects by using combinations of hindered phenolics, arylamines, and peroxide decomposers.

The dilemma in these conclusions is that items 2 and 4 are contradictory. Item 2 discourages the use of sulfur and arylamines while item 4 encourages their use. The lubricant formulators task is then to achieve the most favorable balance where the benefits of specific basestock and additive combinations outweigh the detriments.

The principles discussed in this section are further highlighted by the fundamental oxidation studies presented in Part II.

Part II—Turbine Oil Testing

In Part I of this paper, we discussed the oxidation of basestocks in the presence or absence of selected metal catalysts and how antioxidants disrupt these oxidation mechanisms. In Part I the value of key bench tests such as ASTM D 943 (Turbine Oil Stability Test) and D 2272 (Rotating Pressure Vessel Oxidation Test) were also discussed. Another valuable bench test of interest is the CM-A test (Cincinnati Milacron Thermal Stability Test Procedure A) which looks primarily at the thermal stability of an oil. In all these tests the key environmental variables are temperature, concentration, oxygen delivery mode, or water, or combinations thereof, as well as the presence or absence of copper or iron, or both. Table 1 summarizes the key environmental factors for each of these tests.

TABLE 1—*Key environment conditions for selected turbine oil tests.*

Test	RBOT/RPVOT ASTM D 2272	CM-A ASTM D 2070	TOST ASTM D 943
Temperature	150°C	135°C	95°C
Water Concentration	5 mL	Not Present	60 mL
Copper Catalyst	Copper Coil	Copper Rod	Copper Coil
Iron Catalyst	No	Iron Rod	Iron Coil
Gas	90 PSI Oxygen	Air (No Flow)	Oxygen 3 L/h
Test Parameter	Pressure Drop	Sludge and Rod Rating	TAN
Oil Sample Size	50 g	200 mL	300 mL

In Part II we report the results of a bulk oil oxidation study done on model turbine oil formulations prepared using either a Group I or Group II basestock. To these formulations we added either a phenolic antioxidant, an amine antioxidant, a mixture of these antioxidants, or omitted the antioxidant entirely. Testing was performed at the temperatures used in the ASTM bench tests shown in Table 1. Testing was also done with no oxidation catalyst added, or copper ion added, or iron ion added, or a mixture of copper and iron ions added. We used this approach to mimic the different types of metal ions that are commonly seen in key bench tests. Samples were taken periodically during the bulk oil oxidation test. For these samples we determined the viscosity and recorded the Fourier Transform Infrared (FTIR) spectra. We then used these data to relate the oxidation behavior observed to the fundamentals addressed in Part I and to show how these fundamentals are being manifested under various bench test conditions in different basestocks.

Experimental

Chemical Components

4,4′-methylenebis(2,6-di-tert-butylphenol), MBDTBP (Fig. 3 in Part I) is used as a representative of the hindered phenolic class of antioxidants while nonylated diphenylamine, NDPA (NH in Fig. 5 of Part I, R=nonyl) is chosen as a representative of the arylamine class of antioxidants. The copper catalyst used is a concentrated mixture of copper carboxylates in mineral spirits (12 % copper by weight). The iron catalyst is a mixture of mixed iron carboxylates in mineral spirits (6 % iron by weight). The Group I and II basestocks are available commercially. The Group I basestock had a 40°C viscosity of 30.5 cSt, viscosity index of 99, Noack volatility of 19 wt. %, sulfur content of 0.35 wt. % (ASTM D 2622), and an aromatic content of approximately 24 %. The Group II basestock had a 40°C viscosity of 38.4 cSt, viscosity index of 110 (minimum), Noack volatility of 9 wt. % (maximum), sulfur content of 0.001 wt. % (ASTM D 2622), and an aromatic content of approximately 5 %. The rust and corrosion inhibitors are also commercially available materials.

Equipment and Procedure

The bulk oil oxidation testing was done in large glass tubes similar in dimension to those used in ASTM D 943 that contained approximately 300 mL of test solution. Testing was performed at 95, 135, and 150°C to simulate temperatures of the ASTM standard tests. For the tests that involved copper ion catalyst, 41.7 mg of the copper catalyst solution (equivalent to 5.00 mg of copper) was added to the 300 mL of formulated oil. For the tests involving iron ion catalyst, 83.4 mg of the iron catalyst solution (equivalent to 5.00 mg of iron) was added to the 300 mLs of formulated oil. For tests involving both copper and iron catalyst, these same catalyst loadings were used. Temperature was controlled using an aluminum block heater that could be set to the desired test temperature. Temperature was controlled to within 1°C of the set point. Oxidation was carried out using pure, dry oxygen that was delivered from cylinders to the oxidation cell at a rate of 10 L/h.

Oxidized samples were taken periodically from the glass tubes while leaving the glass tubes in place in the heater block. Viscosity was measured at 40°C in calibrated viscometer tubes using ASTM D 445.

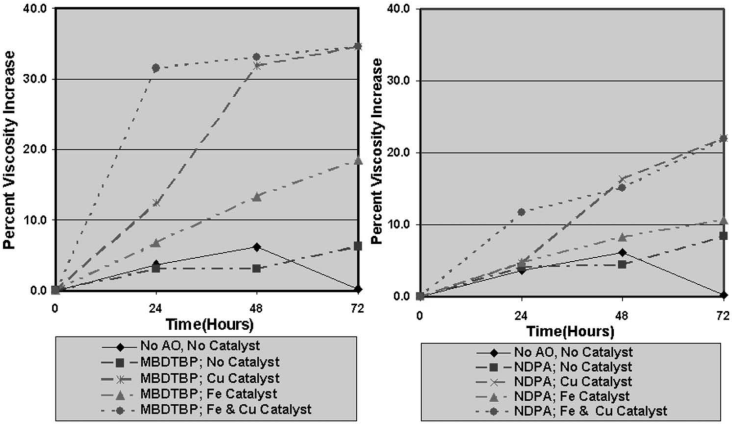


FIG. 11—*Percent viscosity increase at 150°C for a turbine oil formulation with MBDTBP or NDPA in a Group I basestock.*

FTIR spectra were taken in a KBr cell of known path length (usually 0.037 mm) and analyzed in several different ways. For the carbonyl region (1900 to 1560 wavenumbers) we monitored the peak area increase (PAI) using a modification of the method reported by Obiols [27]. For the hindered phenolic region we monitored the intensity of the hindered OH absorption for MBDTBP (3650 wavenumbers) and for what we believe to be hydro-galvinoxyl (3637 wavenumbers). For selected NDPA systems we also monitored the N-H stretch at 3437 wavenumbers in order to follow its behavior. This absorption band is broad and weak and required the use of a long path length cell (2 mm) in order to obtain quantitative information.

The CM-A test (ASTM D 2070) was done using standard protocols, except that the length of the test was increased to further stress the Group II basestock. TANs (Total Acid Numbers) were determined using ASTM D 664. This procedure, which is a potentiometric titration, had to be used carefully in order to avoid false endpoints.

Formulations

For each basestock we added a fixed weight percentage of rust inhibitor (0.10 wt. %) and corrosion inhibitor (0.05 wt. %). To test the value of different antioxidants and antioxidant blends, we used either 0.25 wt. % MBDTBP, or 0.25 wt. % NDPA, or a mixture that contained 0.125 wt. % MBDTBP and 0.125 wt. % NDPA. A system with no antioxidant added was also tested as a reference system. The rest of the formulation was the appropriate amount of Group I or Group II basestock.

Results and Discussion

High Temperature Oxidation

Figures 11 and 12 summarize our percent viscosity change results at 150°C for the simple turbine oil formulations described above with and without different catalysts, with and without different antioxidants, in either a Group I or II basestock. Figures 13 and 14 give the PAI (Peak Area Increase) data for the same systems. In general, the percent viscosity change and PAI data are in very good agreement with each other. For those data points where there is apparent disagreement between the two techniques, we generally prefer the PAI data. In work on engine oil formulations that we have reported elsewhere we have seen the formation of volatiles under certain test conditions that can skew viscosity test results [28]. As long as these volatiles remain in the test solution, the carbonyls that are formed are included in the PAI numbers which generally don't show unusual "breaks" in the data curves as are sometimes seen in the viscosity curves.

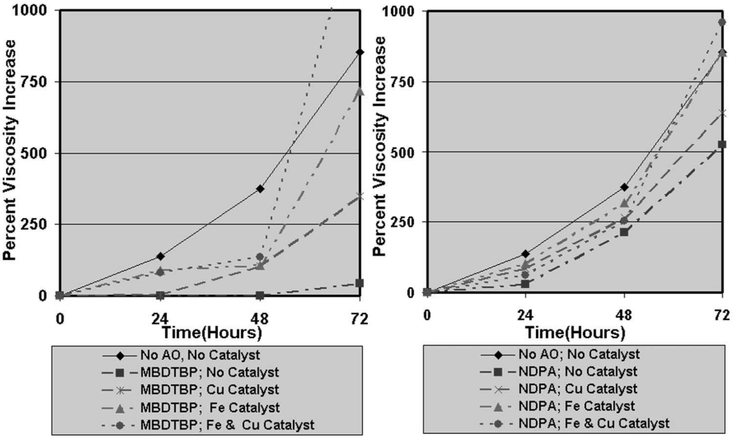


FIG. 12—*Percent viscosity increase at 150°C for a turbine oil formulation with MBDTBP or NDPA in a Group II basestock.*

The figures are organized around basestock and antioxidant type in order to highlight the effects of the key fundamental differences between systems that are discussed in Part I of this paper. In Fig. 11 through Fig. 14 it is clear that the percent viscosity change for the Group I basestock was much less than for the Group II basestock under similar conditions. However, for the Group I basestock, heavy deposits were observed which would have caused these systems to fail in use, while for Group II only a light deposit was seen. There are clearly different "failure modes" for these two classes of basestock. The deposit failure mode is associated with a solvent refined basestock (Group I) which is subject to the mildest form of processing and which usually has relatively high levels of aromatic and sulfur compounds. As discussed in Part I of this paper, it is reasonable that these aromatic and sulfur compounds lead to deposit formation. The viscosity change failure mode is then associated with the more highly refined and processed Group II basestock.

As many standard tests were developed when Group I was the dominant basestock in the marketplace, it is potentially a major issue that Group I behaves so differently from Group II (and actually Group III and IV as well). As much is known about the behavior of Group I basestocks, we did not focus on deposits as the key test parameter, but instead chose viscosity and FTIR analysis (including PAI) as the key determi-

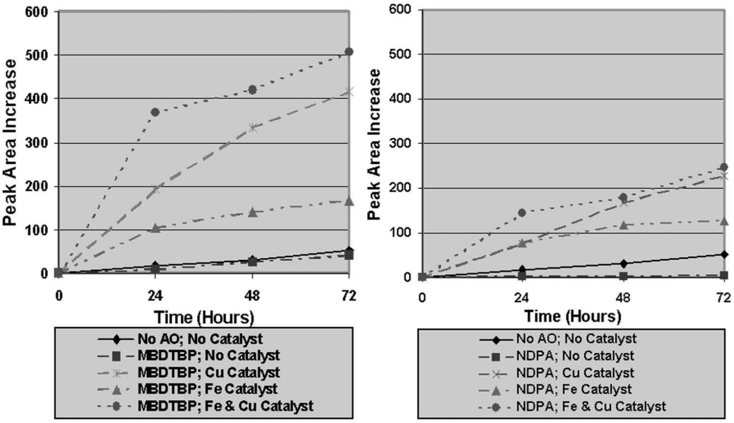


FIG. 13—*PAI at 150°C for a turbine oil formulation with MBDTBP or NDPA in a Group I basestock.*

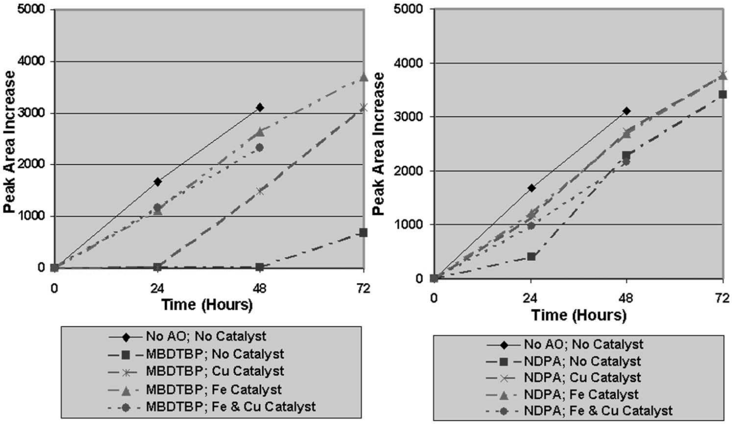


FIG. 14—*PAI at 150°C for a turbine oil formulation with MBDTBP or NDPA in a Group II basestock.*

nants of oxidation behavior. For the Group I results we were concerned that our test procedures did not properly account for the heavy deposits (which contain oxidation products) that were observed in Group I systems. Therefore chloroform was added to a few selected Group I system samples containing heavy deposits in order to dissolve the deposits. The new PAI numbers for these samples, when corrected for sample dilution, showed between about 20 and 70 % increase in the PAI values. This is no where close to the PAI differences seen between Group I and Group II systems (see Figs. 13 and 14). Thus, the order of magnitude difference in the percent viscosity change and PAI data for Group I versus Group II formulations is meaningful and shows that the total oxidation in the Group I system is substantially less than the Group II system at 150°C. As discussed in Part I of this paper, sulfur compounds frequently have antioxidant properties. It's possible that basestock sulfur, at this test temperature, accounts for the overall reduction in oxidation seen in Group I systems [24].

Comparing test results for MBDTBP and NDPA in a Group I basestock (Figs. 11 and 13) shows that NDPA may be more effective than MDBTBP in this basestock. As there are known synergisms between NDPA and sulfur compounds (see Part I), it seems reasonable that the sulfur compounds in the Group I basestocks are also responsible for this observed behavior. However, data on deposits are needed to fully assess the relative merits of the antioxidants in Group I turbine oil systems.

As the effects of metals on viscosity change and PAI are so much larger in Group II than Group I systems and are not complicated by substantial deposit formation, we focused more on Group II data to understand the role of metal ions in our testing. Figure 12 (viscosity data) and Fig. 14 (PAI data) show that adding an antioxidant to the Group II turbine oil formulation at 150°C dramatically decreased the amount of oxidation observed. Addition of copper ion, iron ion or mixtures of these two ions, then increased the rate of oxidation. This is as expected from Reactions 3 and 4 in Part I of this paper and shows how the presence of metal ion promotes the decomposition of peroxides into harmful free radicals. For systems containing MBDTBP, iron ions are more harmful than copper ions on an equal weight basis. For systems containing NDPA, the relative effect of the addition of metal ions is less than with comparable MBDTBP formulations. When mixtures of copper and iron ions were used, the picture gets more complicated with the ordering of the test severity being dependent on the time the observation is made. It is expected that the presence of iron or copper metal, or both, in the tests would complicate the behavior even further [29].

Figure 11 (percent viscosity data) and Fig. 13 (PAI data), which focus on Group I turbine oil formulations at 150°C, suggest that the effect of antioxidants and metal ions may be different in this group. Here the data suggest that copper is worse than iron on an equal weight basis and mixtures of copper and iron can be particularly detrimental early on in the test. However, data on deposits are needed to fully assess the role of metals in Group I turbine oil systems.

Oxidation data for Group II basestock (Figs. 12 and 14) show that for addition of equal weights of MBDTBP or NDPA to the turbine oil formulation, the MBDTBP was superior to the NDPA at suppressing

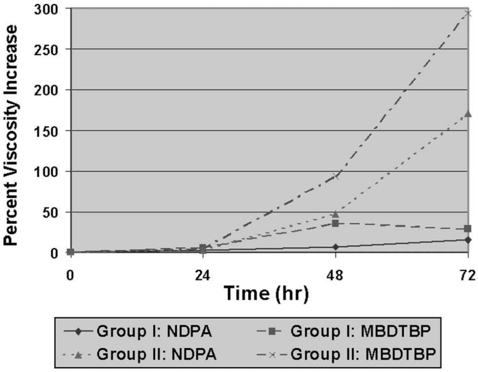


FIG. 15—*Percent viscosity increase test results for Group I and Group II turbine oils at 135°C (Fe and Cu catalyst).*

oxidation without catalyst. As mentioned earlier, when copper or iron ion is added there is a higher relative negative effect of these ions on MBDTBP containing formulations than on NDPA containing formulations, but the MBDTBP system continues to outperform the NDPA system. By the time you reach the high catalyst loadings present in the iron plus copper systems, the NDPA system now outperforms the MBDTBP. These data then support the concept that for Group II basestocks, MBDTBP is a better antioxidant than NDPA, probably because there are no sulfur components in the Group II basestock that behave synergistically with the NDPA. As NDPA handles metal ion containing systems better than MBDTBP, it seems that another effect is also going on. Since amines are known for their chemical coordination properties [30], the data support the idea that NDPA ties up the metal ions and reduces their negative effects. Therefore, the test results can be made to vary widely by choice of metal ion catalyst and the loading level of these metal ions.

As we are interested in the CM-A bench test we also looked at the results for the copper and iron catalyst system in the Group I and II turbine oil formulations at 135°C in the presence of MBDTBP or NDPA. The data are shown in Fig. 15. These data are consistent with the picture obtained at 150°C. It also indicates that total oxidation in the Group I system is much less than in the Group II system. Thus, the sulfur compounds are continuing to exhibit some antioxidant behavior at 135°C.

CM-A Results

To show the relevance of our oxidation test, we then compared the above results with some CM-A test results. As shown in Table 2 for a Group I turbine oil formulation, Group I is known to frequently fail the CM-A test. As Group II generally passes quite easily we decided to do an extended length (up to four weeks) CM-A test in this basestock. Figures 16 and 17 show the CM-A results using either sludge formation, total acid number (TAN), percent viscosity increase or PAI as the measurement tool. As we observed in the bulk oxidation test, deposit or sludge formation, or both, in a Group II basestock is usually low and is significantly lower than what is observed for a Group I based system (compare Fig. 16 with Table 2). Total acid number (TAN), percent viscosity increase, and PAI (Figs. 16 and 17) are all better indicators of the condition of the Group II oil. These three tests are also in general agreement with each other, with only one viscosity data point being an apparent outlier. Figures 16 and 17 also indicate that

TABLE 2—*One week (16 h) CM-A results for a Group I turbine oil formulation.*

Test	Antioxidant System		
Parameter	No AO 0.25 %	MBDTBP	0.25 % NDPA
Sludge (mg/100 mL)	134	31	61
Total Acid Number (mg KOH/g)	0.4	0.2	0.3
Viscosity Change (%)	9.2	6.9	5.8

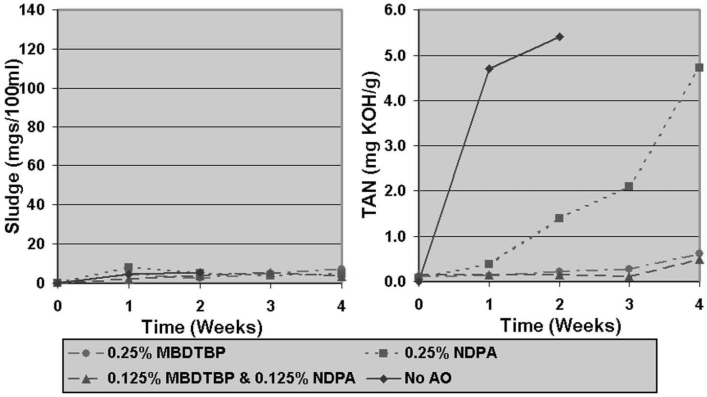


FIG. 16—*Sludge formation and total acid number results for an extended length CM-A test for a Group II turbine oil formulation.*

MBDTBP outperforms NDPA, which is a result that we see under many conditions in the bulk oil test. These figures also show the potential benefit of using a mixed MBDTBP/NDPA system. In general, the mixed system performs equal to or slightly better than the pure MBDTBP system. This is in agreement with the comments made on the mixed system in Part I of this paper.

For the CM-A test we also attempted to rate the copper and iron rods that were used in the test. However, we found that the reference color chart was not appropriate for rating rods aged in Group II systems. The resulting rod color changes, particularly the copper rods, were difficult to match with the reference color chart. We, therefore, have not presented any of our rod corrosion results. These color rating results did, however, reinforce our concerns about the value of some of the tests when applied to Group II systems.

Low Temperature Oxidation

We also performed the bulk oil oxidation testing at 95 °C, as this is the temperature at which ASTM D 943 is run. Figure 18 shows that there is some change in the viscosity of the Group I turbine oil formulations before there is an observed change in Group II formulations. Also, in the Group I formulations, MBDTBP is better than NDPA early in the test, but later on these roles are reversed. Again the use of mixed MBDTBP and NDPA systems shows potential benefits. For Group II systems there is no appreciable

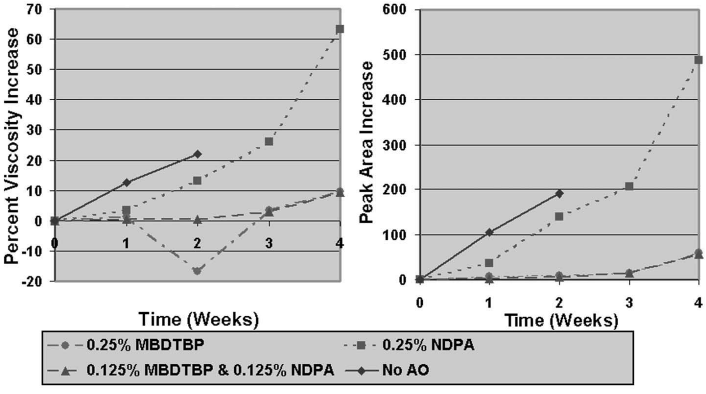


FIG. 17—*Percent viscosity increase and PAI results for an extended length CM-A test in a Group II turbine oil formulation.*

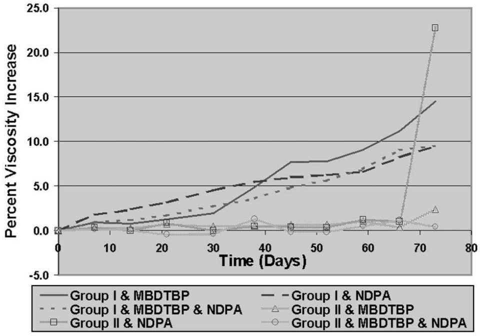


FIG. 18—*Percent viscosity increase results for Group I and Group II turbine oil formulations at 95 °C (Fe and Cu catalyst).*

change in viscosity until day 73 when the viscosity of the all NDPA system shows a break. This suggests that the change in Group II formulations is more catastrophic and not gradual as in the Group I systems. Thus, there is a substantial change in the relative performance of Group I and II systems between 95 and 150 °C that suggests a fundamental change in oxidation mechanisms. It's possible that at 95 °C the sulfur compounds in Group I basestocks are less effective as antioxidants or show less of a synergistic effect with NDPA. Also, the higher bond dissociation energies for the chemical components of Group II basestock (see Part I) may now be causing a significant increase in the usable life of the Group II oil. However, once the antioxidants are depleted from the Group II oil, catastrophic oxidation is possible. This catastrophic effect is not observed in the Group I systems possibly because of the natural antioxidant effects provided by the sulfur and aromatics contained in Group I oils. For the Group I systems, deposits were again observed, while deposit formation in the Group II formulations was significantly lower. PAI data for the same systems were also collected and confirms that the observed viscosity changes are related to the fundamental oxidation behavior.

These dramatic changes caused us to look more carefully at the FTIR spectra of the turbine oil systems at 95 °C. We were able to clearly observe changes in the OH and NH stretching frequency regions (3650, 3637, and 3437 wavenumbers) that substantiate major segments of the proposed mechanisms for the behavior of MBDTBP and NDPA in an oxidative environment (see Fig. 3 and 6 in Part I of this paper). The FTIR data for the mixed MBDTBP and NDPA systems show how these systems work together synergistically.

For the all MBDTBP systems, the hindered phenolic peak at 3650 wavenumbers, attributed to the MBDTBP hydroxyl groups, disappears during the course of the test and is replaced with a new hydroxyl peak at 3637 wavenumbers, which also eventually disappears (Fig. 19). Referring to the mechanism in Fig. 3 of Part I of this paper, we believe that this new hydroxyl peak was hydro-galvinoxyl, GH. GC/MS work on the 10-day sample of the Group II system with MBDTBP confirmed the presence of hydro-galvinoxyl, 3,5-di-tert-butyl-4-hydroxybenzaldehyde (3,5-BA), and 2,6-di-tert-butyl-benzoquinone (2,6-BQ). It also identified a molecular species with an oxygen atom attached to a hydro-galvinoxyl type intermediate. Thus the data obtained during the 73-day test period show that the MBDTBP is consumed, forms hydro-galvinoxyl, which is in turn consumed. Some other oxidation intermediates such as the 3,5-di-tert-butyl-4-hydroxybenzaldehyde may also be active antioxidants (see Fig. 4 from Part I). The data thus support the proposed mechanism for the antioxidant behavior of MBDTBP.

For the all NDPA systems in Group II basestock, the NH stretch disappears during the course of the test (Fig. 20). The loss in intensity of the NH stretch band is consistent with the proposed low temperature mechanism for NDPA that is shown in Fig. 6 of Part I. Also shown in Fig. 20 is the result for the amine peak in the presence of MBDTBP. Note that when MBDTBP is present the amine peak is not significantly depleted for at least the first 30 days of the test. Figure 21 shows the behavior of the MBDTBP and hydro-galvinoxyl hindered phenolic stretch intensities in the same mixed antioxidant system samples. These results show that the phenolics are behaving in a manner similar to what they do when NDPA is not present. Actually the magnitude of the drop in peak intensity early in the test is very similar in the

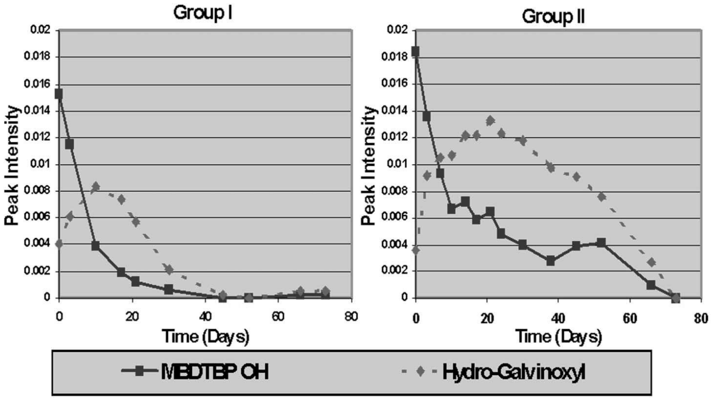


FIG. 19—*Intensity of OH stretching bands in the FTIR spectra of MBDTBP during 73 days of oxidation testing (10 L/h oxygen) at 95°C in a turbine oil formulation based on Group I or Group II basestock (Fe and Cu catalyst).*

MBDTBP systems with and without NDPA. This indicates that the MBDTBP is either handling the oxidation products early on in the test, or—and this is more likely—the MBDTBP is reacting directly with any N· radical formed (see Figs. 5 and 8 of Part I) in order to regenerate the amine. As the NDPA is continuing to be regenerated well after the MBDTBP hydroxyl absorption disappears, it is clear that other molecules in the proposed MBDTBP reaction scheme—particularly the hydro-galvinoxyl—must also be able to regenerate the NDPA. For the Group II system the depletion of NDPA antioxidant (▲, Fig. 20) appears to correspond to the onset of oil oxidation (—☐--, Fig. 18).

Armed with this understanding of how MBDTBP and NDPA act, and interact, we have gone back and looked in more depth at the 135 and 150°C results. By 150°C the oxidation reactions are occurring so quickly that the key FTIR bands we are following disappear in the first 24 hours of testing, thus making mechanistic observations difficult. While there is ample evidence that the high temperature mechanism for NDPA regeneration (see Fig. 5 in Part I) does exist, our FTIR work at 150°C did not clearly identify any unique FTIR bands that let us make any specific comments on this high temperature mechanism.

Conclusions

From the viewpoint of the December 2005 ASTM Turbine Oil Oxidation Symposium, these data have important implications for turbine oil testing. Our results show marked differences in behavior between Group I and Group II basestocks. For those tests that were developed primarily using Group I basestocks,

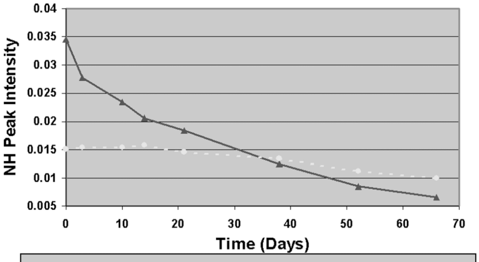


FIG. 20—*Intensity of NH stretching bands in the FTIR spectra of NDPA and mixed MBDTBP/NDPA systems during 73 days of oxidation testing (10 L/h oxygen) at 95°C in a turbine oil formulation based on Group II basestock (Fe and Cu catalyst).*

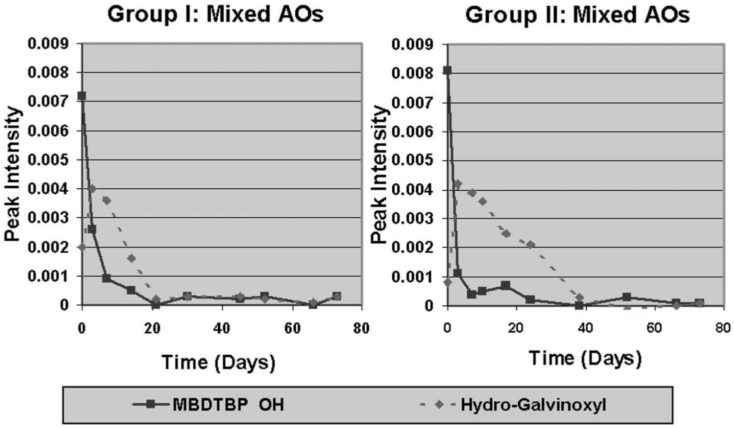


FIG. 21—*Intensity of OH stretching bands in the FTIR spectra of MBDTBP during 73 days of oxidation testing (10 L/h oxygen) at 95°C in a turbine oil formulation based on Group I or Group II basestock which also contains NDPA (Fe and Cu catalyst).*

the question then becomes, "how well are these tests now working in the more highly refined or processed, or both, Group II basestocks?"

Our results also show significant differences between copper, iron, and mixed copper/iron ion catalysts and suggest that they may behave differently in Group I and Group II oils. The challenge now becomes for the turbine manufacturers and users to define what is the proper range and type of metallurgy to explore. How important is it to have both copper and iron present and what is the concentration range and ion type to have in the test? A related issue is for the turbine manufacturers and users to define the range of operating conditions that they encounter. Clearly it is possible to manipulate test conditions to make a phenolic or amine-based antioxidant (and potentially other additives) look better based on test conditions. So the choice of test conditions must ultimately be tied back to real world experiences.

From the viewpoint of primary antioxidants, there is certainly commonality in that phenolic and amine antioxidants are free radical scavengers, but the data presented here show that their relative performance is affected by the choice of test conditions. The data presented here suggest that the tested phenolic in a Group II basestock may be better than the tested amine, but it is clear that the ability of the amine to coordinate with metal ions can readily create situations where the amine will outperform the phenolic. In Group I, NDPA may be better than MBDTBP because of the presence of sulfur compounds, and these sulfur compounds may be acting as antioxidants, particularly at the higher test temperatures. From the data we presented, coupled with what is available in the literature, the understanding of how amine and phenolic-based antioxidants function and interact is in reasonably good shape. Unless there is a better understanding of the range of real world operating conditions that could in turn lead to improved bench tests, then the data suggest that a prudent formulator should consider combinations of the phenolic and amine antioxidants in order to develop a formulation that has the ability to adapt to a wide range of conditions which would seem possible in the field.

References

[1] Henderson, H. E., "Advanced Performance Products from VHVI Specialty Base Fluids," *Symposium on Worldwide Perspectives on the Manufacture, Characterization and Application of Lubricant Base Oils: IV*, 218th Annual Meeting Preprint, American Chemical Society, New Orleans, LA, August 22–26, 1999, pp. 251–256.

[2] Henderson, H. E., Fefer, M., Legzdins, A., Michaluk, P., and Ruo, T., "Compositional Features of High Performance Specialty Base Fluids," *Symposium on Worldwide Perspectives on the Manufacture, Characterization and Application of Lubricant Base Oils: IV*, 218th Annual Meeting Preprint,

American Chemical Society, New Orleans, LA, August 22–26, 1999, pp. 265–269.

[3] Gatto, V. J., Grina, M. A., Tat, T. L., and Ryan, H. T., "The Influence of Chemical Structure on the Physical Properties and Antioxidant Response of Hydrocracked Base Stocks and Polyalphaolefins," *Journal of Synthetic Lubrication*, Vol. 19, 2002, pp. 1–18.

[4] Kramer, D., Rosenbaum, J. M., Krug, R. R., and Lok, B. K., "Evolution of Base Oil Technology," *Lubrication*, ChevronTexaco Products Company, January 2005, pp. 1–11.

[5] Scott, G., *Atmospheric Oxidation and Antioxidants*, Elsevier Publishing Company, Amsterdam, 1965.

[6] Shlyapnikov, Y. A., "Antioxidant Stabilization of Polymers," *Russ. Chem. Rev.*, Vol. 50, 1981, pp. 581–600.

[7] Colclough, T., "Lubricating Oil Oxidation and Stabilization," *Atmospheric Oxidation and Antioxidants Volume II*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 1–70.

[8] Rasberger, M., "Oxidative Degradation and Stabilization of Mineral Oil Based Lubricants," *Chemistry and Technology of Lubricants*, R. M. Motier and S. T. Orszulik, Eds., Blackie Academic and Professional, London, 1997, pp. 98–143.

[9] Migdal, C. A., "Antioxidants," *Lubricant Additives Chemistry and Applications*, L. R. Rudnick, Ed., Marcel Dekker, Inc., New York, 2003, pp. 1–28.

[10] Ingold, K. U., "Inhibition of the Autoxidation of Organic Substances in the Liquid Phase," *Chem. Soc. Rev.*, Vol. 61, 1961, pp. 563–589.

[11] Lowry, T. H. and Richardson, K. S., *Mechanism and Theory In Organic Chemistry*, Harper and Row Publishers, New York, 1976, p. 472.

[12] Osawa, Z., "Metal Catalyzed Oxidation and Its Inhibition," *Atmospheric Oxidation and Antioxidants Volume II*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 327–362.

[13] AL-Malaika, S., "Autoxidation," *Atmospheric Oxidation and Antioxidants Volume I*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 45–82.

[14] Uri, N., "Mechanism of Autoxidation," *Autoxidation and Antioxidants Volume I*, W. O. Lundberg, Ed., John Wiley & Sons, Inc., New York, 1961, pp. 133–170.

[15] Sharp, D. B., Patton, L. W., and Whitcomb, S. E., "Autoxidation of Ketones, I. Diisopropyl Ketone," *J. Am. Chem. Soc.*, Vol. 73, 1951, pp. 5600–5603.

[16] Maslov, S. A. and Blyumberg, E. A., "Liquid-Phase Oxidation of Aldehydes," *Russ. Chem. Rev.*, Vol. 45, No. 2, 1976, pp. 303–328.

[17] March, J., "The Aldol Condensation," *Advanced Organic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1985, pp. 829–834.

[18] Greene, F. D. and Adam, W., "Autoxidation of Galvinoxyl," *J. Org. Chem.*, Vol. 28, 1963, pp. 3550–3551.

[19] Jensen, R. K., Korcek, S., Zinbo, M., and Gerlock, J. L., "Regeneration of Amine in Catalytic Inhibition of Oxidation," *J. Org. Chem.*, Vol. 60, 1995, pp. 5396–5400.

[20] Berger, H., Bolsmann, T. A. B., and Brouwer, D. M., *Developments in Polymer Stabilization—6*, G. Scott, Ed., Elsevier Applied Science Publishers, London, pp. 1–27.

[21] Kozakowski, G. and Kolodziejski, W., "EPR Study of Antioxidant Action of p,p′-Dioctyldiphenylamine," *Synth. Lubr.*, Vol. 7, 1990, pp. 229–234.

[22] Oae, S., *Organic Sulfur Chemistry: Structure and Mechanism*, CRC Press, Boca Raton, 1991, p. 216.

[23] AL-Malaika, S., "Antioxidants—Preventive Mechanisms," *Atmospheric Oxidation and Antioxidants Volume I*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 161–224.

[24] Igarashi, J., Yoshida, T., and Watanabe, H., "Concept of Optimal Aromaticity in Base Oil Oxidative Stability Revisited," *Symposium on Worldwide Perspectives on the Manufacture, Characterization and Application of Lubricant Base Oils*: 213th Annual Meeting Preprint, American Chemical Society, San Francisco, CA, April 13–17, 1997, pp. 211–217.

[25] Scott, G., "Synergism and Antagonism," *Atmospheric Oxidation and Antioxidants Volume II*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 431–459.

[26] Ryan, H. T., "Lubricant Compositions Exhibiting Extended Oxidation Stability," European Patent Application EP 1 006 173 A1, June 7, 2000.

[27] Obiols, J., "Lubricant Oxidation Monitoring Using FTIR Analysis—Application to the Development of a Laboratory Bulk Oxidation Test and to In-Service Oil Evaluation," JSAE Technical Paper No. 20030124, JSAE, Tokyo, Japan, 2003.

[28] Moehle, W. E., Cobb, T. W., Schneller, E. R., and Gatto, V. J., "Utilizing the TEOST MHT to Evaluate Fundamental Oxidation Processes in Low Phosphorus Engine Oils," presented at the STLE 60th Annual Meeting in Las Vegas, Nevada, May 15–19, 2005.

[29] Osawa, Z., "Metal Catalyzed Oxidation and its Inhibition," *Atmospheric Oxidation and Antioxidants Volume II*, G. Scott, Ed., Elsevier Science Publishers B. V., Amsterdam, 1993, pp. 327–362.

[30] Kirk-Othmer, *Encyclopedia of Chemical Technology*, 4th ed., J. Wiley & Sons Publication, Vol. 7, pp. 328–348.

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Modern Turbine Oil Oxidation Performance Limits—Meeting and Measuring Them—A Shell Perspective

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ABSTRACT: This paper outlines some of the significant changes in turbine oil oxidative stability requirements over the past five to ten years, and illustrates how these have been met using mineral oil-based products with differing antioxidant systems. It also considers possible future requirements and how these may be met. Use of a modified Federal Test Method 5308, and ASTM tests D 2272, D 4310, and D 943 in formulating new turbine oils and evaluating their oxidative stability is also described and contrasted. An example of oil condition monitoring on a used turbine oil from the field to assess its oxidative degradation is also given.

KEYWORDS: turbine oil, oxidation, power generation, antioxidant, performance

Introduction

Power generation in all its forms requires outstanding lubrication of the turbines and associated equipment to ensure long, trouble free operational lifetimes, putting stringent demands on the performance of the lubricants. Turbine oil producers such as Shell have responded to this challenge by developing oils with increasing lifetimes using their knowledge of base oil and additive chemistry and with the understanding of how these interact.

This paper outlines some of the significant changes in turbine oil oxidative stability requirements over the past five to ten years, both from the perspective of the OEM and the oil manufacturer, and illustrates how these have been met using API Group I, Group II, and Group III, mineral oil-based products with differing antioxidant systems. It also considers possible future requirements and how these may be met. Use of a modified Federal Test Method 5308, and ASTM tests D 2272 [1], D 4310 [2], and D 943 [3] in formulating new turbine oils and evaluating their oxidative stability and sludge forming tendency is also described and contrasted.

An example of oil condition monitoring on a used turbine oil from the field to assess its oxidative degradation is given, utilizing a number of techniques such as ASTM D 2272 testing, and analytical techniques such as high performance liquid chromatography to quantify specific antioxidant components in the oils. An important factor that will be highlighted here using an example of an aminic antioxidant, is the complexity of trying to establish an analytical method to assess the oxidative condition of an oil. This is because a single pure antioxidant in a new oil degrades in service into multiple compounds which can have varying levels of antioxidancy, and are less readily identified and quantified.

Experimental Test Methods

RPVOT (ASTM D 2272-02)

Fifty grams of oil with 5 mL water is placed in a vessel together with a copper coil catalyst, pressurized with oxygen to 620 kPa, placed in an oil bath at 150°C and rotated at 100 r/min. The time is then measured in minutes for the pressure to drop by more than 175 kPa.

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TOST Life (ASTM D 943-04a)

Three hundred millilitres of oil plus 60 mL of water, in the presence of a copper and a steel coil catalyst, is heated to 95 °C, and is blown with oxygen until the acid number of the oil reaches 2.0 mg KOH/g.

TOST 1000 Hours (ASTM D 4310-06b)

Three hundred millilitres of oil plus 60 mL of water, in the presence of a copper and a steel coil catalyst, is heated to 95 °C, and is blown with oxygen for 1000 h. At this time the weight of insoluble material is determined by filtering the oil through a 5 micron filter.

Modified Federal Test Method 791c-5308 (ASTM D 4636-99, [4] Alternative Procedure 2)

One hundred millilitres of oil, in the presence of a five metal catalyst (Cu, steel, Al, Ag, Mg), is heated to 175 °C, and blown with air for 72 h. At the end of this period the change in viscosity, and acid value, is measured. The weight of insoluble material is determined by filtering the oil through a 5 micron filter.

TABLE 1—*Selected turbine oil specifications.*

Specification	RPVOT (minutes)	TOST life (hours)
GEK 32568F (gt)[a]	500 minimum	3000 minimum
GEK 46506D (st)[a]	>250	>2000
GEK 107395 (stag)[a]	1000 minimum	7000 minimum
Alstom HTGD 90 117 T (st and gt)	>300	>2000
Siemens TLV 9013 04 (st and gt)	n.a.[a]	2500
MHI MS04-MA-CL001 (st and gt)	220 minimum	2000 minimum
DIN 51515-1 (st and gt)	n.a.	2000 minimum (ISO 32/46)
DIN 51515-2 (st and gt)	800 minimum	3000 minimum

[a] gt=gas turbine, st=steam turbine, stag=combined cycle, steam and gas, n.a.=not applicable.

Specifications Regarding Oxidative Stability of Turbine Oils

Table 1 illustrates some of the latest oxidative stability requirements specified by the major turbine OEM's and international bodies, in terms of rotating pressure vessel oxidation test (RPVOT) time as measured by ASTM D 2272-02, and oxidation life (TOST life) as measured by ASTM D 943-04a. These tests were primarily designed to simulate the conditions that a turbine oil would be exposed to in the field, and in so doing provide an assessment of their oxidative stability and lifetime in the application to ensure that the oil is suitable for use.

Five to ten years ago a typical solvent refined Group I (as defined by the API [5]) based turbine oil using either a single or simple two component antioxidant system would be expected to give an RPVOT up to ~400 min and a TOST life of 3000–4000 h. However, to meet the more arduous and extreme operating conditions of the latest generation of turbines most modern turbine oils are based on the more hydroprocessed Group II and Group III base oils. These have reduced aromatic and heterocyclic contents (which are more prone to oxidation and sludge formation than the other base oil constituents) and so tend to be inherently more oxidatively stable [6]; they also exhibit greater antioxidant response when blended with the latest generation of synergistic multi-component antioxidants. RPVOT times for such oils are typically >1000 min but with equal RPVOT retention capability in service, and TOST lives that can far exceed the 10 000 h maximum quotable, specified according to ASTM D 943-04a (indeed, figures of >20 000 h have been achieved when the test has been allowed to continue past the usual end point of 10 000 h).

Formulating a High Performance Oxidatively Stable Turbine Oil

Some of the key lubricant requirements of a good turbine oil are high oxidative and thermal stability, anti-wear performance (for certain geared turbines), rapid water separation, and foaming and corrosion resistance. Base oils on their own tend to have limitations in these areas. Therefore specialist performance

TABLE 2—*Oxidative stability results.*

	Oil A	Oil B	Oil C	Oil D	Oil E
Base oil type	I	I	II	II	III
RPVOT, min	396	443	1100	2000	1400
TOST 1000 h, sludge, mg	41	171	10	57	41
TOST life, h	3900	3553	>10 000 (11 000[a])	>10 000 (>20 000[a])	>10 000
FTM, % kinematic viscosity change	n.a.[b]	n.a.[b]	n.a.[b]	5	1.3
FTM TAN change, mg KOH/g	n.a.[b]	n.a.[b]	n.a.[b]	0.2	0
FTM, sludge, mg per 100 mL oil	n.a.[b]	n.a.[b]	n.a.[b]	100	35

[a] Test allowed to run past usual end point of 10 000 h until acid number of 2.0 mg KOH/g was reached.

[b] n.a.=Not applicable as these are steam turbine oils and this test has been designed to primarily simulate high temperature gas turbine applications.

enhancing additives such as antioxidants, anti-wear, anti-rust, demulsifiers, and anti-foams are carefully selected by lubricant formulators to extend their performance and life in these areas and to ensure that the lubricant exceeds the demanding turbine requirements. The consequences if these demands are not met can be extreme, for example, considering oxidative stability alone. In a poor quality turbine oil that is not sufficiently oxidatively stable, in service, rapid and extensive oxidation can occur resulting ultimately in the formation of oil insoluble oxidation products (giving deposits such as sludge and lacquer), and oil soluble organic acids and polymeric species (giving thickened, potentially corrosive oil), which will both shorten the life of the oil and reduce the service interval of the turbine, potentially giving rise to a costly and time consuming unplanned turbine shutdown. All turbine oils will degrade in service with time, but it is the rate at which this occurs that can be controlled by the lubricant developers knowledge of base oil and additive chemistry.

As previously mentioned oxidative stability tests (accelerated to shorten the test duration) are used in the laboratory during the development of a new oil to replicate field conditions that the turbine oil will encounter, such as variable temperatures in the presence of catalytic metals, water, and air. Parameters assessed can include change in viscosity, change in acidity, sludge formed, etc.; these are used to predict the oils thermal and oxidative behavior in the field. Once an oil's performance has been sufficiently characterized and proven in the laboratory, it will be extensively field tested prior to commercialization. Oxidation screener tests utilized by Shell include [7]: RPVOT, TOST life, TOST 1000 h, (ASTM D 4310-06b), the Mitsubishi Heavy Industries Dry TOST test [8], and a modified Federal Test Method 791c-5308 (see ASTM D 4636-99, alternative procedure 2). Of these tests, the MHI Dry TOST, TOST 1000 h, and FTM 5308 method, are among the few that are routinely used for turbine oils to assess the deposit forming characteristics of the oil as it degrades in service. This is of key importance to the turbine operator, as significant deposit formation can lead to a cycle of restricted oil flow, hot spot generation, and increased deposition, ultimately resulting in an outage.

Table 2 contains RPVOT, TOST life, TOST 1000 h, and modified Federal Test Method 791c-5308 data, for a number of commercial turbine oils (unused oil samples) representative of those in the market today.

Oils A and B are older conventional Group I mineral oil-based turbine oils, and have performances typical of such. Having low starting RPVOT, relatively short TOST lives, and good to poor sludge performance in the TOST 1000-h test. Such oils were acceptable for use in the less severe older steam and gas turbines giving life times up to five to ten years or more depending on the application, but would not give adequate oil lives in the latest steam and gas turbines.

Oil C represents a modern steam turbine oil; this uses a balanced phenolic/aminic antioxidant system in a Group II base oil to more than double the starting RPVOT antioxidancy, and TOST life seen with the older conventional Group I oils A and B. As a result of the increased oxidative stability of the oil, the sludge forming tendency in the TOST 1000-h test is also improved. This oil is designed to cope with the more extreme conditions in today's turbines, such as increased steam temperatures, and smaller lubricant reservoirs with higher recirculation rates and shorter residence times. These can lead to more exposure of the oil to any potential oxidation hot spots in the system such as the bearings (transient temperatures in journal bearings can reach or exceed 120°C).

Oil D is a top tier turbine oil designed for use in the latest combined cycle (steam and gas turbine) systems. This has a patented balanced additive system capable of meeting the conflicting performance requirements of hot and moist conditions in steam turbines and hot and dry conditions in gas turbines. An aminic antioxidant system is used with a Group II base oil to give the excellent oxidative stability results (and RPVOT retention) shown. In addition to the RPVOT, TOST 1000-h, and TOST life test data shown for the previous oils, Federal Test Method 5308 data have also been included for oils D and E. This test was originally developed to determine the resistance of aircraft turbine engine oils to oxidation and corrosion, and has previously been included in OEM specifications for industrial gas turbines [9]. It is the most severe in temperature terms (175°C) laboratory oxidation test used for turbine oils, and involves air being passed through the oil for 72 h in the presence of five catalytic metal coupons. At the end of the test period three criteria are assessed to rank the oils oxidative stability, these are percent viscosity increase, acid number increase, and sludge formation. The OEM specifications have given limits from +20 to −5 % viscosity change, and an acid number increase of 3.0 mg KOH/g maximum. Sludge limits have not been specified by the OEM, although laboratory values for good oils with proven field performance are typically <150 mg sludge/100 mL oil. Oil C demonstrates a very good low viscosity increase of 5 % (other commercial oils examined have given values of up to 75 % viscosity increase) and a low acidity change of 0.2 mg KOH/g(other commercial oils tested have given values of up to 13 mg KOH/g). The sludge at 100 mg is also even low (other commercial oils evaluated have produced up to 2545 mg of sludge in this test).

Oil E is a premium tier gas turbine oil based on a mixed phenol/amine antioxidant system and Group III base oil. Although this has a slightly lower initial RPVOT value than oil D it performs better in the FTM laboratory evaluation test, with minimal thickening, acidity increase, and lower sludge formation indicating even greater oxidative stability and deposit control under the severest gas turbine conditions. As discussed later, it is typically the rate of decline of RPVOT when the oil is in service, rather than the magnitude of the starting value that is of key importance in determining the oils performance. These laboratory predictions of high oxidative stability and resistance to deposit formation have been confirmed by a long and successful field experience with this oil. Maintaining and enhancing oxidative/thermal stability and especially long-term deposit control in turbine oils continues to be a fundamental area of Shell's turbine oil R&D effort, and will be the subject of future publications.

RPVOT Oil Condition Monitoring of Used Turbine Oils

ASTM D 2272 is routinely used in the laboratory to give an overall estimate of the remaining oxidative stability of turbine oils, because it is relatively quick, uses a small volume of oil, and for trending oils in the field over extended periods is reliable. The most severe OEM requirements for RPVOT such as GEK 107395 are >1000 min for a fresh oil, which are comfortably exceeded by most modern turbine oils. Generally speaking, for a turbine oil to perform well in the field, and give a long and trouble free life, it should have a slow and gradual decline in antioxidancy as the oil degrades normally in service. It is therefore the rate of decline of the RPVOT that is more important than the absolute magnitude of the starting RPVOT. This rate can vary due to a number of factors such as, the severity of the application, the duty cycle, the frequency and quantity of oil top-up, type and amount of contamination, etc. Figure 1 shows the results of RPVOT oil condition monitoring from a long-term field trial of a top tier Group II combined cycle turbine oil.

ASTM Standard D 4378-03 (Standard for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines) [10] suggests considering an oil change for either a steam or gas turbine oil, once its RPVOT falls to 25 % of the initial value and a high acid value is found. This level of RPVOT degradation was developed around older turbine oils that typically had low starting RPVOT values, e.g., ~400 min and so at a 25 % residual level of ~100 min (predicted to be reached at 10 000 h or less under these same field conditions as the Group II oil) would have very little remaining antioxidancy left, and so be vulnerable to rapid degradation. Figure 1 shows that after more than 40 000 operating hours in service, even though the RPVOT value is approaching 25 % of its initial value, it still has an RPVOT value in excess of 500 min (well in excess of the starting RPVOT of many of the older generation of turbine oils) and therefore with

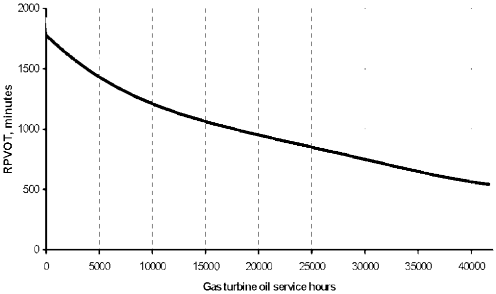

FIG. 1—*RPVOT data for a combined cycle oil running in an Alstom MS6001 Frame 6B gas turbine.*

high remaining antioxidancy. As the other oil condition parameters monitored, such as acid number change, viscosity change, etc., are acceptable, the oil has been approved for continued use, although with an increased frequency of oil condition monitoring (OCM).

Given the laboratory equipment requirements for the RPVOT, the search has been on for a number of years for alternative techniques that could be used in the field to quickly and accurately monitor the oxidative condition of turbine oils. Techniques such as RULER® have been reported to be able to fulfill this function. However, after detailed evaluation of these techniques, Shell has found limitations in their use in terms of accurately quantifying the oxidative condition of used modern turbine oils containing sophisticated multi-antioxidant systems. Such techniques seem more applicable to trending simpler single antioxidant systems. The RPVOT is still Shell's preferred method for trending and determining the remaining oxidative stability of used turbine oils in the field, since it physically oxidizes the oil and directly measures its resistance to oxidation, rather than relying on an indirect measure of antioxidancy.

In addition to using RPVOT to assess the remaining antioxidancy of turbine oils, chromatographic techniques have also been investigated in our laboratories to quantify the amount of remaining original antioxidants. The combined cycle oil above was formulated with two aminic antioxidants to obtain the desired excellent oxidative stability. Unused amine one when analyzed by high performance liquid chromatography (HPLC) gave at least five major readily resolvable peaks attributable to isomers. Fresh amine two gave two main peaks. In the used turbine oil, in principle, these peaks can be tracked and quantified to obtain an estimate of the remaining unused original antioxidant species. In practice such information can be of limited use from an OCM perspective; it needs to be emphasized that frequently no simple linear correlation exists between the quantity of remaining unused antioxidant and the oxidative stability of the oil. This is because as each antioxidant functions it can transform into numerous chemical intermediates; some of these intermediates can be more potent antioxidants than the original starting material, and because they are chemically different to the starting antioxidants may not be detected as readily without detailed complex analysis. Unless each and every antioxidant and their major intermediates are identified, quantified, and their potency as antioxidants established, it is possible that analytical quantification of the antioxidant concentration in a used oil could underestimate its overall oxidative stability, leading to a premature oil change.

Conclusions

Given the present turbine technology drivers, the future trends in turbine oil performance are likely to include maintaining high oxidative and thermal stability in service, longer oil service life expectations, together with enhanced long-term resistance to oil deposit formation over the oil's extended lifetime.

The majority of the high performance turbine oils available in the market place today are based on hydroprocessed Group II or even Group III mineral oils derived from conventional crude oil, which in combination with sophisticated additive packages meet and exceed the latest turbine OEM and international specifications with regard to oxidative stability. Such oils readily outperform the older Group I type turbine oils.

With regard to oil condition monitoring, and directly measuring the effective antioxidant performance remaining in a used turbine oil, in our experience the RPVOT test remains the preferred method. Alternative methods that attempt to quantify the concentration of antioxidants can underestimate the oil's remaining oxidative stability.

References

[1] ASTM D 2272, "Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel," *Annual Book of ASTM Standards*, Vol. 05.01, ASTM International, West Conshohocken, PA, pp. 822–833.

[2] ASTM D 4310, "Standard Test Method for Determination of Sludging and Corrosion Tendencies of Inhibited Mineral Oils," *Annual Book of ASTM Standards*, Vol. 05.02, ASTM International, West Conshohocken, PA, pp. 602–612.

[3] ASTM D 943, "Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils," *Annual Book of ASTM Standards*, Vol. 05.01, ASTM International, West Conshohocken, PA, pp. 347–357.

[4] ASTM D 4636–99, "Standard Test Method for Corrosiveness and Oxidation Stability of Hydraulic Oils, Aircraft Turbine Engine Lubricants and Other Highly Refined Oils," *Annual Book of ASTM Standards*, Vol. 05.02, ASTM International, West Conshohocken, PA, pp. 748–757.

[5] API (2002) "Engine Oil Licensing and Certification System," API 1509.

[6] Schwager, B. P., Hardy, B. J., and Aguilar, G. A., "Improved Response of Turbine Oils Based on Group II Hydrocracked Base Oils Compared with Those Based on Solvent Refined Base Oils," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM Internationals, West Conshohocken, PA, 2001, pp. 71–78.

[7] Guerzoni, F. N., and Graham, J., "The Relationship Between Oxidative Stability and Field Behaviour of High Performance Turbine Lubricants," *The Society of Tribologists and Lubrication Engineers, 56th Annual Meeting*, Orlando, FL, 2001.

[8] Yano, A., Watanabe, S., Miyazaki, Y., Tsuchiya, M., and Yamamoto, Y., "Study on Sludge Formation During the Oxidation Process of Turbine Oils," *Tribol. Trans.*, Vol. 47, 2004, pp. 111–122.

[9] GEK 32568C, "Lubricating Oil Recommendations for Gas Turbines with Bearing Ambients Above 500°F (260°C)," July 1993, and GEK 101941, "Lubricating Oil Recommendations with Antiwear Additives for Gas Turbines with Bearing Ambients Above 500°F (260°C)," March 1995, GE Power Systems.

[10] ASTM D 4378–03, "Standard for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines," *Annual Book of ASTM Standards*, Vol. 05.02, ASTM International, West Conshohocken, PA, pp. 623–633.

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Physical, Performance, and Chemical Changes in Turbine Oils from Oxidation

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ABSTRACT: One of the primary factors in determining the life and performance of turbine oils is its oxidation stability. Oxidation can cause a host of problems for in-service turbine oils, such as sludge, deposits, lacquer, and varnish formation. There is limited published research on the performance of turbine oils once oxidation begins. This paper presents data on the relationship between several turbine oil characteristics during the oxidation process by focusing on the measurable physical and chemical changes that occur. Five turbine oils were chosen, each employing different antioxidants and base oil refining technologies to represent a typical selection of commercially available turbine oils. A 49-day experiment was completed in which the oils were subjected to a controlled and accelerated oxidative process under laboratory conditions. Throughout the testing period, samples were drawn and a range of chemical, physical, and performance tests were performed. The data obtained from this experiment identify several correlations that relate to the performance of each oil. These data are useful in understanding the relationship between turbine oil oxidation and fluid performance and will help end-users in selecting and optimizing their turbine lubricant.

KEYWORDS: anti-oxidants, oxidation, turbine oils, varnish, sludge, lacquer, deposit, condition, monitoring, oil analysis

Introduction

Gas turbines have been subjected to dynamic changes over the past ten years due to their continual evolution of design, which have improved fuel to power efficiency and elevated firing temperatures. This has placed increasing demands on turbine lubricants, especially in the areas of oxidative and thermal stability. In some combustion turbines, the lubricants serve multiple functions in addition to providing bearing lubrication and cooling. These added functions include acting as a sealant for compressed gases, providing hydrostatic lift while the unit is on turning gear and actuation of critical and sensitive hydraulic control valves. Also, many power stations are operated in a peaking or cycling fashion, which places further thermal stress on the lubricant.

Turbine oil formulations have kept pace with these changing operating environments. Most turbine oils on the current U.S market utilize API Group II (hydrocracked) or higher basestocks. These products contain significantly fewer impurities than solvent refined API Group I products. Furthermore, these lubricants employ more sophisticated and robust additive systems to improve oxidative stability and a host of other performance factors, making the formulations more suitable for today's demanding environment.

The advancements in turbine oil chemistries and the criticality of the application require an understanding of oil degradation in order to optimize the formulation and maximize the life of the lubricant. This paper discusses some of the known oxidation principles and the relationships between common testing methodologies, using five different oils as examples. These oil samples were placed in a 120°C bath for seven weeks to accelerate the experiment and to simulate higher than typical bulk circulating oil temperatures of a gas turbine application. A series of analytical tests were performed and visual observations made at set intervals throughout the experiment to monitor the chemical and physical changes. In addition, some comparisons were made regarding the performance of each of the fluids.

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TABLE 1—*Oils tested.*

Oil	Basestock	Antioxidant	Sulfur, ppm
Sample A	API Group II	Phenol, Amine	9
Sample B	API Group II	Phenol	<1
Sample C	API Group I	Phenol, ZnDTP	566
Sample D	API Group II	ADPA, APANA	112
Sample E	API Group II	Phenol, ADPA, PANA	17

The Experiment

Five turbine oils were selected, each with different properties as defined in Table 1. The turbine oils in the experiment consisted of both API Group I and API Group II basestocks. The oxidation inhibitors in the turbine oils consisted of hindered phenols such as 2,6 di-tert-butyl-para-cresol (DBPC), aromatic amines such as phenyl-alpha-naphthylamine (PANA), alkylated-phenyl-alpha-naphthylamine (APANA), alkylated diphenylamines (ADPA), and secondary antioxidants such as zinc dialkyldithiophosphate (ZnDTP). For the purposes of this paper, the groups of antioxidants will be generically classified as either phenols or amines unless the specific additive chemistry is discussed.

Approximately 15 litres of each oil type was placed in an independently controlled and covered circulating bath. The temperature of the fluid in each bath was maintained at 120°C for 49 days. These conditions accelerated the oxidation process while enabling atmospheric evaporation of the lubricant to occur naturally. The ambient temperature of the air in the laboratory was maintained at 22°C.

Description of Analytical Tests

The following analytical tests were performed on the oil samples:

- Acid Number, mg KOH/g—ASTM D 664 (modified)
- Viscosity, mm^2/s (centistokes) at 40°C—ASTM D 445
- Rotating Pressure Vessel Oxidation Test (RPVOT), minutes—ASTM D 2272
- Water Separability, minutes—ASTM D 1401
- Arc Emission Elemental Spectroscopy (Spectroscopy), ppm—ASTM D 6595
- Linear Sweep Voltammetry (LSV), RULER®[1] Number—ASTM D 6971
- Fourier Transform Infrared (FTIR), Absorbance, ASTM E 168
- Ultracentrifuge (UC), Sedimentation Rating—40 millilitres of undiluted sample is placed in a plastic test tube and spun at 20 000 r/min in a centrifuge for 30 minutes. The fluid is subjected to a 34 800 g force. The insolubles are separated from the fluid centrifugally then compared with a visual sediment rating scale. The minimum value of 1 represents no to low total insoluble levels. The maximum value of 8 represents a high amount of insolubles.
- Quantitative Spectrophotometric Analysis (QSA^{sm})[2], Varnish Potential Rating—A sample of oil is mixed with solvent and pulled through a filter-membrane. It is known that the color spectra of the insolubles collected can be correlated to the amount of oxidation byproducts in the oil [1,2]. The insolubles are analyzed with a spectrophotometer and then translated to a Varnish Potential Rating. Results are expressed on a scale of 1 to 100.
- Insoluble Isolation and FTIR, The QSA^{sm} membrane was rinsed with methylene chloride. The filtrate was then allowed to evaporate, leaving behind only the captured insoluble material. This material is then analyzed with FTIR.

Experiment Results and Discussion

Lubricant degradation pathways are complex and difficult to predict due to the wide range of organic species produced. Each product may react with the oil, additive, or other intermediates to yield new byproducts, as depicted in Fig. 1. The laws of thermodynamics and various kinetic constants govern many of these reactions.

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[1] RULER® is a trademark of Fluitec International.

[2] QSM^{sm} is a service mark of Analysts Inc.

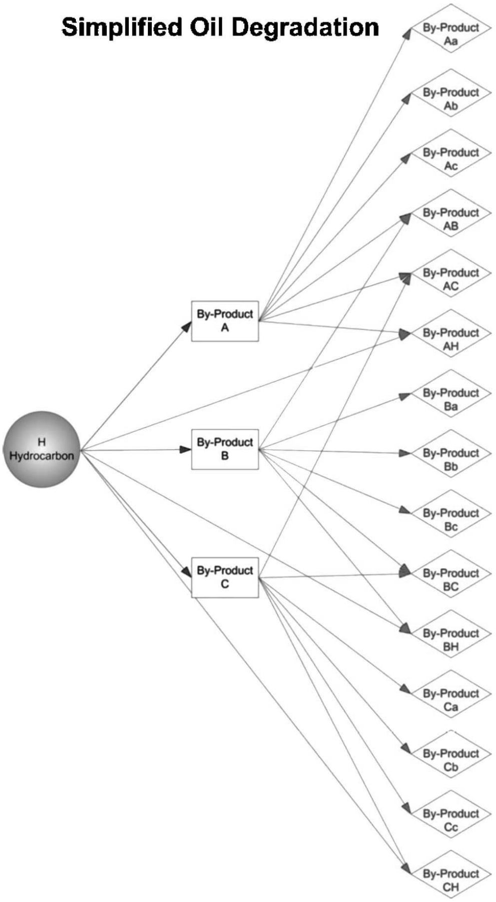

FIG. 1—*Simplified oil degradation example of one hydrocarbon molecule and one level of intermediary degradation byproducts.*

This experiment monitored the degradation of the oils by measuring specific properties. The analysis performed will not detect all of the specific degradation pathways that occurred within this experiment. However, a likely scenario for each oil type is suggested by examining the lab data over the seven-week experiment. In no way is it proposed that these are all of the possible degradation mechanisms.

Results and Analysis of Sample A

The analytical results of Sample A are presented in Table 2.

General Observations of Sample A

Sample A is a Group II, R&O turbine oil with a phenol and amine antioxidant additive package. Following is a summary of the analytical observations made from the data:

- No meaningful change in RPVOT value.
- Constant and gradual depletion of phenol antioxidants.
- There was very little change in amine antioxidants concentration.
- FTIR analysis indicated a build up of byproducts in the carbonyl region — most noticeably carboxylic acids (Fig. 2).

TABLE 2—*Analytical results from Sample A.*

	Start	W1	W2	W3	W4	W5	W6	W7
Physical and Chemical Tests								
Viscosity (mm^2/s @ 40°C)	29.7	29.8	30.0	30.1	30.1	30.0	30.3	30.5
Acid Number (mg KOH/g)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.11
Spectrograph (ppm)	<5	…	…	…	…	…	…	<5
FTIR — Phenol OH (3664–3610 cm^{-1})	1.19	…	…	…	…	…	…	0.29
FTIR — Amine N-H (3500–3370 cm^{-1})	0.08	…	…	…	…	…	…	0.08
FTIR — Acid C=O (1719–1703 cm^{-1})	0.021	…	…	…	…	…	…	0.042
QSA^{sm} (Varnish Potential Rating)	1	3	5	3	3	3	3	38
Ultracentrifuge (Sediment Rating)	1	…	…	…	…	…	…	3
Performance Tests								
RPVOT (min)	458	…	460	493	…	471	491	413
Water Separability (mins)	25	…	20	15	20	15	20	20
LSV — Amines (RUL #)	100.0	80.5	95.8	93.2	79.8	91.0	92.1	92.2
LSV — Phenols (RUL #)	100.0	129.0	102.2	101.4	64.4	54.7	58.1	29.4

- There was a sharp rise in insoluble content between Week 6 and Week 7 as measured by the QSA^{sm} test and UC test.

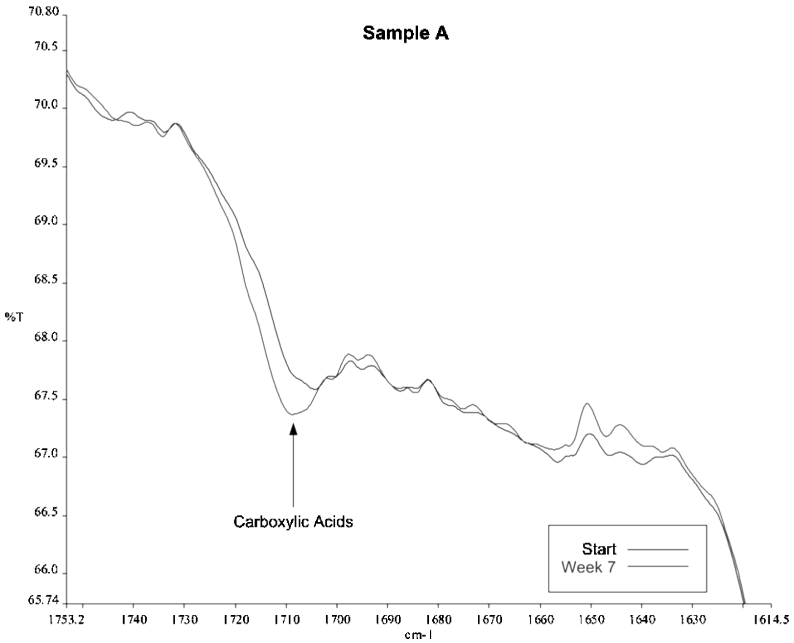

FIG. 2—*FTIR: increases in carboxylic acids.*

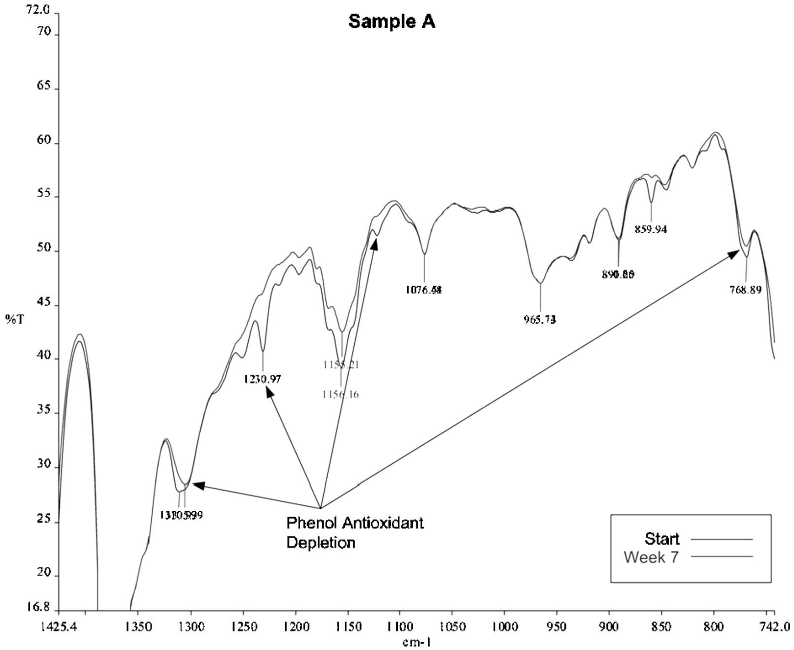

FIG. 3—*FTIR: phenol antioxidant depletion.*

Discussion of Sample A

The RPVOT values remained statistically unchanged throughout the experiment. The amine antioxidants also remained unchanged as reported by LSV. However, the phenol antioxidants depleted. This indicates that RPVOT values have a higher correlation to amine concentration than to phenol concentration. Research confirms that amines are more effective than metallic and phenol-type substances in raising oxidative resistance of lubricants as measured by RPVOT [3].

Amines react quicker than phenols at scavenging free radicals. However, phenols will donate a hydrogen atom to the intermediary amine byproduct, causing the phenol to deplete and the amine to become regenerated [4]. This synergistic effect of formulations containing both amines and phenols is one possible explanation why the level of phenols may deplete quicker than that of the amines.

The LSV results corresponded to the FTIR spectra. All phenol peaks in the infrared spectra showed depletion as depicted in Figs. 3 and 4.

The most notable change throughout the experiment was the increase in insoluble byproducts that occurred between Week 6 and Week 7 as measured by QSA^{sm} and UC. There was evidence of oxidative byproducts at Week 7 visible in the infrared spectrum between 1725 cm^{-1} and 1700 cm^{-1}. The majority of these byproducts are carboxylic acids but were undetected by acid number titrations. Oxidation byproducts are electrochemically polar and have a natural attraction to each other, as well as other polar compounds. The accumulation of several byproducts of lower molecular weight can form a higher molecular weight, long-chained molecule called an oligomer [5]. Due to its increased mass and electronegative properties, an oligomer molecule has limited solubility in a lubricant and contributes to deposit formations. Therefore, in Sample A it is postulated that the increase of insolubles in the experiment can be explained by the accrual of degradation byproducts that amassed together forming oligomers which settled out of the oil.

Results and Analysis of Sample B

The analytical results of Sample B are presented in Table 3.

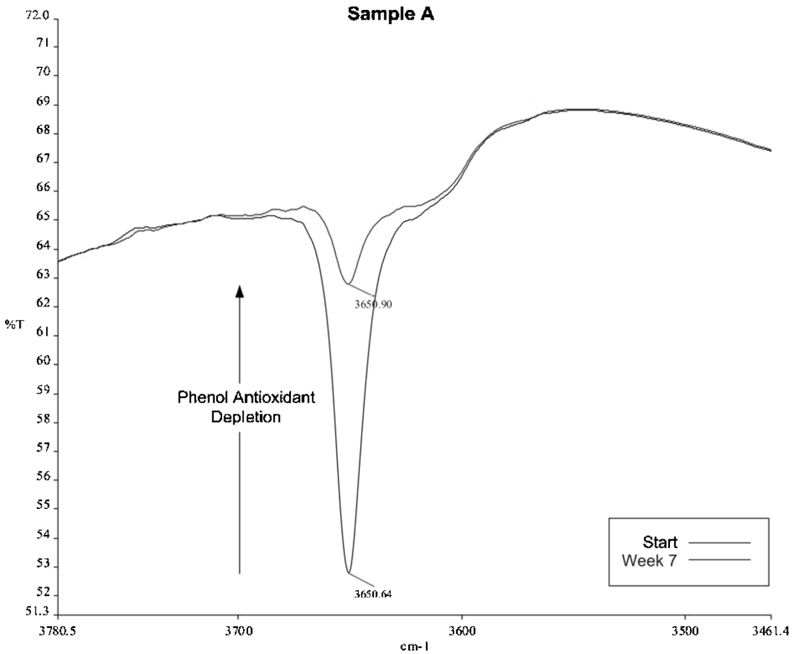

FIG. 4—*FTIR: phenol antioxidant depletion.*

TABLE 3—*Analytical results from Sample B.*

	Start	W1	W2	W3	W4	W5	W6	W7
				Physical and Chemical Tests				
Viscosity (mm^2/s @ 40°C)	30.1	30.1	30.0	30.2	30.2	30.0	30.2	30.3
Acid Number (mg KOH/g)	0.11	0.06	0.06	0.06	0.06	0.06	0.06	0.11
Spectrograph (ppm)	<5	…	…	…	…	…	…	<5
FTIR — Phenol OH (3664–3610 cm^{-1})	0.8	…	…	…	…	…	…	0.34
FTIR — Amine N-H (3500–3370 cm^{-1})	−0.05	…	…	…	…	…	…	−0.04
FTIR — Acid C=O (1719–1703 cm^{-1})	0.005	…	…	…	…	…	…	0.032
QSA^{sm} (Varnish Potential Rating)	1	1	3	1	1	3	1	5
Ultracentrifuge (Insolubles Rating)	1	…	…	…	…	…	…	2
				Performance Tests				
RPVOT (min)	453	…	407	448	371	379	297	287
Water Separability (min)	20	…	10	15	10	10	10	10
LSV — Amines (RUL #)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LSV — Phenols (RUL #)	100.0	68.9	42.2	31.4	25.0	22.8	14.5	8.4

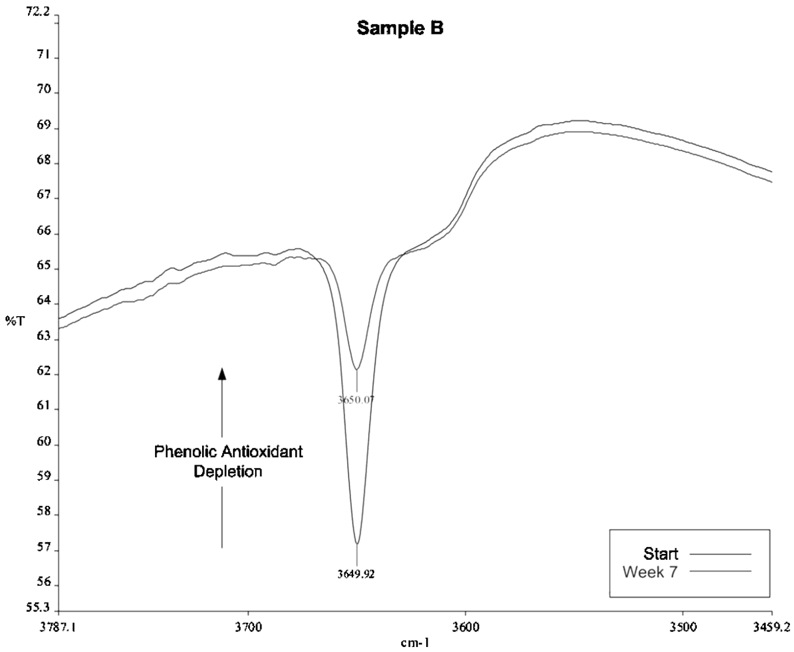

FIG. 5—*FTIR: phenol depletion.*

General Observations of Sample B

Sample B is a turbine oil containing a phenol antioxidant formulated into a API Group II basestock. Following is a summary of the analytical observations made from the data:

- No increase in insolubles or acid number.
- Consistent depletion of phenols over the course of the experiment as evidenced by LSV and FTIR results (Figs. 5 and 6).

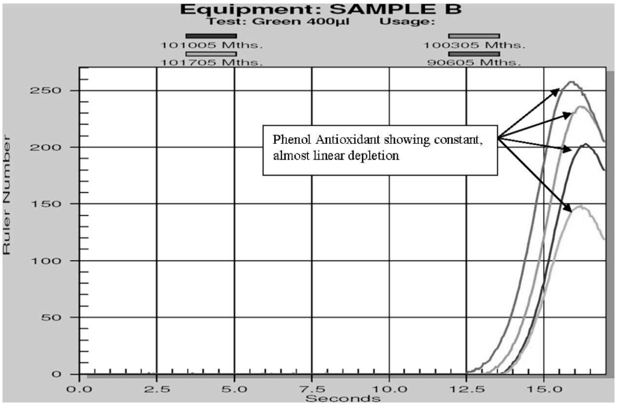

FIG. 6—*LSV graph of Sample B.*

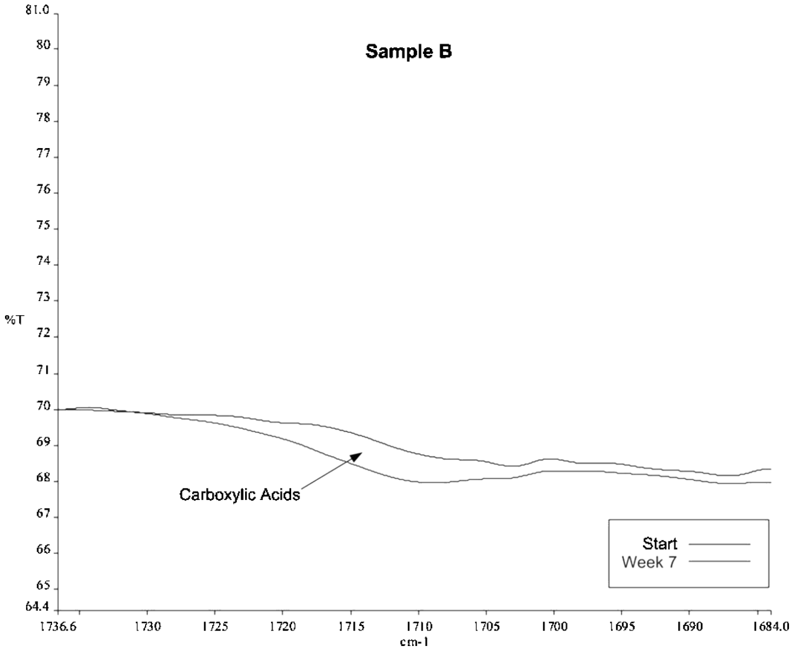

FIG. 7—*FTIR: carboxylic acids.*

- A reduction in oxidative stability as measured by RPVOT.
- Small amounts of oxidation byproducts are visible at 1714 cm^{-1} (Fig. 7).

Discussion of Sample B

The phenol antioxidants appear to do an adequate job of protecting the base oil and preventing the formation of deposits or base oil oxidation. In addition, the phenol intermediaries and degradation byproducts do not create deposits in this experiment. The viscosity and acid number is not impacted throughout the experiment, suggesting a high quality basestock.

This is the only sample in the experiment that uses phenols exclusively as an antioxidant. As a result, a consistent, predictable rate of depletion as measured by LSV can be observed (Figs. 8 and 9). The calculated phenol antioxidant content by FTIR has good correlation with RPVOT in a phenol-only product.

Results and Analysis of Sample C

The analytical results of Sample C can be viewed of Table 4.

General Observations of Sample C

Sample C was formulated with primary (phenol) and secondary (ZnDTP) antioxidants, and had an API Group I basestock composition. The observations made from this sample are:

- There was no measurable change in acid number or RPVOT.
- There was no measurable amount of carboxylic acids or other oxidation byproducts visible in the infrared spectrum.
- There was a rapid increase in insolubles level between Week 6 and Week 7 as identified by QSA^{sm} and UC. The collected insolubles had a yellowish orange appearance.

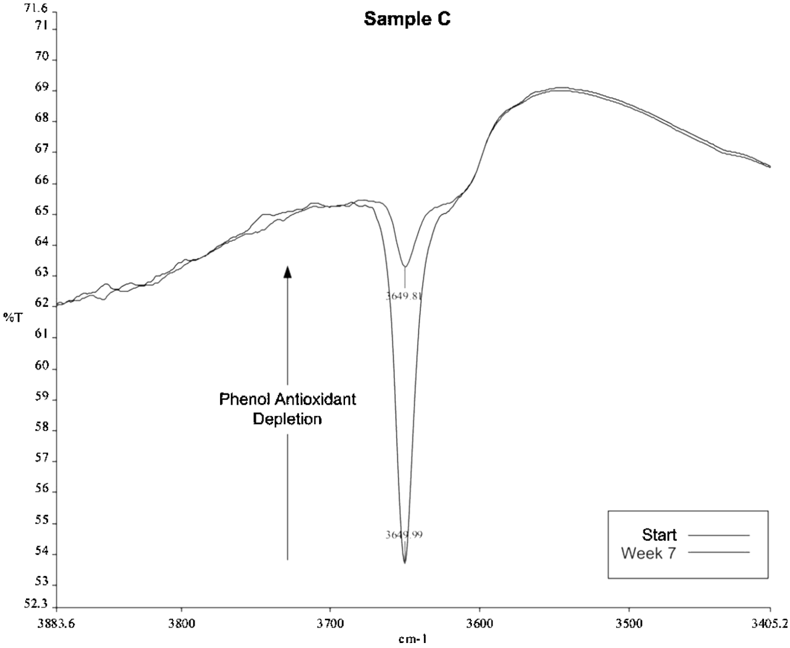

FIG. 8—*Phenol antioxidant depletion.*

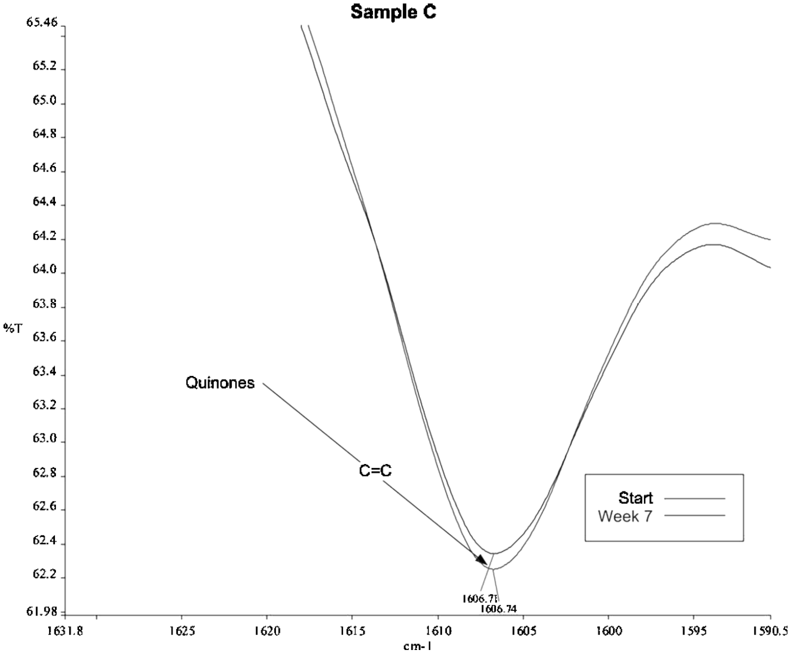

FIG. 9—*Evidence of quinones.*

TABLE 4—*Analytical results from Sample C.*

	Start	W1	W2	W3	W4	W5	W6	W7
				Physical and Chemical Tests				
Viscosity (mm^2/s @ 40°C)	33.5	33.4	33.7	33.6	33.7	34.0	34.2	33.8
Acid Number (mg KOH/g)	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Spectrograph (ppm)	Zn: 89, P: 61	…	…	…	…	Zn: 93, P: 61		
FTIR — Phenol OH (3664–3610 cm^{-1})	1.15	…	…	…	…	…	…	0.27
FTIR — Amine N-H (3500–3370 cm^{-1})	0.03	…	…	…	…	…	…	0.03
FTIR — Acid C=O (1719–1703 cm^{-1})	0.011	…	…	…	…	…	…	0.009
QSA^{sm} (Varnish Potential Rating)	1	1	5	5	7	13	13	44
Ultracentrifuge (Insolubles Rating)	1	…	…	…	…	…	…	5
				Performance Tests				
RPVOT (min)	696	…	620	664	677	…	…	710
Water Separability (min)	15	…	15	15	15	15	10	10
LSV — ZnDTP (RUL #)	100.0	100.0	85.4	59.1	81.1	82.2	75.6	80.3
LSV — Phenols (RUL #)	100.0	91.6	93.1	108.9	75.8	55.1	34.0	12.6

- The phenol antioxidant was almost completely consumed and dropped from 34 to 13 % in the last week of the experiment.

Discussion of Sample C

The depletion of phenol antioxidants over the course of the experiment indicates several reactions with alkyl radicals [6]. Assuming the generation of alkyl radicals was constant, it is likely that the number of alkyl radicals overwhelmed the primary antioxidants creating hydroperoxides. At this point, the ZnDTP additive was activated to decompose the hydroperoxides [7]. It is known that the depletion of ZnDTP results in creation of phosphorus containing intermediaries [8]. The intermediaries proceed to create insoluble phosphate salts and sulfates which form deposits [8].

In order to test this theory, the filter-membrane from the QSA^{sm} test was rinsed with methylene chloride to extract the oil degradation byproducts (Fig 10). This filtrate was reduced to concentrate the

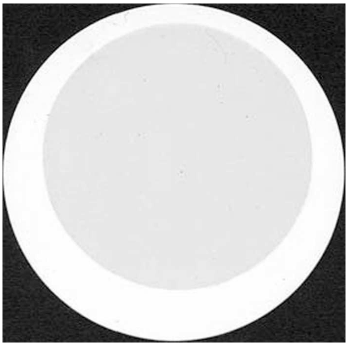

FIG. 10—*Filter membrane from Sample C.*

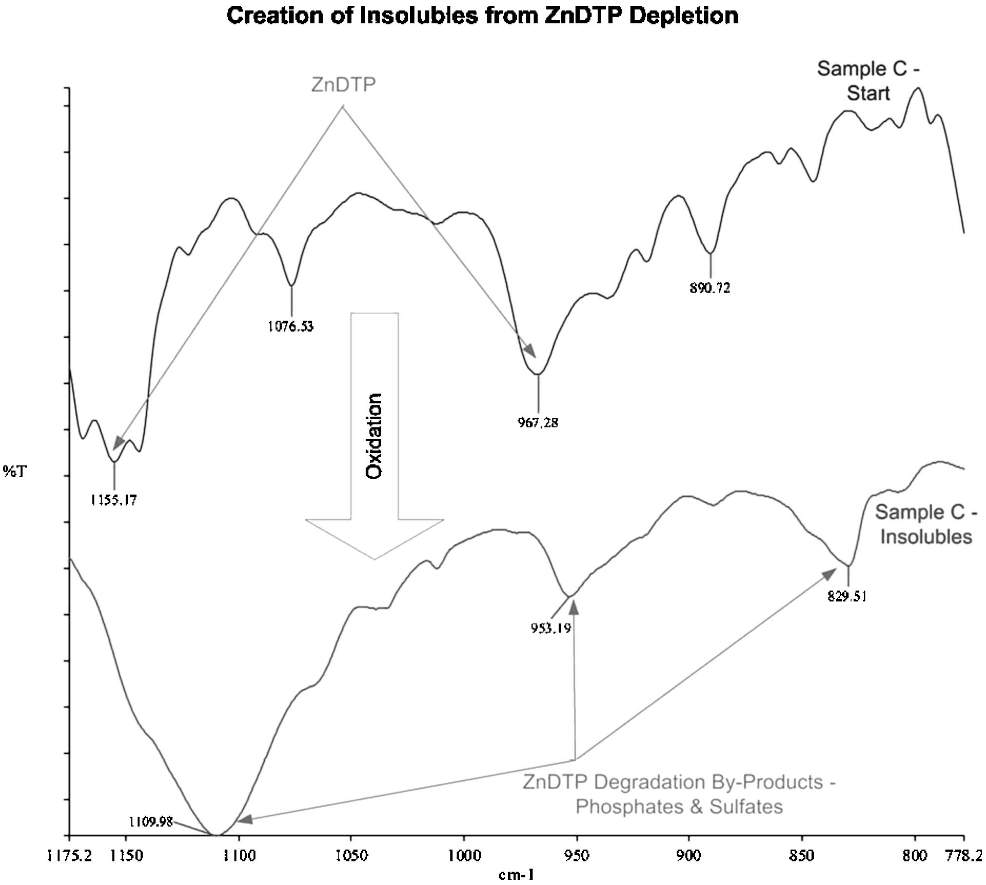

FIG. 11—*Evidence that depleted ZnDTP is responsible for creation of insolubles.*

insoluble materials gathered from the membrane. Finally, a portion of the filtrate was evaporated directly on the FTIR cell and analysis was performed. The analysis indicated a significant amount of sulfates and phosphates, degradation byproducts of ZnDTP, confirming that the rise in insoluble level was due to the depletion of ZnDTP (Fig. 11).

Based on this experiment, it is reasonable to estimate that the majority ZnDTP was activated when the phenol antioxidant dropped below 34 % between Weeks 6 and 7 and subsequently formed insoluble byproducts.

Results and Analysis of Sample D

The analytical results of Sample D can be viewed of Table 5 (see Figs. 12–14).

General Observations of Sample D

This oil was formulated with ADPA and APANA, and used an API Group II basestock composition. The oil also had approximately 35 ppm phosphorus (in the form of either an amine phosphate or thio substituted phosphate) as an extreme pressure additive. This oil had the highest initial RPVOT value in the experiment. The observations made from this sample are:

- No measurable change in acid number or RPVOT.

TABLE 5—*Analytical results from Sample D.*

	Start	W1	W2	W3	W4	W5	W6	W7
				Physical and Chemical Tests				
Viscosity (mm^2/s @ 40°C)	30.3	30.1	30.2	30.2	30.0	30.2	30.4	30.6
Acid Number (mg KOH/g)	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Spectrograph (ppm)	P: 33	…	…	…	…	…	…	P: 20
FTIR—Phenol OH (3664–3610 cm^{-1})	0.05	…	…	…	…	…	…	0.06
FTIR—Amine N-H (3500–3370 cm^{-1})	0.23	…	…	…	…	…	…	0.20
FTIR—Acid C=O (1719–1703 cm^{-1})	0.049	…	…	…	…	…	…	0.011
QSA^{sm} (Varnish Potential Rating)	5	40	50	60	81	85	99	100
Ultracentrifuge (Insolubles Rating)	1	…	…	…	…	…	…	6
				Performance Tests				
RPVOT (min)	2 175	…	…	…	…	2 312	…	1 850
Water Separability (min)	15	…	10	15	15	15	…	15
LSV — Amines (RUL #)	100.0	103.6	108.1	90.5	105.9	104.0	97.9	100.5
LSV — Phenols (RUL #)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

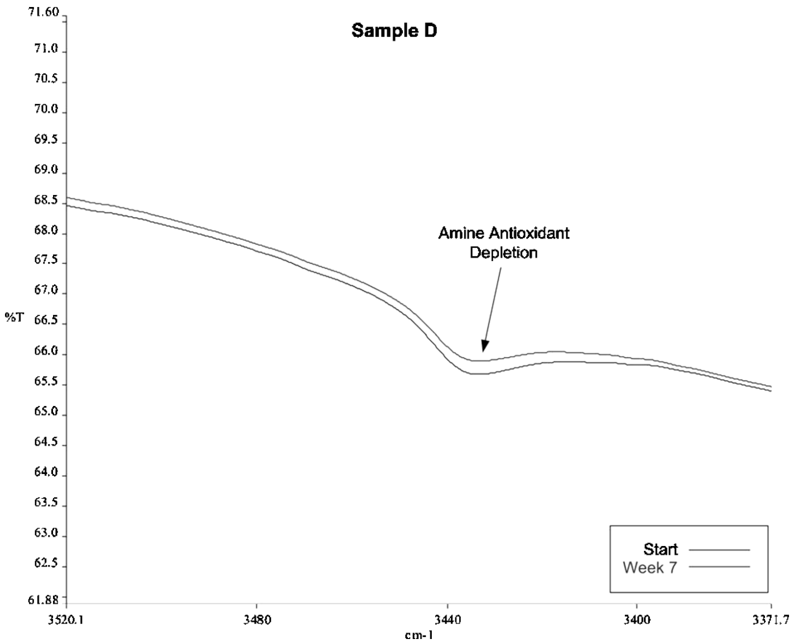

FIG. 12—*FTIR: amine antioxidant depletion.*

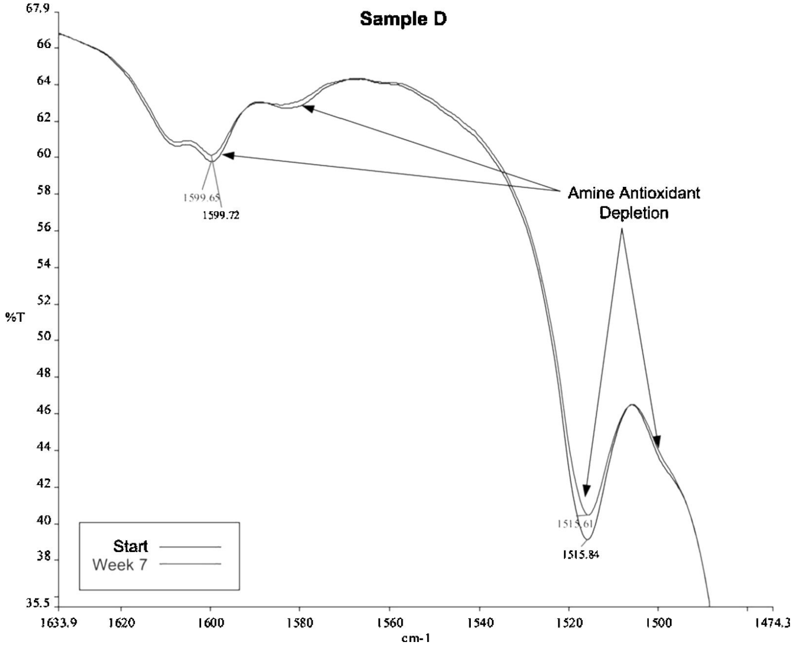

FIG. 13—*FTIR: amine antioxidant depletion.*

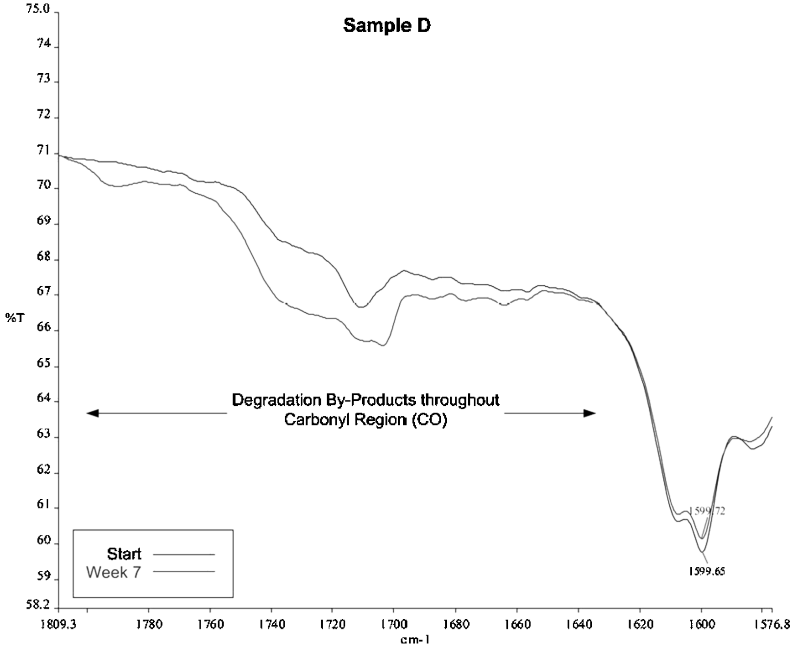

FIG. 14—*FTIR: evidence of degradation byproducts.*

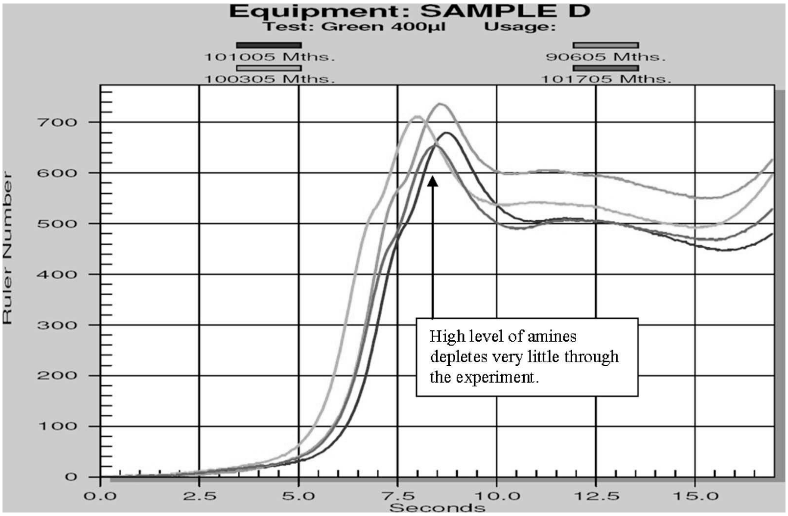

FIG. 15—*LSV results.*

- LSV calculations did not show signs of amine depletion, although FTIR did show some signs and the LSV graphs indicate a shift in peak height and location (Fig. 15).
- After the first week, there was a high level of insolubles as measured by QSA^{sm}.
- The level of insolubles built to a very high level throughout the experiment.
- The QSA^{sm} membrane had a very dark hue.
- While in the 120°C bath, this oil quickly became dark and continued to darken throughout the experiment.

Discussion of Sample D

The high level of insolubles in this sample throughout the experiment indicates that a fluid's potential to produce deposits may be unrelated to the RPVOT value of the oil, as this oil had the highest RPVOT value in the group.

Based on these results, it is reasonable to assume that the insolubles were created by the depletion of amine additives. One of the amines formulated into the product is ADPA, an effective antioxidant, but also known to produce insoluble byproducts [9].

The color of the QSA^{sm} filter membrane had a dark brown hue as seen in Fig. 16. PANA, APANA, and other aromatic amine derivatives are known to produce a reddish purple chromophore after depletion [6]. Therefore the color of the patch and the darkness of the oxidized oil also suggest amine depletion is responsible for the sludge formation.

Results and Analysis of Sample E

The bath used in Sample E had a failure midway through the experiment. Therefore, limited data was collected on this sample. The data that were collected do allow for some interesting interpretation. The analytical results of Sample E can be viewed in Table 6.

General Observations of Sample E

This oil was formulated with phenols, ADPA, and PANA antioxidants, and had an API Group II basestock composition. The observations made from this sample are:

- No measurable change in acid number.

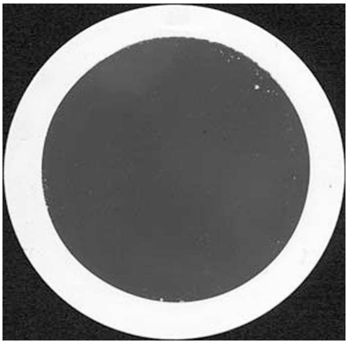

FIG. 16—*Filter membrane from Sample D.*

- Increasing level of insolubles throughout the course of the experiment as measured by QSA^{sm} and UC tests.
- LSV calculations did not show signs of amine depletion, although FTIR did show some signs and the LSV graphs indicate a shift in peak height and location.
- The level of phenols varied considerably but trended downwards throughout the four weeks.

Discussion of Sample E

The level of insolubles in Sample E rapidly became high, especially during Weeks 1 and 2. Sample E was the only turbine oil formulated with PANA. APANA has an alkyl group in the molecular structure increasing its solubility, while PANA has lower solubility and its derivatives will create insolubles [9]. Therefore, based on the experiment, it is reasonable to hypothesize that PANA created the insolubles.

Data Trends

There were several trends observed when viewing the data from the experiment cumulatively.

TABLE 6—*Analytical Results from Sample E.*

	Start	W1	W2	W3	W4
Viscosity (mm^2/s @ 40°C)	29.9	29.9	30.0	30.1	30.1
Acid Number (mg KOH/g)	0.06	0.06	0.06	0.06	0.06
Specrograph	<5	…	…	…	<5
FTIR — Phenol OH (3664–3610 cm^{-1})	0.46	…	…	…	0.35
FTIR — Amine N-H (3500–3370 cm^{-1})	0.06	…	…	…	0.05
FTIR — Acid C=O (1719–1703 cm^{-1})	0.006	…	…	…	0.021
QSA^{sm} (Varnish Potential Rating)	3	15	52	54	64
Ultracentrifuge (Insolubles Rating)	1	…	…	…	3
LSV — Amines (RUL #)	100.0	108.0	103.6	112.2	113.0
LSV — Phenols (RUL #)	100.0	54.2	4.6	15.0	29.8

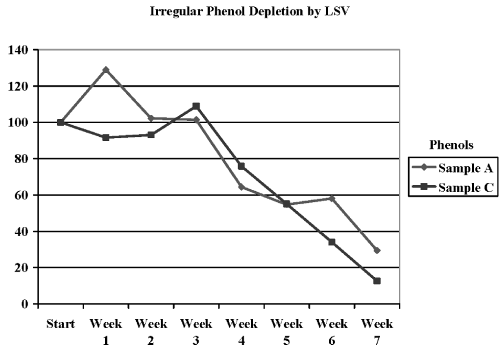

FIG. 17—*LSV results: irregular phenol depletion in the presence of amines.*

Measuring Antioxidant Performance by the LSV Method

In the presence of amines and ZnDTP, phenols do not deplete linearly by the LSV method. Two examples from the experiment where the phenol level rises about 100 % can be seen in Fig. 17.

This can be explained by a synergistic affect that some of the intermediary degradation byproducts of phenol have with amine antioxidants.

LSV is an effective monitoring tool for antioxidant performance. The oils that formed insolubles in the experiment also had significant movement in LSV results. It would be easy to correlate LSV results to an in-service turbine oil's varnish potential and other performance characteristics. This could be accomplished with a large number of trending data points; however, the oil would have to have the same additive chemistry.

Oxidation Testing

Several observable chemical and performance changes occurred throughout the experiment; however, there was virtually no change in RPVOT values for all but one sample. This indicates that RPVOT may not accurately reflect a turbine oil's in-service performance characteristics.

RPVOT has a repeatability value of 12 % and a reproducibility value of 22 % for oils under 1000 minutes. The test has "poor precision for oils with greater results than 1000 min" [10]. This limits the value of the test for a narrow number of commercially available turbine oils.

Another problem with RPVOT is that it does not reproduce the dynamic conditions in a turbine environment. An in-service turbine oil may be subjected to temperatures ranging from a couple of hundred degrees Celsius [11] causing oxidation, to conditions creating localized hotspots of several thousand degrees (such as in electrostatic spark discharge or micro-dieseling), sufficiently hot to crack the hydrocarbon molecule [12]. Each temperature range alters the kinetics of the oxidation process and creates scenarios not measured by RPVOT. Due to these factors, RPVOT may have limited value in a turbine oil condition monitoring program, especially in determining a fluid's varnish potential.

Acid Number

There were no significant changes in acid number throughout the experiment. This illustrates the limitations of the testing method to measure the subtle changes in fluid chemistry and demonstrates its ineffectiveness as a predictive tool for increased sludging and varnishing propensities.

Viscosity

As oils oxidize, byproducts such as ketones and aldehydes undergo Aldol Condensation reactions, which will increase the oil's viscosity [13]. Every oil in the experiment saw an increase in viscosity. These results are significant; however, it is not clear whether the rise in viscosity was due to the evaporation of light ends or an increase in oxidation byproducts. More testing is required to make this conclusion.

Water Separability

It is known that polar contaminants in turbine oils will affect the water separability of a fluid [14]. The authors have field experience showing a relationship between the amount of oxidation byproducts in an oil and its water separability characteristics; however, there were no meaningful changes in water separability values in this experiment. This suggests that either additional contaminants that enter the oil during service may impact this performance characteristic or more severe oxidation, or both, is required to have an impact.

Turbine Oil Varnish Potential

Lubricant varnish is a serious problem in turbine applications [2,9,15]. Turbine equipment manufacturers have also recognized this problem and have issued recommendations to their clients to make them aware of performance and reliability issues associated with varnish [16,17]. Monitoring the varnish potential of in-service turbine oil is an important criteria in a condition monitoring program. The experiment detailed in this paper used two analytical tools to monitor the turbine oil's varnish potential; quantitative spectrophotometric analysis and insolubles by ultracentrifuge. Both tests were demonstrated to be effective in detecting small changes of insoluble contents. Values from these tests can also be correlated to a turbine oil's varnish potential, based on the specific application the fluid is being used.

Summary

Based on this paper's experiment, the following summary points are concluded:

1. Antioxidant Chemistry
    - (a) High amounts of amine-type antioxidants positively affect the product's RPVOT value and oxidative stability. However, amines additives may produce more insolubles than phenols when depleted.
    - (b) ZnDTP antioxidant/antiwear agents appear to produce insolubles when depleted.
2. Oxidation
    - (a) The first performance problem related to oxidation is the production of insolubles. This will cause sludge and varnish in a turbine application.
    - (b) Based on the experiment, an oil's propensity to produce insolubles does not appear to be related to its oxidative stability.
    - (c) When selecting turbine oil, one should consider the fluid's resistance to form sludge and varnish as an important criteria.
    - (d) There is a need for a new industry test standard to measure turbine oil's oxidative characteristics and varnish/sludging tendencies.
3. Turbine Oil Condition Monitoring
    - (a) RPVOT may have limited value in a condition monitoring program due to the lack of correlation to turbine oil varnishing performance.
    - (b) Acid number is unable to detect subtle changes in oil chemistry reducing its value in a condition monitoring program.
    - (c) FTIR is a useful tool in monitoring changes in turbine oil chemistry.
    - (d) A more thorough understanding of the antioxidant characteristics of the fluid may be accomplished by using techniques such as the LSV.
    - (e) An important element of a condition monitoring program is measuring the varnish potential of the turbine oil.

Acknowledgments

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References

[1] Sasaki, A. et al. "Investigation of Oil Contamination by Colorimetric Analysis," *STLE/ASM Tribology Conference*, San Francisco, June 2001.

[2] Livingstone, G. J. and Thompson, B. T., "New Varnish Test Improves Predictive Program," *Practicing Oil Analysis Magazine*, July 2005.

[3] Hashimoto, K., "Turbine Oils," *Tribologist*, Issue 39, No. 10, 1994, pp. 857–863.

[4] Migdal, C., "The Mechanism of Antioxidant Action in Lubricants" *Proceedings of the 4th Annual Fuels & Lubes Asia Conference*, Singapore, Jan. 1998.

[5] 2001 International Union of Pure and Applied Chemistry, IUPAC Compendium of Chemical Terminology, http://www.iupac.org/goldbook/O04286.pdf

[6] Scott, G., *Atmospheric Oxidation and Antioxidants*, Elsevier Publishing Company, Amsterdam, 1965.

[7] Irvine, D. J., "Performance Advantages of Turbine Oils Formulated with Group II and Group III Basestocks," *Turbine Lubrication for the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM International, West Conshohocken, PA, 2001.

[8] Wooton, D., "Trending Additive Depletion," *Proceedings for Lubrication Excellence 2003*, Houston, TX.

[9] Yano, A., Watanabe, S., and Miyazaki, Y., "Study on Sludge Formation During the Oxidation Process of Turbine Oils," *STLE Tribol. Trans.*, vol. 47, 2004, pp. 111–122.

[10] ASTM, Standard D 2272, "Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel," *Annual Book of ASTM Standards*, Vol. 5(1), ASTM International, West Conshohocken, PA, 2002.

[11] "Lubricating Oil Recommendations for Gas Turbines with Bearing Ambients Above 500°F (260°C)," GEK 32568F, Revised February 2002, GE Power Systems.

[12] Sasaki, A. and Uchiyama, S., "Production of Free Radicals and Oil Auto-Oxidation Due to Spark Discharges of Static Electricity," *Proceedings for NFPA International Exposition for Power Transmission and Technical Conference*, April 2000.

[13] March, J., "The Aldol Condensation," *Advanced Organic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1985.

[14] Okazaki, M. "Advantages of Steam Turbine Oils Formulated with Group II Base Stocks," *Proceedings for Lubrication Excellence* 2003, Houston, TX.

[15] Livingstone, G. and Thompson, B. "The Lowdown on the Sticky Subject of Lubricant Varnish," *Combined Cycle Journal*, 3Quarter, 2005.

[16] "Lube Oil Varnishing" Technical Information Letter *1528-3*, GE Energy Services Technology, Customer Technology Services, Nov. 18, 2005.

[17] "Gas Turbine Lube Oil Contamination Problems," TTI no. *05-010*, Thomassen Technical Info Engineering and Product Support, July 14, 2005.

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Studies of the Oxidation Dynamics of Turbine Oils—Initial Data from a New Form of the Rotating Pressure Vessel Oxidation Test

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ABSTRACT: The importance of oxidation-resistant turbine oils in the various applications in which turbines are used is difficult to understate. Turbines in themselves are very costly energy-converting mechanisms which, among many other applications, provide much of the electricity for the power grids of modern society. Most critical to these turbines are the lubricants that are essential to their operation in long, dependable service. Equally critical, then, are the tests that determine the acceptability of these turbine oils and the understanding of the oxidation mechanisms that cause these oils to form deposits and otherwise lose their ability to properly lubricate the turbine. This paper is a first report on a new dry-bath approach to not only determine antioxidation characteristics of turbine oils in the well-known Rotating Pressure Vessel Oxidation Test (RPVOT) but to enable the direct study and modification of the oxidation process as it occurs. The instrument not only eliminates the hot oil-bath associated with the RPVOT but also allows the test fluid to be available for direct monitoring of temperature, chemical content, and the effects of injecting reactants. In the process of gathering the preliminary information for this paper, it was found that significant exotherms may develop in the turbine oil at a critical stage of oxidation response. These exotherms can vary in duration and temperature rise depending on the nature of the antioxidant system and other properties of the formulated turbine oil. Moreover, the fact that these exotherms seem to mark a certain level of the oxidation process, brings the opportunity to more thoroughly investigate and understand oxidation processes as well as the chemistries of other lubricants.

KEYWORDS: turbine lubricant, turbine oil, oxidation, Rotating Pressure Vessel Oxidation Test (RPVOT), Rotating Bomb Oxidation Test (RBOT), quantum oxidation test, dry-bath oxidation test, dry-bath RPVOT, ASTM D 2272

Introduction and Background

Dependence of Society on the Power Turbine

Societies of many countries of the world today are highly dependent on generally available electric power grids produced by various forms and sizes of turbine engines. This form of energy conversion is also the major form of aircraft propulsion and, additionally, is often used in powering ships and railroad engines.

Turbine engines have become so dependable and common that, as a whole, the societies they serve are unaware of how fundamentally dependent such societies are on the service and durability of these sources of power. It is only when some failure or accident occurs involving these power sources and their work output that society regains consciousness of its own vulnerability. Often, the society becomes highly disturbed by this sudden recognition of its degree of its dependence and the potential consequences of its loss of such an important mainstay of social structure and civilized life.

Growth of such dependence has rapidly accelerated over the past half century. This growth in a power-hungry civilization has been assisted by major engineering design improvements in the metallurgy and the manufacturing methods of turbine components and broadened use and refinement of this form of power.

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Dependence of the Power Turbine on Its Lubricant

Undergirding both the turbine and its service to society has been the development of the lubricants upon which the turbine must completely depend. Just as the turbine engine is indispensable to civilization, its lubricant is indispensable to the turbine engine.

The Turbine Engine Lubricant and Its Properties

As turbine engines have improved in efficiency, dependability, and range of applications, a considerable part of that development has been coupled with improvement in the base stocks and additives used in formulating the oils that enable and extend the turbine engine's power-producing function. In many ways, the co-relationship between the turbine engine and its lubricant is basic and very demanding. Essentially, it is lubrication at its simplest and yet most profound required level of dependability.

Desired Properties of the Lubricant—The two major and indispensable properties of the turbine lubricant are:

1. Provision of sufficient viscosity for hydrodynamic lubrication and hydraulic service, and
2. Resistance to oxidation with its accompanying burden of varnish and deposit formation as well as oxidation's concomitant effects on altering other properties of the lubricant.

In addition, vulnerability to foam and air entrainment, or both, is a serious concern accompanying the formulation of the turbine lubricant. Foam and air entrainment can drastically reduce the ability of the lubricant's ability to form as well as maintain hydrodynamic lubrication and, additionally, apply sufficient hydraulic pressure when required. Thus, a third desirable property of a turbine lubricant is the ability to:

3. Reduce or eliminate foaming tendencies and air entrainment.

Viscosity—Viscosity is a physical property that can be readily selected by the formulator of the lubricant from a range of base oils and synthetic oils available. The viscosity of the lubricant is best measured by simulation of the conditions of turbine operation using a high shear rate viscometer at the operating temperatures encountered.

Oxidation—Oxidation resistance of the lubricant is a chemical function of the effectiveness of the additive employed to counteract the various paths of oxidizing decomposition of a turbine lubricant exposed to air and perhaps water at sufficiently high temperatures and any catalyzing effect of the metals present in the turbine.

Foam—Foam, on the other hand, is a somewhat poorly understood physical response to agitation of the turbine lubricant in the presence of air. The molecular composition of the lubricant in conjunction with some additives or organic contaminants may predispose the lubricant to forming foam, particularly when pressure on the circulating lubricant is suddenly reduced. In addition, foaming tendency can be affected by the changes that can occur in viscosity and composition as an indirect result of lubricant oxidation.

To control foam, it is highly desirable to have a particular form of additive present that, because of its limited solubility in the turbine oil, encourages rupture of the foam cell membrane to cause rapid foam collapse or to indirectly block entrained air from developing into foam-forming voids.

Lubricant Formulation and Operating Volume—As a consequence of the evident need for continuous, acceptable service for long periods of time, turbine lubricants should be formulated with careful choices of base stocks and additives, particularly considering the three desired properties previously discussed. Moreover, to extend the lifetime of their acceptable service, the relatively limited areas in a given turbine engine requiring lubrication are served by considerable volumes of these carefully formulated lubricants.

Appraising Life Expectancy and In-service Conditions of Turbine Lubricants—A continuing challenge in the formulation and application of turbine lubricants has been to appropriately define their functionality for service life and rate of depreciation without the need to periodically run very expensive, long full-scale tests. Accompanying the need for prior-service lubricant screening tests is the related need for determining the in-service remaining life of a turbine lubricant. Both of these needs have led to several bench tests for

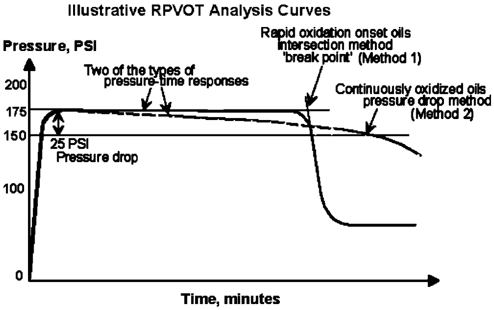

FIG. 1—*Illustrative plots of RPVOT analyses showing two types of oxidation curves and methods of interpreting the oxidation.*

appraising initial and in-service condition of turbine lubricants. Fortunately, the properties of viscosity, and foam formation can be (and have been) relatively simply reduced to bench tests. However, testing the oxidation resistance of turbine lubricants has been considerably more challenging.

One of the most widely used tests is the Rotating Pressure Vessel Oxidation Test (RPVOT) formerly known as the Rotating Bomb Oxidation Test (RBOT), ASTM Method D 2272 originally developed by Von Fuchs et al. [1,2].

The Rotating Pressure Vessel Oxidation Test (RPVOT) Laboratory Test

Test Method

For many years the Rotating Pressure Vessel Oxidation Test (RPVOT) has been applied to the need to appraise the oxidation resistance of new turbine lubricants as well as to measure their rate of depreciation in oxidation resistance while in use.

In essence, this test measures the length of time in minutes that the turbine or other lubricant can withstand the attack of pure pressurized oxygen gas at a relatively high temperature of 150°C while in contact with a coil of copper wire ostensibly serving as a catalyst. Correlation of relatively brief test time in ASTM D 2272 to the actual extended service time in the turbine engine has been established.

More specifically, the RPVOT exposes 50 g of the test lubricant and 5 mL of distilled water to an operating pressure of approximately 1240 kPa (180 psi) of pure oxygen gas in a sealed steel container in the presence of a 55.6 g coil of 99.9 % pure copper wire serving as a catalyst. Internal pressure of the steel vessel is continuously recorded. The special form of glass beaker (into which the lubricant, copper coil, and five mL of water are placed) is rotated at 100 r/min until the oxidation resistance of the lubricant reaches its so-called “break point” or reduced by 175 kPa (25.4 psi) at which time the bench test is ended.

During some period of test time (which may extend to several thousand minutes), the oxidation resistance of the test oil is affected by the oxygen. That is, the lubricant chemically reacts with the oxygen to bind the gas molecules into both organic and inorganic oxidation products. In this process some or much of the free oxygen gas responsible for maintaining pressure in the steel vessel is progressively chemically incorporated in these oxidation products. Consequently, the oxygen pressure is reduced and, if the rate of oxidation of the lubricant for some lubricants is rapid, the pressure may rapidly plunge to a fraction of its former value.

Both slow and rapid oxidation response of lubricants are shown in the simulated sketch of Fig. 1. The criterion of lubricant failure is the time in minutes required to reach either the so-called “break point” or to reach the 175 kPa pressure drop specified in ASTM D 2272. Some lubricants may, in replicate tests, show both forms of failure. In some cases, the failure time may be considerably different.

RPVOT Test Equipment Utilizing Oil Baths

Until recently, all RPVOT tests have been conducted using a technique of immersing the steel pressure vessel containing the prepared and loaded sample beaker into bath oil heated to an average temperature of

150 °C to obtain the operating temperature of the required for the test. Some of these baths are capable of operating with four pressurized steel vessels simultaneously and may contain more than 75 L (20 gallons) of bath oil.

Under the test protocol, the necessary rotation of the steel pressure vessels at 100 r/min often is done by driving the rotating mechanism through the floor of the bath as shown in ASTM D 2272. Unfortunately, this approach is accompanied by problems of seal leakage and subsequently difficult cleanup and repair.

Moreover, these oils baths are normally kept at operating temperature continuously because of the length of time required to reheat the baths to operating temperature. As a consequence, the often expensive bath oil is oxidizing continuously and must be changed at relatively short intervals (unless the bath oil is silicone requiring special operator exposure control). In addition, the odor problem of oxidizing oil baths usually require these to be kept in hoods making bath oil change more difficult when the oxidized oil becomes too thick for effective circulation of heat and temperature control.

Four RPVOT tests are often started at the same time in some of these larger oil baths and the pressure vessels removed when their individual break points were obtained. However, new tests cannot be started until all four tests are completed since the addition of a new steel vessel upsets the critical constancy of the bath temperature.

Perhaps the greatest ongoing problem with any hot oil-bath dependent equipment is in the more or less frequent handling of the steel vessels and supporting equipment into and out of the hot bath oil and the attendant safety precautions.

These considerations of the limitations of present equipment led the authors and their associates to develop a new, nonliquid bath approach to the RPVOT method and this development is the subject of this paper.

A New “Dry-Bath” Approach to the RPVOT Protocol

Basic Considerations

The limitations of oil bath heating the RPVOT pressure chamber led to the concept of an electrically heated, dry-bath, fixed pressure chamber with magnetic drive of the test sample beaker. This approach permitted other simplifications and advantages which became apparent during development:

1. The stainless steel pressure chamber could be stationary and permanently connected to a source of high pressure oxygen as well as another permanent connection for venting the used gases of oxidation.
2. Instead of rotating the whole pressure vessel, only the sample beaker could be rotated at the appropriate speed with use of a magnetic cup.
3. The instrument could be operated outside of a hood although the reaction gases would have to be released into a hood or other intake.
4. The instrument would be most productive in the laboratory when made as single units having a small footprint. This would permit use of one or several units at a time since single units could be relatively quickly returned to analysis of another sample if desired.
5. The stationary pressure chamber and rotating sample beaker would make it readily possible to directly measure the test oil temperature as well as to sample fluid for other analyses by use of a high pressure sampling port.
6. Clean up of the apparatus after test would be reduced to the sample beaker, magnetic cup, and pressure chamber side wall and bottom.

Transition of the Concept into the Dry-Bath Instrument

As with almost all major changes in instrument design, the rendering of the concept into a practical instrument required considerable time. Recognizing its importance as a basic test method, attention was focused on the RPVOT protocol early in the developmental stage. Early prototype units of the dry-bath instrument—trade named the Quantum—were very helpful in teaching appropriate ways of handling the heating of the pressure chamber and control of heat radiation.

Similarly, use of a magnetic drive from the bottom of the pressure chamber led to several techniques

FIG. 2—*Bench top, dry-bath RPVOT and lid cover.*

for close-coupling the drive magnet and the driven magnet as well as effectively reducing the friction of the rotating cup within the pressure chamber with both the walls and bottom of the chamber. Forcing outside air flow through the interior of the cabinet through vents after test completion was found desirable for quick analytical turnaround.

One of the earlier designs of the electrically heated, dry-bath Quantum instrument is shown in Fig. 2.

Careful consideration was given to the pressures developed in the pressure chamber. Consequently, the pressure chamber was made of stainless steel with relatively thick walls. Other metals such as aluminum were avoided because of their vulnerability to distortion under heat and their response to the highly reactive oxidation conditions within the pressure chamber.

The stainless steel access lid to the high pressure chamber was designed to be easily closed and opened while retaining a complete pressure seal when closed. For this purpose, a specially designed O-ring sealing approach simplified the pressure-resistant closure and, as shown, requires only three finger-tightened nuts threaded onto three bolts protruding through the circular flange of the pressure chamber to completely seal the chamber for operation.

Above the pressure chamber lid are two valves for admitting high pressure oxygen (left) and releasing pressure (right). Below the lid are two electronically programmable control meters—temperature measurement, control, and recording on the left and pressure measurement and recording on the right. On the vertical panel are the main, heat and cup rotation switches accompanied by a warning light indicating when pressure chamber temperatures are low enough to avoid hot water spattering when the lid is removed.

The rear panel of the cabinet has connections for oxygen and vented gas as well as connections for data recording by either strip chart or computer program. Shown to the right of the dry-bath instrument in Fig. 2, is the insulated Teflon cover cap for the pressure chamber lid which is used during test to control heat loss and protect the operator from the hot flange and lid surfaces.

Although, as noted, a strip chart or other recorder can be attached to the dry-bath instrument, it is advantageous to use a special computer program placed on an accompanying laptop computer to track pressure and temperature data which can then be readily converted into spreadsheet programs for further analysis and reporting of the collected data, if desired. The combination of computer and program is capable of recording data from four instruments simultaneously.

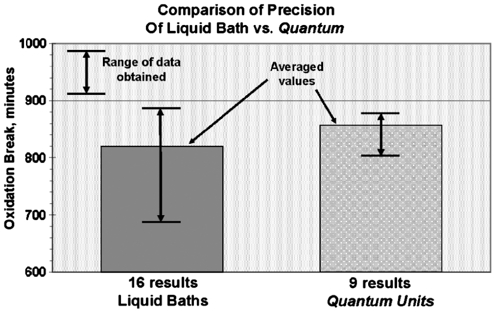

FIG. 3—*Comparative values and precision of oil- and dry-bath heating in the RPVOT protocol.*

Preliminary Experimental Results

Initial Repeatability Studies

Among the first questions of importance when developing a new instrumental approach to a long-standing method are the dual questions of agreement with the older technique and the precision of the newer technique.

For this study, test oil which had previously been used for comparative results in several laboratories was made available through the courtesy of Joseph Franklin, Chairman of the ASTM RPVOT Task Group of Committee D02, Subcommittee 9. Results are shown in Fig. 3.

For this study, data from two earliest prototype dry-bath instruments were used. The multiple runs on these two prototype instruments, as shown in Fig. 3, were obtained by interchange of operators.

In comparison, the oil-bath instrument data in Fig. 3 were obtained by combined multiple data on several instruments in different laboratories manned by different operators. While the comparison shown somewhat favors the dry-bath instrument, the data are not generated in exactly the same way. Thus, the contrast in precision shown in Fig. 3 is between the summed repeatability-reproducibility of the oil-bath data and the semi-reproducibility in the dry-bath units.

However, from the viewpoint of the first question regarding agreement and precision of older liquid-bath and the new dry-bath instruments, the data shown in Fig. 3 gave the following pertinent information:

1. Oil-bath and dry-bath modes of obtaining RPVOT values gave reasonably similar results (the band of values for the dry-bath units fell within the band of data obtained on the oil-bath units.
2. Precision of the prototype dry-bath instruments may be better.

Moreover, as anticipated in the conceptualization of the dry-bath instrument, it was found that return of the instrument to subsequent analyses was relatively rapid, particularly with use of more than one rotating cup.

Observation of Oxidation Exotherms

Unexpected information came to light during early investigations with the dry-bath instrument. Easy access to the rotating sample beaker permitted direct measurement of the sample temperature during a dry-bath RPVOT analysis. In the first experiment conducted using this technique, it was found that the oxidation process produced an evident exotherm of several degrees Celsius during the rapid oxidation step shown in Fig. 1. Moreover, as would be predicted, since the exotherm is a measure of the rate of energy released to the test fluid with oxidation of the fluid ($\Delta H/\Delta t$), the maximum in the exotherm occurs at the maximum of the rate of decreasing pressure change ($-\Delta P/\Delta t$). To assist in visualizing this phenomenon, an idealized re-sketch of the curve of rapid oxidation in Fig. 1 is shown with an accompanying temperature exotherm in Fig. 4.

These exotherms varied in height and breadth depending on the oils analyzed and were repeatable on reanalysis of the same test oil. It is thus evident that these exotherms may have value in identifying and understanding the relationship of type, amount, and effectiveness of oxidation inhibitors in relation to the process of oxidation. The more rapidly the oil oxidizes the more pronounced the exotherms.

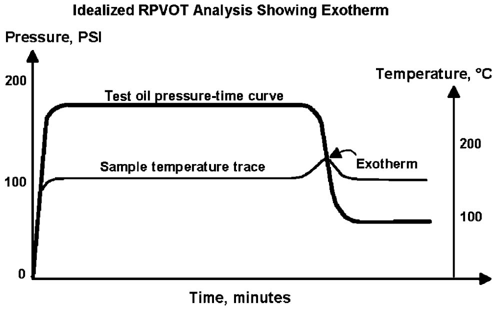

FIG. 4—*Schematic example of appearence of exotherm during analysis of sharply oxidizing oil.*

Analysis of the Process of Oxidation by Sampling During Test

The technique of measuring the sample temperature during RPVOT analysis in the dry-bath instrument led to the further technique of removing small samples of the fluid under test while the analysis was in progress. The authors consider this an important use of the dry-bath technique since the chemistry of oxidation with use of different oxidation inhibitors can be followed closely.

Only a fraction of a milliliter needs to be taken for such information given the sensitivity of today's analytical instruments, such as inductively coupled plasma (ICP) spectrometers, nuclear magnetic resonance (NMR), and Fourier Transform InfraRed (FTIR).

Technique for Sampling Sample During Test—The sampling technique is simple. A long, thin metal hypodermic needle is threaded through the graphite ferrule of a high pressure fitting and a three-way valve connected to the syringe end of the needle. The oxidation test can be performed and very small samples taken periodically and conveniently using this technique.

Figure 5 is a cut-away side view sketch of the pressure chamber of the dry-bath instrument showing this setup for sampling.

Trial Application of Sampling Technique—Fortunately, an opportunity developed to explore this sampling technique concept. During a meeting of the ASTM Committee D02 in June of 2006, a need was expressed during the Subcommittee 9, Section C, to determine whether and to what extent the copper catalyst coil was attacked in the process of catalyzing oxidation by the test oil—particularly when rapid oxidation of the sample was occurring.

This seemed to be an ideal use of the dry-bath instrument. A turbine oil provided for this test was exposed to the RPVOT oxidation conditions in the dry-bath instrument and periodic 0.1 mL samples were

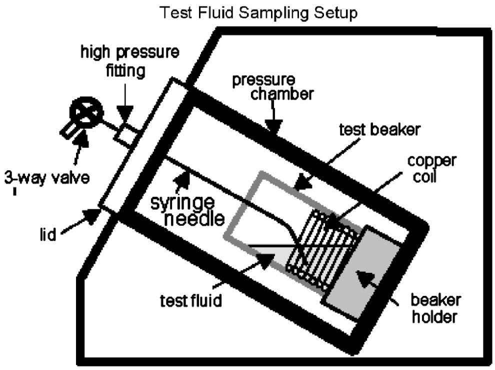

FIG. 5—*Schematic of sampling technique.*

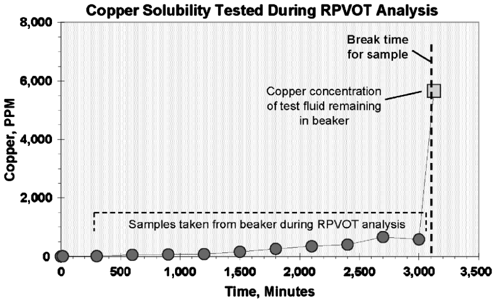

FIG. 6—*Copper dissolution in and RPVOT test protocol on a turbine oil analyzed in the dry-bath instrument.*

taken during the course of the test. These first results in a prototype instrument are shown in Fig. 6.

During the initial portion of the test, copper gradually increased from 6 ppm at 15 min to about 600 ppm in samples taken at 2700 and 3000 min. However, when the turbine oil oxidation break point occurred at just over 3100 min, the copper concentration in the residual fluid in the test beaker was found to be over 5500 ppm—almost ten times the prior sample.

Obviously, rapid attack of the copper catalyst coil occurs when the oxygen is rapidly assimilated into the test oil sample. What progression might occur under the slower oxidation process illustrated in Fig. 1, has not yet been examined but should be interesting.

Discussion

The long standing problems of RPVOT determinations in oil-bath equipment such as bath oxidation, odor, leakage, replacement of oil, and the difficulties of working with hot oil led to the development of a dry-bath instrument. In essentially all respects, the dry-bath instrument protocol was designed to be similar to the oil-bath apparatus regarding exposure of the test sample to the copper-catalyzed oxidation conditions as indicated in the table of Appendix I. However, it was very dissimilar in not having the attendant liquid bath problems previously mentioned, but more so in making simple access to the test fluid possible.

In preliminary studies using a reference oil on which considerable RPVOT data had been collected in liquid baths, two prototype dry-bath instruments have shown reasonable agreement with, and apparently better precision than, data collected on the same fluid in the oil-bath RPVOT equipment of several laboratories. Further work with more modern turbine lubricants is about to begin with production Quantum™ instruments.

It has also been found easier and faster to prepare and load samples in the dry-bath instrument and the elimination of the odiferous bath oil permits hood-free use of the instruments. Venting of the test gas to a hood through plastic tubing or use of a vacuum "snorkel" is a simple approach to the odor of this gas.

The technique of turning the test fluid beaker without turning the pressure chamber has made it possible to use the dry-bath instrument to produce information that, for all practical purposes, cannot be obtained from present oil-bath RPVOT equipment even with tedious and repetitive multiple analyses of a given oil. For example, it has been shown in this paper that by applying the dry-bath instrument, it is possible to follow the process of oxidation by thermal sensors in the fluid being tested or, if desired to sample the fluid for further information of interest.

Conclusions

Preliminary studies with the dry-bath instrument have shown that this approach can produce data that are similar to oil-bath equipment but early data indicate that it may be somewhat more precise.

Of considerable importance, moreover, is the ability to apply the instrument to the observation of the oxidation process through either or both temperature sensors in the test fluid and sampling of the test fluid by direct removal of small samples or conceivably by infrared using glass fiber optical waveguides.

Perhaps equally, or more importantly, is the ability to inject reactants into the test fluid and to observe the consequences.

Essentially, this approach has made the dry-bath instrument a more universal tool for the study of oxidation, nitration, chemical and physical reaction dynamics, and other associated uses in which it is desirable to monitor, alter, and sample, or a combination thereof, the material(s) being investigated.

It is anticipated that the dry-bath technology will produce new understanding of the oxidation processes occurring in the various oleaginous fluids used in lubrication and hydraulics. Moreover, this constant-temperature oxidation technique may have much broader applications in the study of other reactions of interest and importance.

Acknowledgments

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Appendix I

Comparison of Operational Parameters

Operational Parameter	Oil Bath	Dry Bath
Bath Temperature	150 ± 0.5°C	150 ± 0.5°C
Sample Size	50 ± 0.1 g	50 ± 0.1 g
Copper Coil	55.6 ± 0.3 g	55.6 ± 0.3 g
Water in Sample	5 g	5 g
Initial Oxygen Pressure	620 ± 5 kPa (90 ± 1 psi)	620 ± 5 kPa (90 ± 1 psi)
Pressure Recording	Round or Strip Chart Electronic Transmission	Strip Chart or Computer Interfaceand Program
Temperature Recording	Strip Chart or Electronic Transmission	Strip Chart or Computer Interface and Program
End of Test Signal	175 kPa (25 psi) pressure drop or "break point"	175 kPa (25 psi) pressure drop or "break point"

References

[1] Von Fuchs, G. H., Claridge, E. L., and Zuidema, H. H., "The Rotary Bomb Oxidation Test for Inhibited Turbine Oils," *Phys. Rev.*, No. 186, 1952, pp. 43–46.

[2] Von Fuchs, G. H., "Rotary Bomb Oxidation Test," *Lubr. Eng.*, Vol. 16, No. 1, 1960, pp. 22–31.

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Review of Degradation Mechanisms Leading to Sludge and Varnish in Modern Turbine Oil Formulations

ABSTRACT: In recent years, there has been an unusually large number of reported cases associated with varnish and sludge formation in turbine-generator and compressor applications using Group II turbine oil formulations. Explanations for these problems have varied but typically include Group I/Group II incompatibility, additive instability, bulk oil oxidation, adiabatic compressive heating, electrostatic discharge, among others. This paper reviews these failure pathways and discusses actual case history including root cause analysis. Analytical methods for the sludge/varnish and the degraded oil are also reviewed.

Introduction

A wide range of fluid degradation and contamination-related issues can affect turbine lube oil systems. One serious and growing concern is the presence of sludge and varnish. This condition can occur in even the most well-maintained machines. Surprisingly, it can also happen when oils are not particularly old or contaminated. And it can occur with even the most thermally robust synthetic lubricants and hydraulic fluids.

In turbine systems, there are few failure conditions that can disrupt operation as quickly and completely as a varnished and seized-up control valve operation. This can be the cause of a tripped turbine forced outage or other production losses. So too, sludge in many circulating lube oil systems can gum up flow controls, strainers, and critical oil ways. In recent years, there has been a large number of reported cases associated with varnish and sludge formation in turbine-generator applications. Explanations for these problems have varied but typically include Group II mineral oil solubility issues, additive instability, bulk oil oxidation, adiabatic compressive heating, and electrostatic discharge, among others. This paper will review precursor conditions that lead to sludge formation, some of the common lubricant degradation methods, and the role of oil analysis in recognizing the potential risk well ahead of failure.

Brief History

Since the mid-1990s, turbine systems have been increasingly experiencing electro-hydraulic valve stiction: Sticking or erratic action of hydraulic valve components due to the combination of reduced spool clearances and increased friction caused by varnish. This condition can produce a unit trip, leading to an unscheduled shutdown. Stiction of inlet guide vane (IGV) valve positioners is a common cause of unit trips. An example of varnish on an IGV valve positioner from a large-frame turbine is shown in Fig. 1 [1].

Why are varnish problems more commonly occurring today? Around 1990, oil suppliers started switching to more highly refined API Group II mineral oils in the turbine oil formulations. Some of the advantages of Group II oils include superior oxidation stability and viscosity/temperature properties compared to Group I mineral oils. These enhanced performance properties were attractive in meeting the higher temperature requirements of today's advanced technology turbines.

When impurities form in the oil, regardless of the root cause, the ability of the base oil to keep these compounds in soluble suspension will directly affect the likelihood and rate of varnish formation. Because of the highly pure nature of the Group II base oils, they present greater risk of varnish formation once

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FIG. 1—*Varnish formation on inlet guide vane (IGV) valve from a gas turbine.*

degradation has occurred because they have a more limited ability to solubilize polar impurities such as water, oxides, carbon resins, dirt, and similar contaminants.

Additionally, the release of oxide and organic insolubles to machine surfaces forming varnish is more pronounced when the oil is cooled or the oil moves over cool surfaces in contact with the environment. This accelerates the rate of condensation. Such conditions may exist in turbines exposed to peaking and cycling conditions where the oil temperature fluctuates considerably over time.

Sludge and Varnish Defined

Sludge and varnish are insoluble materials typically formed as a result of either deterioration reactions in oil or contamination of oil, or both. Varnish is typically distinguished as a thin, insoluble, nonwipeable film deposit, whereas sludge is soft and tacky and can move about the system. A simplistic illustration of varnish formation is shown in Fig. 2.

Sludge and varnish formation can originate by a number of mechanisms such as oxidation, chemical contamination (cross-contamination), or localized thermal failure (such as microdieseling). The chemical reaction by-products of these failure mechanisms are typically submicron and initially remain soluble at normal operating temperatures. Because they are polar in nature, they begin to coalesce as their concentration builds and the varnish saturation point of the oil is exceeded and eventually become insoluble in the oil. The transition to the insoluble state can be escalated by a cooling of the oil. These polar insoluble and unstable suspensions migrate from the oil to polar machine surfaces, particularly in cool spots in the system or in tight working clearance zones. Over time, these insolubles continue to layer and harden.

Sludge and varnish products are generally unstable in the oil and, as such, are looking for a place to deposit or simply separate from the bulk oil. In certain instances, deposits form on machine surfaces at the exact location where the oil has degraded, for example, thermal degradation known as hot surface cooking. In other cases, the oil degrades in one location, but the insoluble degradation products are carried elsewhere by the moving fluid, forming deposits on surfaces. Over time, some deposits can thermally cure to a tough enamel-like coating. Other types of deposits, generally in cooler zones, remain soft or gummy. Sludge is not always black or even dark. It may appear clear and grease-like, similar to petroleum jelly. The following are examples of where sludge and varnish might occur in turbine lube oil and hydraulic control systems [2]:

- Black crusty deposits on mechanical seals
- Gold adherent films on spool valves in EHC hydraulic systems

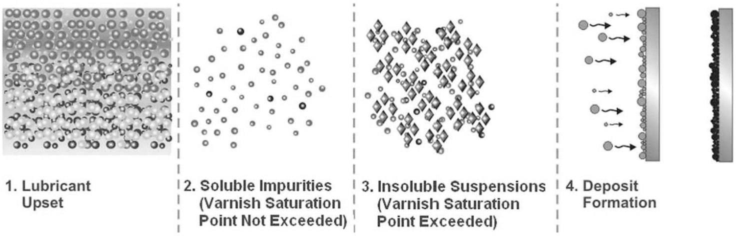

FIG. 2—*Varnish formation stages.*

- Charcoal-like deposits on babbitt sleeve bearings
- Gooey-brown mayonnaise on oil filters
- Black scabby deposits on thrust-bearing pads (Fig. 3)
- Carbonaceous residue of servo strainers

The deposits that form on sensitive machine surfaces interfere with the reliable flow of the fluid and the machine's mechanical movements. They can also contribute to wear and corrosion or simply just cling to surfaces. For example, deposits on the spool and bore of a servo control valve can tighten the interference fit. Compounding this are the adherence properties of varnish, which can attract and stick particles from the oil to silt lands, leading to common silt-lock valve failure. Silt lock refers to particle-induced mechanical jamming of axial spool movement in directional control valves [3].

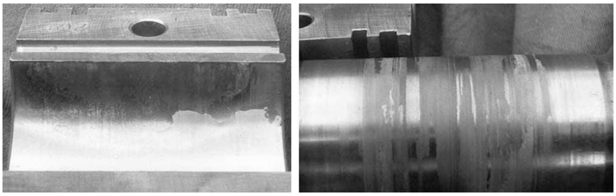

FIG. 3—*Varnish formation on plain bearing and shaft. (Courtesy of Cerestar Deutschland).*

Other types of sludge and varnish-induced failures include plugged orifices, damaged mechanical seals, plugged discharged ports, journal-bearing wear (disrupted hydrodynamic film production), and premature plugging of oil filters and impaired oil cooler performance [2]. Factors that compound the risk of valve stiction in hydraulic systems include the following [4]:

The Presence of Varnish on Valve Spools and Bores

This tightens the interference fit (annular clearance), reducing the particle size and affecting contaminant lock. The varnish also has adherent properties that stick the particles to the silt lands, referred to by one author as the fly-paper effect.

High-Pressure Differential

Zones of high-pressure differential in a valve encourage fluid movement. High-pressure fluids will work through some of the tightest clearances to get to low pressure, carrying particles and sludge en route. These contaminants can pack the clearance, obliterate oil ways, and restrict spool actuation.

Long Dwell Time

The longer a valve holds pressure without actuation, the longer the available time for the valve to silt up (and sludge up), usually nucleated by a single clearance-sized seed particle. Most stiction-related valve failures occur immediately after a long dwell time.

High Population of Silt-Sized Particles

Particles in the two to 6-μm range have a tendency to grow dramatically in population as oils age. These clearance-sized particles increase the propensity of contaminant lock. Slight amounts of moisture in oil can preferentially coat these particles causing them to more readily cling (cake). This phenomenon is associated with hydrogen bonding.

Degradation Methods and Analysis

Before discussing the methods for analyzing sludge and varnish in turbine systems, it is helpful to understand the lubricant degradation methods in turbine lube oil and hydraulic systems.

Bulk Oil Oxidation

Oxidation causes degradation of the bulk oil over time. Under mild machine operating conditions and clean environment, oxidation will occur gradually. However, elevated temperature plays a significant role in accelerating the oxidation process—the general rule of thumb is that for every 10 °C (18 °F) increase in operating temperature, the rate of oxidation doubles (Arrhenius Rate Rule). Water, metals such as iron or copper particles and aeration also act as catalysts to speed up this process. As the rate of oxidation increases, oxidation by-products develop and coalesce into insolubles in the oil (as previously discussed), resulting in sludge and varnish in the system. Oil that degrades through oxidative pathways typically produces metal carboxylates, carboxylic acids,f and similar oxide transformation products. Depending on the nature of the oxidation process and the formulation of the oil, the tendency and severity of sludge production can vary. In fact, studies have shown that some turbine oils will produce sludge long before the onset of base oil oxidation (e.g., during the induction period) [5]. The base oil type and the refining process influence this as well. For instance, naphthenic base oils, normally high in aromatic compounds, tend to more quickly form hydroperoxides, which are sludge precursors.

Thermal and Compressive Base Oil Degradation

Thermal degradation occurs when the oil comes in contact with a hot surface or due to adiabatic compression from entrained bubbles. When the oil comes in contact with machine surfaces greater than 200 °C (400 °F), depending on oil type, thermal degradation can initiate. Such heat can come from gas combustion, steam, and highly loaded frictional surfaces. Often the aeration occurs due to tank agitation, plunging oil returns, or surface lapping. Suction line leaks and venturi zones (vena contracta regions) can introduce air into circulating fluids as well. These conditions can both introduce air into the oil and inhibit efficient detrainment of the air (degassing).

Regardless of the means of entrainment, the forcing function that leads to sludge and varnish is in place. From here, the failure can proceed along one of two pathways. Both involve adiabatic compression in either the load zone of a lubrication system or the pressured zone of a hydraulic control system. Adiabatic compression is what occurs when air bubbles travel from low pressure to high pressure. The air bubble compresses rapidly (implosion), resulting in intense entrapment of the heat and extreme rise in temperature locally in the oil. The temperatures reached (typically greater than 1000 °F) are often more than sufficient to thermally degrade the oil.

A special, though serious situation occurs when fluids are aerated and high compression pressures are experienced. The condition is referred to as pressure-induced dieseling (PID), or microdieseling, and can occur in both hydraulic systems and lubrication systems. The temperature reached with PID leads to microscopic ignition (called partial combustion) of the oxygen-rich oil vapors. The problem is most acute with low-viscosity oils such as turbine oils. Such fluids have low flash points which contribute to the vaporization of the light oil fractions that mix with the air at the bubble boundaries.

During ignition, the pressure in the area of the micro-explosion may reach five to six times the working pressure. A common consequence of dieseling is carbonization of the oil due to the high temperatures and the residue of incomplete combustion. The carbon insolubles that emerge are the fodder that, over time, condense on surfaces to form sludge and varnish.

Electrostatic Discharge

Studies have been conducted on the effects of static discharge in hydraulic systems since at least the 1970s [6,7]. Static discharge is a form of localized thermal degradation as discussed earlier. Recently, much attention has been directed to the potential role of fluid electrification and static discharge as a prominent contributor to sludge and varnish formation in turbine systems [8–11].

Electrostatic charge generation occurs in fluid systems as a result of internal molecular friction and electric potential between the fluid and machine surfaces (particularly where no boundary films develop, such as the interstices of an oil filter). The magnitude of the static charge within the oil will depend on many factors, however grounding of the machine itself has little impact toward mitigating charge propagation. This is because the oil is nonconductive and effectively self-insulates the charged fluid zones from grounded surfaces. Once these charges build up in the working fluid zones, including reservoirs, the subsequent static discharging, similar to lightning strikes through the fluid, may cause localized thermal-

TABLE 1—*Acid number (AN) for turbine oil exposed to static charges after zero, six, and nine months in storage.*

Number of Spark Discharges	0	500	2,000	3,000
AN just after spark discharges	0.08	0.08	0.08	0.08
AN after 6 months in storage	0.08	0.09	0.36	0.59
AN after 9 months in storage	0.08	n.a.	0.40	0.74

oxidative oil degradation. The most obvious noticeable effect may be an audible noise (clicking sound) as the discharge occurs by spark-arcing internally within the system. Less noticeable effects include migration of the electrical charge downstream (streaming currents) of the filter, causing damage to system components and the filter itself when the charge suddenly dissipates to nearby grounded surfaces.

Interesting studies led by Sasaki have been conducted relating to static discharge. According to his research, spark discharges can reach temperatures as high as 10 000 to 20 000 °C. Additionally, he has found that although the initial process is a localized failure mechanism, the chemical degradation process is autocatalytic. In one study, a turbine oil sample was exposed to spark discharges [9]. Acid number (AN) was measured on the oil samples just after exposure to the spark discharges and after six and nine months of oil storage. Results of that test are shown in Table 1. Acid number was measured immediately after the tests were the same regardless of the number of sparks exposed to the turbine oil, suggesting that oil degradation had not yet started. However, there was a significant change in acid number after being stored indicating that the oil oxidation process was continuing to occur even when stored at room temperature in the dark.

The fluid conditions within some turbines may be ideal for generating static discharge and the formation of polar insolubles which contribute to varnish. These ideal conditions for electrification of the oil include the following [8,9]:

1. Higher Combustion Temperatures—In response to higher gas turbine combustion temperatures, flow rates in the lubrication and control system have increased proportionally. The increased flow translates to higher molecular frictional energy and corresponding electrification of the oil (charge accumulation).
2. Low Oil Conductivity—Turbines oils have exceptionally low polar constituents in their additive system and base oil(s) compared to nearly all other types of lubricants.
3. Low Moisture Levels ($<$100 ppm)—Moisture contamination is polar and conductive. The hot environment of gas turbine lubricants drives off both free and soluble water which keeps the oil's dielectric constant low (higher risk for static discharge).
4. Low Level of Entrained Air—New Group II turbine oils have excellent air release and foam suppression features. Such air handling performance is generally good for quality lubrication, except where static discharge is concerned. In other words, the lower the aeration, the higher the risk.
5. Cleanliness—Turbine oils are increasingly being filtered to achieve higher magnitudes of fluid cleanliness. This purification of the oil is good from the standpoint of wear reduction and fluid health, except where static discharge risks occur. Particle contamination is generally conductive and contributes to the bulk conductivity of the oil (lower risk of static discharge). According to one study, particle contamination equivalent to an ISO 18/15 was sufficient to dissipate static charge buildup in contrast to low contaminant levels of ISO 13/10 or cleaner, which led to strong discharges [11]. Compounding the problem is the fact that fine filtration intensifies the internal molecular friction that generates the static charge within the oil, that is, the finer the filter pore size and the higher the flow density, the more pronounced the problem.
6. Sparking Locations—discharging is more likely to occur in high-pressure differential zones (such as in filter elements) and at sharp edges of pipe submerged in oil in the reservoir.

Analysis Techniques for Monitoring Sludge and Varnish

Analytical techniques for measuring sludge and varnish vary depending on the failure mechanism. These methods fall into three categories, according to the stage of contaminant or degradation product they target. The first stage is a precursor condition. Specifically, it relates to the properties (contaminants) that give an oil a propensity to form oxides and other oil breakdown products. Stage 2 is a transitory stage.

TABLE 2—*Methods for analyzing oxidation-induced sludge and varnish.*

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage) —*Root causes that propel the fluid into the next stage*	Measurable Oxidation Root Causes:	
	1. Particle contamination	1. Various laboratory particle counting methods (optical, pore blockage and microscopic)
	2. Wear debris	2. Elemental analysis, ferrography, ferrous density analysis
	3. Water contamination	3. Various laboratory methods including Karl Fischer and FTIR
	4. Antioxidant additive depletion	4. Methods include FTIR, RPVOT, RULER, and HPDSC
Stage Two (transitory stage)—*The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* oxidation products to form:	
	1. Carboxylic acids, formic acids, etc.	1. FTIR (1730 cm^{-1}), AN
	2. High-density resins, polymers, etc.	2. Coagulated oxide insolubles
	3. Chromophoric compounds (color bodies)	3. Spectrophotometry, patch colorimetry
Stage Three (attack stage)—*More advanced oxidation phase where significant risk of varnish, corrosion and impaired lubrication is present*	The presence of both *soluble* and *insoluble* oxidation products to form:	
	1. Metal carboxylate soaps and sludge	1. Analysis of sludge (bottom sediment, organic filter sediment, etc.) by elemental analysis (D5185), FTIR (1730 cm^{-1}), GC/MS (D2786, etc)
	2. Suspended oxide insolubles	2. Ultracentrifuge, patch test, patch colorimetry
	3. Rising oil viscosity	3. Viscometry (D445)

Typically, it consists of soluble oxides and other dissolved impurities that might later synthesize to form insolubles. The condition that aids the transition from stage two (oxide soluble) to stage three (oxide insoluble) may be cold oil temperature or simply a supersaturated state (a concentration of oxides in excess of the varnish saturation point).

Stage 3 is an attack stage. While conditions in stages 1 and 2 may not impart damage to the machine, stage three contaminants are surface active, potentially causing deposits, corrosion, or mechanical wear. Stages 1 and 2 are more proactive, that is, analytical methods detect aberrant conditions before damage or harm to the machine occurs. Stage 3 is a predictive maintenance stage where an incipient or impending machine failure is already in progress.

Oxidation is a well-known oil degradation mechanism and is relatively simple to monitor with traditional oil analysis methods compared to other failure mechanisms. Thermal degradation, although often less understood, is also familiar and can be analyzed with traditional oil analysis. The effects of static discharge are still relatively new to the oil analysis field. It is more difficult to analyze with traditional oil analysis techniques. The degradation stages and analytical scheme for oxidation, thermal and compressive base oil degradation and static discharge conditions are presented in Tables 2–4. Many of the analytical methods listed in Tables 2–4 correspond to international standards. Some of these standards are included in Table 5.

A number of analytical tests have been identified in Tables 2–4. It is of interest to discuss a couple of these tests and how their results can be used to distinguish the various failure mechanisms.

Fourier Transform Infrared (FTIR) Spectroscopy

As oxidation increases, common reaction by-products are carbon-oxygen double bonds, also called the carbonyl group. Carbonyl peaks on FTIR spectra in the 1740 cm^{-1} region (Fig. 4) [12], easily identifying oxidation. As oxidation increases, the absorbance peaks will also increase in this region. Additionally, phenol inhibitors used as antioxidants in the oil show peaks around 3650 [13,14]. Changes in this peak are also noteworthy.

TABLE 3—*Methods for analyzing thermal degradation-induced sludge and varnish.*

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage)*—Root causes that propel the fluid into the next stage*	Measurable root causes:	
	1. Impaired air-release properties	1. Air release tests
	2. Cross contamination (mixed lubricants)	2. FITR, elemental analysis, etc.
	3. Contamination with polar impurities (dirt, water, oxides, etc.)	3. Various standard lab tests for such impurities
Stage Two (transitory stage)—*The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* thermal degradation products:	
	1. Nitric oxides	1. Thick-cell (500 μm) FTIR for nitration (1639 cm^{-1})
	2. Chromophoric compounds (color bodies)	2. Spectrophotometry, patch colorimetry
	3. Localized thermal failure conditions	3. Pattern testing (combining above tests with RPVOT, AN, viscosity, etc.) to differentiate from bulk oil degradation
Stage Three (attack stage)—*More advanced degradation phase where significant risk of varnish is present*	The presence of both *soluble* and *insoluble* thermal degradation products to form:	
	1. Suspended high molecular-weight nitric oxides and similar resinous insoluble compounds	1. Ultracentrifuge, patch test colorimetry, coagulated insolubles
	2. Sludge and deposits	2. Analysis of sludge (bottom sediment, organic filter sediment, etc.) by elemental analysis, FTIR, GC/MS

Because thermal degradation can occur without significant amounts of oxygen, different degradation by-products are often observed. Thus, the 1740 cm^{-1} peak is less likely to be significant. Instead, the by-products of thermal base oil degradation show up in the 1600 to 1640 cm^{-1} region—also known at the nitration peak due to the nitrogenous by-products [4]. This is more pronounced using a thick cell (500 μm path length) spectrometer.

Acid Number (ASTM D974 or D664)

As the number of acids increase due to the oxidation process, acid number will increase accordingly. In large turbine systems, an acid number change as low as 0.3 to 0.4 above the new oil baseline is often sufficient to condemn an oil [15].

Rotating Pressure Vessel Oxidation Test (RPVOT) (ASTM D2272)

RPVOT measures an oil's resistance to oxidation. This information indicates the oil's remaining oxidative useful life (RUL) and is calculated by dividing the in-service sample result by the new oil result. RPVOT values are highly influenced by the type and quantity of antioxidants present in the oil and the oxidative robustness of the base oil. Cautionary and critical limits for turbines are usually at 60 % and 40 % RUL, respectively.

Viscosity (ASTM D445)

During oxidation, cleaved oil molecules combine to form higher molecular weight species. An increase in absolute viscosity can indicate when oxidation becomes advanced. In some cases, oil can be thermally cracked during degradation, where the oil molecules are severed into smaller molecules. As a result, a decrease in viscosity can be detected.

TABLE 4—*Methods for analyzing static discharge-induced sludge and varnish.*

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage)—*Root causes that propel the fluid into the next stage*	Root causes:	
	1. Exceedingly dry oil	1. Karl Fischer, dew point meters
	2. Exceedingly clean oil	2. Particle counters (various), total insolubles
	3. Unoxidized oil	3. AN, RPVOT, FTIR (1730 cm^{-1})
	4. Drop in oil conductivity	4. Conductivity meters, dielectric breakdown testers, dielectric constant meters, etc.
Stage Two (transitory stage)—*The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* thermal degradation products:	
	1. Chromophoric compounds (color bodies)	1. Spectrophotometry, patch colorimetry
	2. Localized thermal failure conditions	2. Pattern testing (combining above tests with RPVOT, AN, viscosity, etc.) to differentiate from bulk oil degradation
Stage Three (attack stage)—*More advanced degradation phase where significant risk of varnish is present*	The presence of *soluble* and *insoluble* thermal degradation products:	
	1. Suspended high molecular-weight similar resinous insoluble compounds	1. Coagulated total insolubles
	2. Sludge and deposits	2. Analysis of sludge (bottom sediment, filter sediment, etc.) by elemental analysis, FTIR (1730 cm^{-1}), GC/MS
	3. Gas evolution	3. Flash point, gas chromatography for acetylene and other gases

Note—Analytical methods for clearly isolating oil degradation in conditions to electrification and static discharge has not been fully developed. The methods listed here are general in nature and may ais in the differentiation.

Flash Point (ASTM D92)

Flash point may also be used to identify thermal degradation if oil molecules have been thermally cracked. As the percentage of lower molecular-weight oil fractions increases due to thermal cracking, the flash point will drop accordingly.

Gas Chromatography (GC)

One of the advantages of gas chromatography is its ability to separate similar molecules based on their size. Thermally cracked oil will show an increased number of light-end molecules compared to the new oil baseline.

Patch Colorimetric Test

The patch test has been used for many years in oil analysis as a qualitative test to assess the condition of oil. Recently, several commercial laboratories have developed a quantifiable scale to trend the varnish potential of oil. For example, on Analyst Inc.'s scale from 0 to 100, a varnish potential rating of 0 to 40 would be considered acceptable. The range 41 to 60 would be a reportable condition, meriting the need to monitor the oil more frequently. Readings above 60 would be considered actionable and should trigger work plans to quickly remediate the condition.

Conclusion

With ever increasing expectations on performance extending oil's remaining useful life, sludge and varnish are serious concerns that must be addressed if present. A number of theories on the degradation methods have been discussed in this paper. Oxidation is commonly understood, and many analytical methods are

TABLE 5—*Corresponding international standards to analytical methods listed in Tables 2, 3, and 4.*

Analytical Method	Corresponding Standard Test Method[a]
Particle Counting	ISO 11500—Determination of Particle Contamination by Automatic Counting Using the Light Extinction Principle
Elemental Analysis	ASTM D5185—Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) ASTM D6595—Determination of Wear Metals and Contaminants in Used Lubricating Oils or Used Hydraulic Fluids by Rotating Disc Electrode Atomic Emission Spectrometry
Karl Fischer	ASTM D6304—Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration
RPVOT	ASTM D2272—Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel
HPDSC	ASTM D6186—Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
Acid Number	ASTM D892—Foaming Characteristics of Lubricating Oils
Patch Test	ASTM F312—Microscopical Sizing and Counting Particles from Aerospace Fluids on Membrane Filters
Viscosity	ASTM D445—Kinematic Viscosity of Transparent and Opaque Liquids
Air Release	ASTM D3427—Air Release Properties of Petroleum Oils
Coagulated Pentane Insolubles	ASTM D4055—Pentane Insolubles by Membrane Filtration
GC/MS	ASTM D2786—Hydrocarbon Types Analysis of Gas-Oil Saturates Fractions by High Ionizing Voltage Mass Spectrometry
Flash Point	ASTM D92—Flash and Fire Points by Cleveland Open Cup Tester ASTM D93—Flash-Point by Pensky-Martens Closed Cup Tester

[a] Note—There may be additional relating standards available for the analytical methods listed.

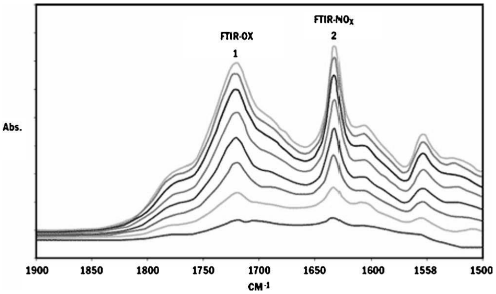

FIG. 4—*FTIR example spectrum showing oxidation peak around 1740 cm^{-1} range.*

available to identify this failure mechanism before the problem becomes advanced. Various forms of thermal degradation failure mechanisms including static discharge are also known to cause sludge and varnish; however, identifying and correcting the root cause can often be difficult. Further aggravating the problem is the poor solubility of Group II mineral oils compared to Group I oils. In order to differentiate between the failure mechanisms and assess varnish potential severity, turbine owners should consider a variety of tests to monitor the oxidative or chemical degradation of their turbine oils, such as the following:

- FTIR
- RPVOT
- RULER (linear sweep)
- Patch colorimetry
- Ultracentrifuge
- Coagulated insolubles
- Acid number

References

[1] Livingstone, G. and Thompson, B., “New Varnish Test Improves Predictive Maintenance Program,” *Practicing Oil Analysis*, July 2005.

[2] Fitch, J., “Demystifying Sludge and Varnish,” *Machinery Lubrication*, January 2002.

[3] Fitch, E. C., *Fluid Contamination Control*, FES, Inc, Stillwater, OK, 1988.

[4] Fitch, J., “Using Oil Analysis to Control Varnish and Sludge,” *Practicing Oil Analysis*, May 1999.

[5] Yano, A. et al., “Study on Sludge Formation during the Oxidation Process of Turbine Oils,” *Tribol. Trans.*, Vol. 47, 2004, p. 111–122.

[6] Yamamoto, Y. and Hirano, F., “Electrical Behavior of Phosphate Esters,” *Wear*, Vol. 50, 1978, p. 349–355.

[7] “Electrokinetic Wear,” *BFPR Journal*, Fluid Power Research Center, Stillwater, OK, 1988, Vol. 21, pp. 137–145.

[8] Sasaki, A. et al., “Generation of Static Electricity During Oil Filtration,” *Lubr. Eng.*, September 1999, p. 14–21.

[9] Duchowski, J. et al., “Overcoming Electrostatic Discharge in Hydraulic and Lubricating Applications by Incorporating a Novel Filter Media,” NCFP I05-19.1, NFPA Technical Paper Series, Presented at International Fluid Power Exposition, March 2005.

[10] Sasaki, A. et al., “Free Radicals and Oil Auto-Oxidation Due to Spark Discharges of Static Electricity,” *Lubr. Eng.*, May 1998, p. 24–27.

[11] White, L., “Snap Crackle Pop,” Hilliard Corporation, Elmira, NY.

[12] Barnes, M., “The Lowdown on Oil Breakdown,” *Practicing Oil Analysis*, May 2003.

[13] Fitch, J., and Barnes, M., “Hydrocarbon Analysis,” *Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing*, G. E. Totten, ed., ASTM International, West Conshohocken, PA, 2003, Chap. 24.

[14] Barnes, M., “Fourier Transform Infrared Spectroscopy,” *Practicing Oil Analysis*, March 2002.

[15] ASTM, Standard D 4378-03, “Standard Practice for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines,” *Annual Book of ASTM Standards*, ASTM International, West Conshohocken, PA, 2005.

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Contamination of Power Generation Lubricants

ABSTRACT: This paper examines the potential sources of fluid contamination that may occur during the manufacture, transportation, delivery, and use of a turbine oil for power generation. A turbine oil is a very precise formulation. If it becomes polluted with other lubricants or water, its performance could be compromised. The paper first identifies the potential sources of contamination that may be found when using a turbine oil. Then the consequences of contamination of the lubricant are considered. In conclusion, the paper proposes possible solutions to some of these practical problems regarding the sources of contamination. The paper will not consider the effects of particulate contamination. Because this is a well documented subject, the need for high levels of cleanliness in turbines is accepted practice.

KEYWORDS: turbine oils, contamination, demulsibility, filterability, metals, calcium, zinc, lubricant, compatibility

Introduction

Lubricants for power generating turbines are formulated to meet very exacting specifications set forth by turbine manufacturers. Depending on the particular additive chemistry and base stocks, the level of contamination by other fluids that can be tolerated without compromising performance can vary widely. Contamination can occur by a variety of means [1–4]:

1. Lubricants are inadvertently mingled due to incomplete flushing of blend tanks, storage tanks, hoses, lines, pumps, filters, or tank cars.
2. Incompatible preservative oils or prelubes are not removed completely. For example, engine oils are sometimes used as prelubes. While one performance level may be compatible, a newer version produced when engine oil specifications change may have adverse effects.
3. Human errors occur with the additive or the finished lube at the blending stage, during packaging if containers are mislabeled, or in service if a reservoir is topped off with the wrong fluid.
4. Containers are left open, allowing moisture, particulates, or both, to enter.
5. Soaps or other surfactants enter the system after wash down.
6. A turbine oil blender changes additive systems, resulting in later shipments that are incompatible with earlier shipments of the same branded lube. This is not technically contamination, but one should still be aware of the possibility.

Contamination can cause a number of problems in turbine system operation including reduced oxidation performance, excess foam, blocked filters and emulsion formation, or a combination thereof. Turbine oils are usually ashless (metal-free) while many other lubricants with which they may come into inadvertent contact are not. In addition, turbine oils may be formulated with acidic rust inhibitors that can react with basic species (such as overbased metal sulfonates or amine-based dispersants) found in other lubricants and may form insoluble materials. It was thus desired to systematically investigate the effects of their contamination with ash-containing fluids. In this paper, we will show the impact on the filterability and demulsibility performance of various commercial turbine oils when contaminated with heavy-duty diesel engine oil or a zinc-based antiwear hydraulic fluid.

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TABLE 1—*Properties of new turbine oils.*

Fluid	Metal Content, ppm	D 1401 (mL oil-H_2O-emulsion (min))	Afnor Filterability, IFE (dry/wet)	IP 19 (Demulsification Number, s)	Primary Performance Claims
1	0	40-40-0 (10)	1.0/2.0	261	GEK 32568, ES 9-224 CM P-38, P-55, P-57
2	0	40-40-0 (10)	1.1/1.3	69	GEK 32568C, ES 9-224, DIN 51515
3	0	40-40-0 (5)	1.0/1.3 (51.7 kPa)	621	GEK 32568E, ES 9-224U, D4304 Type II
4	0	40-40-0 (10)	1.0/1.3 (51.7 kPa)	114	Meets major OEM specifications for nongeared gas turbine applications
5	0	40-40-0 (15)	1.1/1.4 (51.7 kPa)	187	GEK 32568F, ES 9-224, BS 489
6	0	40-40-0 (10)	1.1/2.0 (51.7 kPa)	184	GEK 32568F, ES 9-224, DIN 51515

Experimental Details

Six commercial ISO VG 32 turbine oils that meet a range of performance specifications were chosen for this experiment. Properties of the turbine oils (including their performance in selected filterability and demulsibility tests) are shown in Table 1. The performance claims were taken from the respective marketers' product data sheets. A CI-4 PLUS quality, 15W-40 heavy-duty diesel engine oil (HD oil) and an HF-0 quality, ISO VG 32 zinc-based antiwear hydraulic oil (AWHF) were chosen as the contaminants. They were blended with the turbine oils at levels that added either 100 ppm calcium plus zinc (Ca+Zn) or 10 ppm Ca+Zn, and the performance of the resulting blends was evaluated in the Afnor filterability (NF E48-691 and NF E48-690), the ASTM Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids (D 1401) demulsibility and the Institute of Petroleum Determination of Demulsibility Characteristics of Lubricating Oil (IP 19) steam demulsibility tests. The Afnor test was conducted in accordance with the published procedure [5]. Demulsibility testing was conducted in accordance with ASTM D 1401-02 or IP 19 2003 revision.

A brief summary of each test method, as well as a description of what constitutes passing or acceptable results follows.

Afnor Filterability (Filter Index)

This filtration test is run on two 320-mL samples of fluid—one as is and one with 0.2 % volume distilled water added (wet). Both are run at room temperature, but in the case of the water-containing sample, prior to testing, the water is mixed in and the mixture stored at 70°C for 72 h in the dark, followed by 24 h at room temperature in the dark. The filtration apparatus consists of a pressurizable vessel with a volume of 340 mL and a cellulose filter membrane that is 47 mm in diameter with a mean pore diameter of 0.8 μm fitted in a support such that the effective surface area is 11.3 cm^2.

The fluid to be filtered is charged to this vessel and pressurized to 101.4 kPa with compressed air or nitrogen and the time required to filter 50, 100, 200, and 300 mL fluid is recorded. However, if the time to filter 50 mL is less than 60 s, then the applied pressure is reduced by 50 %; if that time is greater than 600 s, the applied pressure is doubled. Either of these deviations is noted in the report in parentheses after the filter index. If the time to filter 300 mL is longer than 7200 s, the test is stopped, no filterability index is calculated, and instead the total volume filtered is reported.

The filterability index (IFE) is calculated as follows:

$$IFE = \frac{T_{300} - T_{200}}{2(T_{100} - T_{50})}$$

where T_X is the time required for X mL of fluid to pass through the membrane.

TABLE 2—*Results for turbine oils contaminated with diesel engine oil.*

	Test Requirements	Oil 1		Oil 2		Oil 3		Oil 4		Oil 5		Oil 6	
ppm metals		10	100	10	100	10	100	10	100	10	100	10	100
Afnor IFE													
Dry	≤2.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.2	1.1	1.1	1.1
Wet	≤2.0	27 mL filtered	3 mL filtered	267 mL filtered	1.4	1.1	183 mL filtered	33 mL filtered	<300 mL filtered	176 mL filtered	1.4	247 mL filtered	1.4
D 1401													
mL oil-H_2O-emulsion (minutes)	≤3 mL emulsion at 30 minutes	12-0-68 (30)	0-0-80 (30)	1-35-44 (30)	1-0-79 (30)	2-30-48 (30)	15-21-44 (30)	35-20-25 (30)	0-0-80 (30)	39-40-1 (25)	1-0-79 (30)	43-37-0 (15)	0-0-80 (30)
IP 19													
(demulsibility number, s)	≤300	395	>1200	>1200	>1200	570	>1200	895	>1200	237	>1200	330	>1200

A passing filterability index (*IFE*) value is generally considered to be less than or equal to 2.0, and is reported for both the dry and wet tests.

D 1401-02

Forty millilitres each of reagent water and test oil are charged to a 100-mL graduated cylinder. The cylinder is placed in a bath at 54°C (82°C if the oil has a kinematic viscosity at 40°C that is greater than 90 cSt) and allowed to equilibrate. A shaft-mounted stainless or chrome-plated steel stirring paddle (120 by 19 by 1.5 mm) is placed in the cylinder. The mixer is turned on and run at a speed of 1500 ± 15 r/min for 5 min, after which time the stirrer is lifted out of the mixture, allowing the fluid to drain back into the cylinder. At 5-min intervals the cylinder is removed from the heating bath and the volumes of the oil, water, and emulsion layers are recorded. This is continued until complete separation occurs, or until 30 min have passed (60 min if at the higher temperature).

A passing result is generally considered to be one in which the time to 3 mL or less emulsion is 30 min or less (although most oil marketers claim 15 min or less). The ASTM format for reporting results is mL oil-mL water (H_2O)-mL emulsion (time in minutes at which this occurred). For example, a report of 40-40-0 (20) means that at 20 min, the sample had separated into oil and water phases of 40 mL each.

IP 19 Determination of Demulsibility Characteristics of Lubricating Oil

This is a measure of the time it takes for the complete separation of a mixture of 20 mL oil and 20 mL water at 94°C. A test tube containing 20 mL of the test fluid is placed in a water bath with a temperature of 19–26°C. Steam is bubbled into the tube at such a rate that the oil temperature can increase to 88–91°C within 45 to 75 s. The bubbling is continued until the volume has increased by approximately 20 mL (the volumes of the thermometer and steam delivery tube must be accounted for). The operator must begin timing the separation immediately after the steam is discontinued and simultaneously transfer the tube to a separating bath maintained at a temperature of 93–95°C. The volume of the separated oil layer is measured and recorded at 30 s intervals. If complete separation does not occur by 1200 s, the test is stopped and the demulsification number reported as >1200 s.

The passing limit (for ISO VG 32 oils) is a demulsification number ≤300 s.

As shown in Table 1, the samples of fresh turbine oils, except for Oil 3 in the IP 19, met these requirements.

Results

Heavy-Duty Diesel Engine Oil Contaminant (Table 2)

TABLE 3—*Results for turbine oils contaminated with hydraulic fluid.*

	Test Requirements	Oil 1		Oil 2		Oil 3		Oil 4		Oil 5		Oil 6	
ppm metals		10	100	10	100	10	100	10	100	10	100	10	100
Afnor IFE													
Dry	≤2.0	1.3	1.3	1.1	1.1	1.1	1.0	198 mL filtered	1.2	1.1	1.1	1.1	1.2
Wet	≤2.0	21 mL filtered	50 mL filtered	1.3	1.9	1.2	1.1	50 mL filtered	40 mL filtered	1.6	1.6	273 mL filtered	1.6
D 1401													
mL oil-H_2O-emulsion (minutes)	≤3 mL emulsion at 30	38-39-3 (10)	40-40-0 (10)	38-40-2 (15)	40-40-0 (15)	38-40-2 (10)	32-39-9 (30)	40-40-0 (20)	40-40-0 (10)	38-40-2 (10)	38-40-2 (10)	39-40-1 (10)	39-40-1 (10)
IP 19 (demulsibility number, s)	≤300	442	360	143	150	428	137	172	102	285	372	295	194

- 100 ppm total calcium+zinc (Ca+Zn), from the addition of approximately 2.1 % wt diesel engine oil.
  - Three oils (2, 5, and 6) met the generally accepted Afnor filterability requirements.
  - None passed either demulsibility test.
- 10 ppm Ca+Zn (or 0.21 % wt).
  - One sample, Oil 3, met the generally accepted Afnor filterability requirements.
  - Two oils (5 and 6) passed the ASTM D 1401.
  - One oil (5) met the IP 19 demulsibility criterion with a second (Oil 6) giving borderline performance of 330 s.

Thus, when contaminated with heavy-duty diesel engine oil, the ability of these fluids to retain their desired properties can be severely compromised. Specifically, the turbine oils were more resilient in terms of filterability when the contamination was at the higher level but far less capable of maintaining their demulsibility characteristics. At the lower level, filterability suffered more, but some measure of demulsibility was maintained in two of the oils. Interestingly, of the three oils that passed Afnor filterability with 2.1 % contamination, none passed at the lower, or 0.21 % wt level.

Zinc-Containing Antiwear Hydraulic Oil (Table 3)

- 100 ppm Ca+Zn (22 % wt of hydraulic fluid added to the turbine oil).
  - Four oils (2, 3, 5, and 6) met the generally accepted Afnor filterability requirements.
  - Every oil but one (Oil 3) passed the D 1401.
  - Four oils (2, 3, 4, and 6) passed the IP 19.
- 10 ppm Ca+Zn (2.2 % wt added hydraulic fluid).
  - Three oils (2, 3, and 5) met the generally accepted Afnor filterability requirements.
  - All oils passed the D 1401.
  - Four oils (2, 4, 5, and 6) passed the IP 19.

With the hydraulic oil as a contaminant, the trend was similar to what was observed with a high level of diesel oil contamination with respect to filterability characteristics. The same three oils (2, 5, and 6), along with Oil 3, passed at the higher level, and the lower level was somewhat more severe with only three oils passing. Almost all were able to maintain demulsibility characteristics as measured by the D 1401, with only Oil 3 failing at the high level. Using the IP 19, only four passed at either one of the levels and three (Oils 2, 4, and 6) passed at both.

The differences in demulsibility performance, depending on whether the oils were contaminated with diesel engine oil or hydraulic oil, can probably be attributed more to their different additive chemistry than to metal content. Compared to turbine oils, today's engine oils generally have high treat rates of ashless dispersants and overbased metal sulfonates, both of which tend to form emulsions in the presence of water. On the other hand, hydraulic fluids are usually formulated with lower levels of sulfonates and little to no ashless dispersant. Also, hydraulic fluids are often designed to demulsify, so the fact that they generally retain this performance is not too surprising.

Retention of a turbine oil's demulsibility characteristics during its life is important in order to allow any water that enters the system to be drained out of the bottom of the reservoir. The presence of water can reduce the lubricity of the oil, allow bacteria and fungi to grow, cause rust, and hydrolyze some additives. If the water concentration is high enough, the demulsibility characteristics of the oil can be overwhelmed. The result is a significant amount of emulsion, probably with a different (and potentially undesirable) viscosity than the lubricant, which can then adversely affect the lube's pumpability, air release properties, and lubricity.

From the results in Tables 2 and 3, it is clear that even a very low level of contamination with other fluids is likely to cause problems with filterability in some turbine oils; therefore, it is very important to guard against this contact. Given that these levels constitute contamination with less than 1 % of diesel engine oil, it is critical either to use dedicated equipment for handling turbine oils or to thoroughly flush all equipment after its use with ash-containing oils. At its most basic level, filter plugging will result in the system flow going to bypass mode. Initially, this probably won't have significant adverse effects. However, eventually the number of particles will increase to the point where wear of parts will unacceptably increase. In addition, when the system is not being filtered, varnish and sludge particles can agglomerate and deposit on parts such as servo valves where tolerances are very tight. This is likely to cause valve sticking and ultimately the valves will need to be replaced.

Tables 2 and 3 show that some oils performed better than others when contaminated; they are not all created equal.

Recommendations

In an ideal world, contamination of turbine oils would not occur. The reality, however, is that plants have limited resources, so the use of dedicated equipment is not always possible. To minimize the likelihood of contamination, storage and transport containers should be drained as thoroughly as possible and flushed before refilling. Likewise, hoses, lines, pumps, connectors—literally anything that potentially could come in contact with the turbine lubricants—should be drained and flushed between uses. Journal bearing prelubes and preservatives should be checked for compatibility with the turbine oil that ultimately will fill the system. Motor oils should not be used as prelubes or preservative oils because of the frequency with which their specifications (and consequently additive chemistry) change [2]. An earlier version may have been trouble free, but the next API or SAE upgrade may cause problems.

Containers should be clearly labeled. Training should include information about the different types of oil, their uses, and hazards that can occur when mixing them. Purchasers should require all suppliers to provide certificates of analysis (COA) for key analyses. This should be standard practice for lube blenders, additive suppliers, and plant operators. The properties of the incoming products should be known and tested for. The tests chosen should be able to detect a problem. For instance, except for carbon, hydrogen, and oxygen, the only element likely to be found in many turbine oils is nitrogen. However, testing only for nitrogen won't show any metal content, so it is essential to perform some type of elemental spectroscopy to make sure metals are not present. Finally, some basic performance tests should be carried out on new finished lube deliveries, and mixtures of the new and old lubes should be checked for continued performance in those tests [1,3].

References

[1] Fitch, J., "Should New Lubricant Deliveries be Tested?" *Machinery Lubrication*, March-April 2003.

[2] Shugarman, A. L., "Managing the Risk of Mixing Lubricating Oils," *Machinery Lubrication*, Sept.-Oct. 2001.

[3] Johnson, M., "Journal Bearing Pre-lubes During Turbine Startup—Beware the Risks," *Machinery Lubrication*, March 2003.

[4] Duncanson, M., "Controlling Oil Aeration and Foam," *Practicing Oil Analysis*, Nov. 2001.

[5] NF E48-690 and NF E48-691, "Hydraulic Transmission Fluids—Measuring the Filtrability of Mineral Oils," Association Française de Normalisation, Tour Europe Cedex 7 92049 Paris, La defense, 1990.

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Evaluation and Comparison Between Oxidation Stability Test Methods for Turbine Oils

ABSTRACT: Traditionally, long established oxidation tests such as TOST (ASTM D 943-03) and RPVOT (ASTM D 2272-02) in combination with the acid number (ASTM D 974-03) test has been used to screen the oxidation stability of turbine oils. Lately, nevertheless, a new voltammetric method has been applied to measure the remaining useful life (RUL) of turbine oils, RULER™ (ASTM D 6971-03) as it uses microlitre amounts of sample and needs only a short testing time. The aim of this study is to examine the correlation between the RULER™ voltammetric test in comparison to the standing oxidation turbine methods, TOST and RPVOT.Three fully formulated commercially available oils were studied; two were based on synthetic esters and one was mineral oil based. In addition, other oils were tested in our laboratories in Norway and Sweden in order to investigate the correlation between RULER™ and RPVOT oxidation stability tests. Field samples were also used to evaluate those methods.Although those studies have been worthwhile, reaching a definite conclusion regarding correlations has proven to be somewhat difficult. It is clear, however, that by a careful methodology, a useful correlation for the investigated oil types may be obtained. For example, guide limits for RULER™ results and their correlation to RPVOT values were established.

KEYWORDS: oxidation stability, acid number, turbine oil, modified dry-TOST, remaining useful life, linear voltammetry, antioxidants, RULER™, RPVOT

Introduction and Background

Turbine oils, based on mineral oils or synthetic esters, can oxidize or polymerize as a result of the aging processes. In this way, one of the most important chemical reactions affecting oils in service is the progress of oxidation, which very often determines service life. The effect of oxidation is to introduce oxygen atoms into base oil molecules, converting hydrocarbon molecules into aldehydes and subsequently into acids. Since these products are less stable than the original hydrocarbon molecules, they tend to be further attacked and the final products may be highly oxidized polymers or even solid residues, such as the carbonized materials commonly known as sludge [1]. The rate of oxidation depends on the oxidation resistance of the oil and the operating temperature. Oxidation is also catalyzed by certain metals. The presence of antioxidants, either natural or as additives, will reduce the rate of oxidation, but eventually the antioxidants will be consumed, and the rate of oxidation will then increase rapidly [1]. In order to prevent this aging in the oil, a "refill" is needed before this critical point in antioxidant concentration. The measurement of the antioxidants concentration can give important information on the condition of the oil. Some other tests such as acid number, viscosity, water content, contamination level, and the remaining useful life of the oil can be analyzed [2].

Traditionally, long established oxidation tests such as TOST (ASTM D 943-03) and RPVOT (ASTM D 2272-02) in combination with the acid number (ASTM D 974-03) test have been used to screen the oxidation stability of the turbine oils. Lately, nevertheless, a new voltammetric method has been applied to measure the remaining useful life (RUL) of turbine oils, RULER™ (ASTM D 6971-03). The RULER™ employs a linear voltammetry technique, which is used to determine the remaining antioxidant concentration of the test oil. Main advantages with the voltammetric method are: small amount of sample utilized (200–400 μL), easy sample preparation, faster on-site analysis (4–6 min), and a portable instrument which can be used in the field.

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This study investigates the relationships between the remaining useful life of oils and the concentrations of antioxidants. First, a correlation study between the voltammetric techniques in our two laboratories in Norway and Sweden will be discussed. An investigation and correlation between the RULER™ and RPVOT oxidation stability test, using a stressed laboratory oxidation test on three different types of oils will be examined. In the final part of this study, two field samples are investigated using voltammetric techniques and the RPVOT oxidation test, and compared utilizing standard physical analysis such as viscosity and acidity changes.

Ameye et al. [3] investigated a number of laboratory and field samples where they showed a good correlation between RPVOT, DSC standard oxidation methods, and antioxidants using RULER™. They considered the benefit of RULER™ comparing to RPVOT by the fact that voltammetric analyses gave different depletion depending on which antioxidant was considered.

Herguth et al. [4] studied the comparison between ordinary oxidation methods to voltammetric analyses in industrial oils. They concluded also that investigating the antioxidants levels in industrial lubricants by RULER™ correlated well with usual oxidation techniques, such as, RPVOT, DSC, TAN, and viscosity.

Experimental

Test Oils

Three new fully formulated commercial lubricants were used in the laboratory oxidation process. Oil A was a hydraulic oil based on an unsaturated synthetic ester base fluid, with antioxidants and corrosion inhibitors (<1 % wt), ISO VG 32. Oil B was a mineral turbine oil with antioxidants and corrosion inhibitors (<1 % wt), ISO VG 68. Finally, oil C was a saturated synthetic ester based turbine oil with antioxidants and corrosion inhibitors (<1 % wt), ISO VG 46. In addition, mineral turbine oil D with antioxidants and corrosion inhibitors (<1 % wt), ISO VG 32. Oil D was used to study the sensibility and repeatability between our two laboratories, one placed in Sweden and the other one placed in Norway. Remaining Useful Life test RULER™ and RPVOT oxidation tests were used in both laboratories using oil D. Field samples E and F were also investigated using RULER™ and RPVOT in both laboratories. Oil E was mineral turbine oil ISO VG 32 commonly employed in hydroelectric power stations and thermal power plants, especially in the thrust bearings and control systems parts. Oil E was tested after 70 000 h of operation. Oil F was a synthetic ester based turbine oil used in gas turbine engines, ISO VG 32. Samples obtained at different operating hours were investigated in the study of oil F.

Tests Methods

Oxidation Stability Test Dry-TOST—A modified dry-TOST (Waterless Turbine Oil Oxidation Stability Test) ASTM D 943-03, was used to evaluate the oxidation stability of A, B, and C oils. A 360 mL oil sample without any addition of water was submitted to an oxidation process. The samples were subjected to oxygen (at a flow of 3.5 L O_2/h) in the presence of an iron-copper catalyst at an elevated temperature of 120°C. "Oxidation lifetime" was defined to be the time to reach a total acid number (TAN) of 2 (mg KOH/g). The aging time was divided into five stages in oil A and C: Fresh oil (0 %), 25, 50, 75, and 100 % of the time to reach TAN 2. For oil B an extra data point was analyzed, i.e., 10 % of the oxidation time. At each stage an oil sample was drawn.

Oxidation Stability Test RPVOT—For all samples the oxidation stability test RPVOT (ASTM D 2272-98) was employed. The RPVOT test is used to evaluate the oxidation stability of new and in-service turbine oils in the presence of water and a copper catalyst coil at 150°C. Water and copper catalyst coil are placed in a vessel. The vessel ("bomb") is pressurized with oxygen at 620 kPa (90 psi, 6.2 bar). The vessel is rotated axially at 100 r/min at a 30° angle from the horizontal. The number of minutes required to reach a specific pressure drop of 175 kPa is reported as the oxidative stability of the test sample. The estimate of oxidative stability is used to estimate or assess the properties of the sample [5,6].

Remaining Useful Life Evaluation Routine RULER™—RULER™ is a quantitative linear voltammetry method, which determines the remaining utility of the lubricants by measuring the remaining concentra-

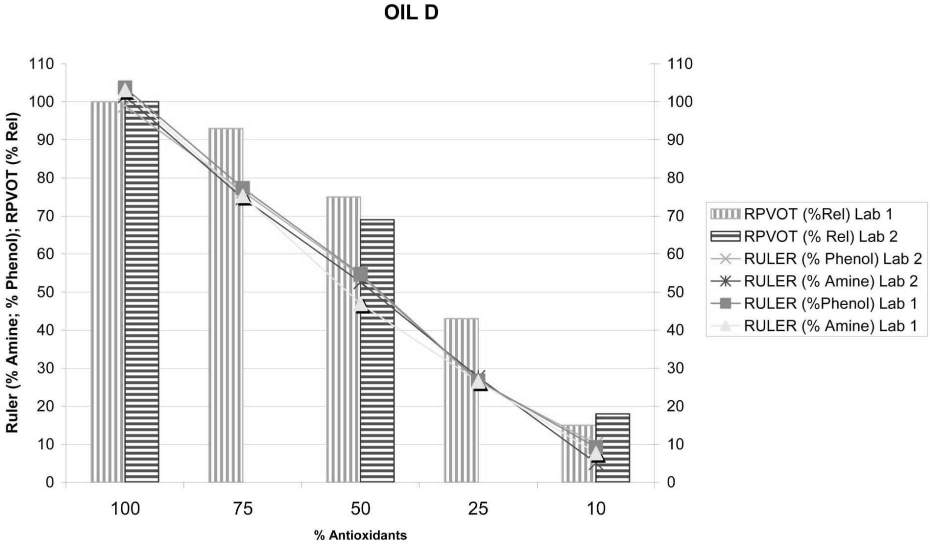

FIG. 1—*Oxidation stability, phenolic and aminic antioxidants tested in two laboratories.*

tions of the antioxidants in a lubricant (ASTM D 6971-03). The rate of antioxidant depletion over time can be monitored, and utilized to predict proper oil change intervals, as well as to detect abnormal equipment operation. Less than 500 μL of test oil is required. The voltammetric method is an electroanalytical experiment in which a sample is mixed with an electrolyte and a solvent, and placed in an electrolytic cell. The result is obtained by determining the current through the cell as a function of the applied potential. Tests results are based on current, voltage, and time relationships at the cell electrodes. As the voltage is increased, the electro-active species, e.g., phenolic and aminic compounds, start to oxidize at the electrode surface, producing an anodic rise in the current. As the potential is increased, the decrease in the electro-active species concentration at the electrode surface and the exponential increase of the oxidation rate lead to a maximum in the current potential curve. The plots produced by the voltammetric method (the oxidation wave) were then used to evaluate the remaining useful life of the aged oil samples. Fresh oils were used as the 100 % reference sample, and the solvent was used as the 0 % standard. The measurements of the aged samples were expressed as percentages of remaining additives. The repeatability of the percentage of remaining additive is between 2.5 and 4 % RSD [7,8].

Acid Number—Acid number (AN, ASTM D 974-03) [9] was determined for oil A, B, C, and E. The method measures the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample (mg KOH/g), needed to titrate the dissolved sample in isopropanol with 0.5 N KOH to reach a color change using a phenolphthalein (pink) indicator solution.

Results and Discussions

Oil D: RULER and RPVOT in our Two Laboratories

In order to investigate the sensitivity of the RPVOT and RULER™ methods in our two different laboratories, samples were prepared of turbine mineral oil D which contained 0, 10, 25, 50, 75, and 100 % relative AO concentrations. All samples were tested by our two laboratories by the RULER™ method. The RPVOT method was employed to further investigate several of these samples: 100, 50, and 10 % relative AO concentration for Laboratory 2; and for 10, 25, 50, 75, and 100 % relative AO in Laboratory 1 (Fig. 1). Duplicate samples of each oil were tested, and an average of both results was used. Good repeatability was found for RULER™ and RPVOT results in both our laboratories as shown in Fig. 1.

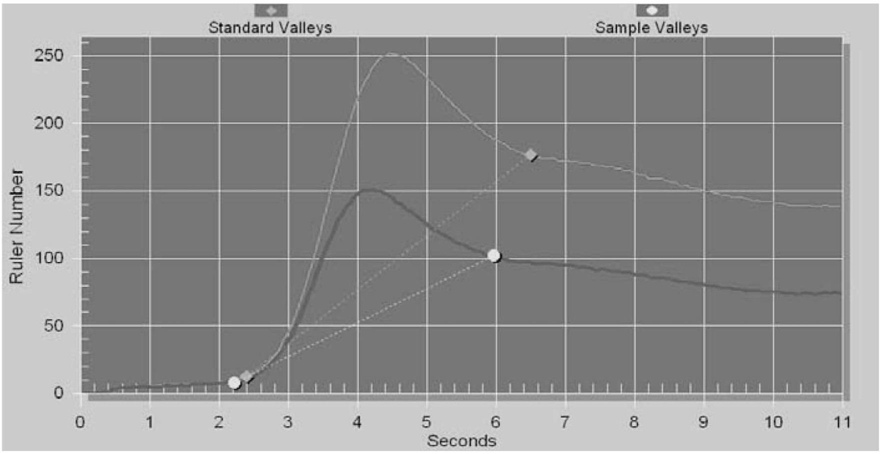

FIG. 2—*RULER™ plot of oil D reference oil 100 % (upper curve) and 50 % (lower curve) phenolic AO, for Laboratory 1.*

Oil D with a concentration of AO set to 100 % was used as reference oil in the RULER™ test. Laboratory 1 and Laboratory 2 obtained fairly similar result for remaining AO amine using RULER™. Oil D with 100 % relative concentration of AO yielded 103 % for Laboratory 1, and 104 % for Laboratory 2, respectively (Fig. 1). Laboratory 1 and 2 obtained similar results also for remaining phenol AO using RULER™. For example oil D with 25 % relative concentration of AO yielded 27 % and 26 % AO, respectively (Fig. 1).

RPVOT results are overall slightly above the corresponding AO percentage levels for each prepared concentration. In Laboratory 1, oil D with 75 % relative concentration of AO gave 93 % relative retention of RPVOT performance. In Laboratory 2, oil D with 50 % relative concentration of AO gave 69 % relative RPVOT retention. This might be explained by the fact that RPVOT method detects the total antioxidant capacity of the test oil, including the natural antioxidancy of the base oil.

Correlation RPVOT and RULER™ *in Accelerated Oxidative Stress Laboratory Tests*

Oil A—Oil A was aged in the modified dry-TOST, and results for the oxidation stability, remaining useful life and acidity (acid number) are shown in Fig. 3. The percentage of remaining phenolic and aminic antioxidants in each sample, for stage 0, 25, 50, 75, and 100 % of the oxidation experiment time needed to reach a final acid number of 2 (mg KOH/g), was measured with RULER™ and plotted against RPVOT results and the acid number in Fig. 3.

A progressive loss of phenolic and aminic antioxidant was observed as a function of increasing oxidation time. However, a different loss rate for the two types of antioxidants was observed. A higher loss rate than expected was found for RPVOT performance, as a function of increasing oxidation time. Since oil A is a hydraulic fluid, based on a synthetic unsaturated ester, one part of the explanation for this observation might be the lack of natural antioxidancy of this fluid. In addition, a plateau was observed between 50 and 75 % progression of the oxidation time (Fig. 3). A considerable acid number increase was observed after 75 % of the oxidation time. Phenolic antioxidant concentration for oil A was less than 30 % after 50 % test progression (36 h). However, for the aminic antioxidant, the concentration was 50 % at the same oxidation stage. At this point, 20 % relative RPVOT retention was obtained.

Similar trends have been confirmed in previous studies using dry-TOST for hydraulic oils [3]. Phenolic and aminic antioxidants depleted at a different rate, and the acid number increased dramatically when the remaining aminic antioxidant was less than 40 % [3] (Fig. 3).

Correlation between antioxidant concentrations and RPVOT results for the unsaturated ester based hydraulic oil A are shown in Figs. 4 and 5. Oil A shows a linear correlation $R^2=0.96$ between RPVOT and

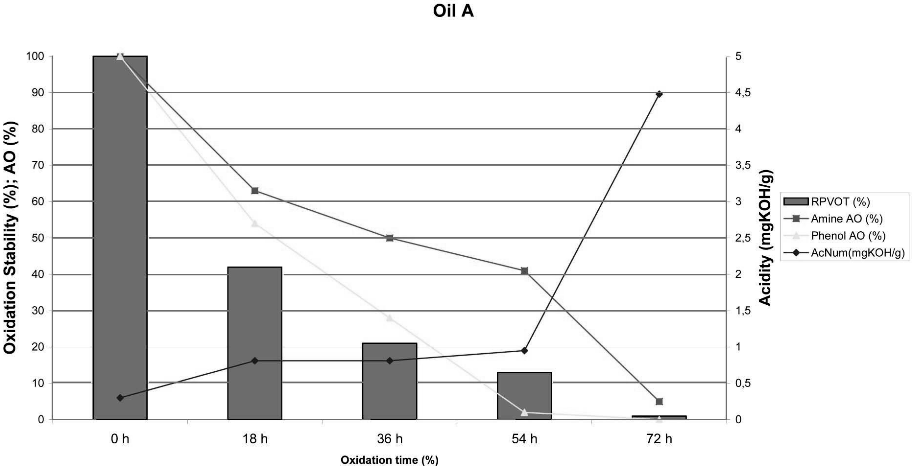

FIG. 3—*Oxidation stability, remaining useful life and acidity (acid number) for oil A.*

phenolic antioxidants using RULER™ (Fig. 4) and a linear correlation $R^2=0.84$ between RPVOT results and aminic antioxidants (Fig. 5). Thus, a better correlation for oil A was obtained between RPVOT results and phenolic AO concentrations.

Oil B—In Fig. 6, the results for the oxidation stability, remaining useful life and acidity change for the aged mineral turbine oil in the modified dry-TOST are shown. A decrease in the levels of phenolic and aminic antioxidants was found, as the oxidation exposure time progressed. Different loss rates for the two types of antioxidants were observed (Fig. 6). After 25 % of the oxidation time, no phenolic antioxidant was detected using RULER™, and less than 30 % of the aminic antioxidant remained. A decrease of the oxidation stability, as measured by RPVOT, was also detected at 25 % of the oxidation time (Fig. 6). After

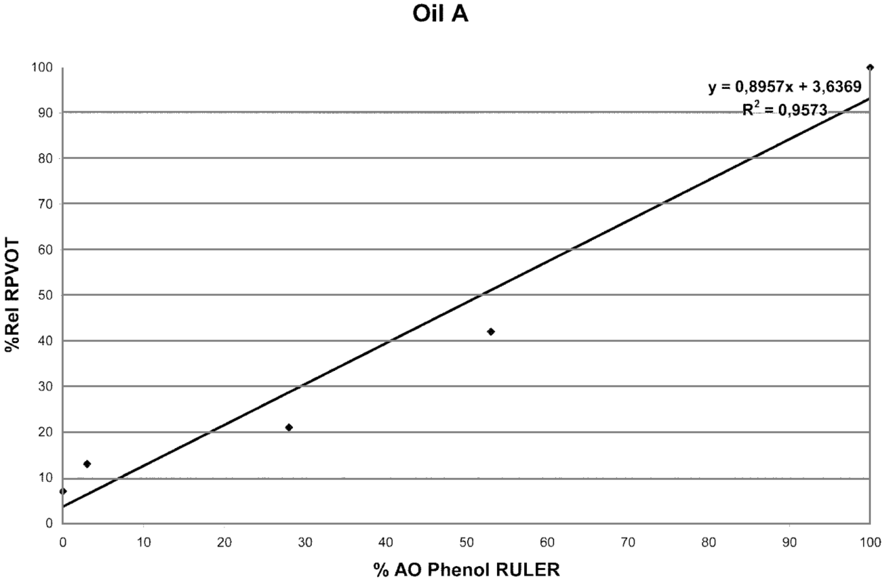

FIG. 4—*Correlation between phenolic AO and RPVOT results for oil A.*

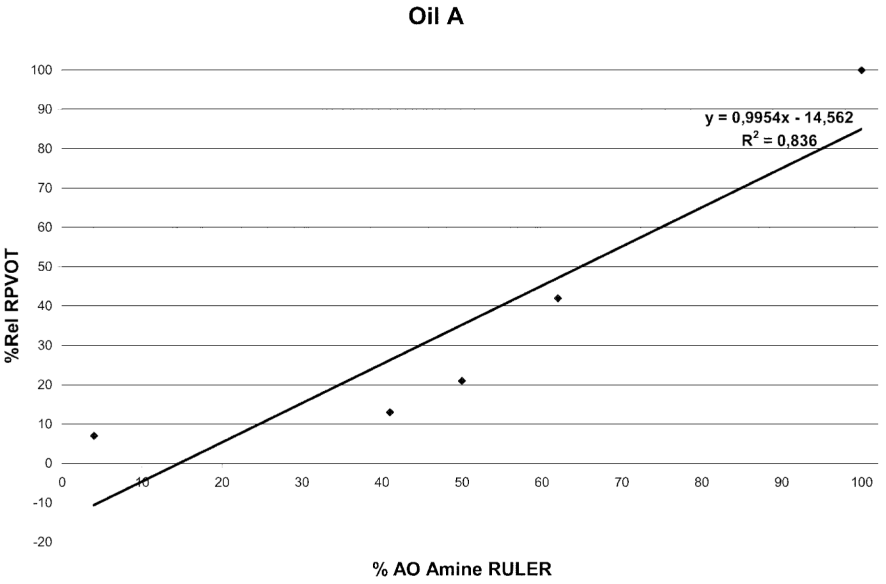

FIG. 5—*Correlation between aminic AO and RPVOT results for oil A.*

25 % of the oxidation time (936 h) both phenolic and aminic antioxidant concentrations were near 0 %, and, of course, for the rest of the remaining test time, as seen in the data from 50, 75, and 100 % oxidation time (Fig. 6). The RPVOT result for 25 % (234 h) oxidation time was down to only slightly above 10 %. After this point, the RPVOT relative results dropped to almost 0 %. In addition, a progressive increase of the acid number was obtained for every stage in the oxidation time until the modified dry-TOST was

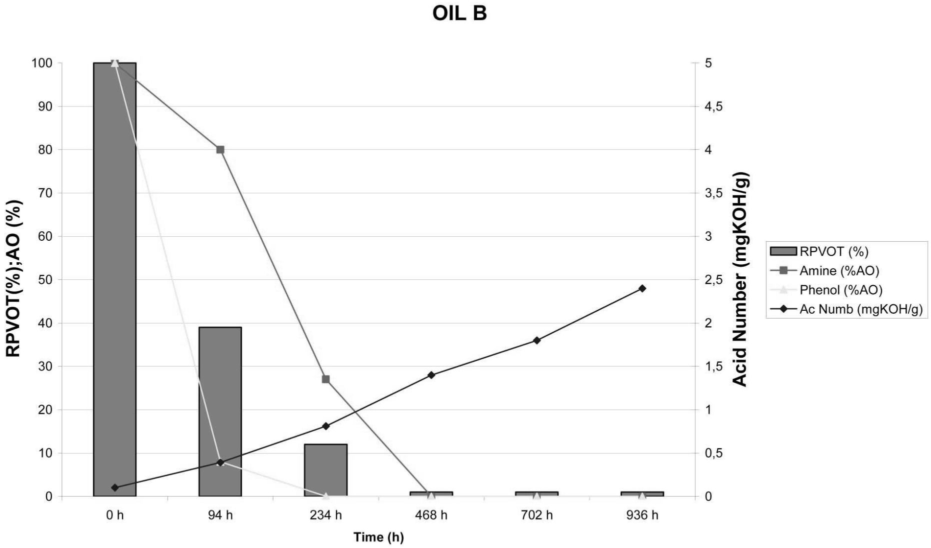

FIG. 6—*Oxidation stability, remaining useful life and acidity (acid number) for oil B.*

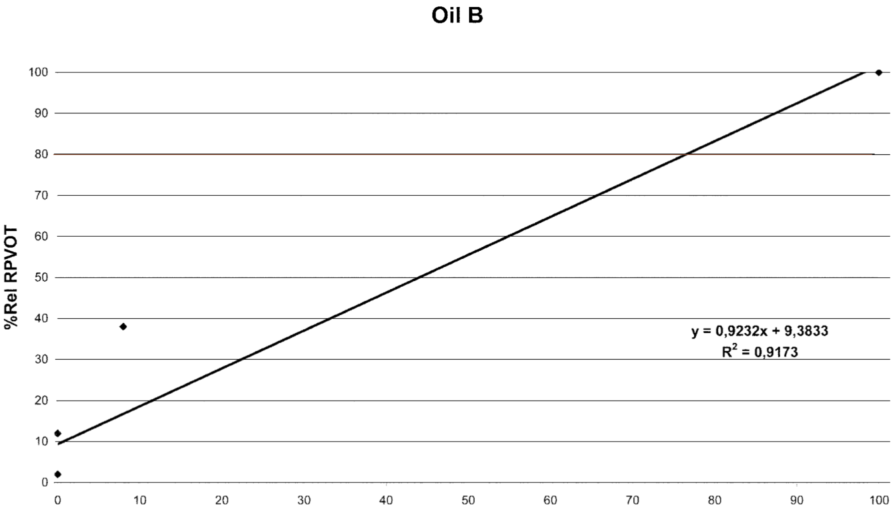

FIG. 7—*Correlation between phenolic AO and RPVOT results for oil B.*

stopped, with the TAN reaching 2 (mg KOH/g) (Fig. 6).

The correlation between RPVOT results and AO concentrations for the mineral oil based turbine oil B is shown in Figs. 7 and 8. For the phenolic AO, a linear correlation $R^2=0.92$ was found. For the aminic AO, the correlation was $R^2=0.84$.

Oil C—The synthetic saturated ester based turbine oil C was aged in the modified dry-TOST, and results for the oxidation stability, remaining useful life, and acidity are showed in Fig. 9. The percentage of remaining phenolic and aminic antioxidants in the oil samples drawn at every stage (0, 25, 50, 75, and

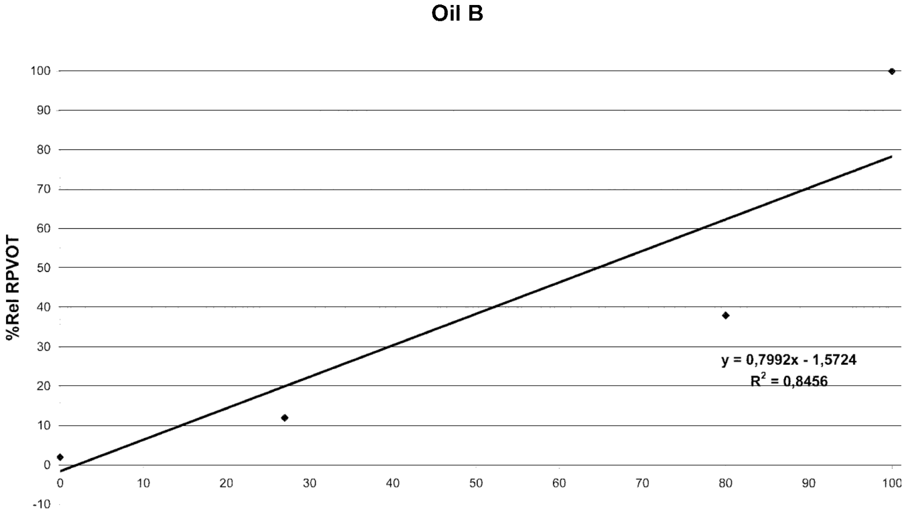

FIG. 8—*Correlation between aminic AO and RPVOT results for oil B.*

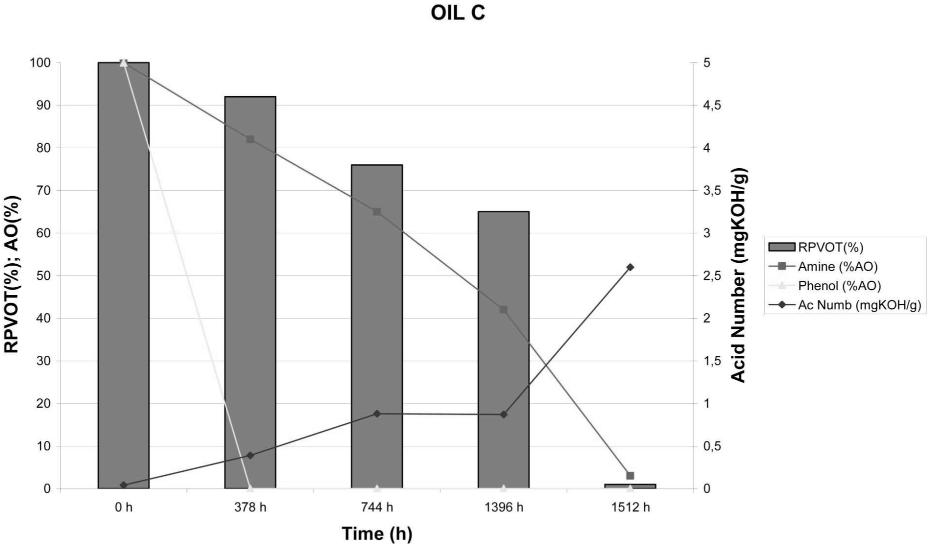

FIG. 9—*Oxidation stability, remaining useful life and acidity for oil C.*

100 %) of the oxidation time (1512 h) to reach the end-of-test acidity set to TAN 2 (mg KOH/g). Again, the RULER™ measurements were compared to the RPVOT results and acid number (Fig. 9). Decreasing AO levels, for both the phenolic and aminic antioxidants, were observed as the test progressed. However, a rather different loss rate was found for the two different AO types. The phenolic antioxidant in oil C decreases dramatically already in the first 25 % of the oxidation time (378 h); near 0 % concentration is detected by the RULER™. However, the aminic antioxidant decreases only gradually by each consecutive measurement point. At 75 % of the oxidation time (1396 h), the aminic antioxidant level is down to slightly over 40 %. After this point, the aminic antioxidant levels decreases drastically so that at the end of test time, 1512 h, a value near 0 % is detected. As seen in oil A, the acid number in oil C increased rapidly once the concentration of the aminic antioxidant fell below 40 % (Fig. 9). Again, this correlated well to earlier findings using dry-TOST for hydraulic oils [3]. Previous tests from field data [3] pointed out the difference in antioxidant depletion behavior between steam and gas turbines. Phenolic antioxidants, used commonly as antioxidant in steam turbine oil, were consumed by evaporation/sublimation and oxidation. Aminic antioxidants utilized in gas turbine oils operating at higher temperatures, had a different depletion rate, corresponding to the findings in Fig. 9 [3]. Only a slight decrease in the oxidation stability using RPVOT method was observed up to the 75 % oxidation time stage (Fig. 9). In addition, a plateau was again seen for the development of the acid number between the 50 % and 75 % time marks (Fig. 9). After this point the acid number increases more rapidly towards the end-of-test value (Fig. 9).

The linear correlation found for the synthetic saturated ester based turbine oil C between RPVOT results and concentration for phenolic and aminic AOs using RULER™ were $R^2=0.22$ (phenolic, Fig. 10) and $R^2=0.99$ (aminic, Fig. 11), respectively. Thus, an extremely low correlation between RPVOT result and phenolic antioxidant concentration using RULER™ was found for this system.

Correlation RPVOT and RULER™ *from Field Oil Samples*

Samples from the field were also used in this study. Oil E was a mineral turbine oil (ISO VG 32) frequently used in hydroelectric power stations and thermal power plants, especially in the thrust bearings and control systems parts. Oil E was tested after 70 000 operating hours. Figure 12 shows oxidation stability, antioxidant concentration, viscosity, and total acidity for oil E, as determined by our two laboratories. Four different samples of oil E were tested. Each sample was drawn from a different part of the system, and all samples had the same field hours of operation. Lower remaining levels of phenolic AO than

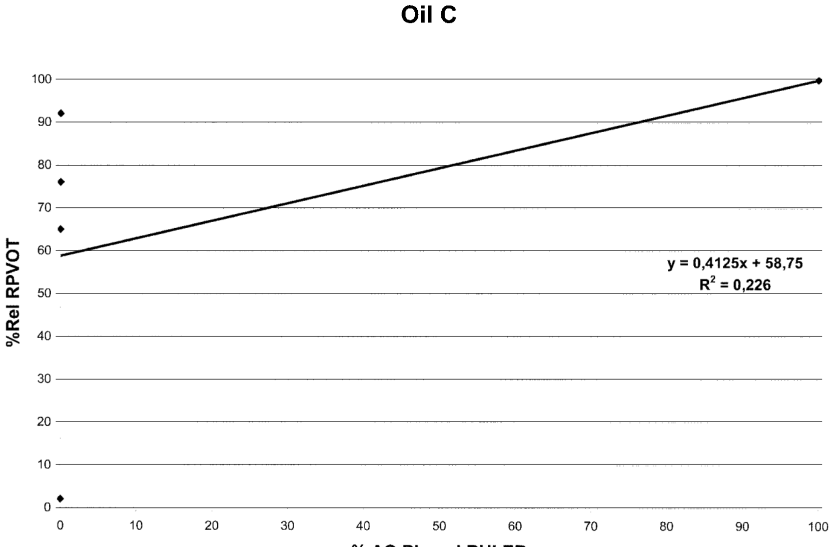

FIG. 10—*Correlation between phenolic AO and RPVOT results for oil C.*

aminic AO was obtained in both laboratories. Phenolic AO concentration just above 20 % by the RULER™ method was obtained for both laboratories. However, the aminic AO levels were above 75 % in all samples. Over 70 % retained relative RPVOT performance was found for all samples. The kinematic viscosity at 40°C and the acid number remained rather constant after 70 000 h of operation. A good correlation is seen for aminic AO results by RULER™ and RPVOT results.

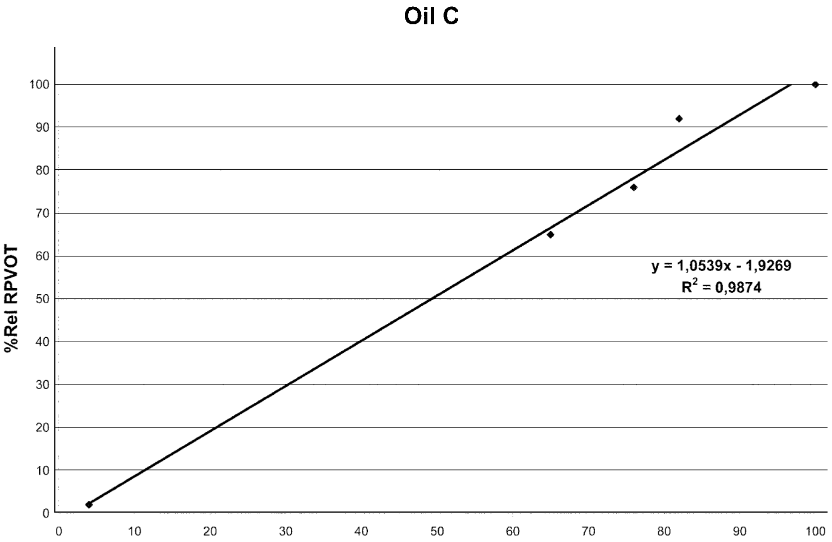

FIG. 11—*Correlation between aminic AO and RPVOT results for oil C.*

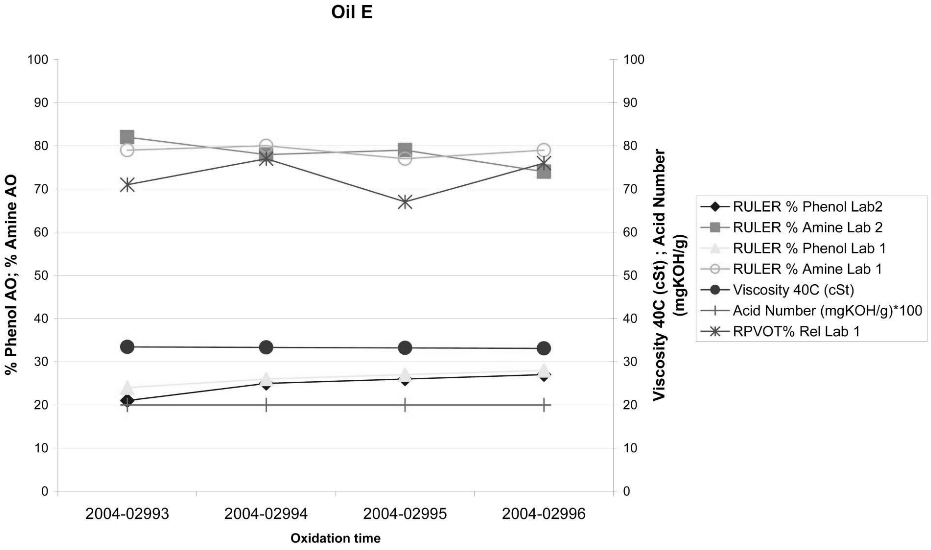

FIG. 12—*Oxidation stability, viscosity, acidity, and remaining useful life for oil E.*

Oil F was a synthetic ester based turbine oil used in gas turbine engines. Sample properties after several different operating hours were investigated. All samples were acquired from different system parts of the sampling site (Table 1). In Table 1, properties of these field samples are listed: oxidation stability (by RPVOT) in Laboratory 1; operating time, viscosity, and aminic AO for both laboratories. Generally, the remaining aminic AO levels by the RULER™ were higher in all tested samples than the corresponding relative RPVOT percentages. In 1b, 2b, and 3b time in field is longer. This is most likely due to top-ups by the system operator, so that new oil was added between the "a" and "b" sampling dates. The same reasoning might explain the (apparent) lowering of the viscosity during operation. In this turbine oil F is also seen as a rather good correlation between aminic AO using RULER™ and RPVOT results.

Conclusions

In order to investigate the correlation between linear voltammetry analyses utilizing the RULER™ methodology and oxidation stability of turbine oils by the RPVOT method, six different oils (A to F) were studied. Some conclusions can be derived from this work:

- An excellent repeatability using test method remaining useful life RULER™ in our Swedish laboratory and Norwegian laboratory was obtained for mineral turbine oil ISO VG 32. Good sensibility in both laboratories was obtained; see Fig. 1 using oil D.

TABLE 1—*Oxidation stability, viscosity, and aminic AO for field sample oil F.*

Sample F	Time in-used (h)	% Amine AO Lab 1 RULER™	% Amine AO Lab 2 RULER™	RPVOT Lab 1 (%Rel)	Viscosity 40°C (cSt)
1 a	7000	85	79	83	35
1 b	10500	88	85	98	30
2 a	8000	65	62	70	35
2 b	11500	73	83	88	30
3 a	3100	80	74	67	37
3 b	6200	80	72	80	33
4 a	3000	70	64	84	28

- Three fully formulated oils A, B, and C were submitted to accelerate oxidative stress laboratory test in form of a modified dry-TOST. Unsaturated ester based oil A showed a correlation between RPVOT and antioxidant depletion using RULER™ better for phenolic than for aminic antioxidants. For mineral oil based turbine oil B had also better correlation for phenolic than for aminic antioxidants. Finally, the saturated ester based turbine oil C showed a vague correlation between RPVOT and antioxidant depletion using RULER™ with phenolic AO, and better correlation for the aminic antioxidant and RPVOT results.
- A comprehensive and obvious correlation between RPVOT and RULER™ proved to be somewhat difficult to obtain. One problem was the very significant dependence on the base oil type used. Apparently, short oxidation lifetime turbine oil had better correlation with phenolic antioxidants and RPVOT results, and longer oxidation lifetime turbine oil had better correlation with aminic antioxidants and RPVOT oxidation test.
- For both field samples oil E and F with longer oxidation lifetime turbine oils also had a rather good correlation with aminic antioxidants using RULER™ and RPVOT.

Acknowledgments

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References

[1] Mortier, R. and Orszulik, S., "*Chemistry and Technology of Lubricant*, 2nd ed.," Blackie Academic & Professional, 1997.

[2] Jefferies, A. and Ameye, J., "RULER™ and Used Engine Oil Analysis Programs," *Lubr. Eng.*, Vol. 54, p. 29.

[3] Ameye, J. and Kauffman, R. E., "Antioxidant Analysis for Monitoring Remaining Useful Life of Turbine Fluids," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, ASTM International, West Conshohecken, PA, 2001.

[4] Herguth, W. and Phillips, S., "*Comparison of Common Analytical Techniques to Voltammetric Analysis of Antioxidants in Industrial Lubricants Oils*," STLE 1994 Annual Meeting, Kansas City.

[5] ASTM Standard D 2272-02, "Oxidation Stability of Steam Turbine Oils by Rotating Bomb," *Book Of Standards*ASTM International, West Conshohecken, PA, Vol. 05.01 2006.

[6] Totten, G., Westbrook, S. R., and Shah, R. J., "*Fuels and Lubrication Handbook: Technology, Properties, Performance and Testing*," ASTM International West Conshohocken, PA, 2003.

[7] Kauffman, R. E., "Remaining Useful Life Measurements of Diesel Engine Oils, Automotive Engine Oils, Hydraulic Fluids, and Greases Using Cyclic Voltammetric Methods," *Lubr. Eng.*, Vol. 51, 1994, p. 223.

[8] Van Leeumen, W., "*Use of RULER™ for the Determination of Critical Antioxidant Concentration in Ester Base Hydraulic Fluids*," Quarker Chemical, presented at the STLE Annual Meeting, Detroit, 1998; and AISE Annual Meeting, September 1998.

[9] ASTM Standard D 974-03, "Standard Test Method for Acid and Base Number by Color Indicator Titration," *Book of Standards*, 05.01, ASTM International, West Conshohocken, PA, 2006.

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Residue Analysis on RPVOT Test Samples for Single and Multiple Antioxidants Chemistry for Turbine Lubricants

ABSTRACT: Antioxidant chemistry is playing an important role in meeting the longer-life and higher temperature performance criteria of modern generation turbine lubricants. Oxidative life assessment is therefore an important parameter as part of today's turbine oil diagnostic services, where methods such as RPVOT, FTIR, and RULER are being applied. With this paper, we will discuss how RPVOT (per ASTM D 2272) testing of turbine lubricants with single antioxidant systems have much better reproducibility and repeatability than comparable RPVOT testing of oils with complex, synergistic mixtures of antioxidants. Both new and used turbine oils obtained from gas and steam turbines were used to assess the effects of antioxidant chemistry on the RPVOT results. In the first part of this research program, we present the analytical results for the residues remaining at the completion of the RPVOT tests of single component antioxidant oils. The RULER, varnish potential index (VPI), FTIR, AN, and viscosity analyses of the residues are very similar indicating that the residues contain no remaining antioxidants and have elevated levels of VPI, AN, viscosity, and FTIR oxidation, i.e., all of the RPVOT residues of the single antioxidant oils are highly oxidized when the test is ended based on oxygen uptake. In the second part, we present the analytical results for the RPVOT residues of complex mixture antioxidant oils. In contrast to the single antioxidant oils, the analytical tests of the complex antioxidant RPVOT residues indicate that the concentration of antioxidant and the level of oxidation varies with antioxidant formulation when the test is ended based on oxygen uptake. The results presented in this paper indicate that the effects of antioxidant chemistry on the residue content of RPVOT tests help explain the poor reproducibility of the RPVOT tests for turbine oils containing different types of antioxidant systems. Consequently, RULER analyses to characterize the antioxidant systems of the turbine oils before and after RPVOT testing would be very valuable in interpreting the RPVOT results and in improving the reproducibility of the RPVOT technique for making oxidative life assessments of modern generation turbine lubricants. VPI assessments of the turbine oils would further improve the oil diagnostic services of turbine lubricants by providing insight into the capability of the lubricants to solubilize the oxidation products of the antioxidants and the highly-refined base-oil.

KEYWORDS: antioxidants, remaining useful life, voltammetry, RPVOT, varnish index potential, oxidation, phenols, aromatic amines, steam turbines, gas turbines

Introduction

There have been countless instances of problematic turbine engine failures that have yielded used oil samples with a darker than normal appearance and a foul odor, yet conventional used oil testing of these samples has shown quite normal test results. Even on normally operating turbine engines, the routine predictive analysis of the lubricant for remaining useful life has been considered to be less of a science, and closer to an art form, for many decades. The most popular test for measuring oxidation stability, Rotating Pressurized Vessel Oxidation Test (RPVOT), has been widely used and touted as an industry standard, while at the same time, the test results are often ignored, especially when the results come into conflict with other test data or other operating criteria. Typical examples of this phenomenon, are when the RPVOT of the new oil is lower in value than the RPVOT of the in-service oil, or when the in-service oil RPVOT results are far out of range with the new oil data, yet the oil has only been in use for a short period of time and no other abnormal parameter can be found with the oil. Some real-life RPVOT data are given

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in this paper in the section titled RPVOT Reproducibility Issues. It is the authors experience that true, blind, interlaboratory round-robin testing for RPVOT, cannot achieve the reproducibility values as specified by ASTM D 2272 method.

The RPVOT test is designed to be a performance test for measuring the remaining test life of in-service oils. It takes into account the natural antioxidative properties of the base-oil as well as the oxidation inhibiting capabilities of the antioxidant additive for the base-oil. The RPVOT does this by stressing the oil in a pressure vessel with oil, water, copper catalyst, heat, and pure oxygen. The test is considered to be complete (formulated and natural antioxidants depleted), when the oxygen pressure drops (base-oil undergoing rapid oxidation) by a specified amount below the maximum pressure developed. Therefore, once the test is completed, the antioxidants should be totally depleted and the base-oil undergoing accelerated oxidation resulting in increased acid number (AN) and viscosity values with respect to the new oil. Since interlaboratory testing found poor reproducibility values for RPVOT, the authors took a closer look at the residual oils from different RPVOT tests and found that the AN and viscosity values of numerous residual oils were not increased with respect to the new oil. Consequently, it was decided to investigate further into this phenomenon by studying the oils as brand name groups, and to widen the scope of testing of the residual oils, to include FTIR spectroscopy (base-oil oxidation), voltammetry (antioxidant depletion) and colorimetric stain (Varnish Potential Index) analyses.

It was discovered that six different types of oils using mono-type antioxidant additive packages were fully oxidized during the RPVOT test, as measured by the AN, kinematic viscosity, FTIR spectroscopy, voltammetry and Varnish Potential Index. These oils are called sensitive to the RPVOT test. In contrast to the mono-type additive packages, three different types of oils using complex (synergistic) antioxidant additive packages were found to not fully oxidize during the RPVOT test, as measured by the same criteria. These oils are called nonsensitive to the RPVOT test.

This paper demonstrates that while the exact antioxidant chemistry of branded turbine oils remains as trade secrets of the oil refiners, there should be an assessment made, by the oil refiner, of whether or not their brand of oil is sensitive or nonsensitive to RPVOT testing. This assessment should then be made part of the product specification sheet. This will help clear up much confusion in the minds of many turbine engine owners and operators. It is also recommended to the ASTM committee that further study may be required to answer the fly question: Can the RPVOT test method be modified to allow testing of nonsensitive oils?

The Important Role of Antioxidants in Modern Lubricants

When modern turbine lubricants are developed, the lubricant manufacturing company has an important role of developing a lubricant which shall correspond to the particular turbine's performance requirements. Basically that means that an important role is dedicated to the development and selection of the base oil in combination with the selection of the additives. Why? In order to meet the basic lubricant requirements, and to protect against oxidation, corrosion, temperature extremes, wear, and deposits, oil additives are blended to the base oil. These are usually known as antiwear, extreme pressure, antioxidant, dispersant, antifoam, and Vl-improver additives, all of which have their own specific roles. On the other side, as a direct result from increasing operating economy parameters, OEMs' have driven the lubricant requirements toward more demanding specifications due to:

Increased load factors on new and existing types of equipment
Extended operational service/maintenance periods
Extended drain intervals
Decreased lube reservoir volume (cost/weight/engineering reasons)

The demanding specifications challenge the new generation of turbine lubricants to possess greatly improved capabilities to inhibit oxidation and explains why in the last decennia a wide variety of new antioxidant technologies have been emerging to respond to this market need. Until the effects of the new antioxidant technologies on long-term lubricant performance and traditional condition monitoring techniques have been fully established, there will be a need of measuring and trending their concentration in order to make proper remaining useful life evaluations of in-service lubricants. For this paper, remaining useful life or remaining oxidation stability is the length of time the lubricant can be used before the antioxidant(s) become depleted allowing rapid base-oil oxidation signified by increased TAN and viscosity

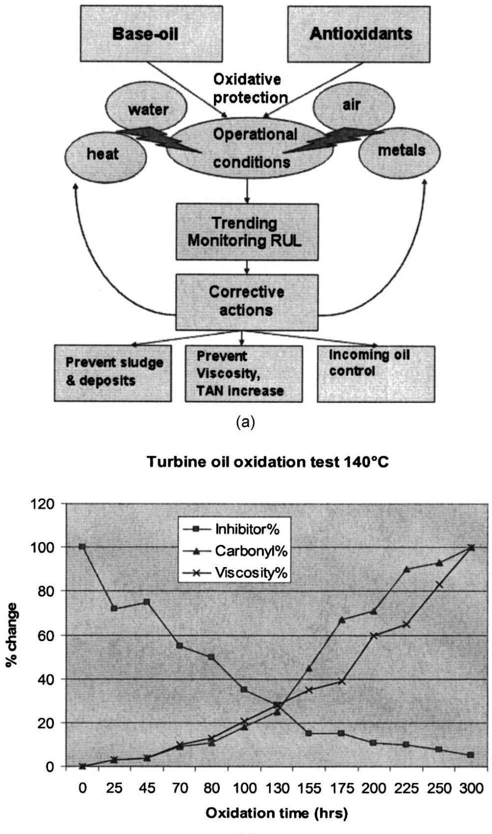


FIG. 1—*(a) Antioxidant function. (b) Turbine oil oxidation test graph.*

values, lubricant darkening, deposit formation, etc. Using this definition, new oil has 100 % remaining useful life and caused oil with elevated TAN values has 0 % remaining useful life.

Which Type/Classes of Antioxidants are Used?

Before explaining in more detail the different classes of antioxidants and their principle of working, it is vital to understand that in many modern lubricants a mixture of antioxidants is applied. Therefore it will be important to understand the total oxidative health of the lubricant, and not just one type of antioxidant.

What is oxidation? Oxidation is the chemical reaction of a lubricant at elevated temperatures between the dissolved atmospheric oxygen and the base-oil (Fig. 1(*a*)). During the oxidation, as hydrocarbon molecules will break down, reaction products will be formed, better known as radicals (very reactive chemical compounds). Subsequent reactions of these radicals lead to the formation of peroxides, and must therefore be quenched by the antioxidants to preserve the lubricant integrity, or its remaining useful life (RUL). Most of us relate the oxidation (or aging) of an oil with the formation of acids (Fig. 1(*b*)), resins, or other nasty chemical compounds which have to be seen as final reaction compounds, or when it's too late to react. We will come back on the importance of RUL in the following paragraph.

The role of antioxidants is to protect the base oil by either scavenging these radicals or decomposing hydroperoxides into stable products. This is very similar to the human body where vitamins (fresh vegetables, fruit, and wheat) are excellent antioxidants to neutralize these reactive compounds. Continuously refreshment of your body with fresh vitamins can be compared with the top-off technique applied on lubricants. At the same time literature refers to negative effects of over-additization, just like for a human body:

Primary Antioxidants—Remove the radicals (known as radical scavengers) that initiate the chain reaction that results in accelerated lubricant oxidation. Hindered aromatic amines and phenols are characteristic types of primary antioxidants, widely used in industrial lubricants. Therefore these types of ashless antioxidants go straight to the root of the problem and prevent deposits from forming in the first place.

Secondary Antioxidants—React with peroxides (known as hydroperoxide decomposers) and to form nonreactive products that do not participate in further oxidation of the lubricant. Zinc dithiophosphates, or better known under the name of ZnDtP or ZDDP, phosphites and phosphonites belongs to this class of antioxidants [1,2].

Mixed Antioxidant Systems—When two or more antioxidants are added to oil, an antioxidant effect is frequently observed in excess of either additive introduced individually. Antioxidants are often used in synergistic mixtures in modern lubricant formulations, to achieve an extended useful life, where one of the antioxidants sacrifices itself in preservation and regeneration of the other. A realistic example is the synergy between amines and phenols [1,3–5] whereby the hindered phenols give excellent protection at low-temperature regimes (and deplete first), while the amine antioxidants are more effective in extending lubricant life at higher temperature ranges.

In the above Fig. 1(*a*), the oxidation accelerators (heat, water, air, and metals) play an important role, as they can act separately or in combination, but are very much application dependent (will also be discussed in the practical case studies). Lubricating oils and greases oxidize in much the same manner, and the oxidation process steps are very much temperature dependent. The antioxidant (inhibitor) reaction mechanism scavenges the free radicals to stop the formation of oxidation products (carbonyl compounds in Fig. 1(*b*)). The actual mechanism will depend upon the type of antioxidants applied and selected.

With the continuous increase of power plants efficiency, as well size of power plants, thermal loads of turbine oils have been rising over the past ten years. This has resulted in a large change in new lubricant specifications for gas and steam turbines lubricants. The gas turbine lubricants inherently work at higher operating temperatures, and are faced with higher oxidative stresses. The steam turbine oils do not follow the same temperature evolution as for the gas turbines, but have also seen an increase of operating temperature over the years, requiring a higher oxidative stability (e.g., combined cycle power plants). Because turbine oils are increasingly required to have longer life at higher operating temperatures, turbine oils with amine additives as a mixture with phenolic antioxidants are coming into use for steam turbine, gas turbines, as well for combined cycle turbines.

Also with the increases of operating temperatures and equipment availability, turbine lubricating equipment manufacturing companies have started to include new proactive parameters in their maintenance specifications. Not only will these parameters result in a better balance between equipment and oil health monitoring, but also increase the availability of the equipment. This explains why oxidative health monitoring will be of high economic value for in-service oils as well for incoming oil batches.

The Value of Monitoring Antioxidants—To Know the RUL or Not to Know the RUL, That's the Question

The answer to this question is found in the basic characteristic of modern maintenance techniques, which require root cause failure analysis. In order to help extend fault free machine operating life, the trending of oxidative health, or antioxidants concentration, we will be required to look at the root causes of lubricant failures. Typically, oxidative health is monitored by AN tests which have a very low proactive value in CBM programs. Viscosity increase, which is a direct result from the polymerization (chain formation) between hydrocarbon (base-oil) chains and enhanced by the oxidation products is a second indicator or signal that heavy lubricant degradation exists.

The main drawbacks of techniques like AN, viscosity, and FTIR-Ox is their inability to predict the operating time from when the fluid was sampled and tested, until a fluid change will become necessary due to additive depletion. These tests have very low-slope rates-of-change, and tend to show completely normal results until the very latter stages of the oils' life. When critical oxidative depletion finally starts to take place in the oil, these tests take on a rapid rate-of-change or slope, but they are usually not noticed because the fluid is not sampled frequently enough to detect the initial rapid rate of change. In addition to that, an AN increase of just 0.1 AN, from 0.1 AN to 0.2 AN, can be significant, yet the AN test has accuracy problems in this range.

By monitoring the antioxidants, lubricant operators will detect additive failure in advance of oxidation, acid formation, thickening, and varnishing so as to avoid secondary component failure caused by accelerated wear, corrosion, filter plugging, and bearing lubricant starvation. And herein lays the major benefit by monitoring the antioxidant concentration or the remaining useful life (RUL), as users will be able to look forward, rather, than look backward by being reactive on changes of parameters like viscosity, AN, or oxidation by FTIR (FTIR-Ox).

This is why, in contrast to conventional fluid degradation techniques, other techniques are required which can routinely monitor the antioxidant concentration in a predictive mode. These tests need to be able to trend results well, with easy to recognize data slopes that give sufficient early warning, warning times that are well within the acceptable sample frequency interval.

For each type of turbine, antioxidant depletion rate will reflect the turbine's characteristic operating conditions enabling operators to look at the root causes for possible abnormal conditions. Experiences [5–7] have shown that with 10–20 % remaining antioxidant concentration, especially with higher temperature applications, large changes in the basestock's physical properties occur, i.e., the useful life of the oil ends. If a lubricant is than used past its end of useful life, excessive basestock degradation can occur, resulting in component wear and eventually equipment/engine malfunction, better known as oxidative accelerators can be divided in three categories:

Temperature Stress—Elevated temperature is an important accelerator to oil oxidation. This can be due to local hot spots (local bearing effects, dieseling), or overall high operating temperature. The impact of high temperature on the rate of oil oxidation (rule of Arrhenius—for operating temperatures higher than 100°C/170°F each increase by 10°C/17°F, will double the rate of oxidation or half the oxidative life of the lubricant.

Solid Contamination (through wear debris or dirt ingestion)—Accelerate the oxidation as being catalysts and decompose hydroperoxides.

Water Contamination Acting as Oxidative Accelerators—Moisture/water contamination (due to ingestion, condensation, and fresh lubricant top-up) and hence the importance of combining antioxidant trend analysis, with predictive maintenance techniques like wear/contamination and water.

These oxidative accelerators will enhance the fluid degradation and will increase the degradation when they work in combination, like water and metals, see Fig. 1(*b*) above:

- With equipment conditions changing continuously lubricant suppliers are changing the lubricant formulations to meet these demands.
- To detect faulty storage conditions of the fluids resulting in fast (auto) depletion of antioxidants.
- To assist lubricant operators during normal oil top-off operation and avoid mixing of lubricants.

Existing Techniques to Monitor Oxidative Health of Turbine Lubricants

For turbine oil oxidation assessment, as part of oil condition monitoring practices, different techniques are applied, from which two will be evaluated in this paper: RPVOT (Rotating Pressure Vessel Oxidation test as per ASTM D 2272), and voltammetric techniques (RULER as per ASTM D 6971).

RPVOT Test Method (per ASTM D-2272)

The most common test for turbine oxidative life measurement is the rotating pressure vessel oxidation test (RPVOT) as per ASTM D 2272. This test involves placing a sample of oil into a rotating pressure vessel along with a concentration of water and a copper coil. The vessel will be pressurized at a pressure of 90 psi with pure oxygen, and placed into a heating bath set at 150°C on a device that rotates at 100 r/min. As the temperature of the pressure vessel and its content increases, the pressure increases, until it stabilizes, and whereafter the test will start. During the RPVOT test, the oil's ability to resist oxidation degrades as a

TABLE 1—*Reproducibility results for RPVOT year 2004.*

Same Sample to Four Different Labs in Four Different Parts of the World			
Lab & Area	New Oil	GT No 1	GT No 2
Lab 1 - SE Asia	750		
Lab 2 - USA	806		
Lab 3 - Europe	920		
Lab 4 - Australia	1490		
Lab 1 - SE Asia		818	
Lab 2 - USA		588	
Lab 3 - Europe		650	
Lab 4 - Australia		1440	
Lab 1 - SE Asia			1009
Lab 2 - USA			596
Lab 3 - Europe			950
Lab 4 - Australia			1385
New Oil Avg	992		
Oil No 1 Avg		874	
Oil No 2 Avg			985

*Note Laboratories 1 and 3 reported higher values for the used oils than the new oil.

result of stress-induced antioxidant depletion, to the point where the base oil starts to react with the oxygen as the oil molecules begin to oxidize. At that point the pressure drop in the pressure vessel starts to accelerate and when the pressure drop reaches a value of 25 psi, this will be known as the end-point of the RPVOT test. The time in minutes is reported as the oil's RPVOT value, and should be directly linear to the depletion of the antioxidant additive package which is degrading during operation. Consequently the number of minutes required to reach the RPVOT end point decreases as an oil begins to age in-service and indicates a loss of the RUL.

Initially the RPVOT test was used on turbine oil formulation using phenolic mixtures resulting in RPVOT test times between 300 and 600 min. Over the past decade, turbine generator sets have been characterized by a significant increase in operating temperature, as well life time, which resulted into the introduction of mixtures of aromatic amines and phenols. With these synergetic mixtures, the RPVOT values have significantly increased to values varying between 800 and 3000 min.

RPVOT Reproducibility Issues

To test the precision and bias statement of ASTM D 2272 (the RPVOT test), it was decided to conduct blind and nonblind testing of new and used turbine oils in four different laboratories in four different parts of the world. Samples of a new gas turbine oil containing a phenolic/aminic mixture antioxidant package with a posted RPVOT value of 1400 and two similar formulation used gas turbine oils were sent to four well established petroleum testing laboratories in different regions. Only one of the laboratories was told the brand and type of oil, and which sample was new oil and which samples were used oils. The results of this testing are given in Table 1.

It is interesting to note that the only laboratory that was able to successfully report the results in the correct sequence of new versus used oils with the expected RPVOT ranges was the one laboratory that was told the oil type and which samples were new and used. A conclusion from this data could be that in true blind situations, the RPVOT test is not capable of detecting new oil from used, on that particular type of oil.

Voltammetric Techniques (RULER, per ASTM D 6810, D 6971) for Direct Detection of Antioxidant Chemistry

The working principle of the RULER^{TM} method is based on voltammetric analysis [5,6,8,9] in which the oil sample is mixed with an electrolyte and a solvent, and placed in an electrolytic cell to detect the

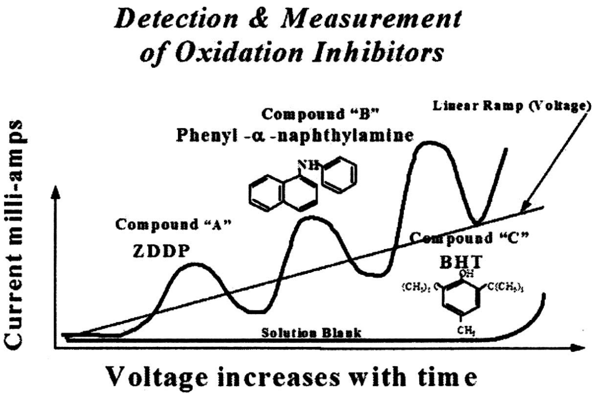


FIG. 2—*Voltammetry as a technique for monitoring antioxidants in oils—voltage versus current for different antioxidant, e.g. ZDDP, amine, and phenols.*

electrochemical (antioxidant activity). The oil samples (max. 400 μL) are diluted in an acetone/electrolyte mixture (RULER^{TM}) Green test solutions) enhancing extraction of the antioxidants (AO[s]) into the solvent phase. When performing a voltammetric analysis, the potential across the electrodes varies linearly with time, and the resulting current is recorded as a function of the potential. With increased voltage to the sample in the cell, the various additive species under investigation in the oil oxidize electrochemically. A typical current-potential curve produced during the practice of the voltammetric test is illustrated in Fig. 2. Initially the applied potential produces an electrochemical reaction with a rate so slow that virtually no current flows through the cell. As the voltage is increased (Fig. 2), the electro-active species (such as antioxidants) begin to oxidize at the microelectrode surface, producing an anodic rise in the current. As the potential is increased (from 0 to 1.7 V at a rate of 0.1 V/s), the decreases in the electro-active species concentration at the electrode surface and the exponential increase of the oxidation rate lead to a maximum in the current-potential curve (Fig. 2); this is the oxidation wave. The data recorded during this oxidation reaction can then be used to predict the remaining useful life of the lubricant, or used to evaluate the remaining antioxidant additives of the used samples. The peak of a zinc dialkyl dithio phosphate (ZDDP) additive is followed by an amine (PANA), and then by a hindered phenol (BHT) (see Fig. 2).

Voltammetric Test Procedures

To enhance the extraction of antioxidants out of the oil phase, the following RULER test procedures have to be applied [6,9–11]:

- Dispense 400 μL of the oil sample inside the vial, containing the electrolytic solution.
- Shake vial for 10 s.
- Let solution settle for about 2 min until clear liquid is evident on top.
- Perform RULER test. The fresh lubricant is used as the 100 % standard and the measurements of the used lubricant samples were expressed as percentage remaining additives (see Figs. 6 and 10.

While ASTM D 6810 [9] specifically covers the measurement of phenolic inhibitors in turbine oils, ASTM has approved a second standard, ASTM D 6971 [11], to measure the concentration of phenolic and aromatic amine antioxidants in nonzinc containing turbine oils. Voltammetric test practices are also part of ASTM practices for steam and gas turbine lubricant monitoring (ASTM D 4378-03 and D 6224-02) [9,12,13]

The RULER instrument is also perfectly capable of measuring the oxidation stability provided by ZDDP and similar antioxidant/antiwear additives [6].

Experimental

With the purpose of developing a balanced formulation between base oil and additives (in this case, more specifically the antioxidants) we can make an assumption that a turbine oil will truly be oxidized up to, or

TABLE 2—*Summary of oil types and information.*

	Viscosity	Type Oil
oil A	32 cSt	GT - dual AO
oil B	32 cSt	GT - dual AO
oil C	32 cSt	GT - dual AO
oil D	32 cSt	ST - mono AO
oil E	46 cSt	ST - mono AO
oil F	46 cSt	ST - mono AO
oil G	32 cSt	ST - mono AO
oil H	32 cSt	ST - mono AO

beyond, the critical point when antioxidants have been consumed, and the base oil will be undergoing secondary degradation (due to the lack of antioxidants to neutralize the C-radicals). It is well accepted that beyond this point, the AN and viscosity oil parameters will show a significant increase over their new oil values.

The experimental work from this paper focuses on the reproducibility issues with RPVOT by taking a closer look at the residual oil that comes out of the RPVOT apparatus, after the test has been completed. The rationale behind doing this is that one could reasonably expect all oils that come out of the RPVOT test apparatus will be depleted of antioxidants and there will be a sharp increase in AN and kinematic viscosity. When it was noted that this was not particularly the case, it was decided to investigate further into this phenomenon by studying the oils as brand name groups, and to widen the scope of testing of the residue, to include FTIR spectroscopy, voltammetry and Varnish Potential Index (colorimetric stain analysis).

Turbine Oils

Table 2 describes the following eight oil types which were evaluated in the program, consisting of three types of gas turbine oil (GT) (with dual antioxidant package), and five steam turbine oils (ST) with mono formulation of antioxidants. All of the oils belong to the Group II or Group III base oils.

Voltammetry

In this research program test results were measured by using a commercially available voltammograph (RULER technology), as per ASTM procedures D 6971. Neutral electrolytic test solutions were used to monitor both aromatic amines as well phenolic antioxidants, and the FLUITEC R-DMS data acquisition software was used for automatic RUL % calculation per additive.

RPVOT Test Instrument

RPVOT tests were performed by using a Koehler 4-vessel RPVOT instrument per ASTM D 2272. The pressure vessels were equipped with newer-style digital transducers. The data inflection points were acquired using the Oxidata V 7.2 software. After completion of the RPVOT test, the residue for the pressure vessel was collected for further analysis.

VPI

A proprietary colorimetric stain technique developed by Focus Laboratories Ltd. The scale is 0 to 100 VPI, with 0 being new clean oil, and 100 being a critical point of varnish residue. The test is a trending tool for the early signs of varnish precursors.

FTIR

Analytical spectra were taken using a Bio-Rad FTIR instrument. The sample pathlength was 0.1 mm. The oxidation area of measurement was 1800–1670 cm^{-1} with two baseline correction points; left of 2200 to

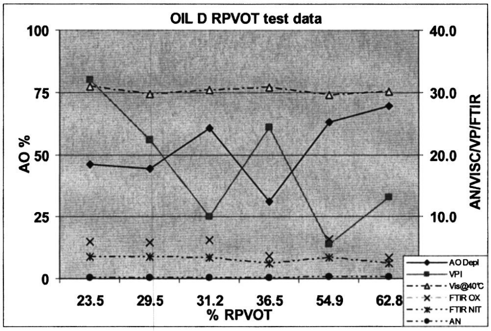


FIG. 3—*RPVOT test data for OIL D, compared to RUL AO, VPI viscosity at 40°C, AN, and nitration.*

1800 cm^{-1} and the right as 650–550 cm^{-1}. The nitration area was 1650–1600 cm^{-1}, with the same baselines as oxidation. The analysis was in accordance with JOAP and the instrument manufacturers' procedures.

Viscosity

Kinematic viscosities at 40°C were measured using a Cannon CT 500 viscosity apparatus, using Zeitfuchs crossarm viscometers. The method conforms to the ASTM D 445 method.

Acid Number (AN)

Acid numbers were performed using ASTM D 974, manual colorimetric titrations. The samples were dissolved in a solution of toluene/isopropyl alcohol/water and titrated to their end points using a standard alcoholic base solution and *p*-naphtholbenzein indicator solution.

Results and Discussions

RPVOT Comparison from Monoantioxidant Formulated Type of Turbine Oils

The first part of the research paper focused on the mono-type of antioxidant inhibited lubricants (voltammetric analysis highlighted that the antioxidants were mostly phenolic type of antioxidants). To assess the feasibility of the RPVOT technique for implementation in a used oil program, the RPVOT results were compared to the voltammetric results (RUL %) per type of antioxidants, AN, FTIR (oxidation), VPI, and

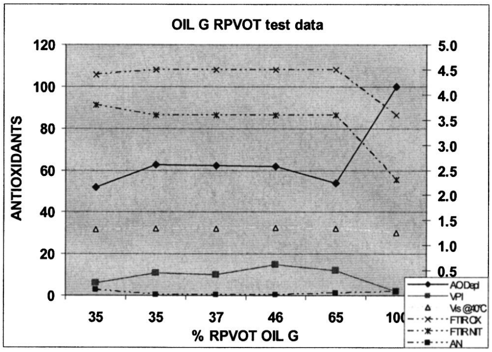


FIG. 4—*RPVOT test data for OIL G, compared to RUL AO, VPI, viscosity at 40°C, AN, and nitration.*

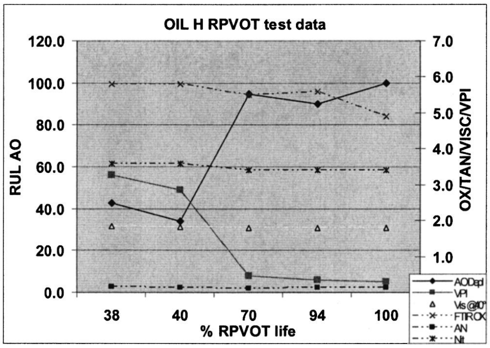


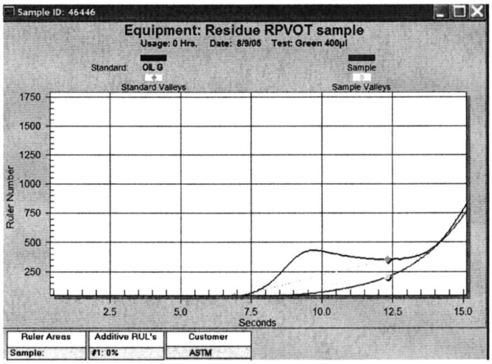
FIG. 5—*RPVOT test data for OIL H, compared to RUL AO, VPI, viscosity at 40°C, AN, and nitration.*

viscosity. For this comparison a total of 26 used oil samples were obtained from different operational power plants and different oil suppliers. Figures 3–5 present the RPVOT test results (% RPVOT = used oil RPVOT result (min)/reference oil result (min) × 100 % versus the analytical test data for the remaining antioxidants (RUL %), viscosity, AN, oxidation by FTIR and VPI, for D, G, and H oils. As all the data were similar in between the oil types D, E, F, G, and H, we only present a selection of data below (Figs. 3–5).

From the graphs (Figs. 3–5) we can see a good correlation between RPVOT and remaining antioxidant activity. Secondly, the VPI test data show the first increase of varnish potential with lower RPVOT and antioxidant concentration. Viscosity, oxidation by FTIR, and acid number test data did not increase very much, as the turbine base oil was still having enough oxidative protection by the remaining concentration of antioxidants. Consequently, to quantify and measure the antioxidant depletion after the RPVOT test, we have analyzed the residue oil samples (residue means that the sample is the oil that was returned from the RPVOT apparatus, after the RPVOT was completed) enabling us to perform the following tests:

- RULER test to quantify the remaining concentration of antioxidants by comparing the voltammetric response for the fresh oil versus the used oil.
- Oxidative degradation by analyzing the VPI, viscosity at 40°C, FTIR oxidation and nitration, and acid number.

On the residue oil samples, the Ruler voltammograph (Fig. 6) shows no remaining antioxidants concentration and is also confirmed by the physical data: high viscosity increase, high acid number increase and high FTIR oxidation, etc. This confirms for these type of turbine oils that we monitored a total depletion of antioxidants after a RPVOT test was performed.


Sample ID: 46446

Equipment: Residue RPVOT sample

Usage: 0 Hrs. Date: 8/9/05 Test: Green 400µl

Standard: OIL G

Ruler Areas	Additive RUL's	Customer
Sample:	#1: 0%	ASTM

FIG. 6—*Voltammograph from RULER analysis on residue oil sample H.*

TABLE 3—*Residue samples analysis for oil H.*

RPVOT Residue Samples OIL H	AO RUL #1(%)	AO RUL #2(%)	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nitr	AN
Residue of 2TGATRB1	0.0	0.0	126	34.4	38.1	6.2	4.20
Residue of 1TGATRB1	0.0	0.0	144	35.2	37.5	6.5	4.19
Residue of 2TGATRB1	0.1	0.0	161	33.3	35.8	6.0	5.01
Residue of 1TGATRB1	0.0	0.0	159	34.4	38.5	6.2	5.60

As the results for the oils D, F, E, G, and H are very similar we only present a selection of the residue oil analysis data— Tables 3–5 present the data from residue oil samples from Oils H, D, and G and with their different monitored analytical parameters.

For all the samples being tested the residue oil samples showed a total antioxidant depletion as well a significant increase of VPI, viscosity, oxidation by FTIR, and acid number. This is a logical consequence of the base oil degradation and lack of antioxidants. In the following paragraph we will start comparing data for multiple antioxidant formulations.

RPVOT Comparison from Synergetic (Multiple) Antioxidant Formulated Type of Turbine Oils

For the second part of this research paper a total amount of 32 oil samples, sampled from different Thai power plants were also first analyzed through the RPVOT test instrument. Three different types of turbine oils, blended with multiple antioxidants, were included in this research program. As stated earlier, we have performed RPVOT testing on their 32 used and new oil samples, including VPI, viscosity, FTIR oxidation and nitration, as well acid number. Figures 7–9 correlates the RPVOT test results (% RPVOT), versus the remaining antioxidants (RUL %), as well as viscosity, TAN, oxidation by FTIR and VPI, for three different types of oil (oils A, B, and C).

To quantify and measure the antioxidant depletion during the RPVOT test, we have taken from all the RPVOT tests that we performed, the residue oil samples, enabling us to perform the following tests:

- Voltammetric (RULER) analysis to quantify the remaining antioxidants.
- Oxidative degradation by analyzing the VPI, viscosity at 40°C, FTIR oxidation and nitration, and acid number.

For the majority of these oils we monitored a partial depletion of antioxidants, as well a difference in increase for the oxidation detected by FTIR, and oxidation acids by AN. A typical example can be seen in Fig. 10 which shows a voltammograph from a RULER analysis, for oil type A residue after performing a 3000 min RPVOT test. The upper curve represents the fresh oil with antioxidant #1 consisting of an

TABLE 4—*Residue samples analysis for oil D.*

RPVOT Residue Samples OIL H	AO RUL #1 (%)	AO RUL #2 (%)	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nitr	AN
Residue of RTGH CTG 2	0.0	0.0	31	33.0	36.1	4.5	8.78
Residue of RTGH CTG 2	0.0	0.0	93	31.9	36.0	5.3	4.63
Residue of RTGH CTG 2	7.7	0.0	150	32.9	38.4	5.5	5.79
Residue of 1TGH CTG 1A	0.0	0.4	125	33.2	35.6	5.3	5.58
Residue of 1TGH CTG 1B	0.0	0.0	135	30.8	34.7	5.4	4.60
Residue of 2TGH CTG 2B	0.0	0.0	145	31.3	37.4	5.6	5.54

TABLE 5—*Residue samples analysis for oil G.*

RPVOT Residue Samples OIL G	AO RUL #1 (%)	AO RUL #2 (%)	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nitr	AN
Residue of Z 660	0.0	0.0	88	36.6	35.8	7.7	5.06
Residue of C 560 3	0.0	0.0	194	35.9	33.6	7.4	3.92
Residue of C 560 4	0.0	0.0	199	35.80	29.90	7.0	3.10
Residue of CT 660 2	0.0	0.0	168	36.2	38.0	8.1	4.3
Residue of Z 660 5	0.0	0.0	183	36.6	35.8	7.8	4.04

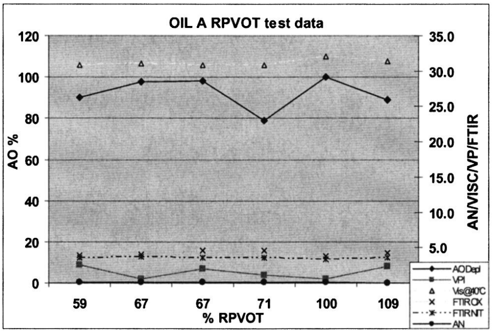


FIG. 7—*RPVOT test data for OIL A, compared to RUL AO, VPI, viscosity at 40°C, AN, oxidation and nitration by FTIR.*

aromatic amine and the antioxidant #2 a phenolic type of antioxidant. The lower curve shows the RULER response for the remaining activity of antioxidants, where a 28.4 % remaining activity of aromatic amines is analyzed, and the phenolic antioxidants are totally depleted. This residue oil sample had also the lowest AN increase, as well as oxidation increase by FTIR, but showed the first signs of Varnish Potential Increase.

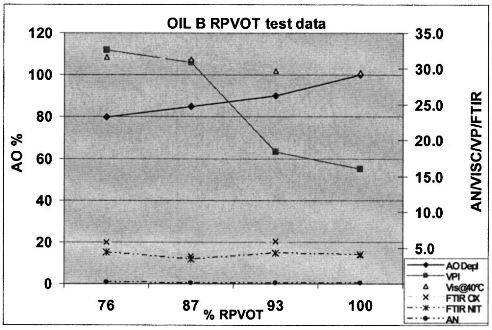


FIG. 8—*RPVOT test data for OIL B, compared to RUL AO, VPI, viscosity at 40°C, AN, oxidation and nitration by FTIR.*

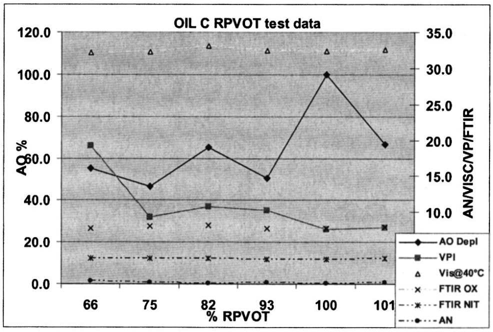
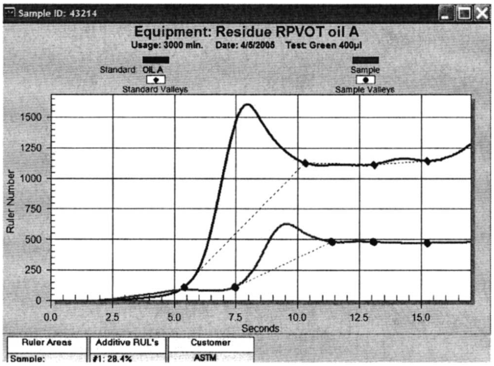


FIG. 9—*RPVOT test data for OIL C, compared to RUL AO, VPI, viscosity at 40°C, AN, oxidation and nitration by FTIR.*



Sample ID: 43214

Equipment: Residue RPVOT oil A

Usage: 3000 min. Date: 4/5/2005 Test: Green 400µl

Ruler Areas	Additive RUL's	Customer
Sample:	#1: 28.4%	ASTM

FIG. 10—*Voltammograph by RULER for RPVOT residue oil sample A.*

The remaining antioxidant activity in the RPVOT residue oil samples is confirmed for the three different oil types (C, B, A—see respective Tables 6–8) where for the majority of the oxidized oil samples, an important part of the antioxidants is still detected by voltammetry. These data are confirmed by a significantly lower increase of acid number and oxidation, in comparison with the oil samples which have total antioxidant depletion. The authors leave for discussion why the residue oil samples A have remaining antioxidant with low AN, but with high VPI, whereas oil C has high AN regardless of AO and oil B has low AN regardless of AO. An explanation for this correlation could be found in the type of base oil which has a difference in the ability to dissolve oxidation products, more specifically when moving from Group I to Group III oil, which may affect VPI independent of remaining AO.

TABLE 6—*Residue samples analysis for oil C.*

RPVOT Residue Samples OIL C	AO RUL (%) #1	AO RUL (%) #2	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nit	AN
Residue of GT 1A	32.1	0.4	100	35.8	13.8	18.2	0.75
Residue of GT 1B	0.0	0.0	155	34.1	39.3	8.4	4.75
Residue of GT 1C	21	0.0	98	35.5	39.2	12.5	4.31
Residue of GT 2B	0.0	0.0	95	33.2	27.3	4.8	3.09
Residue of GT 2C	0.0	0.0	114	33.5	35.6	6.8	4.43

TABLE 7—*Residue samples analysis for oil B.*

RPVOT Residue Samples OIL B	AO Depl (%) #1	AO Depl (%) #2	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nitr	AN
Residue of RTGH CTG 1	2.4	0.0	117	31.2	11.0	4.3	0.61
Residue of GT 2A	31.8	0.2	138	29.5	12.7	5.0	0.96
Residue of RTGH CTG 1	0.0	0.3	128	31.6	10.0	4.3	0.85

TABLE 8—*Residue samples analysis for oil A.*

RPVOT Residue Samples OIL A	AO Depl (%) #1	AO Depl (%) #2	VPI	Visc@ 40°C	FTIR Oxid	FTIR Nitr	AN
Residue of Z 300	24.3	0.0	134	31.9	5.6	3.5	0.36
Residue of Z 460	21.6	0.1	128	31.3	6.7	3.6	1.06
Residue of C 300 4	28.4	0.0	119	31.9	4.8	3.2	0.22
Residue of Z 300 10	22.3	0.1	128	31.8	5.8	3.3	0.63
Residue of Z 300 10	23.1	0.1	169	31.7	7.4	3.9	0.37

Conclusions

From these results, the authors conclude that RPVOT testing of turbine lubricants with single antioxidant systems have much better reproducibility and repeatability than comparable RPVOT testing of oils with complex, synergistic mixtures of antioxidants for both new and used turbine oils obtained from gas and steam turbines.

The results presented in this paper indicate that the effects of antioxidant chemistry on the antioxidant concentration and level of oxidation of the RPVOT test residues help explain the poor reproducibility of the RPVOT tests for turbine oils containing different types of antioxidant systems. Consequently, RULER analyses to characterize the antioxidant systems of the turbine oils before and after RPVOT testing would be very valuable in interpreting the RPVOT results and in improving the reproducibility of the RPVOT technique for making oxidative life assessments of modern generation turbine lubricants.

Based also on the protective function of primary antioxidants in new generation (gas and steam) turbine lubricants, it is of added value to start trending and differentiating the depletion of the individual antioxidants, before excessive base-oil degradation starts to occur with severe known consequences like varnishing and deposit formation [14–16]. Since identifying a fluid's potential to produce varnish is challenging and routine oil analysis does not provide a sufficient warning, the VPI, when used in conjunction with the RULER antioxidant evaluations, can be useful in predicting the formation of varnishing and deposits. Finally, the authors are convinced that the combination of RULER antioxidant analysis, in conjunction with VPI and RPVOT, will be an important contributor to successful maintenance strategies based on root cause analysis leading to the correct alarm levels and maintenance actions for turbine oils regardless of formulation.

References

[1] Mortier, R. and Orszulik, S., *Chemistry and Technology of Lubricants*, Blackie and Son, 1992, p. 94.

[2] Born, M., Hipeaux, J. C., Marchand, P., and Parc, G., "Relationship Between the Chemical Structure and Effectiveness of Some Metallic Dialkyl and Diaryldithiophosphates in Different Lubricated Mechanisms," *Engine Oils and Automotive Lubrication*, W. J. Bartz, Ed., Marcel Dekker, New York, p. 336.

[3] Reyes-Gavilan, J. L. and Odorisio, P., "A Review of the Mechanism of Antioxidants, Metal Deactivators, and Corrosion Inhibitors," Ciba Specialty Chemicals Publication, *STLE 2002* CD-ROM, May 2002.

[4] Hamblin, P. C., Kristen, U., and Chasen, D., "Ashless Antioxidants, Copper Deactivators and Corrosion Inhibitors: Their Use in Lubricating Oils," *Journal of Lubrication Science*, Vol. 2, 1989, pp. 287–318.

[5] Vandenkommer, A., SKF, and Ameye, J., "Predicting Remaining Grease Life—A New Approach and Method by Linear Sweep Voltammetry," ELGI AGM Bern, Switzerland, May 2001.

[6] Kauffman, R. E., "Rapid Determination of Remaining Useful Life of Lubrication Life," in *CRC Handbook of Lubrication and Tribology, 3*, E. R. Booser, Ed., CRC Press, Boca Raton, FL, 1994, p. 89.

[7] Kauffman, R. E., and Ameye, J., "Antioxidant Analysis for Monitoring Remaining Useful Life of Turbine Fluids," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, ASTM International, West Conshohoken, PA.

[8] Migdal, C. A., "The Influence of Hindered Phenolic and Aromatic Amine Antioxidants on the Stability of Base Oils" *213th National Meeting American Chemical Society*, San Francisco, CA, April 13–17, 1997.

[9] ASTM Standard D 6810, "Standard Test Method for Measurement of Hindered Phenolic Antioxidant Content in HL Turbine Oils by Linear Sweep Voltammetry," *Annual Book of Standards*, 05.04ASTM International, West Conshohocken, PA.

[10] Johnson, B., APS Power, and Ameye, J., "Condition Monitoring of Anti-oxidant Chemistry of In-Service Bulk Greases," *NLGI Proceedings*, October 2004.

[11] ASTM Standard D 6971, "Standard Test Method for Measurement of Hindered Phenolic and Aro-

matic Amine Antioxidant Content in Non-zinc Containing Turbine Oils by Linear Sweep Voltammetry," *Book of Standards*, 05.04, ASTM International, West Conshohocken, PA.

[12] ASTM Standard D 4378, "Standard Practice for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines," *Book of Standards*, 05.02ASTM International, West Conshohocken, PA.

[13] ASTM Standard D 6224, "Standard Practice for In-Service Monitoring of Lubricating Oil for Auxiliary Power Plant Equipment," *Book of Standards*, 05.03ASTM International, West Conshohocken, PA.

[14] Livingstone, G. J., Lubrication Excellence 2003, "Detecting Thermal Failure and Varnish Potential," presented at the *Noria Lubrication Excellence 2003 Conference*, April 2003, Houston, TX.

[15] Wurzbach, R. N., "Learning the Basics – Using Oil Analysis to Manage Chemical and Physical Stability of Lubricants." POA *Coanference Proceedings*, 2000, pp. 140–145.

[16] Möller, H., ELSAM, Zeijseink, A. G. L., and KEMA. "Lubricants for Gas Turbine," *Esslingen Conference Proceedings*, January 1996, pp. 379–382.

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Oxidation Testing of Long-Life Turbine Oil Fluids. Can We Do Better?

ABSTRACT: Four turbine oils formulated with varying types and concentrations of antioxidants were aged via D 943 exposure and examined extensively at 1000, 2000, 5000, and 10 000 h. Acid number, Rotary Pressure Vessel Oxidation Test (RPVOT), High Pressure Differential Scanning Calorimetry (HPDSC)RP, and sludge determinations were made at each time interval. Only a combined evaluation of the test results for the 10 000 h oil samples (a "Total Oxidation Products" approach) gave a reasonable estimation of the true oxidative state of the fluids. One shorter term test, ASTM D 6514, was found to give a fair prediction of the overall quality of the fluids at 10 000 h.

KEYWORDS: oxidation, turbine oils, TOST, RPVOT, HPDSC, acid number, sludge, Total Oxidation Products, Universal Oxidation Test

Introduction

The laboratory screening of today's higher quality turbine oils is stretching the capability of existing turbine oil oxidation test procedures. The ASTM test method for Oxidation Characteristics of Inhibited Mineral Oils (ASTM D 943, also called TOST) was originally developed for assessing the oxidative stability of turbine oils in 1943 [1]. The test is catalyzed/accelerated by the use of iron and copper coils, water, oxygen, and heat (95 °C) to simulate the turbine field environment as well as possible in the laboratory. Field data for a series of four turbine oils was related to TOST lives (time to acid number =2.0). The TOST lives of these oils ranged from about 100 to 2100 h. With today's higher quality additives and base stocks, TOST lives can easily surpass 10 000 h (using a modified sampling routine). However, there is little data available correlating ASTM D 943 (or any other lab test) with field data for these long-life turbine oils. The lifetime of a gas turbine oil can be 3–10 years, while that of a steam turbine can approach 30 years. Further complicating the availability of legitimate field data is the heavy fluid make-up rate, as much as 3–10 % per year for steam turbines and up to 30 % per year for the hotter gas turbines [2]. Makeup may not always be conducted with the original fill oil. Additionally, there may be differences in exposures and operating conditions for different turbines—so the task of generating legitimate field data on a set of long-lived turbine oils is a cumbersome undertaking.

Modern turbines are much larger, steam pressures and temperatures are higher, and turbine oil operating temperatures have increased. The use of cogeneration and combined-cycle units has become common to boost turbine efficiency. Yet the TOST procedure still remains the single most trusted laboratory test utilized by the industry for assessing the oxidative stability of turbine oils. Clearly, today's long-life oils exceed the scope or applicable precision ranges originally developed for TOST (and other laboratory turbine oil oxidation test procedures).

By 1983 it was noted that the TOST end point, time to acid number=2.0 was not a sufficient criteria for evaluating turbine oils. A sister test, the ASTM D 4310 [3] sludge determination, was introduced. The procedure uses the same oxidation cell, catalysts, and test conditions as the ASTM D 943 and measures sludge generated after 1000 h. This test served well for determining sludging tendencies of turbine oils formulated with Group I base oils, but may also be deficient for evaluating newer fluids formulated to be long-life turbine oils.

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In this paper, we examine the utility of the TOST test as well as a variety of other laboratory oxidation test procedures for assessing the oxidative capabilities of a set of long-life turbine oils. An approach for improving the way these tests are utilized is proposed.

Turbine Oil Oxidation Testing

Today's increased global demands for electrical power are being met by the development of bigger and more efficient power plants. These units have, in turn, spurred a growing demand for turbine oils with superior oxidation stability. Such oils can be formulated by increasing the content of Group II or higher quality base stocks [4–8]. When coupled with today's improved additive technology, high quality, long-lived turbine oils can be created. The increased purity of these new base stocks results in a reduced generation of oxidation by-products—increasing the lifetime of the base oil and additives. Turbine oils formulated with Group I base oils can routinely reach 7000 TOST hours, and oils formulated with Group II base oils can last double that and beyond [4].

Oil in turbines will eventually undergo catalyzed oxidation and hydrolysis. To ensure the high quality levels of turbine oils, turbine manufacturers and standards organizations such as the following include a variety of oxidation evaluations in their specifications:

- Alstom
- Asea Brown Boveri
- ASTM
- British Standards
- DIN
- ISO
- JIS
- Mitsubishi
- Ontario Hydro
- Siemens Westinghouse
- Solar Turbines
- General Electric
- US MIL Specifications

The laboratory oxidation tests referenced by these organizations use a variety of techniques to stress and accelerate the evaluations, e.g., addition of solid metallic catalyst, soluble metal catalyst, pressure, heat, water, and oxygen. These are necessary components of oxidation test procedures, required in order to complete laboratory evaluations within a reasonable period of time. However, the more artificial stress utilized, the higher the probability that the oxidation pathway will be altered and correlation with real field experience will be compromised. Among the oxidation tests noted for turbine oil evaluations are the following:

- ASTM Standard D 943-02, "Test Method for Oxidation Characteristics of Inhibited Mineral Oils" (TOST, D 943-02)
- ASTM Standard D 4310-03, "Test Method for Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils" (TOST sludge, D 4310-03)
- ASTM Standard D 2272-02, "Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel" (RPVOT, D 2272-02) [9]
- Modified RPVOT (GEK-32568E)
- ASTM Standard D 2070-91, "Test Method for Thermal Stability of Hydraulic Oils (Cincinnati Machine Thermal Stability," D 2070-91) [10]
- CIGRE (IP 280/89)
- Panel Coker (FTMS 791B 3462)
- Dry TOST at 120 °C (plus periodic RPVOT)
- Universal Oxidation Test (UOT, D 5846-02 and D 6514-03)
- Oxidation Stability of Straight Mineral Oils (IP 306/89)
- ASTM Standard Test Method for Corrosiveness and Oxidative Stability of Hydraulic Oils, Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils (OCS, D 4636-99)

Certain oxidation type tests are recommended for in-service monitoring of used oils:

- Rotary Pressure Vessel Oxidation Test (RPVOT)

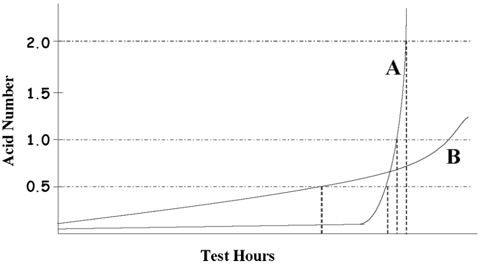

FIG. 1—*Impact of shortening TOST end point.*

- Fourier Transform Infrared (FTIR) (e.g., peak area integration—PIA)
- High Pressure Differential Scanning Calorimetry (HPDSC) (D 6186-98)
- Voltammetry ("RULER," D 6810-02 and D 6971-04)

In fact the scope of RPVOT, ASTM D 2272 [9], clearly states "It is not intended that this method be a substitute for the ASTM Test Method D 943 or be used to compare the service lives of new oils of differing compositions." Rather it is appropriately used "to assess the remaining oxidation test life of in-service oils."

D 943 TOST

Of all the laboratory tests noted, the ASTM D 943 probably comes closest to approximating turbine oil running conditions. The test involves the percolation of oxygen through a sample of oil that contains water and an iron-copper oxidation catalyst at 95 °C. The test continues until the measured acid number reaches 2.0. However, with current long-lived turbine oils, it is also the longest running of the laboratory tests. It is common for formulations to reach 10 000 h with acid numbers still considerably below 2.0.

Several discussions were held in ASTM Working Group 9.C.1 concerning the lowering of the D 943 end point to an acid number increase of 1.0 or 0.5. This would shorten, but not accelerate the test. The impact of such a modification may be seen in Fig. 1. A formulation that degrades by an induction controlled process (Type A) and a formulation that degrades via a steady state process (Type B) are depicted.

For the Type A fluid, very little is gained in terms of test hours by shortening the test to end at an acid number of 1.0 or 0.5. For a Type B fluid, the formulation would be prematurely condemned without justification. There are many long-lived Type B fluids being successfully used in the field. The proposal therefore was never adopted.

There were two undertakings by ASTM Working Group 9.C.3 to accelerate the ASTM D 943 test by using the equipment described in the ASTM Standard Guide ASTM Guide for Universal Oxidation/ Thermal Stability Test Apparatus (ASTM D 4871) [11]. These resulted in ASTM Standards D 5846 [12] and D 6514 [13]. Both use air and are catalyzed by shortened lengths of ASTM D 943 copper/iron coils. The former is run at 135 °C and the latter is run at 155 °C in place of the original ASTM D 943 temperature of 95 °C. As a result, test times are considerably shortened but water may not be used in the tests. Neither of these tests has yet received wide acceptance for evaluating the oxidative stability of turbine oils.

It has been noted that ASTM D 943 oils reaching a longevity of 10 000 h can be very sludgy; oil/water separation can be degraded and the catalyst coils can be corroded despite the low acid number at 10 000 h [5]. The inadequacy of the ASTM D 943 acid number determinations was also pointed out by Stringer and Brown [14]. Acidic oxidation products can rapidly become insoluble and hence will not be detected by acid number determinations.

The newer Group II base oils have better inherent oxidative stability [5–8], but are poorer solvents for degradation products such as sludge [4,15–17]. Stabilizers utilized in turbine oils can "steer" the degradation products from acidic species to sludge. Oils that do not generate much sludge within 1000 ASTM D 4310 hours can generate various and sometimes excessive amounts of sludge if the test time is extended. In the field, severe problems can be encountered by turbines when excessive sludge is generated [14,17].

While the TOST environment remains attractive for oxidation evaluations in that it minimizes unrea-

TABLE 1—*Composition of test formulations.*

Component[a]	A	B	C	D	E
Phenolic AO	0.097	0.097	0.097	0.097	0.097
Corrosion Inhibitor + Metal Deactivator	0.12	0.12	0.12	0.12	0.12
Amine AO-1	0.09	…	0.09	…	…
Amine AO-2	0.12	0.12	…	0.30	…
Amine AO-3	…	0.09	0.12	…	…

[a] Base oil is a 150N Group II.

sonable stress on the lubricant, there clearly are deficiencies in the way the test is currently being used for long-lived turbine oils.

Experimental Design

A series of five turbine oil formulations (Table 1) were assembled in order to make a closer assessment of the value of 10 000 h ASTM D 943 evaluations.

Each formulation contains a fixed amount of phenolic antioxidant, corrosion inhibitor, and metal deactivator. Different amine antioxidant(s) were used to supplement formulations A though D. Formulation E contains no amine antioxidant.

Replicate ASTM D 943 test tubes were set up to run for 1000, 2000, 5000, and 10 000 h. The following determinations were made on the fresh fluids and on the fluids removed from the ASTM D 943 tubes at each time frame:

- Acid number
- Viscosity
- RPVOT value
- HPDSC (isothermal at 180 °C)
- Sludge (as per ASTM D 4310 test protocol)

Additionally, CIGRE (IP 280), UOT (D 6514), and Corrosiveness and Oxidation Stability (D 4636) determinations were made on the fresh (unaged) fluids. All test results represent an average of duplicate determinations and met the precision requirements for their respective procedures.

Results

The results of initial tests on the five formulations indicated a wide spread in oxidative stability among the formulations (Table 2).

At first glance, Formulation D seems to be the most stable of the five formulations with regard to oxidative stability, and Formulation E, without any amine antioxidant, is clearly the weakest. Formulation C would also seem to be on the weak side.

In ASTM D 943 testing, Formulation E only lasted for 3240 h before the acid number exceeded 2.0. All of the remaining formulations ran for the full 10 000 h with very little change in acid number or viscosity. HPDSC and RPVOT results for the formulations after 1000, 2000, 5000, and 10 000 h exposure in the ASTM D 943 apparatus are shown in Figs. 2 and 3, respectively.

The deterioration in oxidative stability of the formulations as measured either by HPDSC or RPVOT is severe—despite the absence of significant acid number or viscosity increase. In fact, if these oils had been in an actual turbine, they would have reached the RPVOT warning values noted in ASTM D 4378 Standard Practice for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines [21] at which one should consider an oil change (e.g.—25 % of the original value) long before 10 000 h is reached. These "lifetimes" are noted in Fig. 3 with an X. In most cases—this level of deterioration is observed within 4000–6000 h. Oil C is anomalous in that it began with a low RPVOT value, lost most of it within the first 1000 h, and then plateaued for the duration of the test.

Figure 4 shows the progression of ASTM D 4310 type sludge formation for the duration of the test program. The amounts of sludge generated at 1000 h are fairly similar and acceptable for all the formulations. However, significant amounts of additional sludge are generated and discrimination between the oils is seen by 5000 h. Furthermore, Oil C, which looked to be the least sludging formulation at 5000 h, gave the largest amount of sludge at 10 000 h.

TABLE 2—*Evaluations of the fresh oils.*

Test/Designation/Units	A	B	C	D	E
Acid number (ASTM D 664)[a]	0.09	0.05	0.06	0.03	0.06
RPVOT, (ASTM D 2272) min[b]	1270	1337	481	2442	113
HPDSC, (ASTM D 6186) min[c]	42.3	73.6	35.5	79.2	6.9
CIGRE (IP 280), TOP	0.36	0.57	0.57	0.27	high
UOT (ASTM D 6514)[d]					
Δ AN	3.4	2.1	1.9	0.07	6.9
Δ % Visc increase	1.66	0.26	19.6	0	94.7
Sludge, mg	6	6	56	80	16
Tube rating	1	1	1	1	1
OCS (ASTM D 4636)[e]					
Δ AN	8.5	5.9	8.4	2.2	16.6
Δ % Visc increase	73.3	46.9	54.9	30.6	325
Sludge, mg	8.6	3.2	2.4	2.6	21.6
Metals attacked	Mg	Mg	none	none	Fe, Al, Mg, Cu

[a] Reference 18.
[b] Reference 9.
[c] Reference 19
[d] Reference 13.
[e] Reference 20.

The condition of the final, 10 000 h aged oil samples is summarized in Table 3.

Clearly there is no relationship between the acid number and viscosity increase alone and the remaining oxidative stability of the aged oils. The only way to obtain a comprehensive and accurate evaluation of the oxidative state of the ASTM D 943 used oil is to combine at least three key test assessments made on the aged fluid:

(1) Acid number

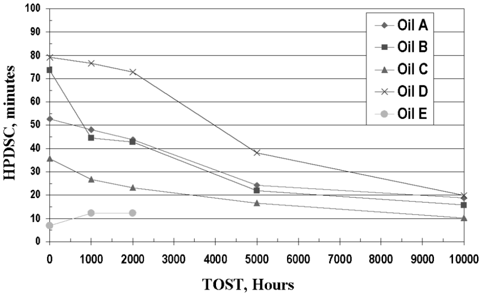

FIG. 2—*HPDSC history of aged oils.*

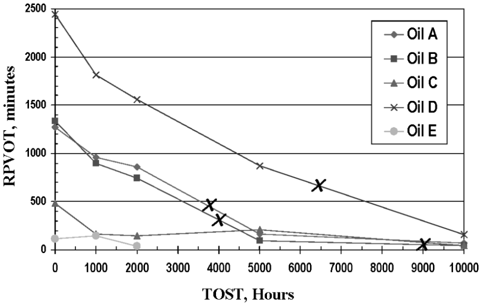

FIG. 3—*RPVOT history of aged oils.*

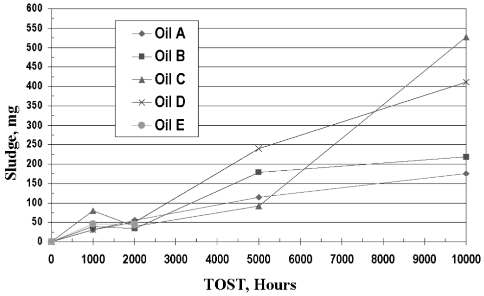

FIG. 4—*Sludge generated by aged oils.*

(2) Sludge

(3) Percent of original capacity lost (e.g., RPVOT, HPDSC, or RULER measurement)

This Total Oxidation Products (TOP) type of evaluation combines several assessments made on the end-of-test oil to estimate its overall oxidative condition. IP 280 and IP 306 combine measurements of volatile acidity, soluble oil acidity, and sludge. Yano et al. [17] measure retained RPVOT and sludge on aged oils. Jayaprakash et al. [22] recommended assessing ASTM D 943 oils run to a fixed time for acid number, viscosity increase, color darkening, acidity of the water layer, insolubles, and dissolved metals.

One may create a formula to combine the parameters being measured for a used oil into a single rating factor, for example,

$$\text{TOP} = x(\text{acid number}) + y(\text{sludge}) + z(\text{percent original oxidative capacity lost})$$

where x, y, and z are weighting factors. Both the time of aging and appropriate weighting factors are best determined by running a series of turbine oils with known field history. For evaluating the formulations tested in this project, we arbitrarily assigned the values, $x=200$, $y=0.5$, and $z=2.0$. By setting the value of x at 200, one prevents the impact of numerically small changes in acid values (typically 0.1–2.0) from being dwarfed by the other test parameters. Sludge values ranged from 20–600 so a weighting factor of 0.5 brings them in line with the magnitudes of the other test TOP values. For determining the percent of original capacity lost we used percent HPDSC value lost. These results ranged from about 20 to 90, so a weighting factor of 2 kept them on a scale with the other tests. Viscosity was not included in the TOP calculation since there were virtually no changes in viscosity for this set of chemistries for the time frames evaluated. It is conceivable that for different chemistries changes in viscosities would be observed. It would then be deemed proper to add a viscosity term to the TOP calculations. It should be stressed that these weighting factors are for illustration only and should not be used for analyzing turbine oil performance. As noted above, a proper selection of weighting should be done via data gathered on oils with known field history. The relative importance of each test's contribution could then be properly incorporated into its weighting factor.

Using the 10 000 h ASTM D 943 data found in Table 3, we calculated the illustrative TOP ratings and rankings for the test oils shown in Table 4.

It is of value to examine the initial oxidation test results conducted on the unaged fluids to see if any of these gave reasonable predictions of the rankings determined at 10 000 h. Using the data noted in Table

TABLE 3—*Evaluation of 10 000 h aged fluids.*

Test/Designation/Units	A	B	C	D	E[a]
Acid number (ASTM D 664)	0.09	0.04	0.33	0.05	⋯
Viscosity Increase, percent at 40 °C	0	0	0	0	⋯
Sludge, mg (ASTM D 4310)	175	219	526	411	⋯
RPVOT, (ASTM D 2272) minutes	68	47	44	156	⋯
percent of original	5.4	3.5	9.1	6.4	⋯
HPDSC, (ASTM D 6186) minutes	18.9	15.9	10.1	19.9	⋯
percent of original	44.7	21.6	28.5	32.4	⋯

[a] Formulation only lasted 3240 h.

TABLE 4—*TOP and rankings for 10 000 h ASTM D 943 test oils.*

	A	B	C	D	E
TOP	216	274	472	351	v. high
Ranking	1	2	4	3	5

2, one can match the rankings of the fluids made by the various test techniques utilized with those obtained for the 10 000 h ASTM D 943 TOP rankings (Table 5). Note that the CIGRE rankings are based on a TOP determination and the UOT rankings are based on an overall assessment of acid number, viscosity increase, sludge, and tube varnish.

The high sludge generated by fluid D in the UOT enabled it to correctly rank it as a poorer performer than fluids A and B. This closely matched the TOP rankings of the 10 000 h ASTM D 943 fluids. All the other tests incorrectly ranked fluid D the best. This suggests that more attention should be paid to the UOT test techniques as screeners for the longer term evaluations.

Conclusions

It is very possible to improve the capability of laboratory tests to assess the oxidative stability of long-lived turbine oils. Better utilization of test methods already in hand can lead to improvements in the significance of the results. The ASTM D 943 TOST apparatus provides the single best laboratory simulation environment for turbine fluids. In assessing today's long-lived turbine oils, misleading conclusions can be drawn from ASTM D 943 testing if they are based solely on acid number evaluations. Furthermore, ASTM D 4310 sludge generation data gathered only at 1000 h is inadequate for such oils. A more comprehensive evaluation of fluids aged in the ASTM D 943 apparatus for 5000–10 000 h can yield information that is more meaningful and worth the lengthy investment in time. The evaluation of the used fluids should consist of a Total Oxidation Products assessment including minimally acid number plus sludge generated plus a measure of lost oxidative capacity. The weighting of each of these parameters needs to be determined by laboratory evaluations of oils with known field performance.

TABLE 5—*Oxidative ranking of project fluids by various techniques.*

	A	B	C	D	E
D 943—TOP	1	2	4	3	5
RPVOT	3	2	4	1	5
HPDSC	3	2	4	1	5
CIGRE	2	3	3	1	5
UOT	2	1	4	3	5
OCS	4	2	3	1	5

ASTM D 6514, which uses the Universal Oxidation Test apparatus, may be used as a quick screener to estimate long term ASTM D 943 TOP performance. An overall assessment of the oil's performance can be obtained by considering together the UOT acid number increase, viscosity increase, and sludge and varnish formation.

References

[1] Dantsizen, C., "Report of Section III on Oxidation of Turbine Oils," *Proceedings ASTM*, 1943, Vol. 43, p. 263.

[2] Thibault, R., "Use Specification Tests to Select Turbine Oils," *Lubrication and Fluid Power*, Vol. 6, No. 2, 2005, pp. 25–31.

[3] ASTM Standard D 4310–03, "Standard Test Method for Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils," *Annual Book of ASTM Standards*, Vol. 5.01, ASTM International, West Conshohocken, PA, 2004.

[4] Kramer, D. C., Lok, B. K., and Krug, R. R., "The Evolution of Base Oil Technology," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM

International, West Conshohocken, PA, 2001.

[5] Swift, S. T., Butler, K. D., and Dewald, W., "Turbine Oil Quality and Field Application Requirements," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM International, West Conshohocken, PA, 2001.

[6] Irvine, D. J., "Performance Advantages of Turbine Oils Formulated with Group II and Group III Basestocks," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM International, West Conshohocken, PA, 2001.

[7] Schwager, B. P., Hardy, B. J., and Aguilar, G. A., "Improved Response of Turbine Oils Based on Group II Hydrocracked Base Oils Compared with Those Based on Solvent Refined Oils," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM International, West Conshohocken, PA, 2001.

[8] Okazaki, M. E., and Militante, S. E., "Performance Advantages of Turbine Oils Formulated with Group II Base Oils," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., ASTM International, West Conshohocken, PA, 2001.

[9] ASTM Standard D 2272–02, "Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel," *Annual Book of Standards*, Vol. 5.01 ASTM International, West Conshohocken, PA, 2004.

[10] ASTM Standard D 2070-91, "Test Method for Thermal Stability of Hydraulic Oils," *Annual Book of Standards*, Vol. 5.01, ASTM International, West Conshohocken, PA, 2004.

[11] ASTM Standard D 4871–00, "Standard Guide for Universal Oxidation/Thermal Stability Test Apparatus," *Annual Book of Standards*, Vol. 5.03, ASTM International, West Conshohocken, PA, 2004.

[12] ASTM Standard D 5846–02, "Standard Test Method for Universal Oxidation Test for Hydraulic and Turbine Oils Using the Universal Oxidation Test Apparatus," *Annual Book of Standards*, Vol. 5.03, ASTM International, West Conshohocken, PA, 2004.

[13] ASTM Standard D 6514–03, "Standard Test Method for High Temperature Universal Oxidation Test for Turbine Oils," *Annual Book of Standards*, Vol. 5.04, ASTM International, West Conshohocken, PA, 2004.

[14] Strigner, P. L., and Brown, K. J., "Some Properties of Canadian Steam Turbine Oils," *Lubr. Eng.*, Vol. 43, No. 4, 1987, pp. 283–289.

[15] Galiano-Roth, A. S., and Page, N. M., "Effect of Hydroprocessing on Lubricant Base Stock Composition and Product Performance," *Lubr. Eng.*, Vol. 50, No. 8, 1994, pp. 659–664.

[16] Barber, A., Butke, B., and Oliveto, C., "The Lubrication of Power Generating Turbines: An Additive Supplier's Perspective," *Tribology and Lubrication Engineering, 14th International Colloquium Tribology*, W. J. Bartz, Ed., 2004, Vol. 3, pp. 1505–1511.

[17] Yano, A., Watanabe, S., Miyazaki, Y., Tsuchiya, M., and Yamamoto, Y., "Study on Sludge Formation during the Oxidation Process of Turbine Oils," *Tribol. Trans.*, Vol. 47, 2004, pp. 111–122.

[18] ASTM Standard D 664–01, "Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration," *Annual Book of Standards*, Vol. 5.01, ASTM International, West Conshohocken, PA, 2004.

[19] ASTM Standard D 6186–98, "Standard Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry," *Annual Book of Standards*, Vol. 5.03, ASTM International, West Conshohocken, PA, 2004.

[20] ASTM Standard D 4636–99, "Standard Test Method for Corrosiveness and Oxidation Stability of Hydraulic Oils, Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils," *Annual Book of Standards*, Vol. 5.02, ASTM International, West Conshohocken, PA, 2004.

[21] ASTM Standard D 4378–03, "Standard Practice for In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines," *Annual Book of Standards*, Vol. 5.02, ASTM International, West Conshohocken, PA, 2004.

[22] Jayaprakash, S. P., Srivastava, S. P., Anand, K. S., and Goel, P. K., "Oxidation Stability of Steam Turbine Oils and Laboratory Methods of Evaluation," *Journal of the American Society of Lubrication Engineers*, Vol. 40, No. 2, 1984, pp. 89–95.

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Varnish Formation in the Gas Turbine Oil Systems

ABSTRACT: The authors have investigated hydraulic and lubricating oil filter elements used in gas turbine systems which had varnish problems. The hydraulic filter elements were completely plugged with varnish and other degradation products at the first layer of the elements but the lubricating oil filter elements were not plugged with such contamination. However, the proofs of spark discharges of static electricity were found on the lubricating oil filter elements. This paper discusses the details of the investigation of the filter elements and one of the root causes of varnish formation in gas turbine oil systems.

KEYWORDS: gas turbine, lubrication, hydraulics, filter, varnish, electrostatic charge

Introduction

Combined cycle power generation has recently become popular under the pressure of environmental protection, because of high-energy efficiency and immediate start-up when it is necessary. In order to raise energy efficiency, the combustion temperature has become higher and higher. It makes bearing temperatures higher and requires efficient bearing cooling. Currently, varnish problems are highlighted on both bearing lubrication systems and hydraulic systems. Deposits on bearings raise bearing temperature. Deposits on the surfaces of control valve pistons and sleeves cause valve sticking and those on last chance filters and pencil filter block oil passages and make valves out of function. ASTM has several important standards about turbine and mineral oil oxidation stability tests like ASTM D 943 (Oxidation of Inhibited Mineral Oil at 95°C), D 2272 (RPVOT at 150°C) and D 5846 (Universal Oxidation Tests at 135°C).

Although all oils that are used for gas turbine systems satisfy these standards, these varnish problems happen very often. Therefore it is important to investigate the other factors to produce varnish. The authors consider that there must be some hot spots in the systems, which locally cause much more severe conditions than these ASTM standards expect. The authors have investigated the hot spots in the gas turbine systems and have confidence that spark discharges of static electricity in filter elements would be one of the important factors to cause oil oxidation. It is because static electricity will be generated when oil passes through mechanical filters on the main stream and on the by-pass lines of lubrication and hydraulic systems [1] and that the spark discharges of static electricity cracked the oil molecules to accelerate oil oxidation [2,3]. The findings of generation of static electricity during filtration and spark discharges of it in filter and oil were not new. Ernsberger reported electrification of oil when oil passed through filter media in 1956 [4]. Goodfellow and Graydon and Leonard and Carhart confirmed in 1968 and in 1970, respectively, that the magnitudes of charging current were dependent on solution conductivity and fluid velocity when oil passed through small orifices or filter media [5,6]. Green confirmed that high electrostatic charge was built up in the hydraulic oil and blue cracking discharges of it were seen when oil passed through filter media [7]. However, these past studies have not been taken into consideration in the designs of hydraulic and lubricating systems of power plants.

This paper reports the results of the examination of used hydraulic and lubrication oil filters from gas turbines in order to investigate the root causes of varnish formation.

Review of the Current Design of Lubricating Oil and Hydraulic Oil Systems

Gas turbines and steam turbines use lubrication oils and hydraulic oils. There are two types of oil systems: One uses the same oil from a common oil tank for lubrication and hydraulic control, and the other

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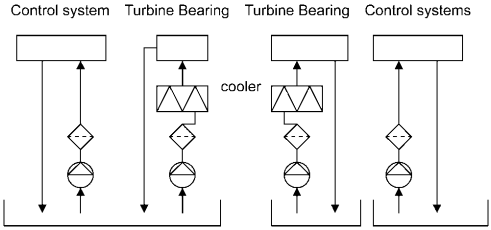

FIG. 1—*Common oil for lubrication. Independent systems of lubrication and hydraulics.*

independent and different oils as shown in Fig. 1. The oil flow velocity of bearing cooling systems is very fast. Some of them are in the range from 2000 L/min to 3900 L/min. On the contrary, the oil flow velocity of hydraulic systems is not so high compared with that of lubricating oil, as the operation of hydraulic control systems is very seldom in the case of gas and steam turbines.

Both lubricating oils and hydraulic oils are required to be very clean, as the rotating speed of turbines is high and the servo control valves are sensitive to contaminants. In order to maintain very clean oils, fine filters are used for the systems.

For the purpose of removing particulate contaminants in oil, the current oil cleaning system with mechanical filters on the main stream of oil are good. But it has been overlooked that filters generate static electricity when oil passes through filter media [1,4–7]. The higher the oil flow velocity, the higher the potential of static electricity [8]. The static electricity will be accumulated on the dielectric materials like filter fibers and oils and will be discharged with sparks [1,7]. As the spark temperature is extremely high, the oil molecules will be cracked to produce free radicals and oil oxidation will be promoted to produce varnish [2]. The varnish deposits on the bearing, a valve spool, and a pencil filter are shown in Figs. 2–4.

The varnish on a bearing causes the rise of bearing temperature. The varnish on valve spools and valve sleeves causes valve sticking. The varnish on the last chance filter prevents oil flow. There is another factor to promote oil oxidation. The current design of the oil circulating systems has an oil cooler after an oil tank, as shown in Fig. 1. This means that the hot oil stays in the oil tank without cooling. It is well known that chemical reaction speed or oil oxidation speed becomes almost twice as high at every 10°C. Therefore, the current design of oil circulating systems has a risk of accelerating oil oxidation, although they have an advantage of easy air releasing with low viscosity.

FIG. 2—*Bearing with varnish.*

FIG. 3—*Valve with varnish.*

Examination of Filters on Gas Turbines

The authors received used filters from a Frame 9 FA gas turbine user and examined them. The maximum oil flow of hydraulic oil was 8 gal/min (18.9 L/min) and that of lubricating oil was 1050 gal/min (3975 L/min) at PQ 1-1 and PQ 1-2, and 750 gal/min (2839 L/min) at PQ 2-1.

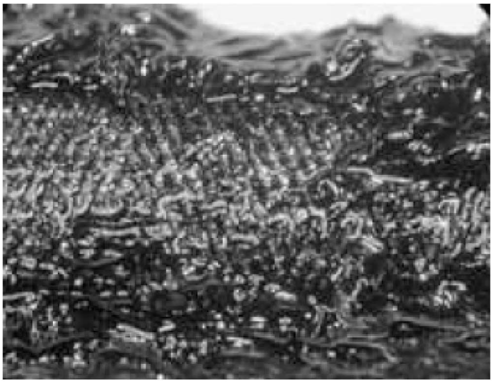

FIG. 4—*Plugged pencil filter.*

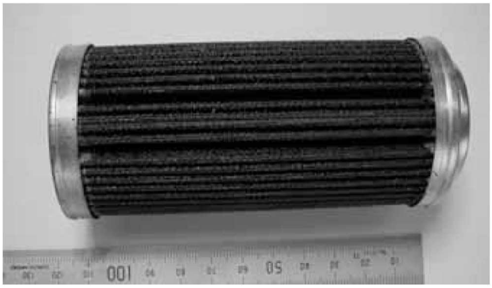

FIG. 5—*General view of last chance filter.*

Filters on the Hydraulic System

The plugging of last chance filters and pencil filters, which prevents oil flow, is one of the problems of gas turbine hydraulics. The general view of the last chance filter is shown in Fig. 5. A last chance filter element was cut and examined. The cut filter element is shown in Fig. 6. The filter element consists of the first layer part, the second layer part, and the metal core part from the outside. The first layer part is composed of (a) metal mesh, (b) glass fiber layers, and (c) a paper layer from the outside. Figure 7 is the close up photo of the outside surface of the first layer part with glass fiber and metal mesh, which is coated with black materials. The first layer part was washed with petroleum ether. The outside surface (glass fiber part: upper photo) and the inside surface (paper part: lower photo) of the first layer part after separating the metal mesh are shown in Fig. 8. The outside surface of the glass fiber layer was black and heavily contaminated. This suggests that the black materials on the glass fiber layer are not soluble in petroleum ether, which is nonpolar. The inside surface of the paper layer (lower photo of Fig. 8) was brown-tinted but

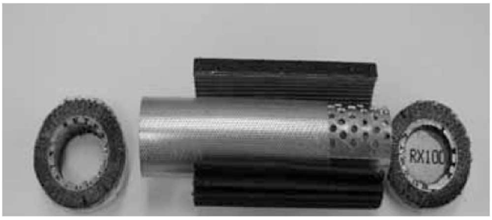

FIG. 6—*Cut view of last chance filter.*

FIG. 7—*Close up photo of the outer face.*

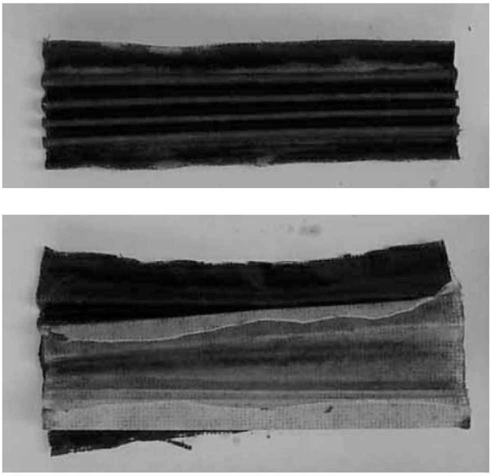

FIG. 8—*The first layer, outside (upper) and inside (lower).*

not contaminated when the paper layer was separated from the glass fiber. The fact that the outside surface of the glass fiber was black and contaminated but that the paper surface was not contaminated indicates that the contaminants were removed by the outside surface of the glass fiber layer. The glass fiber layer was dipped in toluene and almost all black deposits were washed off, as shown in Fig. 9. This shows that the black materials on the glass fiber were soluble in toluene (polar solvent). The toluene soluble fraction was examined by IR spectrum. The chart is shown in Fig. 10. The strong absorption at 1735 cm^{-1} suggests that the toluene soluble fraction was oil oxidation products with carboxylic acid.

The second filter layer is composed of a paper layer and metal mesh from the outside. The outside surface (paper layer) and the inside surface (metal mesh) of the second filter layer were also compared, as shown in Fig. 11. There were almost no black deposits on both the surfaces of the second layer.

The metal core part is composed of (a) a metal tube with fine holes, and (b) the center core with punched holes, as shown in Fig. 12. The surface of the metal tube with fine holes was examined. There were no visible deposits. The surface of the center core with punched holes was also examined. There was a thin layer of deposits. However, there were no traces of spark discharges of static electricity between the filter fiber and the metal.

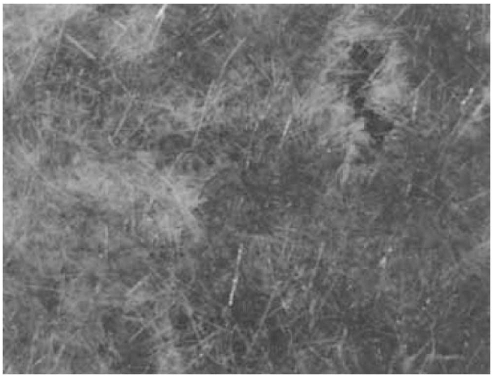

FIG. 9—*The glass fiber layer after washing in toluene.*

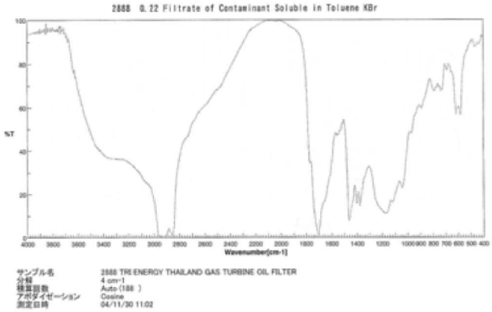

FIG. 10—*IR spectrum of toluene soluble fraction.*

The results of the examination indicate that the contaminants on the last chance filter were produced somewhere outside the hydraulic system and caught by the outer surface of the first layer of the last chance filter.

Filters on the Lubrication System

The filter elements removed from the lubrication oil line were cut and examined. The used filters are shown in Fig. 13 and the internal surface of the filter center core metal is shown in Fig. 14. The outside surfaces of the used filter elements were not contaminated with dirt but the internal surface of the filter

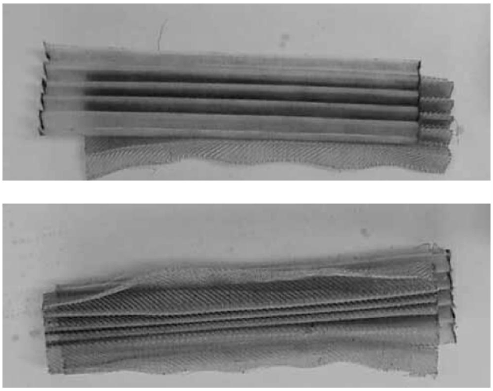

FIG. 11—*The second layer; the layer adjacent to the first layer (upper) and the core side (lower).*

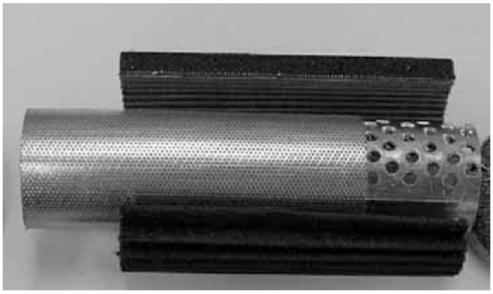

FIG. 12—*The center core pipe of the last chance filter.*

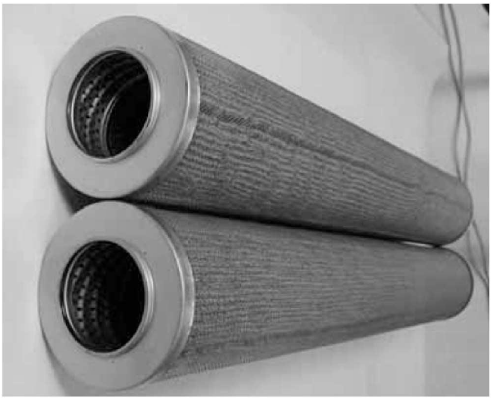

FIG. 13—*Filter elements for lubricating oil.*

center core was coated with brown deposits, as shown in Fig. 14. The deposits were examined by IR spectroscopic analysis and found to be oil oxidation products with sharp absorption at 1735 cm^{-1}. The filter elements were cut and examined. The center core with punched holes had a spiral construction. One spiral line on the center core was high by about 0.5 mm from the surface and coated with brown deposits as shown in Fig. 15. The internal circumference of the filter fiber exactly facing the brown-colored spiral on the metal center core was also brown as shown in Fig. 15. The pleated fiber of the filter element was stretched. The filter fiber was composed of three parts: (a) nylon net, (b) synthetic fiber, and (c) nylon net as shown in Fig. 16. The synthetic fibers of the outside and the inside layers were compared as shown in Fig. 17. The surface of the inside fiber facing the center core metal was black and dirty, but that of the outside fiber was not too dirty. The nylon nets of the inside and the outside were examined. As Fig. 18 shows, there was no damage to the outside nylon net. But the inside nylon net facing the brown-colored spiral of the metal center core was etched sharp like the stumps as shown in Fig. 19. Some droplets like dew were also seen at the root of the stumps. This suggests that the high temperature might have etched the nylon net. One of the candidates to etch the nylon net in the oil may be the spark discharge of static electricity, which can generate high temperature. If so, spark discharges of static electricity may vaporize the nylon net but the oil may quickly cool the vapor. Such being the case, there must be small balls somewhere in the oil. The outside synthetic fiber was statically submerged in petroleum ether to remove oil and in toluene to dissolve oil oxidation products. The prepared synthetic fiber was washed with petroleum ether in an ultrasonic bath. The washed petroleum ether was evaporated in a laboratory dish. The surface of the dried laboratory dish was examined under a microscope and many small balls were

FIG. 14—*The internal surface of the filter center core metal.*

FIG. 15—*The spiral construction of the center core and the contacting line on the internal surface of the fiber part.*

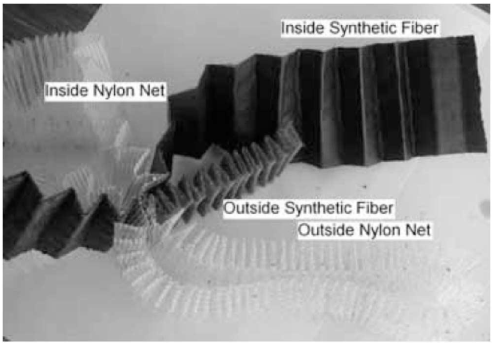

FIG. 16—*Disassembled pleat part.*

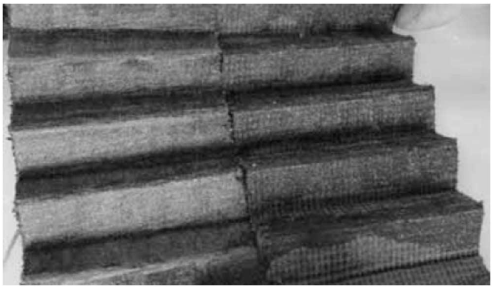

FIG. 17—*Comparison of the outside fiber (left) and the inside fiber (right).*

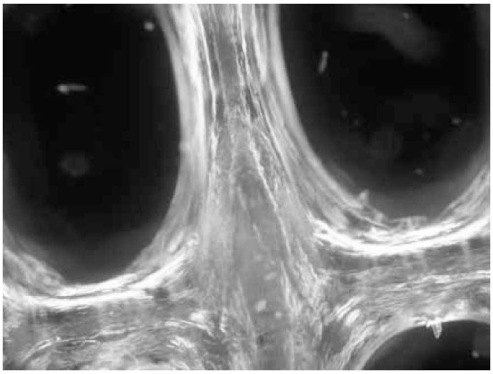

FIG. 18—*Normal nylon net.*

found as shown in Figs. 20 and 21. The user of the gas turbine independently found balls in the contaminants in the oil. These photos suggest that the hypothesis that spark discharges of static electricity damaged the nylon net was correct.

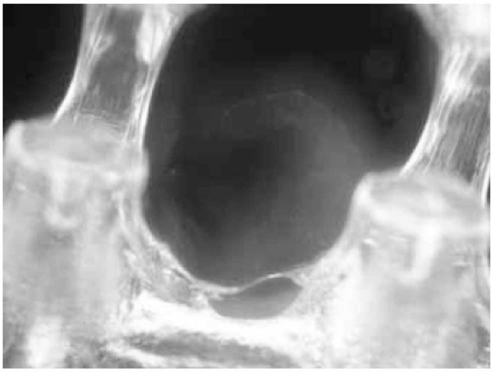

FIG. 19—*Damaged nylon net adjacent to the spiral of the center core.*

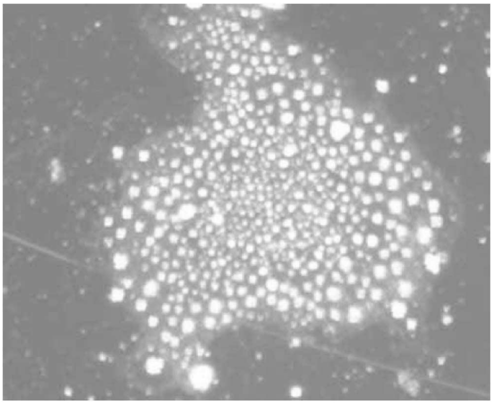

FIG. 20—*An example of collected fine balls.*

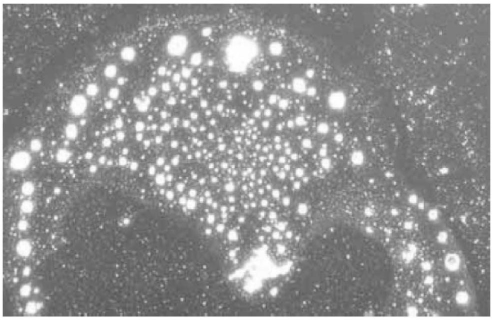

FIG. 21—*Another example of collected fine balls.*

Discussion

The Problem of Spark Discharges of Static Electricity

The combustion temperature of gas turbines has become higher and the bearing temperature has become higher. On the other hand, the oil volume has become less. Therefore, it is inevitable to make the flow of lubricating oil high in order to cool the bearings. The current designs of gas turbines use the lubricating oil for hydraulic systems. As the hydraulic systems use servo valves, which are sensitive to contaminants, fine filter elements are used on the main stream of oil. Because of the high flow of oil, both the filter elements and the oil are electrified. As the synthetic fiber and the oil are dielectric, static electricity will be accumulated on them. The filter housing is connected to the pipe, which is a part of the grounded machine. Therefore, the metallic center core of the filter element can be considered to be a kind of a grounded electrode. The charges of static electricity will be accumulated on the dielectric fiber during filtration, as they cannot move on the dielectric material. The higher the intensity of electrostatic charges on the filter fiber becomes, the more the counter charges will come to the filter center core metal from the ground. When the intensity of the charges exceeds the breakdown strength of the oil between the center core metal and the synthetic fiber, the charge on the metal will rush to the electrostatic charge on the fiber like the return stroke of lightning. It is the reason why the nylon net was etched sharp like the stumps as shown in Fig. 19. As the temperature of spark discharges of static electricity is higher than 10 000°C, oil molecules will easily be cracked to produce free radicals to lead chain reactions of oil oxidation as shown below [2].

Initiation of Oil Oxidation:

$$\mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{H}\cdot \tag{1}$$

Chain Reaction:

$$\mathrm{R}\cdot + \mathrm{O_2} \rightarrow \mathrm{ROO}\cdot \tag{2}$$

$$\mathrm{ROO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}\cdot \tag{3}$$

where

RH = representing hydrocarbon
R = representing free radical
H = representing cracked gas including low molecular weight hydrocarbon gases
ROO = Peroxi-radical

These equations suggest that oil oxidation must be discussed at two stages: one is the "initiation" stage and the other is the "chain reaction" stage.

When the authors made experiments of spark discharges of static electricity during filtration as shown in Fig. 22 [1], each spark discharge of static electricity generated an average of two pieces of gas bubbles in the oil. The diameter of each gas bubble was about 1 mm. Then the volume of the bubble is about

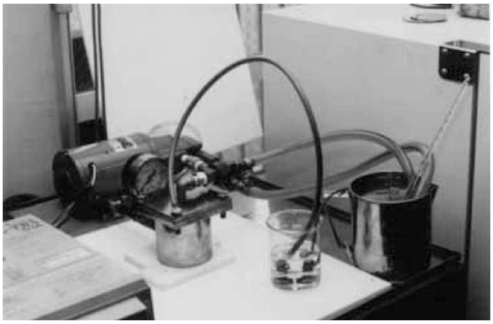

FIG. 22—*Filter spark discharge test apparatus.*

0.5 mm^3. In accordance with Avogadro number, the number of the gas molecules can be calculated to be 1.4×10^{16}. Equation 1 suggests that the number of free radicals is almost the same as that of gas molecules.

The authors made another experiment. They divided the same oil into two groups and prepared them for comparison tests. One of them was heated at 80°C for six months and the other was filtered at room temperature for 30 days. These oil samples were kept at room temperature for 24 h to cool to room temperature and were put in plastic bottles, respectively. The plastic bottles with 150 mL oil each were turned upside down and kept at room temperature in the dark for four months. The plastic bottle with the filtered oil was found deformed, although the one with heated oil remained unchanged as shown in Fig. 23 [2]. The finding suggests that the filtered oil consumed more oxygen than the heated one and that the filtered oil had more free radicals to react with oxygen than the heated one. This means that spark discharges of static electricity are more active to crack oil molecules than ordinary heating and that the filtered oil oxidizes faster than the heated one, as filtration generates more free radicals than 80°C heating. Therefore, spark discharges of static electricity have a strong influence on oil oxidation.

Summary and Conclusion

1. ASTM has good standards to examine oil oxidation stability but the oils that satisfy the ASTM standards have varnish problems.

FIG. 23—*Comparison of a plastic bottle with oil heated at 80°C for six months (left) and the one with oil filtered for 30 days.*

2. The authors consider that there are overlooked factors like “hot spots” to produce varnish in the gas turbine systems.
3. The authors investigated the last chance filter elements of hydraulic systems and the filter elements of lubricating systems of gas turbines and found the proofs of spark discharges in the lubricating oil filter, through which oil passes through at high velocity.
4. The authors verified that filtration generates static electricity and that the oil which was filtered for 30 days at room temperature oxidized faster than the heated oil at 80°C for six months.

References

[1] Sasaki, A., Uchiyama, S., and Takashi, Y., “Generation of Static Electricity During Filtration,” *Lubr. Eng.*, Vol. 55, No. 9, 1999, p. 14.

[2] Sasaki, A., Uchiyama, S., and Takashi, Y., “Free Radicals and Oil Auto-Oxidation Due to Spark Discharges of Static Electricity,” *Lubr. Eng.*, Vol. 55, No. 9, 1999, p. 24.

[3] Sasaki, A., “Contaminants in the Used Oils,” *Special Issue on Contamination in Tribology of J. Eng. Tribology*, Proceedings of the IMechE PART J, Vol. 220, No. J5, August 2006, pp. 471–478.

[4] Ernsberger, F. M., “Mechanism of Frictional Electrification of Dielectric Liquids,” *J. Appl. Phys.*, Vol. 27, 1956, pp. 418–419.

[5] Goodfellow, H. D. and Graydon, W. F., “Electric Charging Current for Different Fluids Systems,” *Chem. Eng. Sci.*, Vol. 23, 1968, pp. 1267–1281.

[6] Leonard, J. T. and Carhart, H. W., “Effect of Conductivity on Charge Generation in Hydrocarbon Fuels Flowing through Fiber Glass Filters,” *J. Colloid Interface Sci.*, Vol. 32, No. 3, 1970, pp. 383–394.

[7] Green, W. L., “Electrostatics and Hydraulic Oils,” *J. Electrost.*, Vol. 1, 1975, pp. 95–96.

[8] Sasaki, A., “Electrical Phenomena at the Interface of Solid and Oil,” *J. Japan. Soc. of Tribologists*, Vol. 49, No. 1, 2004, pp. 30–35.

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