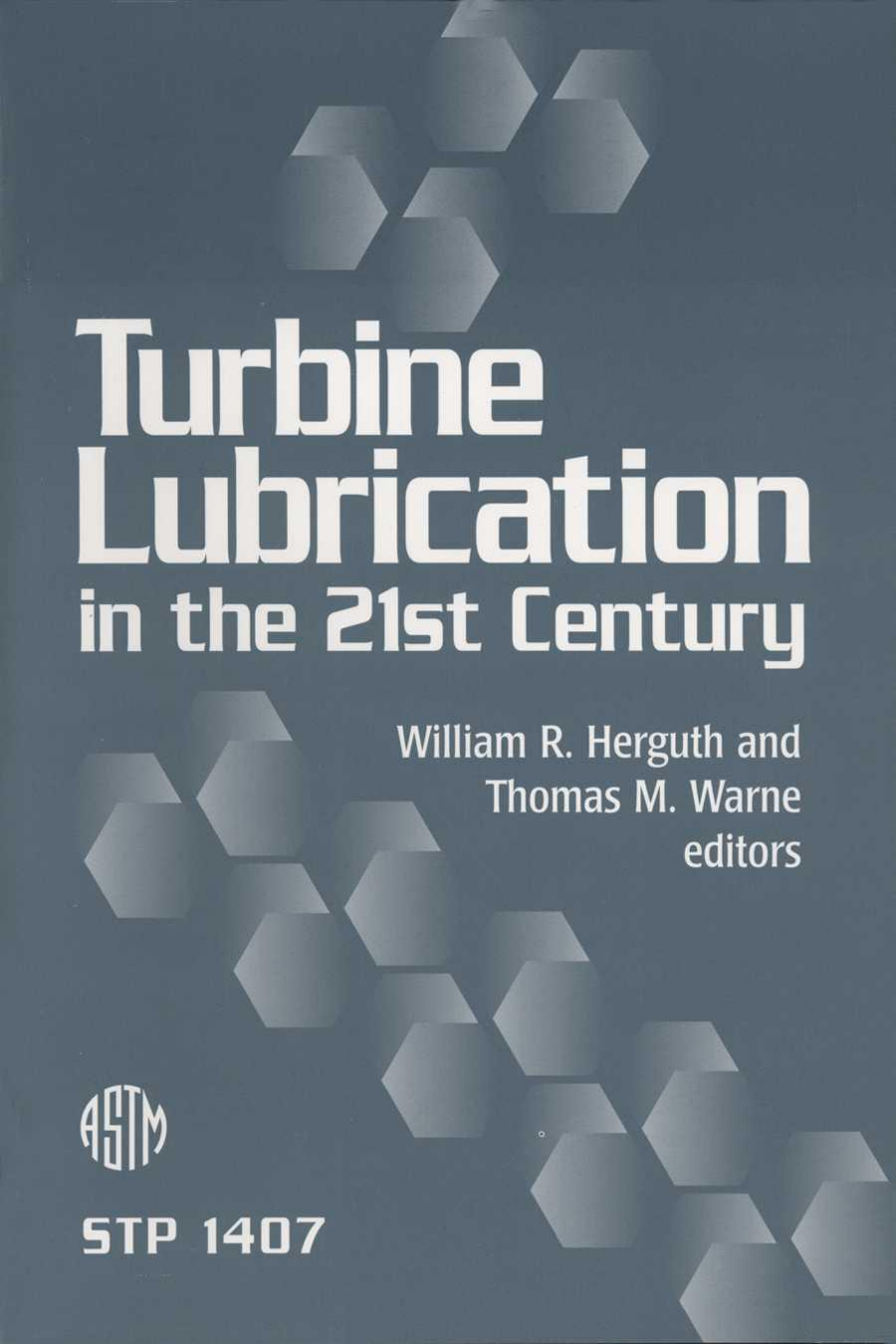

Turbine Lubrication in the 21st Century

William R. Herguth and
Thomas M. Warne
editors

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Foreword

This publication, *Turbine Lubrication in the 21st Century,* contains papers presented at the symposium of the same name held in Seattle, Washington, on June 26, 2000. The symposium was sponsored by ASTM Committee D-2 on Petroleum Products and Lubricants and its Subcommittee D02.C0 on Turbine Oils. The symposium chairman was William R. Herguth, Herguth Laboratories, Inc., Vallejo, California. The symposium co-chairman was Thomas M. Warne, Chevron Global Lubricants, Richmond, California.

Contents

Overview

This publication summarizes the presentations delivered at the "Symposium on Turbine Lubrication in the 21st Century," held in Seattle, Washington on June 26, 2000. The symposium was sponsored by ASTM Committee D-2 on Petroleum Products and Lubricants and its Subcommittee D02.C0 on Turbine Oils.

In the final years of the 20th Century, the lubrication requirements of turbines used for power generation increased significantly. In response, two trends emerged. One was the production of more stable lubricants; the second was the development of improved techniques for monitoring the condition and suitability for use of turbine lubricants.

For some applications, users have turned to synthetic, non-hydrocarbon fluids, such as polycarboxylic acid esters and phosphate esters. Two of the presentations describe current and future directions for some of these fluids. Phillips describes current and future applications of Fire-Resistant Turbine Lubricants, with particular emphasis on European actions to improve the safety of turbine operation. Gschwender, Snyder, Nelson, Carswell, Fultz and Saba address the special case of aircraft turbine engine lubrication and the evolution of new military specifications for Advanced High-Temperature Turbine Engine Oils.

Conventional mineral oil lubricants, produced by solvent extraction and dewaxing of heavy petroleum fractions, still constitute the largest volume of turbine lubricants. However, as we enter the 21st century, petroleum refiners have developed new processing methods; these lead to more stable hydrocarbon fluids which show great promise for the production of more stable turbine oils. One route to these hydrocarbon base fluids is through the oligomerization of olefins; the second involves the catalytic hydrocracking and isomerization of petroleum fractions. Kramer summarizes the history and current state of the Evolution of Base Oil Technology.

The use of such highly paraffinic, low heterocycle hydrocarbon base stocks can lead to steam and gas turbine lubricants with significantly improved oxidation resistance and better thermal stability. Three papers from different lubricant suppliers address some of these performance advantages these formulators have discovered using new technology base oil. Irvine discusses the Performance Advantages of Turbine Oils Formulated with Group II and Group III Basestocks; Schwager and Hardy address the Improved Response of Turbine Oils Based on Group II Hydrocracked Base Oils, while Okazaki covers the Performance Advantages of Turbine Oils Formulated with Group II Base Oils.

Regardless of the stability of lubricating fluids, successful use requires that the lubricant be regularly monitored to ensure continued suitability for use. Swift, Butler, and Dewald present new information on Turbine Oil Quality and Field Application Requirements. Kauffman and Ameye describe the use of a new instrument for oil analysis, in Antioxidant Analysis for Monitoring the Remaining Useful Life of Turbine Fluids.

This publication would not have been possible without the contributions of time, knowledge, and enthusiasm from our authors; the willingness of their employers to support this effort; the reviewers who read the papers and offered suggestions for improvement; and the ASTM personnel who provided editorial assistance and a firm hand to keep us on schedule. The co-Chairs wish to thank all who made this Symposium a success.

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W. David Phillips[1]

The Use of a Fire-Resistant Turbine Lubricant: Europe Looks to the Future

Reference: Phillips, W. D., "**The Use of a Fire-Resistant Turbine Lubricant: Europe Looks to the Future,**" *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W. R. Herguth and T. M. Warne, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: Turbine oil fires continue to cause concern. Although not frequent occurrences, a serious fire can have an enormous financial impact. To reduce the risk of hydraulic oil fires in steam turbines, phosphate esters are now widely used, but large volumes of inflammable mineral oil remain in the lubrication system. In order to decrease the fire risk still further, phosphates have also been used in both steam and gas turbines as fire-resistant lubricants. This paper reviews the need for these products and the experience in both trials and commercial operation. It examines the reasons for their slow adoption by industry but also why current market pressures, particularly in Europe, are likely to accelerate their use.

Keywords: safety, fire-resistant turbine lubricants, turbine fires, fire protection, phosphate esters, steam turbines, gas turbines, fluid conditioning, life-cycle costs

Introduction

In 1944, at a meeting of the Machines Technical Committee of the German Power Station Association, a report was made on the operation of a 6 MW steam turbine with a new fire-resistant lubricant based on tricresyl phosphate. After 6000 hours the experience was regarded as totally satisfactory [*1*]. This is the first known use of a phosphate ester-based turbine lubricant. The objective then, as it remains today, was to find a way of overcoming the main disadvantage associated with mineral turbine oils, namely their inflammability, and to avoid the occurrence of turbine oil fires with their impact on operator safety; the often huge cost of repairs and reduced availability of equipment.

In the intervening period much work has taken place to demonstrate the technical feasibility of using fire-resistant turbine lubricants based on aryl phosphate ester fluids as

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alternatives to mineral oils. Not only have trials in both steam and gas turbines taken place but substantial commercial use has arisen in certain market segments. Their favorable impact on safety has also been confirmed during this period following widespread use as turbine control fluids-particularly in large steam turbines of 250-1500 MW where steam temperatures have risen close to 600 °C.

This paper summarizes the latest position with regard to the remaining "trials" on these fluids; their current commercial use and, particularly in Germany, the factors which are resulting in their promotion by some large utilities, their trade association and by the insurance industry.

Turbine Fires

To many people in the power generation industry, the idea that turbo-generator fires are a concern comes as a surprise! Some utilities, in fact, would go as far as to suggest that fires are unknown in their stations. It is true that large fires are not a frequent occurrence. On closer investigation, however, the situation may be somewhat different as fires can go unreported if they are quickly extinguished and cause neither an unscheduled outage nor casualties. Obviously a severe fire is not good publicity and can shake shareholder confidence but even small fires are important as they can be symptomatic of a greater problem which could eventually lead to a more serious incident. In examining the limited statistics available we should therefore be aware that they may not truly represent the extent of the problem.

Unfortunately few detailed investigations into the origins and frequency of turbine fires have been undertaken. The most rigorous was published in 1983 as an Electric Power Research Institute (EPRI) report entitled "Turbine Generator Fire Protection by Sprinkler System" [*2*]. This was based on 151 responses of 210 U.S. utilities and related to 1181 turbines (principally steam turbines) of >60 MW output. Between 1930 and 1983 some 175 fires were reported of which 121 involved oil either as a primary or secondary source of ignition. Six of these fires involved nuclear units. The study also revealed that in the early 1980s only 285 turbines (24%) of those surveyed had any form of fire protection around the bearings while 350 (30%) had some form of protection on the oil piping. Recent discussions with the author of this report and other authorities in the USA suggest that, while fire protection has improved, there are still many units which are unprotected.

The frequency of turbine fires in the EPRI report appeared to increase from about 1 in 200 unit years in the 1950s through 1 in 145 unit years in the 1960s to about 1 in 100 unit years in the 1970s. (These are probably conservative estimates.) The increase in frequency is thought to be due mainly to better reporting but could also be the result of, for example, higher steam temperatures. These figures are also to be considered against the increasing use of fire-resistant control fluids which were introduced in the mid-1950s. Unfortunately there does not appear to be any published data for the 80s and 90s which would confirm, or otherwise, this trend.

Apart from the above study little detailed data on turbine fires appears publicly available. Some reports are published by the insurance industry, for example the brokers Marsh and McLennan have issued periodic reports [*3*]. While the utility industry normally avoids publicizing information on fires, in Europe the large German-based utility association (the Technische Vereinigung der Grosskraftwerksbetreiber-VGB) maintains a list of major fires. This currently identifies 78 that have taken place, mainly in the USA and Europe, since 1972 [*4*]. In the former Soviet Union about 140 incidents took place between 1980 and 1986 [*5*] and this was after many units had already converted to fire-resistant control fluids!

The costs of turbine fires can, in severe cases, be enormous. One publication [*6*] reported on the costs of twenty large fires occurring between 1982 and 1991 where the total property damage was $417 million–an average of $22.7 million per incident. These figures did not take outage costs into consideration which could be up to double the repair costs. The average outage period in the cases cited was 200 days. Although these figures are for the worst incidents, a risk-benefit analysis undertaken for the EPRI report [*4*] indicated that in 1983 dollars the potential cost to the utility of operating a turbo-generator unit without fire protection for 30 years would be $1.62 million and $0.87 million for a 600 MW and 900 MW turbo-generator respectively. Today these figures would be closer to $6 million and $3 million (or $200 000 and $100 000/year). In the UK, two 500 MW sets have been extensively damaged as a result of turbine oil fires in the last four years.

While repair costs can normally be covered by insurance, outage or business interruption costs, particularly during the commissioning of new equipment when the fire risk is probably at its highest, may not necessarily be insured. Large utilities also tend to carry their own insurance and to be able to rely on excess capacity in times of need, a situation that is changing with privatisation. Even when insurance is available, one of the results of a fire can be a substantial increase in premiums as the insurance companies attempt to recover their losses. Significant inconvenience in the post-fire period can also be expected as alternative power supplies are sourced and the site is cleared.

Clearly, in view of the danger to life and the high financial cost, adequate fire protection should be a priority for the utility and for many years sprinkler systems have been used with steam turbines and gas inerting systems with combustion turbines. These are both forms of "active" fire protection where the fire is extinguished after ignition and can be expensive to install and maintain. The cost of mechanical fire protection for a large steam turbine, for example, would be in the region of $40 000-100 000.

Although they are effective when correctly installed and maintained there are occasions when availability can be impaired e.g. as a result of incomplete maintenance [*7*]. The possibility of false alarms may be low but they are reported [*8*]. Lightening, for example, is known to have activated detection systems and resulted in the unscheduled shutdown of gas turbines with considerable damage to the bearings. As a result there may be a reluctance to operate these systems automatically; indeed in some stations a visual observation of a fire is relied on more than automatic means. Even the best "active" systems are, however, of little use in the event of a catastrophic failure of the turbine with the expulsion of blades through the turbine casing when both oil and water lines in the vicinity of the turbine can be destroyed.

Fire protection techniques that eliminate the possibility of fire are clearly to be preferred. An example of a "passive" protection measure would be the use of guarded piping but this is expensive.

Fire-Resistant Lubricants

An alternative approach has been to consider the use of fire-resistant lubricants. Such products offer:

- built-in protection
- protection throughout the whole of the lubrication system
- protection which is available 100% of the time the fluid is in the system and which does not deteriorate with time.

Several types of synthetic turbine oil have been considered in the past. Due to the necessity for operation at high temperatures and high bearing loads the focus has been on non-aqueous fluids. Initially polychlorinated biphenyls were evaluated but, while they possessed excellent fire resistance, lubrication problems were found when used alone [9]. To overcome this deficit they were blended with triaryl phosphates and successfully tested. However, when pcbs were banned in the 1970s for toxicity and environmental reasons, the subsequent development concentrated on phosphate esters. The fact that they were already widely used in turbine control systems was an obvious advantage as it meant that the same fluid could possibly be used for both systems.

Synthetic carboxylate esters from trimethylolpropane or pentaerythritol and short chain acids (C_{5-9}) are used as low viscosity base-stocks for aviation gas turbine oils, while higher viscosity esters from trimethylolpropane and C_{18} unsaturated acids are occasionally used in turbine control systems. However, this type of product does not possess the same level of fire resistance as the phosphate esters (see Table 1) and where it has been used in the hydraulic systems of large steam turbines, fires have resulted. Consequently, to date, this type of fluid has not been considered as a fire-resistant turbine lubricant.

The main advantage of triaryl phosphate esters is undoubtedly their fire-resistance. For example they have autoignition temperatures in the region of 550-590 °C and possess inherent self-extinguishing properties. This means that if, under severe conditions, they do ignite the flame does not propagate once the fluid has moved away from the source of ignition. Additionally these fluids possess excellent lubricating characteristics, demonstrated by their wide use as anti-wear additives for improving the lubricating properties of both mineral and synthetic oils. A summary of their fire resistance properties in comparison with mineral oils and carboxylate esters is given in Table 1.

Although the phosphate esters have some characteristics in common with mineral oils (see Table 2), there are aspects of their performance that are quite different. These include:

- viscosity/temperature characteristics where phosphates normally have much lower viscosity indices. This difference requires that tank heating be available in order to ensure that the viscosity is low enough for pumping on start-up. This aspect of design is, however, fairly common in conventional systems.
- density. Phosphates have values ~30% higher than mineral oil possibly necessitating more powerful pumps and a higher static head to avoid cavitation.
- hydrolysis of the phosphate. This is a chemical reaction of water with the phosphate which results in the production of acidic degradation products. If not controlled this reaction can have an adverse impact on fluid life as the acid produced has an auto-catalytic effect on fluid breakdown as well as promoting corrosion at high levels. In

order to overcome this disadvantage the fluid is normally conditioned by circulating through an adsorbent media on a by-pass system (see below)

Table 1-*A Comparison of the Fire-Resistance Properties of an ISO VG 46 Mineral Turbine Oil and Triaryl Phosphate Ester and an ISO VG 68 Carboxylate Ester*

Property	Test Method	Mineral Oil	Polyol Ester	Phosphate Ester
Flash point-Open Cup (°C)	ISO 2592	220	266	270
Fire point (°C)	ISO 2592	245	313	365
Auto-ignition temperature (°C)	ASTM D2155	340	430	575
Hot manifold ignition (°C)	AMS 3150C	350	395	>800
Wick ignition	ISO 14935	Fail	Fail	Pass
Factory Mutual Spray test	FM Std. 6930			
-Persistence of burning		Fail	Pass	Pass
-Spray Flammability Parameter		Group 3	Group 2	Group 1
Persistence of burning	ISO 15029-1	Fail	Pass	Pass
Ignitability Index	ISO 15029-2	Group H (worst)	Group G	Group D
Compression ignition test	MIL-PERF-19457D			
-ignition ratio		10	18	>42

- incompatibility with conventional paints and seals. Fortunately a range of suitable seals are now available, in particular fluorocarbon elastomers which are increasingly used in turbine applications. The interior surfaces of systems for use with phosphates are preferably left unpainted as rusting is not normally a problem. However, the industry trend is towards the use of stainless steel which would obviate the need for coatings.

In the same way that mineral oils can vary in their chemical composition and performance, so phosphate esters can also vary depending on the raw materials from which they are produced. There are three basic types of product used in turbine applications, trixylyl phosphate, isopropylatedphenyl phosphate and tertiarybutylphenyl phosphate ester. A comparison of the main properties which are structurally influenced is given in Table 3 and the stability properties are seen to vary significantly. As a result TXP-based products are preferred for applications where water contamination is likely to be a concern, while for applications where high temperature stress is unavoidable, for example in gas turbines, the tertiarybutylphenyl phosphates may be preferred

The differences in properties in comparison with mineral oils require that systems be designed for use with phosphates. It is unfortunately not normally possible to convert a system from mineral oil to phosphate by draining the oil and refilling with the new fluid, due mainly to compatibility aspects, and system modifications may also be needed e.g. to the pump train as a result of the higher fluid density. Contact with the turbine builder is necessary to determine what equipment modifications are required.

Table 2-*A Comparison of Some Typical Properties of an ISO VG 46 Mineral Turbine Oil and Phosphate Ester*

Property	Mineral Oil	Triaryl Phosphate
Viscosity at 100 °C (cSt)	6.7	5.0
at 40 °C	46	43
at 0 °C	450	1700
Pour Point (°C)	-9	-20
Acid number (mgKOH/g)	0.15	0.05
Specific Gravity at 20 °C	0.870	1.135
Air release (min)	3	1
Foaming tendency /stability-24 °C (ml)	250/0	30/0
Water content (%)	0.001	0.06
Rust prevention (distilled water)	Pass	Fail
Specific heat at 20 °C (J/gK)	1.76	1.69
Thermal conductivity (W/mK)	0.134	0.132

Fire-Resistant Turbine Control Fluids

Following a number of turbine fires in the early 1950s, the concept of a split hydraulic and lubricating oil system with the use of a fire-resistant hydraulic fluid in the control system, was introduced. This move was based on the assumption, since shown to be erroneous, that the great majority of turbine fires originate from the hydraulic system as a consequence of the high hydraulic pressures and the proximity of high temperature steam pipes. In fact the statistics show that there is little difference between the hydraulic and lube oil systems as sources of fires-at least in steam turbines [*4,10*].

The earliest fluids used were blends of polychlorinated biphenyls (pcbs) and phosphates. The latter were added to reduce the viscosity and density of the pcbs without significantly adversely affecting their fire resistance. The use of pcbs was, however, quickly discontinued in view of valve erosion problems as well as toxicity and environmental concerns. Since the early 1970s, phosphate esters have been the only fire-resistant fluids approved by the turbine builders for this application although small amounts of more flammable carboxylate or synthetic esters have been used in refurbished systems. It is thought that there are over 1000 large steam turbines (>250 MW output) currently in operation worldwide with fire-resistant hydraulic fluids based on phosphate esters and the use of these fluids has largely eliminated the risk of fire arising from ignition of the hydraulic fluid.

Experience with Fire-Resistant Lubricants

a) *Steam Turbines*

As suggested earlier, while the use of a fire-resistant hydraulic fluid is effective in reducing the fire hazard associated with the control system, the risk of fire associated with the mineral turbine oil remains. Large volumes of oil, possibly up to 100 m^3 in the very largest sets, remain in the bearing lubrication system. Of particular concern in this respect is the common use of shaft-driven oil pumps which can continue to feed a fire with oil as long as the shaft is turning. A leak of fire-resistant lubricant obviously does not pose the same threat.

Table 3-*The Effect of Chemical Type on the Performance of Phosphate Esters*

Chemical Type	Autoignition Temperature (°C)	Air Release (mins)	Hydrolytic Stability	Oxidative Stability
Isopropylphenyl	540	5	Moderate	Moderate
Tertbutylphenyl	580	5	Poor-Moderate	Excellent
Xylyl	570-590	1	Good-Very good	Good

The very earliest use of a fire-resistant lubricant appears to have occurred during the 1930s when pcbs were investigated [*9*] as a result of a series of fires. Although some satisfactory operating experience was obtained, interest lapsed and nothing further was done until the 1950s when a further series of fires "sparked" a revival of interest. The topic was then taken up by some U.S. utilities and also in the late 1960s by General Electric who converted a 12.5 MW set at their Medium Steam Turbine Division. Over a decade of valuable operating experience was obtained with phosphate esters in this industrial set which, after initial teething problems ran very successfully [*11*]. Subsequently, in Western Europe, several trials were also carried out in the UK, Germany and France [*12*]. In the earliest of these dating from 1974, the Technical University of Munich began to test a phosphate ester in a small steam turbine of 1.5 MW and this was followed in 1979 by the conversion of another unit of 5.5 MW [*13*]. The larger of these units is still in operation today and has operated on two charges of fluid in this time period.

In 1982 in Basel, a 10 MW back-pressure turbine was converted from mineral oil to phosphate after experiencing foaming and deposition problems. In this unit the new fluid was used not only for the turbine control and lubrication systems but also for the gears, the jacking system, and the air-cooled generator. Today, after about 60000 hours of operation involving frequent starts which place increased stress on the fluid, the turbine continues to operate on the same fluid charge filled into the unit in 1982. The quality of the fluid is still as good as new and it is only necessary to replace the conditioning medium used to remove fluid degradation products, annually. Table 4 shows some of the analytical data obtained over the period of service to date. Examinations of bearings and reduction gear have not revealed any significant wear and the occasional severe water contamination has not caused any unscheduled shutdown or significant change to the fluid properties. More details on this experience are available in the relevant references [*12,14*].

A very serious incident during operation was avoided as a result of using the fire-resistant lubricant. A boiler failure occurred which led to a loss of steam pressure. Unfortunately, the circuit breaker which should have automatically isolated the generator, failed to trip. The generator therefore now operated as an "engine", motoring the turbine. It was not immediately possible to switch-off the power remotely because of the impact this would have on the rest of the manufacturing site. This resulted in the turbine overheating and the heat generated at the blade tips began to produce local welding with subsequent jamming of the blades in the housing. At this stage the generator was consuming about 3 MW of power! Eventually it was possible to open the switch but the damage cost about 1 million SFr to repair. Outage costs were about 0.5million SFr and the equipment was out of operation for about 1 year. Although fluid escaped from the lubricant system there was no fire and when the unit was eventually returned to use, the same fluid charge was re-installed.

Table 4-*Analytical Data on a Phosphate Ester Used for the Lubrication of a 10MW Steam Turbine*

Property	Units	0 hrs 4/83	3000 hrs	14000 hrs	26000 hrs	40000 hrs	55000 hrs 5/99
Viscosity	cSt	42.7	42.7	41.6	42.4	43.5	43.4
Acid Number	mgKOH/g	0.02	0.05	0.02	0.02	0.01	0.03
Water Content	%	0.05	0.08	0.16	0.11	0.05	0.07
Air release Value	min	2	1	1	1	1	1
Foaming	ml	190/0	240/0	280/0	210/0	370/0	400/0
Cleanliness	SAE Class	4	0	1	0	0	1

While the tests in Europe and the USA focussed on small industrial sets it was in the FSU that the most significant developments took place. Following trials in a 16.5 MW industrial unit in 1959, a 300 MW set (including the generator) belonging to the All Russia Thermal Engineering Institute in Moscow was converted to use phosphate ester and a trial started in the early 1970s [*15*]. The operating experience obtained led directly to the first commercial use of phosphate esters in large steam turbines with the conversion of a 220 MW nuclear unit at Kolskaya in 1982.

Today, the same operating charge is still in use and the turbine continues to function satisfactorily. This has been achieved without any off-line conditioning which is common in Western control and lubrication system design when using phosphate esters. This is a result of the improved hydrolytic stability of the phosphate developed by the All Russia Thermal Engineering Institute [*5*]. Since 1982 other large steam turbines of up to 1000 MW have been converted or operated from new [*16*]. Table 5 indicates those units currently in operation. Although it was originally planned to convert all the existing 220/800 MW sets to phosphate, capital limitations have forced the postponement of this programme. Most of the units to date have continued to use mineral oil for the generator bearings in view of incompatibility with the insulants used in the hydrogen-cooled units, but the latest generator designs also use phosphates for bearing lubrication.

Outside the FSU, interest in the lubrication of large steam turbines was limited to detailed studies by EPRI in 1983 of the feasibility of adapting a large steam turbine [*17*]. It was concluded that such a conversion was possible and that phosphate esters would be suitable but that the modifications would be expensive. A further review of the existing experience with fire-resistant lubricants by EPRI some six years later [*18*] also concluded that phosphate esters could safely be used to lubricate small–medium sized units with the knowledge then available.

Table 5-*Use of a Fire-Resistant Lubricant in Turbines of the CIS*

Power Station	Type	Output (MW)	Date Installed	Conversion to Phosphate	Operating hours on Phosphate
Kola Unit 1	Nuclear	220	1982	1983	110000
Zaporojie Unit 6	Thermal	800	1977	1985	77500
Zaporojie Unit 5	Thermal	800	1975	1992	61000
Perm Unit 1	Thermal	800	1986	1986	95200
Perm Unit 2	Thermal	800	1987	1987	86350
Perm Unit 3	Thermal	800	1990	1990	68200
Perm Unit 4	Thermal	800	1994	1994	42500
Rovny Unit 5	Nuclear	1000	1986	1986	95100
Khmelnitsk Unit 1	Nuclear	1000	1987	1987	86450
Yuzhno-Ukraine Unit 3	Nuclear	1000	1989	1909	70500

b) Gas Turbines

Although the experience in steam turbines with fire-resistant lubricants is probably better known, there is far greater experience in gas turbines. The earliest known operation with fire-resistant lubricants in this application commenced in 1958 when Texas Eastern Corporation decided to test phosphate esters in [*19*]. The trials were successful and Texas Eastern then planned the conversion of the remainder of their turbines. In Canada, the new pipelines that sprang up for gas transmission in the 1960s also decided to use fire-resistant lubricants and companies such as TransCanada Pipelines. Great Lakes Gas, Alberta Gas (subsequently the Nova Corporation), West Coast Transmission, Dome Petroleum etc. introduced these fluids into their equipment where possible–many from their initial installation. If industrial turbines were installed, the phosphates lubricated both the turbine and the associated compressor but if an aero-derivative unit was the prime mover, then the phosphate ester, if used, was only for lubrication of the compressor.

In the area of power generation, phosphates were used by General Electric (GE) as the combined hydraulic fluid and lubricant in some Frame 7 units produced in the 1970s. For a period there was a hot middle bearing which resulted in fires with mineral oil. Before the problem was "designed out," phosphate esters were used as lubricants and about ten units still run on these fluids today with some turbines approaching 100 000 hours operation.

The number of gas turbines/ compressors currently operating on phosphates in North America is about 150 and includes equipment from G.E., Canadian Westinghouse, Nuovo Pignone and Solar. The introduction of dry gas seals in the 1990s encouraged some users in Canada to return from phosphates to mineral oils but a series of fires with these units resulted in government pressure to move all possible equipment to phosphates-including those units that had been supplied with mineral oil.

In Europe, by comparison, the experience in gas turbines is very limited. A 5 MW Sulzer Type 3 unit was installed by Ciba-Geigy in Basel in 1986, in the same power station as the steam turbine. The turbine, reduction gears and generator have operated successfully on the same fluid charge since commissioning. Table 6 shows the results of analyses on fluid samples taken from the turbine over this period.

Two incidents have occurred during operation with the fire-resistant lubricant which, had mineral oil been used, would have resulted in fires. The first involved a screw coupling failure on the line from the high pressure lifting pump which resulted in fluid being sprayed over the hot end of the turbine. Because no fire occurred it was possible to follow normal shutdown procedures. The second was a leakage from the power turbine shaft seal and oil escaped onto the hot housing. Instead of having to shut the unit down to replace the seal, operation continued with the fluid being collected until a convenient shutdown occasion occurred, thus avoiding an unwanted outage [*14*].

Fluid Maintenance

As with existing turbine oils it is necessary to adequately maintain phosphates in order to ensure efficient operation of the system and an acceptable fluid life. The parameters that are of most concern are the increase in acidity, water content and particulate contamination level. When triaryl phosphates degrade the most common result is an increase in acidity with little effect on viscosity change. Consequently this latter property is not one that requires regular attention. Water and acidity, however, need monitoring. To date there are no specifications for used fire-resistant turbine lubricants but there is a tendency to adopt the limits already in existence for phosphate esters when used as turbine control fluids i.e. a maximum acidity of 0.2-0.3 mgKOH/g.

While the presence of some dissolved water can be tolerated if the acidity is low, free water is to be avoided in view of the potential adverse effect on rusting, emulsification etc. As the solubility of water in phosphates is very much higher than in oil (reaching about 2500ppm at 25 °C) this is not usually a problem and the level of fluid acidity will normally determine the suitability of the fluid for continued use.

Table 6-*Analytical Data of a Triaryl Phosphate Ester Used for the Lubrication of a 5 MW Industrial Gas Turbine*

Property	Units	Jan '86 0 hrs	'88	'90	'92	'94 42000 hrs	'96	'98	12/99 82000 hrs
Viscosity at 40 °C	cSt	45.2	46.3	46.4	46.0	46.0	45.8	45.0	45.4
Acid Number	mgKOH/g	0.07	0.08	0.01	0.01	0.01	0.04	0.04	0.08
Water Content	%	0.03	0.03	0.03	0.06	0.06	0.08	0.06	0.07
Air release Value	min	1	2	2.5	2	2	3	2	2

The key to the cost-effective use of phosphate esters is the use of conditioning media to remove acid degradation products. Initially, fullers earth and activated alumina were used for this purpose, but experience with these adsorbents has been unsatisfactory in systems where the acidity was allowed to rise too high. Deposits occurred and the air release/foaming properties deteriorated. The reason for this behavior was that the filter media, for example fullers earth, contained calcium and magnesium carbonates. These components reacted with the acidic decomposition products from the phosphate to produce soluble, and eventually insoluble, metal phosphate salts [*20*] which had an adverse effect on the surface-active properties of the fluid.

These treatment methods could substantially increase the life of the fluid where the system was well maintained and a low fluid acidity level was achieved. However, in cases where the fluid was severely stressed and it was impossible to maintain a low level of acidity this would eventually lead to an early fluid replacement and possibly the necessity of physically removing the deposits from internal surfaces by flushing and manual cleaning. Fortunately this problem is now solved. With the introduction of new adsorbents based on ion-exchange resins [*21*], it is now possible to keep the fluid in the system for many years. TransCanada Pipelines for example have reported units accumulating over 200 000 hours (25 years) on the same fluid charge. In 1998 they had over 14 million operating hours on these fluids [*22*]. With this length of fluid life, the life-cycle costs become very favorable and concerns regarding the disposal of the fluid are minimized. The resins used are however, wet and it is necessary to use a vacuum dehydration unit downstream to remove the displaced water. This equipment replaces the centrifuge used to remove water from wet turbine oil.

Fire-Resistant Fluids and Lubricants–Features and Benefits

As a result of the operating experience to date the principal features and benefits associated with phosphate ester fire-resistant fluids and lubricants are summarized in Table 7.

Table 7-*The Principal Features and Benefits of a Phosphate Ester Turbine Lubricant*

Feature	Principal Benefit
Fire resistance	• Improved safety/worker protection • Avoidance of fires leading to reduced downtime/ increased availability • Elimination of mechanical fire protection around the turbine with space saving and no maintenance requirements • Avoidance of shutdowns due to spurious alarms • Reduction in insurance premiums • Simpler building construction e.g. removing the need to isolate the reservoir • Greater shareholder confidence
Very long life when used with state of the art fluid conditioning	• Favorable life-cycle costs • Reduced downtime for replacement and (in most applications) lower maintenance requirements • Minimizes fluid disposal costs.
System modifications possible with favourable cost impact	• Single hydraulic and lube oil system • Reduction in tank capacity of up to 25% with certain fluid types • Possibility of higher bulk fluid temperatures • Simpler line construction leading to improved accessibility for repair etc.

Obstacles to Progress with Fire-Resistant Lubricants

With such a large amount of satisfactory operating experience it is perhaps surprising that industry has not adopted these fluids more widely. There are several reasons for this as follows:

1) The power generation industry is extremely conservative.

2) As suggested earlier there is no wide acceptance that turbine fires are a continuing problem. The builders argue, as a result, that there is no pressure from the market. In fact there have been a number of enquiries in recent years in which the builders have, at least initially, shown little interest.

3) Although the capital cost of the equipment when using a fire-resistant lubricant is not significantly different from when mineral oil is used, the turbine builder is understandably

reluctant to introduce "design specials". Moving to a new fluid can result in considerable effort in modifying drawings, seeking alternative components, logistics problems with carrying different spares etc. At a time when competition is fierce such changes are unwelcome to the manufacturers, particularly if they have no spare capacity for their standard designs.

4) If the builders are involved in maintenance contracts, they are insisting that these contracts will be invalidated if phosphates are used and problems occur!

5) A fire-resistant lubricant is significantly more expensive than one based on mineral oil. However, the cost savings associated with the elimination of fire-protection around the turbine, favorable life-cycle costs and the safety benefits associated with the new fluids are not necessarily understood or taken into consideration when deciding what lubricant shall be used.

6) There is a perception that phosphate esters are noxious and require special precautions for handling. This is not the case. Extensive toxicity and ecotoxicity data are now available on these fluids [*23*] which have failed to reveal a significant risk and the handling precautions are the same as are recommended for mineral oil.

7) With the emphasis today on the high availability of equipment, users are not prepared to compromise that availability. If therefore the builder shows a reluctance to offer phosphates and to guarantee equipment availability with these fluids, the user will naturally think twice about their adoption.

Technical and Commercial Drivers Towards Fire-Resistant Lubricants

In spite of the reluctance of some turbine builders to introduce fire-resistant lubricant technology there are a number of factors, particularly in Europe, which are steadily influencing the market in this direction. For example, in the search for higher equipment efficiency, operating temperatures, and therefore also the fire risk, are continuing to increase. Gas turbine inlet temperatures have increased from 700 °C in 1950s to 1500 °C today [*24*] while steam temperatures are now at about 600 °C with the intention to increase still further to 650 °C when the metallurgy permits. In an attempt to reduce generating costs, the number of operatives in the utilities has decreased dramatically–by up to half in some cases. Consequently there are now fewer people 'walking the lines' and looking for leaks and signs of other potential problems. Less time is available for training and maintenance programmes are now targeting specific pieces of equipment rather than a 'holistic' approach to the system.

With the drive to increased margins there is a tendency to keep existing plant in economical operation for as long as possible. In the USA for example ~70% of fossil units are currently more than 30 years old. With age comes a greater chance of metal fatigue and an escape of oil. The current trend of refurbishing old units may also result in extending the life of existing pipework with the same effect.

In Europe, because of a number of fires, the German utility association (VGB) is now promoting the use of fire-resistant lubricants in both gas and steam turbines following advice from their technical committees [*25*]. Also in Europe a series of Commission Directives aimed at improving worker protection have been published. In the UK, for example, the Supply of Machinery (Safety) Regulations arising from the Machinery Safety

Directive state "*Machinery must be designed and constructed to avoid all risk of fire posed by the machinery itself or by gases, liquids etc. produced or used by the machinery*". A similar statement appears in the legislation of all EC member states. The legislation also contains provisions for the imposition of penalties in the event of a fire arising as a result of a lack of implementation.

The insurance industry in Europe is very supportive of the use of the new fluids. Allianz Insurance, for example, is offering substantial discounts on insurance premiums and also technical support to the customer in the event that they use fire-resistant lubricants [*26*]. In the USA, the NFPA (National Fire Protection Association) and Factory Mutual already recommend fire-resistant lubricants for use in gas turbines as an alternative to mineral oil and mechanical protection [*27,28*] and the scope of the latter's standard for "Less Flammable Hydraulic Fluids" is being extended to include turbine lubricating oils.

In order to examine the likely cost-effectiveness of phosphate esters, a committee was set up in Germany in 1998 under the chairmanship of Allianz GmbH and consisted of members of some of the German utilities, European turbine builders and fluid suppliers. It concluded that "the use of a fire-resistant fluid in the control and lubrication system of a 500 MW steam turbine offers a cost advantage against mineral oil and is at least cost neutral in combined cycle equipment" [*29*]. The author's experience in industrial gas turbines would support this conclusion.

The Future

There is no doubt that the industrial trends indicated above, particularly the regulatory aspects, will encourage the wider use of fire-resistant lubricants. Utilities will also see their application as a means of avoiding fires and maintaining safe working conditions under strong competitive pressures. In fact there is already a move in this direction from some of the larger utilities in Europe particularly when considering investment in new plant. New industrial steam and gas turbines are also expected to be in operation in the next twelve to eighteen months and, as the advantages become clearer and more quantifiable, the momentum is expected to gather pace.

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Advanced High-Temperature Air Force Turbine Engine Oil Program

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Abstract: Military and commercial jet aircraft engines operate hotter than in the past to increase fuel efficiency. Also, advanced structural engine materials permit hotter burning, more efficient engines. These trends are expected to continue. Many current gas turbine engines experience oil system coking and other problems related to the limited thermal and oxidative stability of the conventional, ester-based gas turbine engine oils. This is because most engines operate on gas turbine oils limited to 150°C. The best current oils have a maximum operating temperature of about 200°C. We initiated a program to develop a new class of ester-based lubricants to meet current and future high-temperature requirements. The target temperature range of this new oil is –40°C to 232°C. Target requirements were established and communicated to industry. This paper presents those requirements and initial results on the most promising candidates.

Keywords: gas turbine engine oil, lubrication, antiwear additive, antioxidant, ester, base oil

Background

Hermann Zorn, of Germany, first investigated ester oils as engine lubricants in the 1930s to replace castor oils, notorious for sludge formation and cold temperature flow problems [*1*]. Esters can be tailor-synthesized to have specific desirable properties, allowing great flexibility for a unique application. Also, esters are naturally oxidatively

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stable and engine oils are subjected to high airflow over thin films of oil, making esters a good match for aircraft engines. In 1951, United States military specification MIL-L-7808, Lubricating Oil, Aircraft Turbine Engine, Synthetic Base, first outlined ester oil performance requirements. Initially diesters were the base fluids. As aircraft performance became more rigorous, thermal and oxidative demands on the engine oil increased and more complex esters were used as engine oil base fluids. The progression of complexity goes from diesters to trimethylolpropane esters to pentaerythritol esters to dipentaerythritol esters. As the ester complexity increases, the cost and stability increase. Pentaerythritol and dipentaerythritol esters have excellent low temperature viscosity, high viscosity index (VI) and very high autogenous ignition temperature (AIT) characteristics [*1*]. This high AIT makes them highly desirable as engine oils, because of fire threats from very hot engine nacelles. High AIT oils allow engine weight savings because less insulation and oil cooling is needed.

Over the years, esters used in gas turbine engines have advanced until now the US Navy has a –40°C to 204°C gas turbine engine oil (GTO), as defined in MIL-PRF-23699 specification, Lubricating Oil, Aircraft Turbine Engine, Synthetic Base, the HTS (high thermal stability) type. The US Air Force has a –51°C to 204°C GTO, as defined in MIL-PRF-7808, Grade 4 (4 cSt at 100°C). Both of these higher thermal stability oils are used where better oxidative stability is required, as they are more expensive than the Navy STD (standard) version and the Air Force Grade 3 (3 cSt at 100°C) version, both with an upper temperature oxidative stability limit of only 177°C.

This oxidative stability is defined in the military specification MIL-PRF-7808 by Corrosiveness and Oxidation Stability of Hydraulic Oils, Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils (ASTM test method D4636) but this test, as often the case with bench tests, does not define the entire problem with GTO stability. Another important related issue is the oil coking tendency. Engine coke is insidious black carbonaceous deposits formed from oil oxidation and thermal decomposition. Coke causes high engine maintenance because it interferes with heat transfer in the engine and clogs critical engine breather tubes and nozzles that spray lubricant on the bearings. Oil can perform well in the oxidative stability test, but produce high coke in a coking test or in an engine. Also, conversely, low coking oil may not have bulk oil temperature oxidation stability.

For this program, we needed a very oxidatively stable, low coking, ester-based GTO, with the very broad target temperature range of –40°C to 232°C. While more oxidatively stable fluid classes than esters exist, esters are preferred because any new ester fluid will be compatible with any existing engine and currently used ester oil. In other words, it would be a "drop-in" replacement, requiring no new hardware or seals, nor cleaning the system of the old fluid to add the new fluid.

Other performance properties are also critical as will be described. Besides the base fluid, the performance-improving additive package must be carefully considered. For example, the antioxidant and antiwear additives affect coke and oxidative stability. A balance of the base fluids and additives is critical to produce a successful candidate fully formulated GTO.

In the 1970s, the US Air Force sponsored research and development of a GTO, designated MIL-L-27502, Lubricating Oil, Aircraft Turbine Engine, Ester Based, similar in target properties to the desired oil of this current program. The prototype oil successfully passed a 100-h J57-P29W engine test, with the bulk oil temperature maintained at 220°C and with 330°C hot spots. Post-test inspection found clean, very low-coked parts [*2*].

That oil was never transitioned to actual use because, after several months, it developed a haze that was the additive package agglomerating. Also at that time, the Air Force required aircraft to operate down to −54°C and MIL-L-27502 would only operate down to −40°C. Although the GTO was never transitioned to use, the program demonstrated the optimum thermal and oxidative stability possible with a −40°C ester-based GTO.

Based on the experience of the MIL-L-27502 development program, the MIL-L-27502 properties were selected as target values. This new ester-based GTO would be the most stable ester based fluid possible.

While the GTO is being developed for primarily jet engines for aircraft, other jet engines and engines for power generating turbines will also benefit from a better oil that provides better fuel efficiency and less maintenance.

Advanced Ester Target Properties and Results

Target properties are established as ideal goals. In trying to meet those goals, some may become obviously impossible to meet. Others may change because input from the customers changes the original thinking. Pratt & Whitney, a major military engine manufacturer, has been involved with this program from the start, providing valuable recommendations. The final product is usually the best compromise lubricant, where less important properties are relaxed to allow achievement of the more important properties. Tables 1 and 2 contain the latest target properties and data from the most promising candidate from three potential fluid suppliers. Numbers in bold fall short of the target requirements. These are the more easy-to-conduct bench tests. The most critical or difficult to meet among these properties are viscosity-temperature, antiwear, static coking, bearing deposition, and corrosion-oxidation. More system-like and expensive tests are also listed (Table 3), which will be conducted on the most promising candidates.

Viscosity-Temperature

The higher temperature viscosity is targeted at 7.0 cSt minimum at 100°C, but down to 5.0 cSt is acceptable at this time. Higher is better because better film thickness in bearings comes from more viscous oil. A higher film thickness means less asperity contact and lower bearing wear. The low temperature viscosity is targeted at 20,000 cSt maximum at −40°C to meet critical cold weather starting. Obviously the high and low temperature requirements work against each other. It is critical to have the best viscosity index possible. The best candidates from Sources A and B are well over the low temperature target, but have the better higher temperature viscosity. The fluid from source C is much closer to 20,000 cSt at −40°C, but is less viscous at 100°C, where higher viscosity is highly desired. The temperatures at which the candidates are 20,000 cSt are interpolated in Table 1. We have ongoing dialogue with Pratt & Whitney concerning all of the target properties, but especially the low temperature viscosity,

Table 1 - Fluid Target Properties and Candidate Data

				SOURCE	
PROPERTY	TARGET REQUIREMENT	TEST METHOD	A	B	C
Kinematic Viscosity (cSt)		ASTM D445			
at 232°C	report			1.18	1.06
100°C	7.0 min target 5.0 min acceptable		6.45	6.32	5.48
40°C	report		37.23	35.95	29.6
-40°C	20,000 max		**30899**	**24950**	**20280**
-47°C(-54°F)	report			129600	93710
20,000 cSt interpolated temp, °C			-36.6	-38.5	
Acid Number (mg KOH/gm)	0.5 max	ASTM D664	0.00	0.0	0.00
Pour Point (°C)	-54 max	ASTM D97	−54[a]	**-50**	-57
Flash Point (°C) Open Cup	230 min	ASTM D92	290[a]	268	260
Autogeneous Ignition Temp. °C	395 min[b]	ASTM E659	404[a]	402	399
Evaporation at 232°C (6.5 Hrs), %	15 max	ASTM D972	5.3[a]	12.7	**20.0**
Four Ball Wear Scar (mm)		ASTM D4172			
1 hr, 40 Kg load, 600rpm					
52100, 75°C	0.7 max		0.47	0.39	0.66
M-50, 200°C	1.0 max		0.52	0.37	0.84
Static Coking, total mg coke/gm oil	49.4 max	(see text)	44.7	45.6	20.5
Shear Stability (% Viscosity Loss)	4.0 max	ASTM D2603	0.8[a]	1.1% +chg	1.00

[a] Similar formulation data - not expected to be significantly different

[b] Recently revised from 410°C

asking if the 20,000 cSt at –40°C is a critical need. In other words, would 20,000 cSt at –38.5°C for Source B candidate be acceptable for engine start-up capability?

Antiwear

We have selected the four ball wear test, Wear Preventive Characteristics of Lubricating Fluid, D4172, for 52100 steel at 75°C and M-50 steel at 200°C, for the GTO development program as it is a good screening test for boundary lubrication. The ultimate test is in the engine performance.

A good phosphorus-containing antiwear additive is required to assist in boundary lubrication of GTOs. Higher molecular weight phosphates are commercially available from several sources and seem to meet the requirements, when properly selected.. If a phosphate is too volatile, it evaporates and is not available in the application. Antiwear additive selection must be made carefully. We have observed that different antiwear phosphates can negatively impact the corrosion-oxidation test, the amount of static coking and the low temperature viscosity (Table 1). Table 4 is an example of 2.5% by

Table 2 - Corrosion-Oxidation Fluid Target Properties and Candidate Data
ASTM D4636

	TARGET		SOURCE	
PROPERTY	REQUIRMENT	A	B	C
Corrosion-Oxidation Stability, 10 L/h air flow				
Temperature, 220°C, 48 hr, 165 ml				
Viscosity Change, (%)	-5 to 25	8.3	15.3	18.2
Acid Number Change (mg KOH/gm)	4.0 max	0.87	3.38	1.4
% Fluid loss	8.0 max	2.9	2.1	2.7
Metal weight Change (mg/cm^2)				
Al (Alloy 2024)	0.2 max	0.03	-0.01	0.00
Ag (99.9% pure)	0.2 max	0.00	-0.04	-0.05
Bz (Si-Fe, AMS 4616, AZ31B)	0.2 max	-0.01	-0.03	-0.01
Steel (grade 1010)	0.2 max	0.02	0.02	-0.03
M-50 (AMS 6490)	0.2 max	0.02	0.01	-0.02
Mg - WE 43	0.4 max	0.01	-0.04	0.00
TI (Alloy 8% Mg)	0.2 max	-0.01	0.00	0.00
Inconel 718	0.2 max	0.00	0.01	0.00
Fluid Appearance	Report	dark brown	dark brown	dark brown
Corrosion-Oxidation Stability, 10 L/hr air flow				
Temperature, 232°C, 48 hr				
Viscosity Change, (%)	-5 to 25	18	23.3	**40.10**
Acid Number Change (mg KOH/gm)	4.0 max	1.6	3.83	**8**
% Fluid loss	8.0 max	4	3.75	**4.8**
Metal weight Change (mg/cm^2)				
Al (Alloy 2024)	0.2 max	0	-0.01	0.01
Ag (99.9% pure)	0.2 max	-0.03	-0.06	-0.08
Bz (Si-Fe, AMS 4616, AZ31B)	0.2 max	-0.03	-0.05	-0.01
Steel (grade 1010)	0.2 max	0.02	0.02	0.02
M-50 (AMS 6490)	0.2 max	0.00	0.02	0.02
TI (Alloy 8% Mg)	0.2 max	0.00	0.00	0.01
Inconel 718	0.2 max	-0.02	0.00	0.01
Fluid Appearance	Report	dark brown	dark brown	dark brown

weight of two of the better antiwear additives, both produced by the same company, in otherwise the same formulation. With these, the largest difference is in the –40°C viscosity and in the post test corrosion-oxidation test acid number change.

Coking

Engine coke involves complicated variables such as airflow, temperature, resonance time, chemistry of the base oil and additives, fluid film thickness, and whether the GTO is in the vapor phase or liquid phase. Coking tendency of GTOs can be different for different engines, i.e., a GTO may be better for coking tendency in one engine than another engine, while a different GTO may be worse for coking in the first engine and better in the second engine.

As a screening tool, we are using a static coking test [3]. The static coker consists of a coker base mounted on a hot plate, a 0.005-inch thick, 2-inch diameter steel specimen, and a programmable temperature controller with the necessary thermocouples for monitoring and controlling temperature. Approximately 0.5 gm of the oil sample is loaded at the 150° C presoak temperature. The temperature is held at 150°C for 30 minutes, then ramped at 10°C per minute to the 300°C test temperature and held for 3 hours. After cooling, the amount of deposit is weighed and reported as mg coke/g oil. This test is extremely sensitive to the volatility (and therefore, the viscosity) of the base fluid: the higher the volatility, the lower the coking value. Only

Table 3 - Fluid Target Properties for Later Testing

PROPERTY	REQUIREMENT	METHOD	SOURCE B
Foaming Characteristics (static)		FTM 791c	
Foam volume, ml	100 max	method 3213	
Foam collapse time, sec	60 max		
Foaming Characteristics (dynamic)		FTM 791c	
Foam vol, ml / collapse time, sec		method 3214	
80°c (176°F) at 1000 ml/min	100 max/ 60 max		
80°c (176°F) at 1500 ml/min	150 max/ 60 max		
80°c (176°F) at 2000 ml/min	200 max/ 60 max		
110°c (176°F) at 1000 ml/min	100 max/ 60 max		
110°c (176°F) at 1500 ml/min	150 max/ 60 max		
110°c (176°F) at 2000 ml/min	200 max/ 60 max		
Elastomer Compatibility, % swell		ASTM D 471	
AMS 3383	25 max		17.16
MIL-R-83248	25 max		15.7/8.26
MIL-R-83485	25 max		12.96
Dynamic Coking	(to be determined)	(to be determined)	
Bearing Deposition, Oil sump, 220°C; Bearing 275°C		FTM 791c	
Deposit Rating	45 max	method 3450	
Filter Deposit weight (gm)	1.0 max		
Oil consumption (ml)	960 max		
Viscosity change at 400C	-5 to +15		
Acid Number change (mg KOH/gm)	1.0 max		
Metal Weight Change (mg/cm^2) (metals as in MIL-L-7808K)	0.2 max		
Mini-Engine Simulator	(to be determined)	(to be determined)	

Table 4 - Effect of Anitwear Phosphate Additive on Formulation Properties
(2.5% by weight antiwear additive in same base formulation)

Oil Additive	1	2
Wear scar, mm		
52100, 75°C	0.45	0.62
M-50, 200°C	0.42	0.38
Viscosity, -40°C	36,390	40,660
Static coke	31.8	38
Corrosion-Oxidation (232°C)		
Visc. Chg., 40°C, %	5.6	7.2
Acid No. Chg., mg KOH/gm	1.36	-0.12

oils of similar viscosity (and presumably volatility) should be compared in coke formation. The static coking value of the original MIL-L-27502 was 49.4 mg coke/g oil. This static coking value was selected as the target for the new oils since that oil passed a full-scale engine test with remarkably clean parts. All of the candidate GTOs (Table 1) meet this requirement.

Since low coke is one of the primary goals of this GTO development program, further testing will be conducted. These tests include an in-house developed dynamic coking test, mini-turbine engine lubricant simulator test, a bearing deposition test and a hot-tube deposition test at Pratt & Whitney. The hot-tube deposition test also investigates vapor phase coke, besides the liquid phase coke investigated by the static coke test.

Corrosion-Oxidation

The corrosion-oxidation test (ASTM D 4636) is called for in the military GTO specifications. We have seen GTOs that pass the 232°C corrosion-oxidation test, but, contrary to what one might expect, gave very high static coke results. We do know that the performance improving additives can have a negative effect on the corrosion-oxidation test, as with the coke test. Currently we are conducting the corrosion-oxidation test at both 220°C and 232°C. In the 220°C test, we use a corrosion-resistant magnesium (Mg) alloy, WE-43, to represent a magnesium alloy in a modern or future gas turbine engine. Since the Mg alloy is not used in the hottest engine sections, its testing was limited to the 220°C corrosion and oxidation test. Mg alloys, even the relatively stable WE-43, tend to be reactive, as we learned when some of them actually dissolved completely in the tests. (Obviously, formulations that dissolved the Mg coupons required more modification/improvement.) The 232°C test contains the same coupons as the 220°C test except without the Mg alloy, as the remaining metal alloys will likely be exposed to higher temperatures.

Sources A and B GTO candidates now meet the corrosion-oxidation test target limits. It was, however, very challenging to meet these limits, taking many formulation modifications, in some cases. The Source C GTO candidate is over the limit in post-test acid number, but may be fine-tuned to meet the limit in the future.

To pass the corrosion-oxidation test, the optimum blend of base fluids and additives must be selected without causing the low temperature flow properties to become too viscous. Antiwear and antioxidant additives can also have a negative effect in this test, so must be selected carefully and used in not too large of a loading. The antioxidant additive may cause excessive coking in the coke test and also in the further coke-related tests, to be conducted in the near future.

Summary

The US Air Force is progressing to meet target goals for an advanced high-temperature, low-coke GTO for current higher temperature and future engines. Significant progress has been made towards the goals established. Current and future high-temperature engines will require less maintenance using the new GTO.

Acknowledgments

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The Evolution of Base Oil Technology

Reference: Kramer, D. C., Lok, B. K., 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., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: From its humble beginnings over 3000 years ago, lubrication technology has seen many phases of evolution. As it continues to evolve at an ever-increasing rate, base oil performance is making a larger contribution to finished lubricant performance. Turbine oils are perhaps the most dramatic example because they typically contain over 99% base oil.

Early lubrication began with animal fats and oils and slowly evolved to petroleum-based oils. Many generations of refining processes have since improved on Mother Nature. Early processes such as acid treating and solvent extraction improved the quality of base oils by removing some or most of the worst molecules from the oil. Later processes like hydrotreating, catalytic hydrocracking, catalytic dewaxing, and modern wax hydroisomerization transformed feed molecules into molecules with improved lubricating qualities.

Modern wax hydroisomerization, in particular, makes base oils with very low impurities and typically water-white appearance. Now, about one third of all base oils manufactured in North America are of such high quality.

Looking to the future, the trend is toward even higher base oil purity, higher viscosity index (V.I.), lower volatility, and longer life. The distinction between heavily processed mineral oils and traditional "synthetic" oils will continue to blur.

The evolution and future of base oil technology will be discussed in more detail in this paper.

Keywords: base oil, evolution, history, hydrocracking, solvent

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Early Base Oil Processing

Base oil technology has undergone many phases of evolution. In the first phase, animal fats were used as lubricants. Ancient inscriptions dating back to 1400 BC show beef and mutton fat (tallow) being applied to chariot axles. Very little changed over the next 3000 years except that the oils sometimes came from more exotic animals such as whales.

In 1852 petroleum-based oils first became available. They were not widely accepted at first because they did not perform as well as many of the animal-based products. Raw crude did not make very good lubricant. The base oil industry was on the very steep part of the learning curve.

But as the demand for automobiles grew, so did the demand for better lubricants. Soon lubricant manufacturers learned which crudes made the best lubricants. Then they improved on Mother Nature by refining the crude into narrow distillation cuts with varying viscosity. By 1923 the Society of Automotive Engineers classified engine oils by viscosity: light, medium, and heavy. Engine oils contained no additives and had to be replaced every 800-1000 miles.

In the 1920s more lubrication manufacturers started "processing" their base oils to improve their performance. Three popular processing routes were:

Clay Treating

Clay similar to kitty litter was used to soak up and remove some of the worst components in the petroleum base oil. These compounds were usually aromatic and highly polar compounds containing sulfur and nitrogen.

Acid Treating

Concentrated sulfuric acid was used to react with the worst components in the base oil and convert them into a sludge that could be removed. Although this process effectively cleaned up the oil, it was expensive. This technology has virtually disappeared from North America due to environmental concerns about the acid and sludge [*1*].

SO_2 Treating

SO_2 treating was a primitive extraction process to remove the worst components in the lube oil using a recyclable solvent. Unfortunately, the solvent was highly toxic. Although it also has been virtually phased out [*1*], it was a useful stepping stone to conventional solvent extraction.

Solvent Refining

By approximately 1930 solvent processing emerged as a viable technology for improving base oil performance using a fairly safe, recyclable solvent. Most base oil producers in the world today still use this process.

Approximately two-thirds of the base oil in North America is currently manufactured using this route. Solvent refined base oils are commonly called Group I base oils which are characterized as those having less than 90% saturates (>10% aromatics) and more than 300 ppm sulfur. Table 1 shows all the base oil groups as defined by the American Petroleum Institute (API) Publication 1509.

Table 1 – *API Base Stock Categories (API Publication 1509)*

Group	Sulfur, Wt %		Saturates	V.I.
I	>0.03	and/or	<90	80-119
II	≤0.03	and	≥90	80-119
III	≤0.03	and	≥90	≥120
IV	All Polyalphaolefins (PAOs)			
V	All Stocks Not Included in Groups I-IV (Pale Oils and Non-PAO Synthetics)			

The solvents and hardware used to manufacture solvent-refined base oils have evolved over time, but the basic strategy has not changed since 1930. The two main processing steps are:

1. Remove aromatics by solvent extraction.
2. Remove wax by chilling and precipitation in the presence of a different solvent.

Aromatics are removed by solvent extraction to improve the lubricating quality of the oil. Aromatics make good solvents but they make poor quality base oils because they are among the most reactive components in the natural lube boiling range. Oxidation of aromatics can start a chain reaction that can dramatically shorten the useful life of a base oil.

The viscosity of aromatic components in a base oil also responds relatively poorly to changes in temperature. Lubricants are often designed to provide a viscosity that is low enough for good cold weather starting and high enough to provide adequate film thickness and lubricity in hot, high-severity service. Therefore, when hot and cold performance is required, a small response to changes in temperature is desired. The lubricants industry expresses this response as the viscosity index (V.I.). A higher V.I. indicates a smaller, more favorable response to temperature. Correspondingly, many turbine manufacturers have a minimum V.I. specification for their turbine oils. Base oil selection is key for meeting this specification because turbine oil additives do not normally contribute positively to the V.I. in turbine oil formulations.

Aromatics are removed by feeding the raw lube distillate (vacuum gas oil) into a solvent extractor where it is contacted countercurrently with a solvent. Popular choices of solvent are furfural, n-methyl pyrrolidone (NMP), and DUO-SOL™. Phenol was another popular solvent but it is rarely used today due to environmental concerns. Solvent extraction typically removes 50-80% of the impurities (aromatics, polars, sulfur and nitrogen containing species). The resulting product of solvent extraction is usually referred to as a raffinate.

The second step is solvent dewaxing. Wax is removed from the oil to keep it from freezing in the customer's sump or crankcase at low temperatures.

Wax is removed by first diluting the raffinate with a solvent to lower its viscosity to improve low-temperature filterability. Popular dewaxing solvents are methyl-ethyl ketone (MEK)/toluene, MEK/methyl-isobutyl ketone, or (rarely) propane. The diluted oil is then chilled to -10 to -20°C. Wax crystals form, precipitate, and are removed by filtration.

Additives Improve Performance

Over the next several decades, the solvent refining process did not change very much. Finished oil quality improved mainly due to the addition of additives. Additives began to be widely used in 1947 when the API began to categorize engine oils by severity of service: regular, premium, and heavy duty. Additives were used to extend the life only in premium and heavy-duty oils.

Regular engine oils were unadditized and were intended for 80-100 hours of low-severity service. Premium engine oils were additized to extend the life of passenger car engine oils. Heavy duty engine oils were more heavily additized to extend the engine oil life in more severe applications such as commercial trucks and construction equipment.

In 1950 multigrade oils were first introduced which were additized with polymers to enhance the V.I. of the oil which improved the hot and cold performance of the oil.

For several more decades, the lubricants industry continued to rely heavily on additive technology to improve the performance of finished oils. Lubricant quality improved significantly only when the additive chemistry improved. This was the only viable strategy until a significant improvement in base oil technology was available.

Hydrotreating

Hydrotreating was developed in the 1950s and first used in base oil manufacturing in the 1960s by Amoco and others. It was used as an additional "cleanup" step added to the end of a conventional solvent refining process. Hydrotreating is a process for adding hydrogen to the base oil at elevated temperatures in the presence of catalyst to stabilize the most reactive components in the base oil, improve color, and increase the useful life of the base oil. This process removed some of the nitrogen and sulfur containing molecules but was not severe enough to remove a significant amount of aromatic molecules. Hydrotreating was a small improvement in base oil technology that would become more important later.

Hydrocracking

Hydrocracking is a more severe form of hydroprocessing. It is done by adding hydrogen to the base oil feed at even higher temperatures and pressures than simple hydrotreating. Feed molecules are reshaped and often cracked into smaller molecules. A great majority of the sulfur, nitrogen, and aromatics are removed. Molecular reshaping of the remaining saturated species occurs as naphthenic rings are opened and paraffin isomers are redistributed, driven by thermodynamics with reaction rates facilitated by catalysts. Clean fuels are byproducts of this process.

A primitive version of the hydrocracking process was attempted for lube oil manufacturing in the 1930s but was soon abandoned for economic reasons after the solvent refining process was commercialized. But hydrocracking technology continued to improve [*2*].

After WWII, predecessors to modern hydrocracking catalyst technology were imported from Germany. Chevron commercialized this technology for fuels production in the late 1950's [*3*]. In 1969 the first hydrocracker for Base Oil Manufacturing was commercialized in Idemitsu Kosan Company's Chiba Refinery using technology licensed by Gulf [*4*]. This was followed by Sun Oil Company's Yabucoa Refinery in Puerto Rico in 1971, also using Gulf technology [*2*].

Catalytic Dewaxing and Wax Hydroisomerization

The first catalytic dewaxing and wax hydroisomerization technologies were commercialized in the 1970s. Shell used wax hydroisomerization technology coupled with solvent dewaxing to manufacture extra high V.I. base oils in Europe. Exxon and others built similar plants in the 1990s. In the U.S., Mobil used catalytic dewaxing in place of solvent dewaxing, but still coupled it with solvent extraction to manufacture conventional neutral oils. Catalytic dewaxing was a desirable alternative to solvent dewaxing especially for conventional neutral oils, because it removed n-paraffins and waxy side chains from other molecules by catalytically cracking them into smaller molecules. This process lowered the pour point of the base oil so that it flowed at low temperatures, like solvent dewaxed oils. Hydroisomerization also saturated the majority of remaining aromatics and removed the majority of remaining sulfur and nitrogen species.

Chevron was the first to combine catalytic dewaxing with hydrocracking and hydrofinishing in their Richmond, California, base oil plant in 1984 [*5*] (Figure 1). This was the first commercial demonstration of an all-hydroprocessing route for lube base oil manufacturing.

In 1993, the first modern wax hydroisomerization process was commercialized by Chevron [*6*]. This was an improvement over earlier catalytic dewaxing because the pour point of the base oil was lowered by isomerizing (reshaping) the n-paraffins and other molecules with waxy side chains into very desirable branched compounds with superior lubricating qualities rather than cracking them away. Hydroisomerization was also an improvement over earlier wax hydroisomerization technology, because it eliminated the subsequent solvent dewaxing step, which was a requirement for earlier generation wax isomerization technologies to achieve adequate yield at standard pour points. Modern wax hydroisomerization makes products with exceptional purity and stability due to extremely high degree of saturation. They are very distinctive because, unlike other base oils, they typically have no color.

By combining three catalytic hydroprocessing steps (hydrocracking, hydroisomerization, hydrotreating), molecules with poor lubricating qualities are transformed and reshaped into higher quality base oil molecules. Pour point, V.I., and oxidation stability are controlled independently. All three steps convert undesirable molecules into desirable ones, rather than have one, two, or all three steps rely on

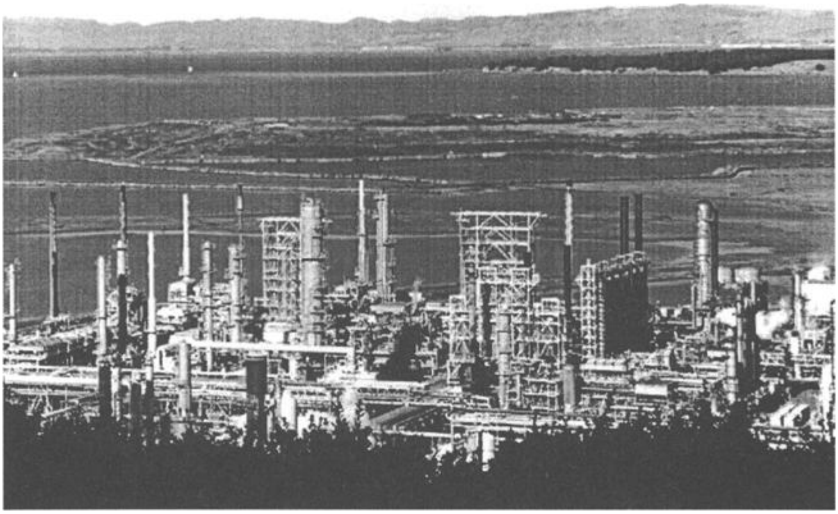


Figure 1 – *Richmond Lube Oil Project*

subtraction. Among the many benefits of this combination of processes is greater crude oil flexibility; that is, less reliance on a narrow range of crude oils from which to make high-quality base oils. In addition, the base oil performance is exceptionally favorable and substantially independent of crude source, unlike solvent-refined base oil.

Group II – Modern Conventional Base Oils

Lube base oils made by hydrocracking and early wax isomerization technologies showed favorably differentiated performance which prompted the API to categorize base oils by composition (API Publication 1509) in 1993, as shown earlier in Table 1. Table 1 shows that Group II base oils are differentiated from Group I base oils because they contain significantly lower levels of impurities (<10% aromatics, <300 ppm S). They also look different. Group II oils made using modern hydroisomerization technology are so pure that they have almost no color at all. From a performance standpoint, improved purity means that the base oil and the additives in the finished product can last much longer. More specifically, the oil is more inert and forms less oxidation byproducts that increase base oil viscosity and react with additives.

The modern hydroisomerization process licensed by Chevron under the name ISODEWAXING gained acceptance rapidly since its introduction in 1993. In fact, about one-third of all base oils manufactured in North America are now manufactured using this process (Figure 2). A similar trend can be seen in the rest of the world as well.

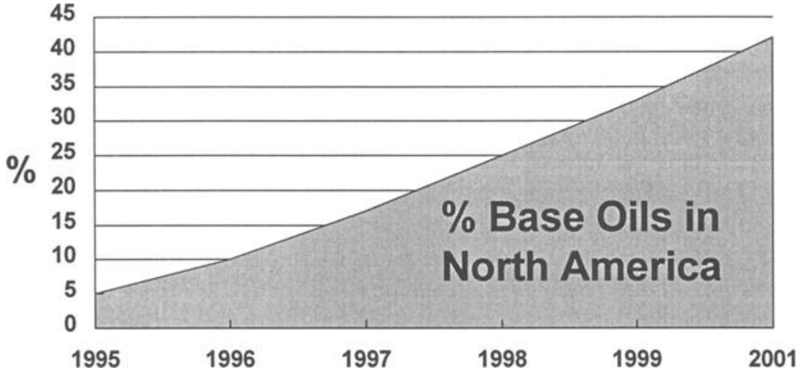


Figure 2 – *Greater Availability (Chevron + Licensees = 42% by 2001)*

More recently, Mobil (ExxonMobil) added to this trend by commercializing an all-hydroprocessed route for Group II production {Mobil Selective Dewaxing (MSDW™)} which they installed in their Jurong Refinery in Singapore in 1997. ExxonMobil also added a hydroprocessing step (Raffinate Hydroconversion or RHC) to a solvent refining plant in Baytown, Texas, to upgrade its capability to Group II.

Group II base oil technology, along with specially designed additives has already had a tremendous impact on finished oil performance. In some applications including turbine oils, lubricating oils formulated with Group II base oils can outlive expensive traditional "synthetic" oils made from PAO.

Group III – Unconventional Base Oils

Table 1 shows that the API defines the difference between Group II and III base oils only in terms of the V.I. Base oils with a "conventional" V.I. (80-119) are Group II and base oils with an "unconventional" V.I. (120+) are Group III. Group III oils are also sometimes called unconventional base oils (UCBOs) or very high V.I. (VHVI) base oils.

Solvent-dewaxed Group III base oils have been produced in Europe for more than 10 years, primarily by Shell and BP [*7*]. Group III base oils were not widely available in North America until a few years ago when Chevron and its licensees began making them using the all-hydroprocessing route. These modern Group III oils have greatly improved oxidation stability and low temperature performance relative to the solvent-refined Group III oils. Consequently, many of these older plants are now being upgraded to enable them to make the modern hydroisomerized Group III oils [*8*].

From a processing standpoint, modern Group III base oils are manufactured by essentially the same processing route as modern Group II base oils. Higher V.I. is achieved by increasing the temperature or time in the hydrocracker. This is sometimes collectively referred to as the "severity." Alternatively, the product V.I. could be increased simply by increasing the feed V.I., which is typically done by selecting the appropriate crude.

Group III base oils are now widely available in North America because they can be manufactured in large quantities by most of the companies that currently make

Group II oils. Many of these companies have started adding them to their "synthetic" product lines.

Modern Group III base oils have properties which allow them to perform at a level that is significantly higher than "conventional" Group I and Group II base oils, and they substantially match existing levels of performance in finished lube applications already established by traditional synthetic oils. The most notable exception is arctic oils, which have extremely low pour point requirements and a very small market presence.

Group IV – Traditional "Synthetic" Base Oils (PAO)

The use of the word "synthetic" in the lubricants industry has historically been synonymous with polymerized base oils such as poly-alpha olefins (PAOs), which are made from small molecules. The term "synthetic" was given a special meaning by the lubricants industry because these types of oils were the only components available for high-performance lubricants at that time. Later in this paper it should become apparent how PAOs directly influenced the evolution of mineral-based base oil technology which in turn has influenced the evolution of the term "synthetic."

The first commercially viable process for making PAO was pioneered by Gulf Oil in 1951 using an $AlCl_3$ catalyst. Mobil patented an improved process using a $BF_3/AlCl_3$ catalyst in the 1960s. Mobil first used this new base oil in specialty products such as Mobilgrease 28, which solved a wheel bearing failure problem on aircraft carriers in cold climates [*9*].

In the 1970s PAOs became a major consumer-sought lubricant component when Mobil Oil commercially marketed its Mobil 1™ engine oils 25 years ago. For the next 15 years, the PAO market traveled a long and winding road battling a slow, steady growth and criticisms of justification for the higher cost compared to conventional oils. In the last 10 years, the PAO market significantly increased, first in Europe and then in North America experiencing periods of double-digit growth. In part, the growth might be attributed to the stricter lubricant specifications in Europe that created a market niche for synthetics and semi-synthetic products [*9*].

As the lucrative PAO market grew, some base oil manufacturers began using higher-V.I. feedstocks (usually byproducts from wax manufacturing) to make mineral oils with V.I.s that matched the PAOs. These new Group III oils were not manufactured from small molecules like traditional synthetics but they bridged most of the performance gap at a lower cost. Therefore, some lubricant manufacturers, primarily in Europe, began replacing PAOs with these newly available Group III base oils in their "synthetic" engine oils. This created a controversy in the lubricants industry as some synthetic base oil producers and lubricant manufacturers believed that polymerized base oils were the only true synthetics.

The trend toward globalized lubricant specifications and worldwide OEM specifications is now creating more demand for Group III base oils in North America and other continents as well. This is particularly true in North America due to the recent ruling by the National Advertising Department of the Better Business Bureau that Group III base oils can be considered "synthetic" and because modern Group III base oils, made using hydroisomerization technology, have most of the attractive performance features of early synthetics.

Group III Versus PAO Performance

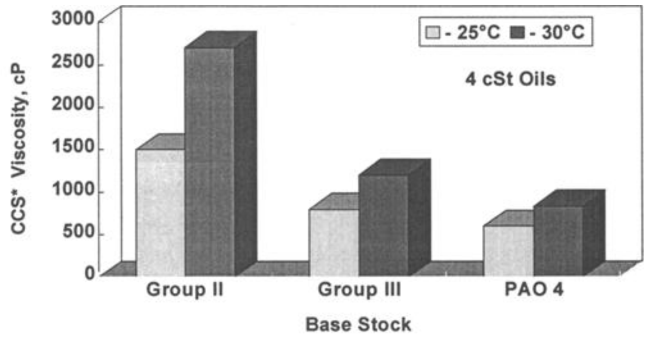
Historically, PAOs have had superior lubricating performance characteristics such as V.I., pour point, volatility, and oxidation stability that could not be achieved with conventional mineral oils. Now, in modern base oil manufacturing, V.I., pour point, volatility, and oxidation stability can be independently controlled. Modern Group III oils today can be designed and manufactured so that their performance closely matches PAOs in most commercially significant finished lube applications.

As well-designed Group III base oils become abundant in the marketplace, the performance gap between Group III and PAO (Group IV) is closing. Here are some key examples:

Pour Point – Pour point is the one property where Group III oils allegedly fall short of PAO. While it is certainly true that the pour point of the neat Group III base oil is substantially higher than that of a PAO of comparable viscosity, it is important to understand that the pour point of the fully formulated lubricant (base oils plus additives) is the critical property. Base oils manufactured with modern isomerization catalysts respond very well to pour point depressant additives. For example, turbine oils formulated with conventional Group II base oils (-12°C base oil pour point) are available with a formulated pour point of -36°C. Fully formulated Group III based lubricants can be made with pour points of -50°C or below.

Products such as motor oils made with the lighter-grade PAOs, on the other hand, typically have ***higher*** pour points than the base fluid, so the gap in final product pour point between PAO-based and UCBO-based lubricants is much smaller than in the base fluids themselves. Moreover, it is entirely possible with modern Group III manufacturing technology to produce base oils of even lower pour point. However, this is not common practice in the industry, because it is more economical to meet finished lube low temperature performance using pour point depressant additives rather than using special Group III oils having exceptionally low pour points.

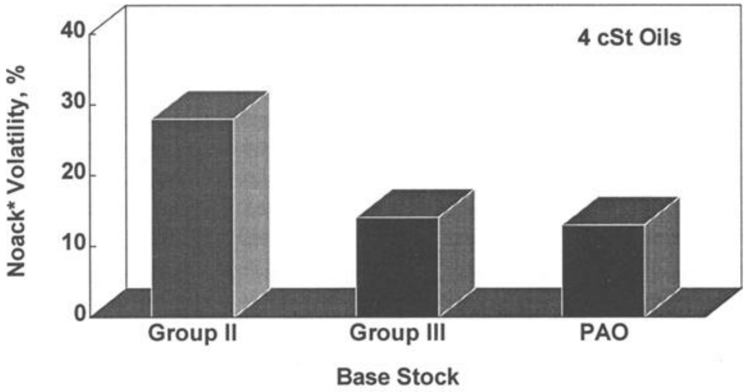
Cold Crank Simulator – Viscosity in engine journal bearings during cold temperature startup is a key factor in determining the lowest temperature at which an engine will start. Cold Cranking Simulator (CCS) viscosity, as measured by ASTM Method D 5293, is determined under conditions similar to those experienced in engine bearings during starting. For base oils, this viscosity is determined almost entirely by viscosity and V.I. Since Group III stocks typically have V.I. comparable to that of 4 cSt PAO, one would expect comparable CCS performance. This is demonstrated in Figure 3, where it can be seen that a 4 cSt Group III base oil, with a kinematic viscosity of 4.2 cSt at 100°C and a V.I. of 129, and PAO 4, with a viscosity of 3.9 cSt and V.I. of 123, have similar CCS values, both about half that of a 4 cSt Group II base stock of about 100 V.I. This performance makes the Group III stock very effective for formulating fuel-efficient multi-viscosity engine oils in the 0W-20 to 0W-50 range, one that has historically been achieved only with PAO-based product.



*ASTM D 5293

Figure 3 – *Cold Cranking Performance, Group III Comparable to PAO*

Noack Volatility – Noack volatility of an engine oil, as measured by ASTM D 5800 and similar methods, has been found to correlate with oil consumption in passenger car engines. Strict requirements for low volatility are important aspects of several recent and upcoming engine oil specifications, such as ACEA A-3 and B-3 in Europe and ILSAC GF-3 in North America. Figure 4 shows that from a blender's perspective, Group III base oils are similarly effective as PAOs for achieving these low volatility requirements in engine oil applications. The V.I. of modern Group III oils typically match or exceed PAO, so they can match the volatility of PAOs at a reasonable distillation cut width.



*ASTM D 5800

Figure 4 – *Group III Performance Versus PAO, Comparable Noack Volatility*

Oxidation Stability – Oxidation and thermal stability are among the most important advantages that "synthetics" bring to the table. Better base oil stability means better additive stability and longer life. High stability is the key to making the premium-quality finished oils of the future with longer drain intervals. Here Group III oils routinely challenge PAO performance.

The stability of modern Group III stocks depends mostly on their V.I., because V.I. is an indication of the fraction of highly stable isoparaffinic structures in the base oil [*10*]. However, because modern Group III stocks also undergo additional severe hydrofinishing after hydrocracking and hydroisomerization, they achieve an additional boost in stability because only trace amounts of aromatics and other impurities remain in the finished stocks. On the other hand, PAO performance seems to depend largely on residual olefin content. Olefins are an intermediate in PAO production that contribute to instability.

Figure 5 illustrates that base oil quality can have a big impact on the oxidation stability in turbine oils. The Turbine Oil Stability Test (TOST), or ASTM D 943, measures the time required for a turbine oil to oxidize to the point where the total acid number reaches 2.0 mg KOH/g. Unadditized Group I base oil fails in about 200 hours. A modern high-quality turbine oil formulated with Group I base oil typically fails in less than 7000 hours. A high-quality Group II formulated oil can run more than twice as long before it fails.

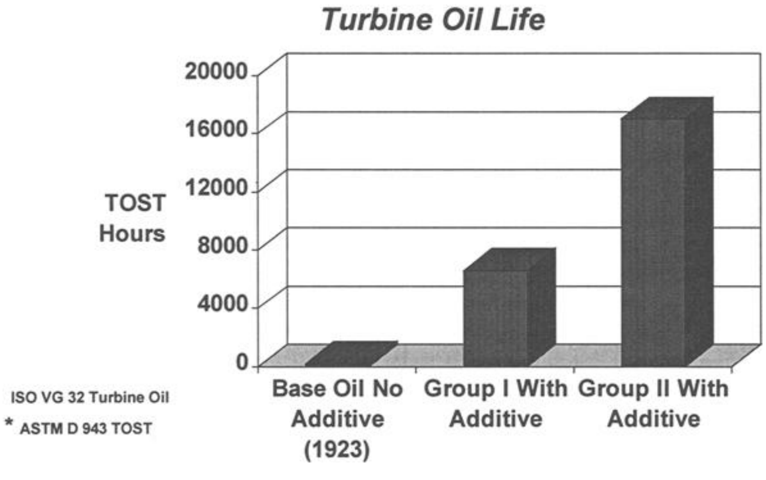
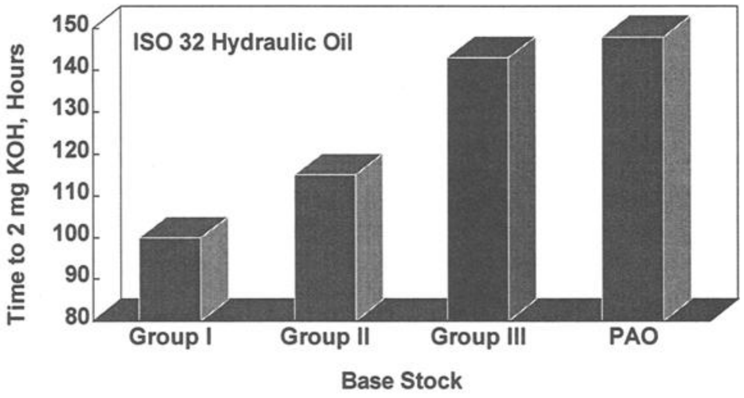


Figure 5 – *Higher Base Oil Quality Extends Turbine Oil Life*

The benefit of all-hydroprocessed Group III base oils in oxidation stability is illustrated in Figure 6 for hydraulic oils formulated by using the same additive system in four different base oils. Here, the time required to reach an acid number of 2.0 (defined by neutralization of 2.0 mg of KOH/g of oil) in the Universal Oxidation Test (ASTM D 4871), a common measure of oil oxidation, was substantially longer for the Group III formulation than for either the Group I or II products. Moreover, the performance of the Group III product was essentially the same as that for the oil formulated with PAO.



Universal Oxidation Test, ASTM D 4871, at 170°C

Figure 6 – *Oxidation Stability, Acid Number in Hydraulic Oils*

Table 2 lists a variety of North American lubricants which are based upon all-hydroprocessed Group III base stocks. These products include engine oils, industrial oils, and driveline fluids, and are targeted at the same performance levels achieved by traditional synthetic formulations.

Table 2 - *Synthetic Quality Products Utilizing All-Hydroprocessed Group III Base Stocks*

Available Now	Upcoming
Semi and Full Synthetic PCMO	GF-3 PCMO (Semi and Full Synthetic)
Semi-Synthetic HDMO	Extended Drain Gear Oil
DaimlerChrysler ATF+4®	High Performance Automotive (Racing) Oils
Ford Mercon® V ATF	Motor Oils
Compressor Oil	Gear and Transmission Oils

Future Evolution

Looking to the future, the trend is toward lubricants and base oils with even higher purity, lower volatility, and longer life. The molecular structure of base oils will probably look even more like PAO as they become more concentrated in the most favorable molecular species needed for superior lubrication performance. It is likely that recent and ongoing developments in base oil technology will enable lubricants with exceptional performance to be marketed in much greater volumes than was feasible when PAO was the only stock capable of such performance levels.

There are many possible routes for improving base oil quality. Continued evolution of the all-hydroprocessing route is one likely possibility. Selectivity toward desired molecular compositions could be improved by improving the catalysts and the processing technology. Improving the feedstock can also improve the product. Very paraffinic (waxy) feedstocks such as Fischer-Tropsch wax from natural gas-to-liquids plants can potentially be further processed into high quality base oils. Volumes and applications are expected to grow, as ultra-waxy feedstocks become more widely available.

Other competing technologies are likely to emerge. New routes for manufacturing PAOs have been proposed that use cheaper feedstocks such as ethylene and propylene rather than 1-decene [*11*].

Future improvements in base oil technology will assuredly lead to further improvements in the performance of turbine oils and other sensitive applications with low additive treat rates.

Conclusions

Lubrication technology evolved slowly from ancient times until the middle of the 20th century. Then solvent refining technology emerged and displaced naturally occurring petroleum distillates due to its improved refined properties. Starting in the 1960s, hydroprocessing technologies were introduced which improved base oil purity and performance further. In the 1970s and 1980s, Group II base oils were manufactured and recognized as a separate API category in 1993, due to their positive differentiation over conventional stocks. Modern hydroisomerization technologies, such as ISODEWAXING, became widely accepted and grew rapidly since it was first commercialized in 1993. Widespread licensing of this technology has created an abundant supply of Group II oils that have exceptional stability and low temperature performance relative to their Group I and Group II predecessors. This technology is now used to make about one-third of all base oils in North America.

A similar trend appears to be emerging with Group III base oils, especially those made using modern hydroisomerization. They offer most of the performance advantages of traditional PAO-based “synthetic” oils and can be manufactured in volumes unachievable by PAO. Most manufacturers of modern Group II base oils can make modern Group III base oils as well.

Selected top-tier lubricants requiring PAO should continue to coexist with Group III oils as they have for years in Europe. But widespread availability of modern Group II and III mineral oils is accelerating the rate of change in the finished oil markets. New improved base oils are helping the engine and equipment manufacturers meet increasing demands for better, cleaner lubricants. This is particularly true for turbine oils because turbine oils usually contain more than 99% base oil. Turbine oils made from hydroisomerized Group II base oils and the appropriate additives have demonstrated significantly longer TOST lives than turbine oils made with Group I base oils. In fact, they commonly outperform the traditional “synthetics” made with PAO.

As base oil technology continues to evolve and improve, consumers will enjoy even greater protection of automobiles, trucks, and expensive machinery such as turbines. Lubrication performance that currently can be achieved only in small-volume niche applications, using PAO and other specialty stocks, will be more widely available using the new generation of Group II and Group III oils.

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Turbine Oil Quality and Field Application Requirements

Reference: 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., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: Power generation and other types of industrial turbines have always required the use of high quality lubricants. This paper will discuss the evolution of turbine oil formulation technology, and the use of different quality products in different applications. The original "R&O" type circulating oils, which are suitable for use in many hydraulic and steam turbine systems, have a long and successful history. Next came high performance products, designed for increased operating life. Finally, products have been introduced recently that provide the high stability needed for systems which operate under severe conditions of thermal stress, such as may occur in certain gas turbine operations.

Selecting a suitable turbine oil requires meeting the application requirements of equipment and service environment, while balancing initial and life cycle cost considerations and oil performance history. Field experience with different types of equipment and different turbine oil types will be described, with examples of situations where each oil type has performed successfully. Experience with field performance problem-solving will also be addressed, such as a gas turbine filter plugging problem which was resolved by selecting the appropriate turbine lubricant.

Turbine equipment manufacturers generally specify the properties and performance requirements of turbine oils according to the type and severity of operation. Standardized laboratory tests provide an indicator of an oil's performance, although such performance needs to be confirmed by field experience. New testing tools are needed which will better correlate to the performance requirements of new generation equipment.

Keywords: turbine oil, steam turbine, combustion turbine, oxidation, antioxidant, testing, oil service life, field application, turbine severity, cyclic operation, deposits

Industrial turbines, commonly used for applications such as power generation and natural gas transmission, have always required the use of high quality lubricants. These are manufactured using a blend of highly refined or converted petroleum base oils of

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appropriate viscosity - generally of ISO 32 or 46 grades - with chemical additives that control properties of the oil which are important to the successful operation of the turbine equipment. This paper discusses the evolution of turbine oil formulation technology, and the use of different quality products in very diverse end uses.

Uninhibited refined petroleum oils were used until the 1940's when they were upgraded to the "R&O" type circulating oils by the addition of chemical additives. These are suitable for use in many hydraulic and steam turbine systems, and have a long and successful history. Such products are still available, but are now mostly used as general purpose circulating oils. Next came higher performance products (herein referred to as "Conventional turbine oils"), designed for longer operating life, and these started to become available in the 1970's and are still widely used in hydraulic, steam and low severity combustion turbines. Finally, products ("Next-Generation turbine oils") were introduced in the late 1980"s that provide the high stability needed for turbine systems operating under severe conditions of thermal stress, such as may occur in high efficiency gas turbines. Land-based aircraft turbine engines are also used sometimes for industrial applications, but their very high operating temperatures mandate the use of highly stable and very expensive synthetic lubricants. In reality, these changes evolved continuously in parallel with the evolution of turbine equipment. The historic data shown in Table 1 represent quality levels that are only broadly associated with time.

Table 1 - *Historic Industrial Turbine Oil Formulations*

	"R&O"	Conventional	Next-Generation
Basestock	Group I	Group I / II	Group II
Antioxidant	Phenolic	Phenolic + Diphenylamine	DPA, PANA, Phenolic
Supplemental Antioxidants	--	Benzotriazole	Benzotriazole, Thiadiazole, Phosphite
Rust Inhibitors	Succinic Acid / Ester	Succinimide, Succinic Acid / Ester	Succinimide, Succinic Acid / Ester
Antifoams	Silicone	Acrylate, Silicone	Acrylate, Silicone
Other	Pour Depressant, Antiwear	Pour Depressant, Antiwear, Demulsifier	Pour Depressant, Antiwear, Demulsifier

Turbine Oil Formulation

A combination of additives is used in turbine oils to control various important properties that are required for reliable, relatively trouble-free operation for an extended time period. Indeed, many low severity steam turbines have a history of requiring a full lubricant changeout only every 10 to 20 years or longer, with periodic top-up with fresh oil, of course. Antioxidants are the additives which have the strongest influence on the useful life of turbine oils. The earliest formulations used hindered phenolics for this purpose [*1*]. These molecules function by trapping reactive radical materials which are generated by oxidation of the oil hydrocarbons by air. This prevents the propagation of chain reactions which generate acids and sludge, making the oil unusable for further service. Later it was found that, at temperatures below about 110°C, the phenolics could be made more effective by adding a low level of diphenylamine antioxidant which synergistically regenerated the phenolic additive [2].

In the search for oils which could function well in turbines operating under very severe, high temperature operating conditions, basestocks with different compositions were investigated. So-called API Group II basestocks, which are manufactured by high pressure, catalyzed hydrogenation refining processes, have higher levels of saturated hydrocarbons in their composition. These are now becoming much more widely available, and they do offer some potential advantages for lubricants used in certain circumstances. However, they also have some limitations not experienced by Group I basestocks, which are manufactured from distillates by solvent extraction processing. Group II basestocks do not necessarily respond to the same antioxidants that are effective in Group I basestocks, and carefully tailored additive combinations are needed if superior oxidation resistance at high temperatures is to be achieved. The patent literature indicates that aromatic amines of various kinds are being used at increasingly higher levels in such applications, although still in combination with phenolics in some cases [*3* - *6*]. Phosphites have also been developed as supplementary antioxidants to boost the action of phenolics in Group II formulations [*7*].

It has also been discovered that other types of additives can be used to further extend the useful life of turbine oils by suppressing oxidation of the hydrocarbons [*6, 8*]. Iron and copper, which are used in the construction of turbine equipment, may slowly dissolve at parts-per million (ppm) levels in lubricant oils in service [9]. Solubilized metal ions act as catalysts for oil oxidation, so additives that actively prevent metals from dissolving, or which bind the metal ions once they are dissolved, were developed. Benzotriazoles and thiadiazoles are now commonly used for this purpose.

Interfacial properties have always been important for the successful functioning of turbine oils. Fast and complete spontaneous separation of oil and water in steam turbine systems is essential so that water does not reach key elements such as bearings and gears. If this property is not adequate, then a demulsifying additive may be employed. Air is not a good lubricant, so it is equally important that the oil does not produce a lot of foam, and that it also rejects air bubbles from the body of the oil quickly. This latter property, known as air release, has become even more important in recent years since turbine systems are being constructed with ever smaller oil reservoirs. The residence time of the oil in the sump is now much shorter, with less chance of entrained air being adequately released. Foam suppressant additives need to be carefully selected in order to prevent excessive foam formation, but still retain short air release times. Antifoam additives are moving from silicone types to acrylate types since the latter seem to give a better balance between these opposing effects.

Other important additives commonly used in turbine oils are rust inhibitors and pour point depressants [*10*]. If a turbine oil is to be used in geared equipment, then antiwear additives are also required, such as ashless phosphorus and/or sulfur compounds. Wear protection is generally specified in terms of four-ball wear (D2266) and FZG gear test (D5182) performance.

Turbine Oil Oxidation Testing

Standard testing methods developed and maintained by ASTM Sub-Committee D02.C on Turbine Oils, and other ASTM sub-committees, have made major contributions for several decades in the science of turbine oil formulation and performance assessment. Two particular standards have been widely used by formulators, product quality labs and turbine operators to determine the useful life of turbine oils. These procedures use techniques that accelerate effects that are encountered in turbine operations. They are intended to be used for particular situations, but cannot possibly directly simulate the environment encountered by oils in the multitude of turbine systems that operate under very diverse conditions.

The ASTM Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel (D 2272), sometimes referred to as "RBOT", was designed for monitoring in-service turbine oils, to warn the equipment operator when the oil was near the end of its useful life. Oil that is allowed to remain in a turbine system after degradation begins can be very damaging. Acids will attack metal surfaces, sludge will plug filters and tubes, and oxidation products can form varnish on hot surfaces such as bearings. This test is run at 150°C under pure oxygen at 620 kPa pressure and in the presence of a solid copper catalyst, in order to promote measurable oxidation in a short time. This makes it unrepresentative of most steam turbines which operate below 100°C. On the other hand, oil is mixed with water in the test, making it unrepresentative of higher temperature combustion turbines. The test is sensitive to particular additive chemistries so that differently formulated oils cannot be validly compared using this test. Further, it is not so much the initial RBOT value of a fresh turbine oil which is important, but how well the turbine oil retains its RBOT value during extended service. Nevertheless, the RBOT has been widely used for many years for controlling a wide variety of turbine and other mechanical equipment.

The ASTM Test Method for Oxidation Characteristics of Inhibited Mineral Oils (D943), sometimes referred to as "TOST", was designed to give an indication of the life of steam turbines by using a test temperature of 95°C, which is closer to that experienced in real steam turbine applications. It is run using pure oxygen, water and a combination solid iron/copper catalyst, and is reputed to be less dependent on additive chemistries than the RBOT. With Next-Generation Turbine Oils exceeding 10000 hours (almost 14 months) in the TOST test, it has become too long to be of practical use for formulating new products or evaluating turbine oils from the field. Further, the test conditions do not simulate those in high severity combustion turbines.

The formation of sludge and varnish by thermal-oxidative processes has become more critical as operating temperatures have increased. The ASTM Test Method for Determination of the Sludging and Corrosion Tendencies of Inhibited Mineral Oils (D4310) test has been used to measure sludge formation, but once again it is run under the same relatively mild conditions as the TOST and for a much shorter, 1000 hour test duration. Recently ASTM Subcommittee D02.9 on Oxidation has begun to develop the use of the ASTM Standard Guide for Universal Oxidation / Thermal Stability Test Apparatus (D4871), sometimes referred to as the "UOT", at 155°C to address the need for a determination of the tendency of turbine oils to degrade at high temperatures. It measures the formation of sludge, varnish and acids, and monitors viscosity increase.

As shown in Table 2, RBOT and TOST lives have increased for each succeeding generation of turbine oils. However, the RBOT and TOST methods do not necessarily correlate well with each other. In the same way, oils with long oxidation lives in either RBOT or TOST do not necessarily give the lowest levels of sludge formation in either the D4310 or UOT procedures.

Table 2 - *Turbine Oil Oxidation Tests*

- Typical Oxidation Test Values

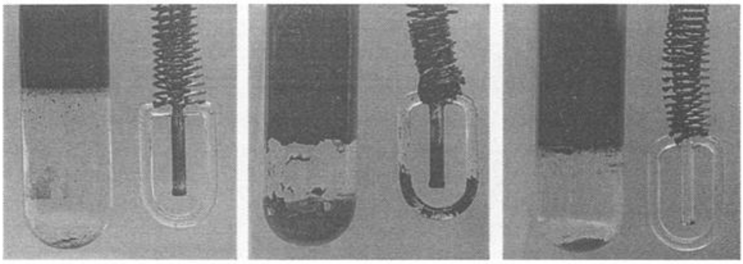
	"R & O"	Conventional	Next-Generation
D2273 (RBOT), min	250	600	1500
D943 (TOST), hr	1500	4000	10,000

- RBOT, TOST, and UOT results are not well correlated

ISO 32 Turbine Oils	RBOT (min)	TOST (hr)	D4310 (mg sludge)	UOT (155°C) (sludge)
A (Group I)	611	6564	<10	Medium
B (Group I)	880	6228	29	High
C (Group I, AW)	875	7040	60	High
D (Group II)	1675	7000	19	Low
E (Group II)	1450	>10,000	14	Low
F (Group II, AW)	1455	>10,000	96	High

It was noted previously that the TOST is most representative of steam turbine operating conditions, so that claims of very long lives - sometimes as long as 20000 hours or more - for high temperature combustion turbines, are of limited value. In addition, consider that the end-point of this test is an oil total acid number of 2.0 mg KOH/gm of oil. Figure 1 shows photographs of the oil/water interface of turbine oils formulated with Group II basestock from different manufacturers in the TOST, all at 10,000 hours test time and all with a TAN of less than 0.5 mg KOH/gm of oil. It is readily apparent that each shows characteristics which would be highly undesirable for an oil in an operating turbine, whether it be a high level of sludge and varnish, severe corrosion of the metal catalyst, or partial emulsification with the water. In addition, we know from experience in this and other tests that acidic products of oxidation often rapidly become insoluble in the oil and may not be titrated by methods D664 or D3339. This is not to say that the oils would not work well in turbine applications, just that TOST data may give an over-optimistic estimate of performance.

All Oils on Test Show T.A.N. < 0.5 mg KOH/g Oil



OIL A OIL B OIL C

- Oils which "Pass" the TOST @ 10,000 hrs are Degraded
  - Significant Sludge Formed
  - Oil / Water Separation Degraded
  - Catalyst Metal Corroded

Figure 1 - *TOST (D943) at 10000 Hours*

As discussed above, turbine oils formulated with Group II basestocks do offer some benefits compared with Group I based turbine oils, but they may also have some inherent limitations. Many turbine oil suppliers continue to offer both types of products to allow end-users to select the one that is most suited to their application. Products formulated with Group II basestocks offer longer RBOT and TOST lives, and are especially suited to high severity turbine applications. At the same time, Group II basestocks are poorer solvents than Group I, as is illustrated by their higher aniline points. This can have important consequences in at least two ways. Firstly, highly polar additives, such as rust inhibitors, may be more sparingly soluble in Group II basestocks, so that additive selection will be more limited. Dispersed additives, such as antifoams and demulsifiers, are more difficult to maintain as suspensions in Group II basestocks and have an increased tendency to drop out. Secondly, the oxidation products which gradually accumulate in all oils during service will have a greater tendency to separate from the oil and form deposits.

When a turbine oil lubricating system is drained of one turbine oil and refilled with another turbine oil, as much as 10 to 15% of the previous oil can remain in the system due to clingage, low-spots, and piping dead-legs. Compatibility between products is an important consideration when converting from one type of turbine oil to another, either from different suppliers or for different types from the same supplier. This is even more critical with Next-Generation turbine oils, where incompatibilities can result in severely downgraded turbine oil performance. Carryover from the previous product in a lubricating system conversion was simulated by adding 15% of either a Group I or Group II based turbine oil to Next-Generation turbine oils from different suppliers. As shown in Figure 2, the resulting RBOT value of the blend was significantly lower than would be expected from simple linear blending, indicating incompatibility between the additives in the two products. Significant pre-screening is required before converting a lubricating system from one product to another, including testing of all critical properties. Without such care the performance of the resultant turbine oil combination may be significantly lower (in this case, RBOT) than that anticipated from fresh oil values.

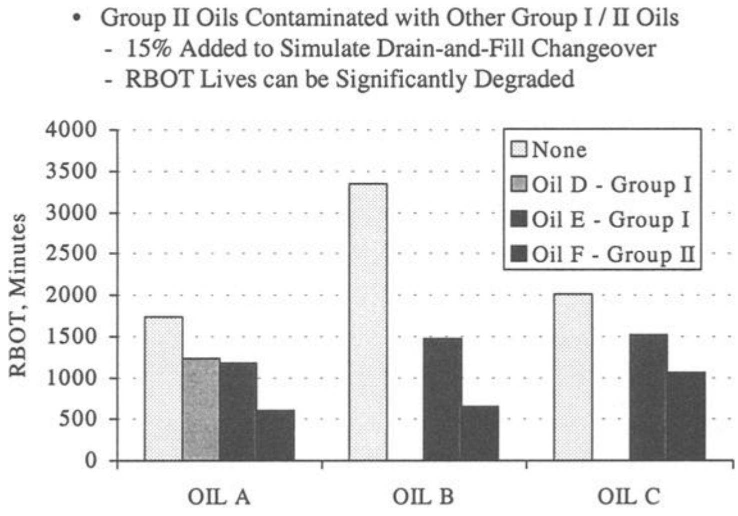

- Group II Oils Contaminated with Other Group I / II Oils
  - 15% Added to Simulate Drain-and-Fill Changeover
  - RBOT Lives can be Significantly Degraded

Figure 2 - *Turbine Oil Cross-Contamination*

Steam Turbine Applications

The lubricating oil in both steam and combustion turbines is responsible for proper lubrication of the journal and thrust bearings, and may also serve as the lubricant for peripheral equipment [*11*]. The oil must be able to remain stable during its long operating life, retaining its viscosity, rust prevention, demulsibility, and oxidation resistance. The ASTM Practice of In-Service Monitoring of Mineral Turbine Oils for Steam and Gas Turbines (D4378) provides guidance on tolerable limits for changes in the turbine oil performance properties during normal service [12]. Although laboratory testing is useful in defining the quality of fresh turbine oil, the ultimate test of robustness is in actual field applications.

Typical bearing temperatures in a steam turbine range from 50 - 70°C, although local temperatures may be much higher. These temperatures accelerate turbine oil oxidation, although not to the extent found in combustion turbines. During normal operation of a steam turbine water can enter the turbine oil through leaks in the shaft seals or cooling coils, becoming entrained in the oil, and it is important that the oil retain its ability to shed water (demulsibility). Water can collect on metal surfaces, especially during start-up and shutdown, and the turbine oil needs to retain its rust protection. Particulates can enter the system through open air-breathers or improper oil addition procedures, and the turbine oil performance must not be impacted by typical inorganic contaminants (which are ultimately removed by external filtration systems). Despite these many deleterious factors, a robust turbine oil can remain in steam turbine service for several *decades*!

In one example, two 125 MW steam turbines have been successfully operating on a Conventional turbine oil since 1957. The turbine oil in the two 4000 gallon reservoirs had not been changed during the 40+ years of operation, except for normal make-up for oil losses. During recent routine sampling the turbine oil showed very little degradation from the original product. The viscosity remained in the ISO 32 range and the oil showed very low levels of particulates (ISO 15/11 - 17/13) and low metals content. Low water levels (less than 100 ppm) confirmed the retention of water shedding ability over this period. Very little oxidative degradation had occurred during this period, as confirmed by the low Total Acid Number of 0.11 mg KOH/gm, which was similar to the original turbine oil. However, slow oxidation over this long period had begun to deplete the oxidation inhibitors, with RBOT values at 13 - 25% of the original product level, indicating that a turbine oil change or sweetening should be considered. This long term reduction in oxidation life was confirmed by FT-IR analysis, which showed that the antioxidant was near depletion. Nevertheless, it is important to note that this extremely long life in this steam turbine was obtained with a Conventional turbine oil. It is unlikely a Next-Generation turbine oil would have provided longer service, given the variety of factors (temperature swings, water ingression, contamination, etc.) which can adversely impact a steam turbine oil system.

A second example comes from a 45 MW steam turbine operated as part of a combined cycle cogen facility. In this case, an anti-wear Conventional turbine oil was used due to the gearing on the companion combustion turbine. The turbine oil has continued to perform successfully in continuous operation for over 23000 hours. Samples taken at the end of 1999 showed excellent resistance to oxidation, with a TAN of 0.11 mg KOH/gm oil, and excellent demulsibility. Figure 3 confirms the oxidation resistance of the turbine oil, showing the RBOT of the oil from the steam turbine sump over a two year period, with the oil still retaining ~70% of its original RBOT value.

Continuously Operated Combustion Turbines

A continuously operated, or baseloaded, combustion turbine is kept running on an ongoing basis providing power at that location or supplying into the utility grid. Turbine oil temperatures range from 70 - 100°C, although newer, more severe combustion turbines can produce oil temperatures of 120°C (12). In continuously operated combustion turbines Conventional turbine oils have also shown excellent performance.

In the cogen example cited above, the companion 70 MW geared combustion turbine also operated with an anti-wear Conventional turbine oil, with a separate turbine oil sump. Again, after over 23000 hours of operation the turbine oil shows excellent oxidation resistance, with a TAN of 0.11 mg KOH/gm of oil, and excellent demulsibility. Figure 3 confirms the oxidation resistance, with the RBOT retaining ~85% of its initial fresh oil value.

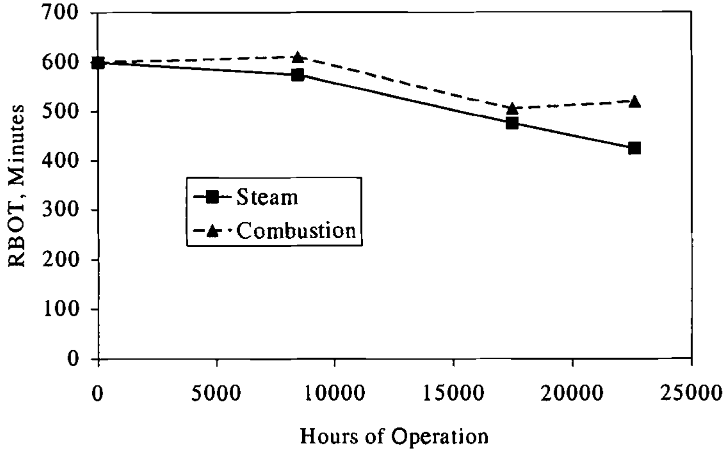


Figure 3 - *Performance of Conventional Anti-Wear Turbine Oil in Cogen Steam and Combustion Turbines*

A second example is from a series of eight 35 MW combustion turbines running continuously in a municipal utility. The units ran with a Conventional turbine oil which had not been changed during the 20+ years of operation, except for normal make-up for oil losses. In a recent sample the turbine oil showed very little degradation from the original product. The viscosity remained in the ISO 32 range and the oil continued to demonstrate good rust protection. Retention of water shedding ability over this period was confirmed by low water levels (less than 30 ppm). Very little oxidative degradation and sludge formation had occurred during this period, as confirmed by the low Total Acid Number of 0.01 mg KOH / gm which was similar to the original turbine oil. However, slow oxidation over this long period had begun to deplete the oxidation inhibitors, with RBOT values at <15% of the original product, indicating a turbine oil change or sweetening should be considered. Again, it is worth noting that this extremely long service life was obtained with a Conventional turbine oil.

Cyclically Operated Combustion Turbines

One application where the enhanced oxidation stability of the next-generation turbine oils has proven to be of value is in combustion turbines that are cyclically operated in peak-loading operations. The turbine oil is subjected to high temperatures during turbine operation, and then is allowed to cool during the stand-down period. When this cyclic operation is combined with more severe, high temperature combustion turbines, the lubricating oil is subjected to extreme thermal and oxidative stresses.

In one field example, a series of 80-90 MW combustion turbines were peak operated on a weekly cycle. During weekday operation the turbine oil was subjected to typical operating temperatures of 70 - 80°C, with isolated peaks approaching 120°C, in the main shaft bearings, then returned to ambient temperature when idled over the weekend. In addition to lubricating the shaft bearings, the turbine oil also provided hydraulic power to the fuel ratio servo control valves. A Conventional turbine oil was used in the system for approximately two years, at which time a non-start condition occurred due to loss of hydraulic pressure to the servo-valve. The hydraulic failure was traced to plugging of the fine pencil filter immediately upstream of the servo-valve.

Infra-red analysis of the deposits removed from the pencil filter showed oxidation by-products, with no significant additive or metals content. The turbine oil itself (Table 3) was in relatively good condition, with low TAN and satisfactory RBOT. The oil was clear at normal turbine operating temperature, but slightly cloudy at ambient temperature. When filtered through a 5 micron filter the oil contained about 90 ppm of an organic particulate.

Table 3 - *In-Service Turbine Oil Analysis*

Viscosity, cSt @ 40°C (ASTM D 445)	32.8
Neutralization No., mg KOH / gm (ASTM D 664)	<0.1
Rotary Bomb Oxidation Test - RBOT, minutes (ASTM D 2272)	360
Particulates, 5 µm filtration at ambient temperature, ppm	90

It was concluded that the organic deposits were the result of normal high temperature oxidation of the turbine oil. During turbine operation these organic particulates would either be removed by the oil filtration system or remain in solution at the 70+°C operating temperatures. However, when the turbine was idled the oil temperature would fall to near ambient and the low level particulate would come out of solution, building up over time in the pencil filter which protected the fuel ratio servo-valve. This situation is unique to cyclic operation, since in base loaded, or continuously operating, combustion turbines the oil temperature is not subject to wide fluctuations on a routine basis.

Next-Generation Turbine Oil

Several approaches were considered to address the pencil filter plugging issue. The most obvious approach would be to use finer filtration media in the turbine oil circulating system. However, since the oxidation by-products were soluble at operating temperatures, improved filtration during operation would not remove the particulates that formed only when the turbine was idled.

The approach selected was to utilize the enhanced oxidation stability of a Next-Generation turbine oil to slow the build-up oil oxidation by-products. The turbine oil utilized a Group II basestock with a balanced additive package providing good foam, rust, and demulsibility performance. The oil showed exceptional resistance to oxidation in both the RBOT and TOST tests, and to sludge formation.

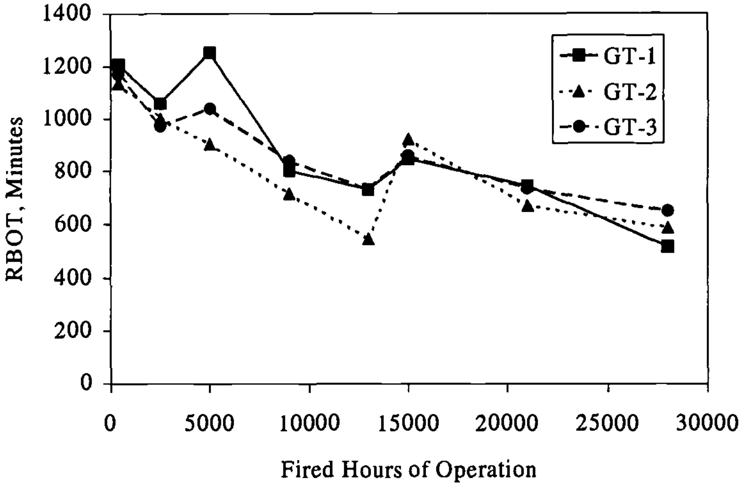


Figure 4 - *Performance of Next-Generation Turbine Oil in Cyclically Operated Combustion Turbine*

The Next-Generation turbine oil was installed in three identical high temperature combustion turbines in 1996. The turbines have continued to run in the weekly cycled mode since that time, with no evidence of sludge formation, pencil filter plugging, or non-start conditions. Table 4 shows the periodic oil monitoring for one of the three turbines, with the other two systems showing similar results. Overall performance has been excellent, with retention of demulsibility, foam resistance, and rust protection properties. Over the 3+ year period, TAN has remained low and RBOT remains at 60% of the original (see Figure 4), well above the recommended oil change-out limits.

Conclusions

Turbine oil quality, for both steam and combustion turbine applications, has continuously evolved over the last two decades. Improvements have been made in both the additive chemistry and basestock selection. While laboratory testing is useful in developing turbine oil formulations, field performance validation is essential to validating the ultimate service life. Interactions between turbine oils need to be considered when changing out the turbine oil in the lubricating system.

Conventional turbine oils have shown excellent, cost effective field performance, with service lives which can be in excess of 20 years for steam turbines and 10 years for combustion turbines. Next-Generation turbine oils show benefits in cyclically operated, high temperature combustion turbines, where the higher oxidation stability provides resistance to the formation of oxidation by-products which can settle out when the turbine is idled. Both types of turbine oils provide the turbine operator with the flexibility to select a product which suits a particular application.

Table 4 - *Monitoring of Next-Generation Turbine Oil in Cyclically Operated Combustion Turbine*

Months in Combustion Turbine	1	6	10	18	22	27	38
Hours of Fired Operation	400	2800	4700	9200	12700	14500	21300
Number of Fired Starts	3	16	27	54	81	102	175
Viscosity, cSt @ 40°C (ASTM D445)	32.4	32.7	32.7	32.7	32.9	32.8	33.1
Neutralization Number, mg KOH / gm (ASTM D974)	0.04	0.06	0.03	0.04	0.06	0.01	0.02
Rotary Bomb Oxidation Test - RBOT, minutes (ASTM D2272)	1207	1061	1256	803	732	847	744
Particle Count - ISO Classification	20/17	13/10	14/11	18/9	12/8	15/13	14/11
Rust Test, Seq. A (ASTM D665)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Foam Tendency / Stability, Seq. II, mL (ASTM D892)	0/0	20/0	20/0	30/0	30/0	-	60/0
Demulsibility, minutes to 37 mL H2O (ASTM D1401)	15	15	20	15	30	24	30

Finally, new laboratory tests need to be developed for the formulation and evaluation of turbine oils. The TOST test (D943) runs too long to be an effective screening tool, and the conditions are too mild to simulate a combustion turbine. The RBOT test (D2272) is effective as a field monitoring tool, but does not correlate well with other oxidation tests. We encourage the ASTM Subcommittee D02.C on Turbine Oils to take on the challenge of developing a rapid laboratory oxidation test that can be correlated to field turbine performance, allowing turbine operators to evaluate and select robust turbine oils for their equipment.

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Douglas J. Irvine[1]

Performance Advantages of Turbine Oils Formulated with Group II and Group III Basestocks

Reference: 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., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: High temperature gas turbine applications, such as GE Frame 7 turbines, place high demands on the thermal and oxidative stability of turbine oils. Successful products not only start with a superior quality basestock, but must also employ a carefully balanced, low volatility, thermally stable additive system. The excellent properties of Group II and Group III basestocks such as high viscosity index, low volatility, superior oxidative resistance, and high thermal stability make them ideal choices for this service. Turbine oils formulated with severely hydrocracked Group II and Group III basestocks offer performance on par with those formulated with synthetic hydrocarbons.

A brief review of the role and requirements of modern turbine oils is given together with a more extensive look at current basestock technology versus traditional solvent refined basestocks. Additive selection for high temperature turbine oils is also discussed.

In addition, data presenting the impact of poly-cycloparaffin content on the stability of highly saturated Group II and Group III basestocks is presented. The oxidative stability of additized basestocks increases as poly-cycloparaffin content decreases.

Keywords: turbine lubricant, antioxidants, basestocks, high temperature, hydrocracked, iso-dewaxed, cycloparaffins

Introduction

There have been steadily increasing demands placed on turbine lubricants over the past few decades. As turbine power outputs have increased, oil volumes in turbine reservoirs have decreased. Bearing temperatures have risen to over 315°C (600°F) and elaborate labyrinth air sealing systems have been developed to shield the lubricant from these high temperatures [*1*]. The lubricant, however, still sees relatively high

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temperatures, as it must cool the bearing and bearing housing. In addition, the lubricant is exposed to the hot sealing air from the labyrinth seal, which tends to strip out volatile oxidation inhibitors [*2*]. The end result is increased thermal stresses on the lubricant and increased bulk operating temperatures. These demands have led to the development of high-temperature lubricants specifically designed for heavy-duty gas turbine service [*3*].

General Electric's Frame 7 gas turbine oil specification (GEK 32568) highlights the severe requirements of gas turbine oil service and the need for thermally stable, low volatility antioxidants.

The increased occurrence of cogeneration or combined cycled turbine operation (in which the waste heat from the gas turbine exhaust is used to drive a steam turbine) has also placed new demands on turbine lubricants. Lubricants are now commonly required to meet both steam and gas turbine oil performance specifications.

Historically turbine lubricants have been simple rust and oxidation inhibited solvent refined oils. Wet seal designs led to high oil make-up rates, which served to replenish the oil's additive system. Hence oil change outs were infrequent, and even oils of moderate stability had long service lives.

Today's heavy-duty high temperature gas turbines use dry seals and hence have very low oil make-up rates. This coupled with the increased severity of operating conditions necessitates close monitoring and more frequent oil change outs.

Turbine Lubricant Role and Requirements

The three main roles a turbine lubricant must fulfill are 1) bearing lubricant, 2) heat transfer fluid, and 3) hydraulic control fluid. Oxidation of the lubricant can change its physical and chemical properties making it less efficient at, or preventing it altogether from performing these key functions. Physical changes include viscosity increase, which leads to excess friction in the bearings and an accompanying generation of heat. Higher viscosity in itself also leads to reduced heat transfer. This heat buildup serves to further accelerate fluid oxidation and breakdown, leading to varnish, sludge, and deposit formation. Sludge and varnish can plug filters and prevent proper operation of hydraulic control devices. Sludge and varnish buildup also tends to insulate the bearings, further exacerbating the problem of poor heat transfer.

Chemical changes due to oxidation lead to formation of acids and other oxygenated species. These oxidation products can cause rust and corrosion, attack seals, and promote foaming and poor demulsibility. Polar oxidation products can also compete with EP/anti-wear additives and corrosion inhibitors for surface activity leading to poor performance.

In addition to accelerating oxidation, high temperatures also lead to additive breakdown and evaporation. Examples of heat sources that turbine lubricants are exposed to include: the bearing oil film (93°C), bearing housing inner surfaces (149°C), sealing air entering the oil spaces (204°C), and the hot turbine shaft (204°C). Smith [*3*] concluded that about 2% of the oil flow in a turbine at temperatures above 204°C accounts for more than 90% of the used oil life (i.e. high temperature exposure of small quantities of oil dictates the bulk oil life).

In order to function effectively over long periods of time a turbine lubricant must, therefore, have excellent thermal and oxidative stability. One of the key factors to achieving this stability is the selection of a highly refined, high purity basestock. This alone, however, will not yield a long life turbine fluid. The antioxidant system employed must also possess excellent thermal stability and have low volatility.

Basestock Technology

Base Oil Type

Refined base oils are complex mixtures of various hydrocarbon structures including paraffins, cycloparaffins, and aromatics. Depending on the refining process used they can also contain significant amounts of sulfur, nitrogen, and oxygen containing compounds. The two main types of base oils available in the marketplace today are naphthenic and paraffinic. Naphthenic base oils are characterized by high aromatic and cycloparaffin content, but have low wax content. They have low viscosity indexes, low pour points, and good solvency, but suffer from poor oxidative stability due to their high aromatic content. Because of their poor oxidative stability, naphthenic base oils do not find their way into most lubricant applications.

Paraffinic base oils are characterized by high paraffin, cycloparaffin, and wax content. They have higher viscosity indexes and good oxidative stability, but have poorer solvency and pour points. Highly refined paraffinic base oils with their high degree of saturates and low sulfur, nitrogen, oxygen, and aromatic content, have been used for years in turbine lubricants. Recent advances in refining and dewaxing technology, however, now offer paraffinic base oils with even higher levels of saturates, and almost no sulfur, nitrogen, oxygen, and aromatic content.

Base oil chemical structure and its impact on lubricant performance is shown in Table 1. Careful molecular tailoring in the refining process can optimize performance by selective removal or transformation of undesirable components via ring saturation and ring opening processes. Desirable paraffins and cycloparaffins yield high viscosity indexes and good oxidative stability, while undesirable aromatics and hetero-atoms lead to instability and deposit formation.

Table 2 gives a more detailed overview of the impact of hydrocarbon structure on viscosity index, pour point, and oxidative stability.

Removal of the undesirable sulfur, nitrogen, oxygen, and aromatic components in paraffinic base oils can be accomplished via solvent refining or hydrocracking, although hydrocracking is more effective. Severe hydrocracking offers almost complete removal of these compounds. The use of iso-dewaxing technology offers further refinements through increasing desirable iso-paraffin content. These refining steps have been described in further detail elsewhere [*4*, *5*]. Severely hydrocracked and iso-dewaxed basestocks have high viscosity indexes and respond well to pour point depressants. This makes them ideally suited to operating environments with wide temperature ranges.

Table 1. *Impact of Chemical Composition on Lubricant Performance*

Chemical Composition		Performance Impact
Saturates		Viscosity Index
- Paraffins (N- & ISO-)	→	
- Cycloparaffins (Naphthenes)		Oxidation Stability
		Pour Point
Aromatics	→	
- Alkyl Benzenes		Volatility
- Naphtheno-Aromatics		
- Multi-Cyclic Aromatics		Solubility
	→	
Hetero-atoms		Seal Characteristics
- Sulphur, Oxygen, Nitrogen		
		Response to Additives

The American Petroleum Institute (API) classifies basestocks according to sulfur content, saturates, and viscosity index as shown in Table 3.

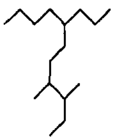
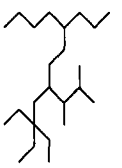
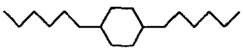
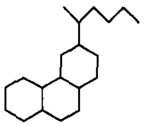
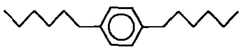
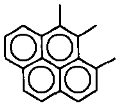
Typical chemical compositions of 4 cSt (approximate viscosity at 100°C) API Group I through IV basestocks are shown in Table 4. As the degree of refining is increased from solvent refining to severe hydrocracking significant reductions in aromatic content are achieved. Moving from solvent dewaxing to iso-dewaxing yields significant increases in iso-paraffin content, and hence viscosity index. Refining and dewaxing technology now allows production of Group III basestocks which are closer akin to synthetic Group IV basestocks than solvent refined Group I basestocks. Recent rulings in the United States, in a well known dispute between Castrol and Mobil, have indicated that these new basestocks may in fact be called "synthetic" (April 1999 decision by the National Advertising Division of the Council of Better Business Bureaus).

Basestock Research

Increasing performance demands can only be met up to a point by increasing additive treat rates. At some point the formulator must look at the limitations of the basestock being employed. Solvent refined oils cannot meet today's heavy-duty high temperature gas turbine performance requirements. Mobil [*6*] notes that they have used high-quality hydrotreated basestocks in their premium turbine oils worldwide since the mid 80's. They comment that the low sulfur and aromatic levels provide excellent oxidation and colour stability.

Attributes of severely hydrocracked/hydrotreated basestocks include: 1) extremely low aromatic contents, 2) very low sulfur levels, 3) water white colour, 4) low DBD/DBF levels (dioxin precursors), 5) excellent high temperature stability, and 6) excellent water and air separation characteristics.

Table 2. *Effect of Hydrocarbon Structure on Selected Lubricant Properties*

Chemical Type	Structure	Viscosity Index	Pour Point	Oxidation Resistance
n-Paraffin (Wax)		Very High ~ 175	Solid @ 50°C	Excellent
Iso-Paraffins with branched chains		High ~150	Good	Excellent
Iso-Paraffins with highly branched chains		Good ~130	Good	Excellent
Cyclo-Paraffin - single ring with long chains		Good ~130	Good	Good
Naphthenes, polycondensed		Poor ~60	Good	Medium
Monoaromatics, long chains		Poor ~60	Good	Medium
Polyaromatics		Very Poor <0	Good	Very Poor

It is well known that aromatic and sulfur contents have a strong influence on the oxidative stability of base oils. Unadditized solvent refined oils have better oxidative stability than hydrocracked base oils and PAOs (polyalphaolefins), which have very low aromatic and sulfur contents. Certain natural sulfur and aromatic compounds present in solvent refined base oils act as oxidation inhibitors, and it has been found that there is also an optimal aromaticity level [7]. However, it has also been noted that higher aromatic contents lead to increased deposit formation in oxidized base oils [8]. The presence of aromatics can also lead to the formation of insoluble compounds if oils are exposed to high temperatures.

Table 3. *API Base Oil Categories*

Base Oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	< 90	80 to 119
Group II	≤ 0.03		≥ 90	80 to 119
Group III	≤ 0.03		≥ 90	≥ 120
Group IV	All polyalphaolefins (PAOs)			
Group V	All basestocks not included in Groups I, II, III, or IV			

Table 4. *Chemical Composition of Various Classes of 4 cSt API Basestocks*

Basestock	A	B	C	D	E	F	G	H
API Classification	I	I	II	II	II	II+	III	IV
Description	Solvent Refined	Solvent Refined	Hydro-Cracked	Hydro-Cracked	Severely Hydro-Cracked	Severely Hydro-Cracked	Severely Hydro-Cracked	PAO
Dewaxing Method	Solvent	Solvent	Solvent	Iso	Solvent	Iso	Iso	None
Mass Spec Analysis								
Paraffins, n & iso-	25.7	29.0	23.7	30.2	32.6	51.4	76.1	100.0
Mono-Cycloparaffins	20.8	25.0	30.8	30.5	34.2	24.4	14.7	--
Poly-Cycloparaffins	27.9	31.7	39.1	35.3	32.8	23.9	9.2	--
Aromatics	24.9	14.2	6.4	4.0	0.4	0.3	--	--
Thiophenes	0.7	0.1	--	--	--	--	--	--
Paraffins + Mono-Cycloparaffins	46.5	54.0	54.5	60.7	66.8	75.8	90.8	100.0

While natural aromatic and sulfur content in solvent refined base oils enhances their inherent oxidative stability, it is a strong liability in their response to antioxidant additives. Rasberger [9] noted that the oxidative stability and sludge forming tendency of additized hydrotreated basestocks, with low aromatic and sulfur content, are clearly superior to that of solvent refined oils. It was also noted that polar compounds present in solvent refined oils (especially aromatics and nitrogen containing compounds) reduce antioxidant efficacy through interactions. In addition, solvent refined oils contain naturally occurring pro-oxidants, which have a further negative impact on basestock stability.

Gatto and Grina [*10*] noted large differences in the response of different hydrocracked basestocks to an optimized hindered phenol/alkylated diphenylamine ratio. A very high viscosity index Group II basestock significantly outperformed other Group I and II basestocks tested.

Galiano-Roth and Page [*11*] show the superior response of two-stage hydroprocessed oils to antioxidants. The oxidative performance increased as total and polynuclear aromatics decreased. Galiano-Roth and Page noted that while oxidation stability is increased by hydroprocessing, solvency (for additives and oxidation products) is decreased. Solubility problems were observed when an additive system typically employed in solvent refined basestocks was examined in the hydroprocessed basestocks.

It was also noted by Deckman et al [*6*] that hydroprocessing reduces the natural dispersancy of basestocks because aromatic levels are decreased. This can be offset by the use of dispersants in certain classes of lubricants, but not in turbine oils where excellent air and water separation are required. They note that the very low aromatic levels in severely hydrocracked basestocks can lead to problems in terms of additive solubility (especially with high-temperature antioxidants needed for gas turbine oils) and oxidation product solubility.

Recent work comparing the performance properties of low aromatic content hydrocracked basestocks and PAOs indicates that performance properties (including oxidative stability of the additized basestocks) can be predicted from their chemical composition [*12*]. It was observed that oils containing low levels of condensed multi-ring naphthenic structures exhibited superior oxidative performance and lower volatility, but had poorer solvency. The Group III basestocks tested had oxidative performance on par with the PAOs. It was also noted, as in previous work, that these highly saturated basestocks can cause solubility limitations with certain additives.

The comparable performance of Group III basestocks and PAOs is in agreement with a previous study by researchers (Henderson et al) at the author's company [*13*]. In this study a wide range of commercially available industrial oil additive packages, designed for synthetic basestocks, were used to compare the performance of Group III and Group IV basestocks. In all packages tested the Group III basestock showed very comparable oxidative performance to the synthetic Group IV basestock (Figure 1).

Table 5 shows a more exhaustive comparison of the Group III and Group IV basestocks in commercial circulating oil additive package A (CIRC OIL A). Again the Group III basestock showed comparable oxidative performance to the Group IV basestock on all tests.

Additive Selection for Turbine Oils

Additive selection is an integral part of formulating a high temperature turbine oil using Group II and higher basestocks. The additive system must be carefully balanced, be of low volatility, and have good thermal stability, but must also have adequate solubility in the basestocks employed in the turbine oil formulation. This last requirement can be one of the greatest challenges facing the formulator as performance requirements become more demanding necessitating higher treat rates and/or different additive chemistries.

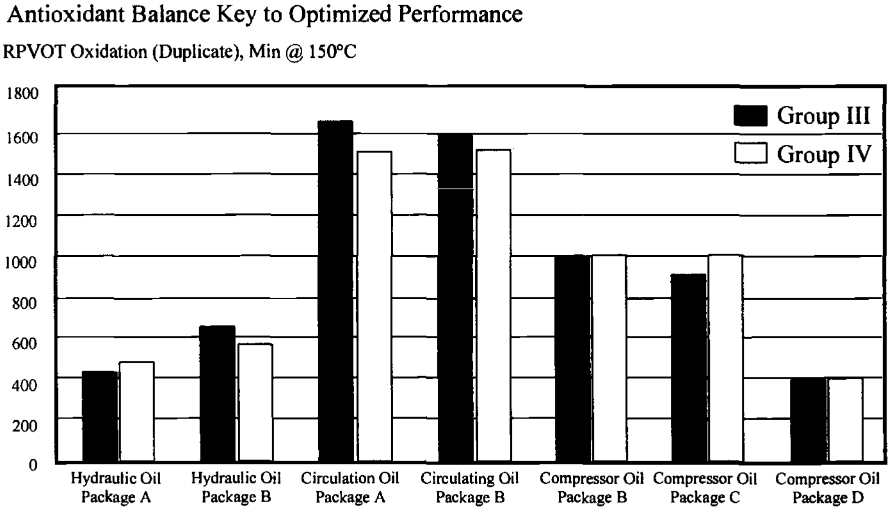


Figure 1. *RPVOT Performance Comparison Using Various Commercial Additive Packages (Henderson et al [13] with Permission)*

Table 5. *Commercial Synthetic Circulating Oil Additive Package (Henderson et al [13] with permission)*

Finished Oil Properties	Group III	Group IV
Kinematic Viscosity@40°C, cSt	32.5	32.0
Viscosity Index	134	137
Pour Point, °C	-39	<-51
RPVOT @150°C , Min.	1628	1492
Oxidation Stability (ASTM D-4310)		
mg Sludge	31.6	791.2
CIGRE Oxidation (IP280)		
Volatile Acidity, mg KOH/g	0.02	0.03
Sludge, %	0.10	0.06
Top. %	0.12	0.07
Thermo-oxidative stability (FTMS 591C5308.6)		
72 Hrs. @204°C , 5L AIR/HR		
Vis. Inc. @40°C, %	2.0	2.4
Sludge, mg/100 mL	202.4	221.7
Solids, %	<0.01	<0.01
IP48 Oxidation (170°C, 48HR)		
Vis. Inc. @40°C, %	2.8	1.7
Δ TAN, mg KOH/g	0.1	0.1
Wt. Loss%	3.1	1.4
Solids, %	0.03	0.03

Additive balance encompasses the concepts of additive interaction and reaction, and optimization to take advantage of additive synergies in order to minimize treat rates. While minimizing the additive treat rates required to achieve a given performance level makes good economic sense, it also has other important benefits. Low treat rates help alleviate additive solubility concerns with these highly non-polar basestocks, which have low aromatic levels and high aniline points. Using high treat rates of antioxidants to achieve oxidative performance can lead to problems with sludge and deposit formation.

Current Trends

Traditional turbine lubricants consist of solvent refined oil and 2,6-di-tert-butyl-para-cresol (DBPC), or DBPC plus an amine. This chemistry, however, cannot meet modern high temperature gas turbine demands due to its high volatility. It has been noted that DBPC, even in lower temperature steam turbine service, is largely consumed through evaporation [*14*]. The inadequacy of DBPC based formulations is highlighted by Smith [*3*], who presents data on a dozen commercial DBPC containing turbine oils, which failed after short periods of service (< 1 year) in high temperature gas turbines. The average bearing housing temperature in the turbines was 300°C, with a range of 289°C to 311°C.

Some OEM turbine oil specifications make explicit reference to low volatility phenolic antioxidants such as DBPC (e.g. GEK 32568), prohibiting or warning against their use. The specifications include tests designed to preclude the use of formulations employing volatile antioxidants. One example is the inclusion of a modified RPVOT (Rotating Pressure Vessel Oxidation Test) test in which before being tested, the lubricant is first stripped of any volatile additives by heating it to 121°C and blowing it with nitrogen for 48 hours. Low volatility necessitates the use of high molecular weight antioxidants, which typically have limited solubility in hydrocracked basestocks.

Rasberger [*9*] presents data highlighting the improvements that can be achieved in turbine lubricants using new generation lower volatility difunctional antioxidants. It is not clear, however, how strong a role decreased volatility plays.

Antioxidants

It is well known that combinations of hindered phenols and alkylated diphenylamines have synergistic antioxidant effects. This synergy, however, is dependent on the characteristics of the basestocks and the oxidative environment employed. The optimal phenol/amine ratio employed in one type of basestock may not be optimal for another. Simply taking an off the shelf additive package designed and tested for traditional solvent refined oils and employing it in Group II and higher basestocks is likely to have sub-optimal results. While Group II and higher basestocks will almost certainly yield superior performance to traditional solvent refined oils using a given package, balancing the phenol/amine ratio using individual components will yield superior results [*10*].

Attempting to use an off the shelf additive package also raises the distinct possibility of incurring additive solubility problems.

Further optimizations of oxidative performance can be achieved by the inclusion of a different class of antioxidant. Hindered phenols and alkylated diphenylamines both represent free radical scavengers. Peroxide decomposers (traditionally organosulfur and organophosphorus compounds) such as phosphites and selected sulfur compounds represent this other class of antioxidant.

As noted previously, the oxidative stability of unadditized base oils is dependent on their aromatic and sulfur contents, with solvent refined base oils outperforming PAOs. Practical experience in the laboratory has shown that the sulfur content of additized base oils is also very important. While the oxidative stability of additized PAOs and hydrocracked base oils is far superior to solvent refined base oils, it can be further optimized with the inclusion of a carefully selected synthetic sulfur carrier.

Gatto and Grina [*10*] observed strong synergies between hindered phenols and diphenylamines when hindered phenols containing sulfur and aliphatic amines were used. These functional groups within the hindered phenols act as peroxide decomposers. The sulfur containing hindered phenol, however, did not have any significant effect in solvent refined basestocks which were also tested. Gatto and Grina also noted an extremely strong synergism when a synthetic sulfur source was used in combination with an optimized phenol/amine ratio. The sulfur carrier mimics the role of naturally occurring sulfur found in less highly refined base oils which acts as a peroxide decomposer.

Phosphorus type chemistry can also effectively fill this role as shown in a patent [*15*], which deals with the stabilization of hydrocracked basestocks and PAOs using a hindered phenol and a phosphite. In this work it was noted that while the antioxidants offered significant benefits in hydrocracked basestocks and PAOs, no significant improvement in oxidative stability was realized when the antioxidants were employed in a solvent refined basestock.

Testing and Materials

The oxidative performance of three severely hydrocracked basestocks was compared to that of a PAO using RPVOT [ASTM Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel (D 2272)], and pressurized differential scanning calorimetry (PDSC). The additive systems employed were a commercially available turbine oil package, and two experimental antioxidant systems which exhibit good solubility in the basestocks tested.

RPVOT test conditions used were in accordance with ASTM D 2272: 150°C, 90 psi oxygen, 50 g sample, 10 mL water, and a polished copper coil catalyst.

PDSC test conditions were 500 psi oxygen at 100 mL/min, isothermal operation at 175°C and 190°C with a 10°C/min initial temperature ramp, 1.5 mg sample, and open aluminum pans.

The basestocks employed in this study were representative of Group II through Group III basestocks. Their basic physical properties are shown in Table 6.

Table 6. *Basestock Properties*

Property	Basestock 1	Basestock 2	Basestock 3	Basestock 4
API Category	Group II	Group III[1]	Group III	Group IV
Viscosity @ 40°C, cSt	34.02	31.36	32.48	30.48
Viscosity @ 100°C, cSt	5.52	5.76	5.99	5.83
Viscosity Index	97	127	132	138
Density @ 15°C, kg / L	0.8674	0.8398	0.8372	0.8270

[1] Blend of Group II and Group III basestocks.

Basestocks 2 and 3 represent blends of 100 Neutral Group II+ and Group III basestocks, respectively, with a 325 Neutral Group III basestock. Group II+ refers to Group II basestocks with a viscosity index close to the Group II upper limit of 120. An ISO 32 viscosity grade (28.8-35.2 cSt at 40°C) was chosen as this is a commonly used viscosity grade for turbine oils. A chemical analysis of the basestocks as well as details on the refining and dewaxing methods used in their manufacture is given in Table 7.

Table 7. *Basestock Chemical Characteristics*

Basestock	1	2	3	4
API Classification	II	III (blend)	III	IV
Description	Severely Hydro- Cracked	Severely Hydro- Cracked	Severely Hydro- Cracked	PAO
Dewaxing Method	Solvent	Iso	Iso	None
Mass Spec Analysis				
Paraffins, n & iso-	21.7	52.9	59.4	100.0
Cycloparaffins	78.2	47.1	40.6	--
Mono-Cycloparaffins	26.9	25.1	23.3	--
Di-Cycloparaffins	20.3	12	10.6	--
Tri-Cycloparaffins	14.9	6	4.2	--
Tetra-Cycloparaffins	10.6	2.5	2.2	--
Penta-Cycloparaffins	4.1	1.4	0.2	--
Hexa-Cycloparaffins	1.3	0.1	--	--
Hepta-Cycloparaffins	0.1	--	0.1	--
Aromatics	0.1	--	--	--
Paraffins + Mono-Cycloparaffins	48.6	78.0	82.7	100.0
Poly-Cycloparaffins	51.3	22.0	17.3	0

The severity of the hydrocracking process used in the production of these basestocks results in negligible aromatic, sulfur, nitrogen and oxygen content. Moving from solvent dewaxing to catalytic iso-dewaxing increases the content of the more desirable iso-paraffins and decreases the poly-cycloparaffin content, bringing the chemical composition closer to that of a polyalphaolefin.

Results and Discussion

A commercially available turbine oil additive package was evaluated using basestocks 1 through 4 using RPVOT and PDSC. TOST (Turbine Oil Stability Test), the ASTM Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils (D 943), was not performed in this study due to time constraints. Previous experience with the commercial turbine package shows TOST performance greater than 5,000 hours in Group II basestocks. Figure 2 shows increasing RPVOT stability as we move from basestock 1 to basestock 4. PDSC oxidation induction times at 175°C showed a similar trend (Figure 3).

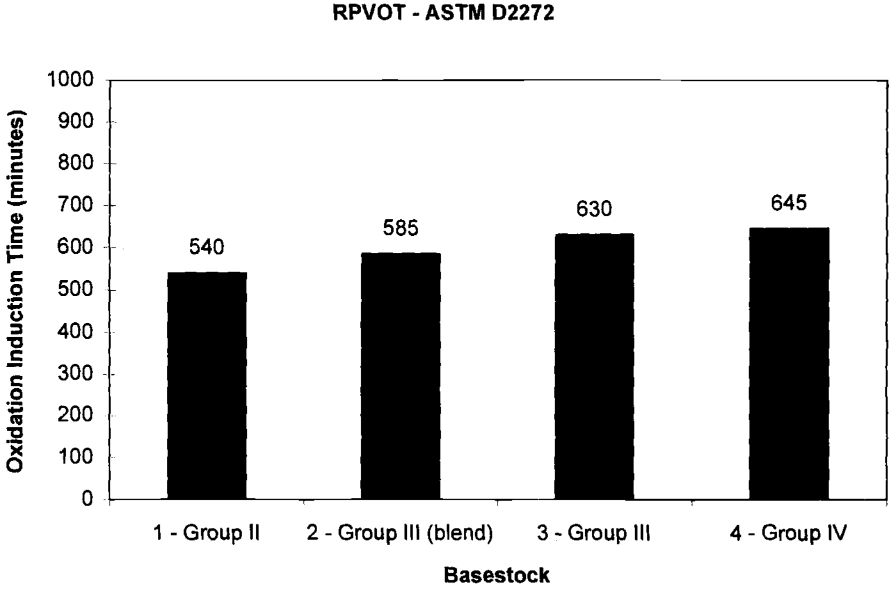


Figure 2. *RPVOT Performance Using Commercial Circulating Oil Additive Package*

Both the RPVOT and DSC performance of basestock 3 (Group III) was closest to that of basestock 4 (PAO), as expected. Figure 4 compares the observed oxidative stabilities with the poly-cycloparaffin content. The oxidation induction times increase as the poly-cycloparaffin content decreases.

Many low volatility antioxidant additives are solids at room temperature, and have poor solubility in severely hydrocracked basestocks. They often require high temperatures in order to be dissolved, and are difficult to handle in manufacturing environments. In this work, a low volatility antioxidant system was developed which exhibited good solubility in severely hydrocracked basestocks.

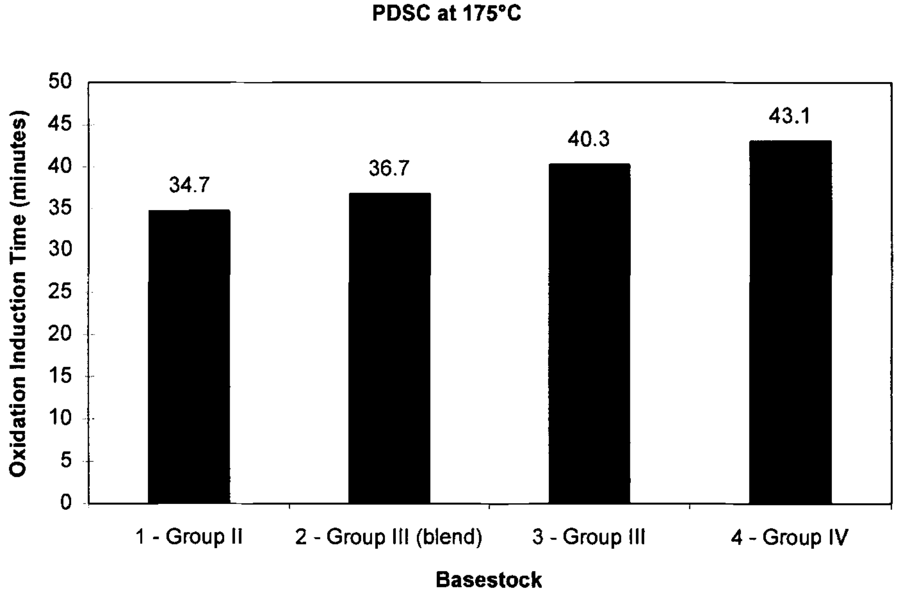


Figure 3. *PDSC Performance at 175°C - Commercial Turbine Oil Additive Package*

When the new antioxidant system was examined in the same series of basestocks as the commercially available turbine package, significantly improved RPVOT response was observed (Figure 5). This significant improvement in oxidative performance is confirmed via PDSC at 190°C (Figure 6). Interestingly, while the PDSC results showed the same trend as with the commercial turbine package, the RPVOT results did not. In this case, basestock 3 (Group III) had superior performance to basestock 4 (PAO). As before, TOST performance was not evaluated for the new antioxidant system, but based on previous experience with similar chemistries this additive system is expected to yield results greater than 15000 hours.

Further work on optimization of the sulfur carrier contained in the new antioxidant system produced a slight increase in PDSC oxidation induction times for the Group II and Group III(blend) basestocks. No significant effect, however, was observed in the Group III and IV basestocks (Figure 7).

RPVOT testing with this modified antioxidant system was inconclusive. A clear oxidative induction breakpoint was only observed for the Group II basestock. In this case, a dramatic increase in RPVOT performance was observed, with the oxidation induction time going from the previous 2160 minutes to 3300 minutes.

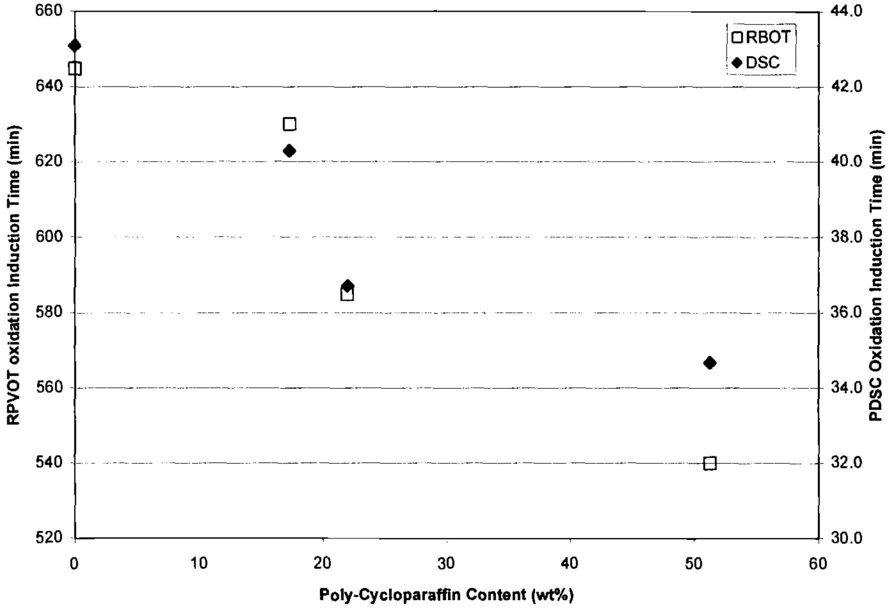


Figure 4. *Oxidation Induction Times versus Poly-Cycloparaffin Content*

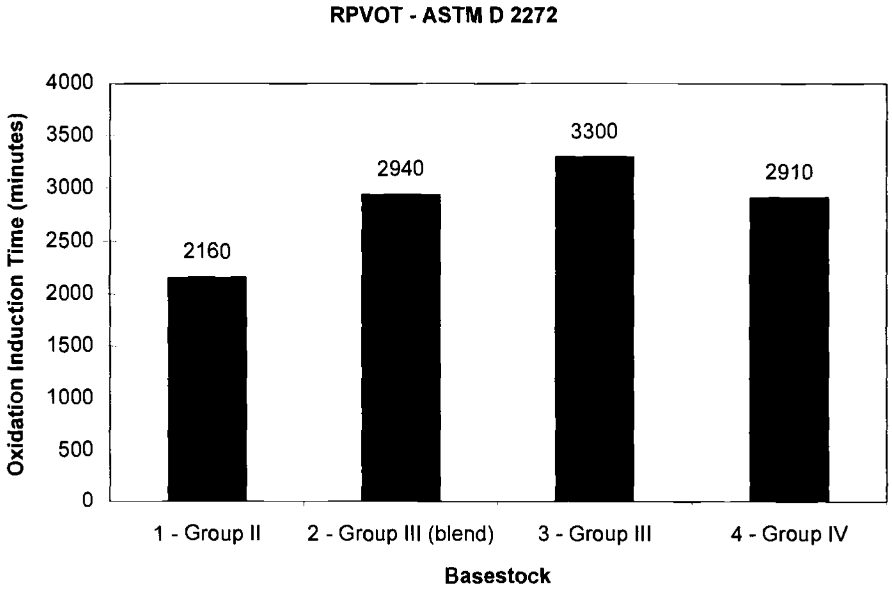


Figure 5. *RPVOT Performance Using Antioxidant System 1*

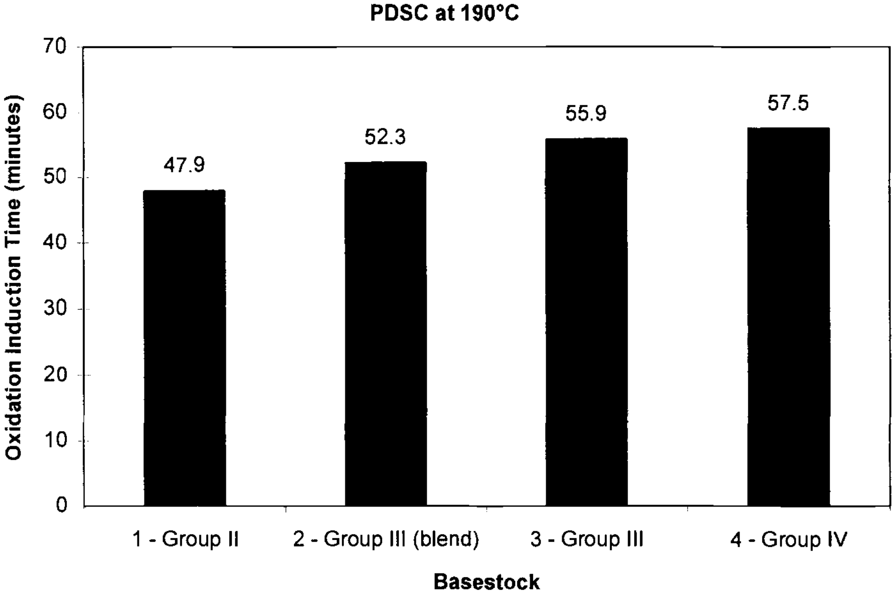


Figure 6. *PDSC Performance Using Antioxidant System 1*

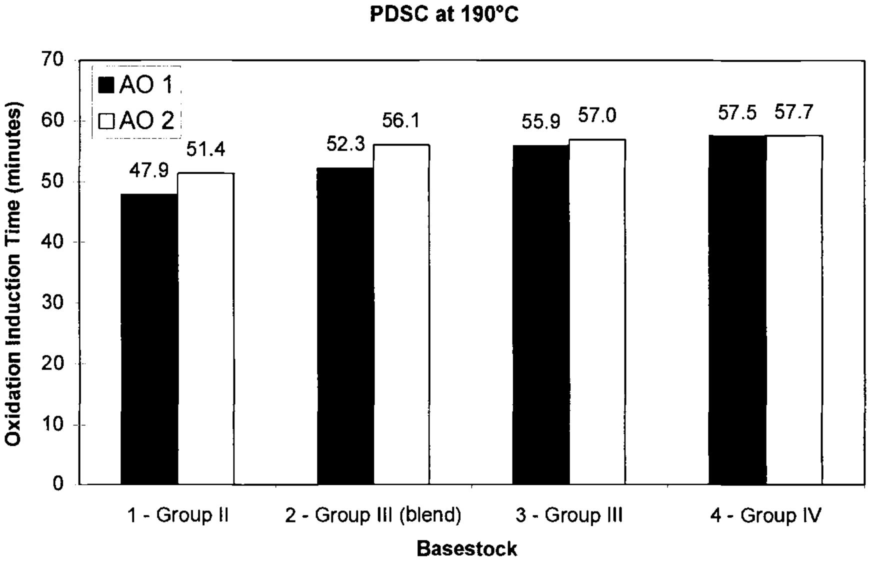


Figure 7. *PDSC Performance Using Antioxidant System 2*

As with the commercial turbine additive, the new antioxidant systems showed the same general trend of increasing oxidation induction times with decreasing poly-cycloparaffin content (Figure 8).

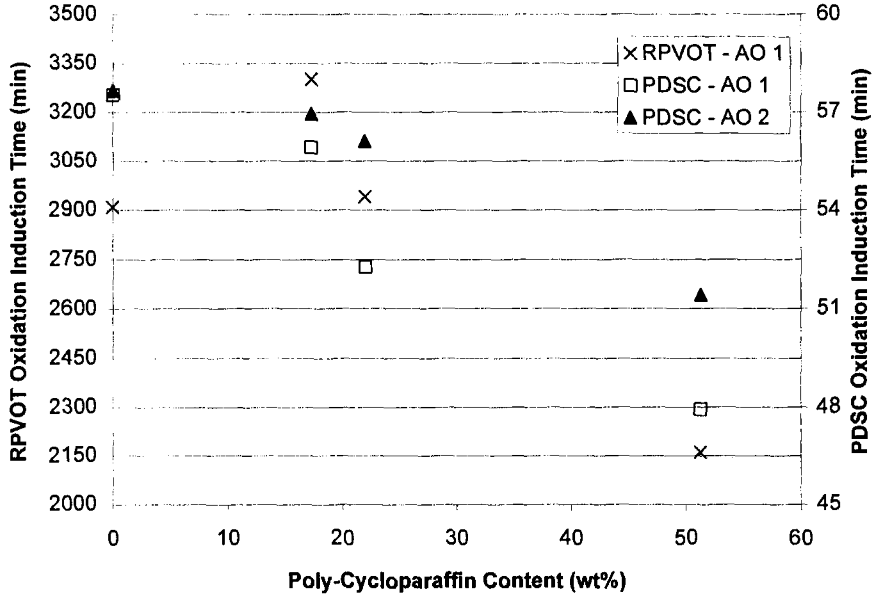


Figure 8. *Oxidation Induction Times versus Poly-Cycloparaffin Content for New Antioxidant Systems*

Conclusions

The demands of modern high temperature gas turbine applications require thermal and oxidative stability performance beyond the capabilities of previous generation turbine oils. Modern turbine lubricants require highly refined basestocks and carefully selected, low volatility, thermally stable additive systems.

Highly refined basestocks, with very low aromatic and hetero-atom content, have been shown to have superior oxidative stability to previous generation solvent refined oils, when additized. Oxidative stability increases and solvency decreases as total aromatic content decreases. When formulating with these highly non-polar basestocks one must be cognizant of their decreased solvency.

This poorer solvency must be assessed in terms of additive and oxidation product solubility. The formulator must carefully screen additive systems and must set firm condemning limits for used fluids.

Condemning limits for turbine oils formulated with these basestocks should not be exceeded. New-generation oils will take a long time to reach their condemning limits, but once they do reach them, action must be taken. The highly non-polar nature of these fluids means that they have very limited solubility and dispersing power for polar oxidation products. These solvency issues are not new, however, and have been faced by formulators using PAOs.

Among highly refined Group II and Group III basestocks, with very low hetero-atom and aromatic content, poly-cycloparaffin content is a key indicator of oxidative performance. Oxidative stability of additized basestocks increases as poly-cycloparaffin content decreases. Group III basestocks with low poly-cycloparaffin content offer oxidative stability on par with PAOs.

It was also observed that the use of sulfur-based peroxide decomposers can yield significant improvements in the oxidative stability of hydrocracked basestocks.

The use of severely hydrocracked iso-dewaxed basestocks together with thermally stable, low volatility, additive systems is a clear method of meeting modern gas turbine lubrication requirements.

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Bruce P. Schwager,[1] Bryant J. Hardy,[1] and Gaston A. Aguilar[1]

Improved Response of Turbine Oils Based on Group II Hydrocracked Base Oils Compared with Those Based on Solvent Refined Base Oils

Reference: 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., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: Modern industrial equipment makes increasingly severe demands on the lubricating oils used to keep the equipment running. Higher operating temperatures, smaller oil reservoirs, and decreased downtime all help create a severe environment for the lubricant. In response, base oil manufacturers have developed new technology to provide more saturated, high-performance base oils using catalytic hydrocracking technology. Lubricants based on these base oils and properly matched with the right additive technology have longer oxidation life, less deposit forming tendencies, and overall higher performance than solvent refined products.

In this paper, the performance properties of lubricants based on hydrocracked Group II base oils are compared with those of more traditional products based on solvent refined base stocks. Laboratory tests such as the Rotating Pressure Vessel Oxidation Test (ASTM D2272), the Turbine Oil Oxidation Stability Test (ASTM D943), and the Water Separability Test (ASTM D1401) were used to predict performance. The lubricants tested were all from the general category of rust and oxidation inhibited oils (R&O oils), and included turbine oils. In some cases, actual performance was verified in field trials. The data presented confirm the performance advantages of a properly formulated lubricant based on Group II hydrocracked stocks.

Keywords: turbine oil, R&O oil, hydrocracked, power generation, performance

Introduction

Lubricate the moving parts. Cool hot spots. Remove contamination. Break out water. Prevent metal-to-metal contact. Avoid varnish and sludge. Remain fluid at low

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temperatures… The job description of a lubricant in a turbine system is very demanding. Conventional lubricants formulated with solvent refined base oils have done an effective job of meeting the challenge over the years. However, changing conditions in the power generation industry are making the demands even tougher.

Cogeneration plants and combined-cycle units add more heat to the system, requiring a lubricant that can stand up to hot spots in excess of 150°C (300°F). Oil reservoirs are smaller, increasing the stress on the lubricant. Control systems are sensitive to even the smallest amounts of contamination or varnish. Plants are often called upon to start up quickly in response to increased demand. When this happens and it is cold outside, the lubricant must be fluid enough to flow to the bearings and other critical moving parts [*1*].

Lubricants formulated with hydrocracked base oils have what it takes to respond to these increased demands. In the traditional solvent refining process, petroleum fractions are "washed" with solvents to remove impurities, leaving behind the desirable lubricant fractions. Due to the nature of the process, 10 – 15 percent impurities are often left in solvent refined oil, in the form of aromatic compounds and heteroatoms, such as sulfur and nitrogen. In the hydrocracking process, the petroleum fractions are reacted with hydrogen under high pressure and temperature. The aromatic compounds are chemically reduced to cycloparaffins and rearranged to form linear paraffins. The heteroatoms are also removed in the process. The result is a lubricant base oil that is greater than 99 percent pure saturated paraffins (Table 1) [*2*].

Table 1 – *Properties of Light Neutral Base Oils*

	Solvent Refined 100N Base Oil	Hydrocracked 100N Base Oil
Clay Gel Analysis (ASTM D2007)		
- Saturates, wt. %	85 – 90	> 99
- Aromatics, wt. %	9 - 15	< 1
- Polars, wt. %	0 – 1	0
Sulfur, wt. %	0.05 – 0.11	<0.001
Nitrogen, ppm	20 – 50	<2
Color (ASTM D1500)	0.5 – 1.0	<0.5

Several early studies have shown that some aromatic compounds and sulfur-containing material can act as "natural" antioxidants [*3-6*]. However, these studies looked at base oils alone, in the absence of any additives. Saturated hydrocarbons respond dramatically to the addition of primary antioxidants, such as amines and phenols, which interrupt the chain reaction that leads to base oil oxidation [*7*]. Aromatic compounds interfere with this mechanism and reduce the effectiveness of the additives [*8*]. Sulfur and aromatic compounds have also been shown to cause the formation of insoluble material in the oil, which leads to sludge or varnish [*9*]. Basic nitrogen compounds, too, have been shown to accelerate oxidation and increase the amount of sludge [*10*]. Overall, hydrocracked base oils result in formulated products that are much more resistant to oxidation and the problems it causes.

Aromatic compounds and non-hydrocarbons such as sulfur and nitrogen-containing materials are all surface-active compounds, compared to saturated hydrocarbons. These surface-active compounds degrade the demulsibility of the base oil, so that water takes longer to separate from the lubricant. The same surface-active compounds also degrade the air-release time of the oil. Both of these properties are important to the performance of turbine oil [*11*].

The hydrocracking process is often paired with catalytic dewaxing, which uses a catalyst to remove any paraffin wax from the oil. This process is also called hydrodewaxing. Because this process is more effective and more selective in removing paraffin wax, hydrodewaxed oils have improved low temperature properties [*12*].

In short, hydrocracked base oils give the lubricant the extra boost they need to meet the challenges of today's power systems. This paper will present several examples demonstrating the performance advantages of lubricants formulated with hydrocracked base oils.

R&O Oils

Rust and oxidation inhibited oils (R&O Oils) are frequently used in less demanding applications in power plants. These applications can include steam turbines, air compressors, pumps and gearboxes. The data below (Table 2) shows typical properties for two general-purpose R&O oils. Both products are made with the same R&O additive package, at the same treat rate. The first product is made with solvent refined base oil and is a commercial product. The additive package was optimized for use in this base oil. The second product was made by switching to hydrocracked base oil, without optimizing the additive package. A simple base oil substitution led to the improved properties shown in the table.

Table 2 – *Properties of R&O Oils (ISO 32 Viscosity Grade)*

	Solvent Refined	Hydrocracked
Viscosity, cSt at 40°C	33	31
Viscosity, cSt at 100°C	5.4	5.4
Viscosity Index	95	108
Pour Point, °C	-34	-40
Color (ASTM D1500)	1.0	0.5
Oxidation Control (ASTM D943), hours	2 500	4 000
RBOT Life (ASTM D2272), minutes	530	750
Rust Test (ASTM D665 A&B)	Pass	Pass
Emulsion Characteristics (ASTM D1401)		
- minutes to 40-40-0	10	5

The results from both the Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils (ASTM D943) and the Standard Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Pressure Vessel (ASTM D2272) illustrate the improved oxidation resistance of the product formulated with a hydrocracked base oil. This increase may translate into a longer life for the hydrocracked product. The pour point for the hydrocracked product is lower than that of the solvent refined product, indicating better low temperature performance, even though 25 percent less pour point depressant is used in the hydrocracked formulation. This product also sheds water faster, as demonstrated by the results from the Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids (ASTM D1401).

A lower viscosity grade R&O oil formulated for a special application highlights the improvement in expected life that can be obtained from hydrocracked base oils. The typical properties of the product formulated with both solvent refined and hydrocracked base oils (Table 3) show the same advantages discussed previously.

Table 3 – *Properties of R&O Oils (ISO 15 Viscosity Grade)*

	Solvent Refined	Hydrocracked
Viscosity, cSt at 40°C	18	17
Viscosity, cSt at 100°C	3.8	3.7
Viscosity Index	92	100
Pour Point, °C	-37	-43
Color (ASTM D1500)	1.0	0.5
Oxidation Control (ASTM D943), hours	-	12 000
RBOT Life (ASTM D2272), minutes	550	750
Rust Test (ASTM D665 A&B)	Pass	Pass
Emulsion Characteristics (ASTM D1401)		
- minutes to 40-40-0	10	5

Both products were also tested in a proprietary bubbling tube oxidation test run at 95°C. This test was developed to simulate the conditions the product experiences in actual use. The depletion of the antioxidant is monitored with infrared spectroscopy. The data in Figure 1 show the additive is depleted much more quickly in the solvent refined base oil. Again, this should translate directly into longer life for the hydrocracked product.

Steam Turbine Oil

The previous examples showed the benefits from switching to hydrocracked base oils, while using the same additive package. Even greater advantages can be obtained by optimizing the additive package to take advantage of the unique properties of hydrocracked base oils.

Steam turbine oils are special grades of R&O Oils, formulated to give better oxidation resistance and longer life in a steam turbine. ASTM D943 is the most common test used to predict the life of these products. Water shedding ability as measured in D1401 is also important.

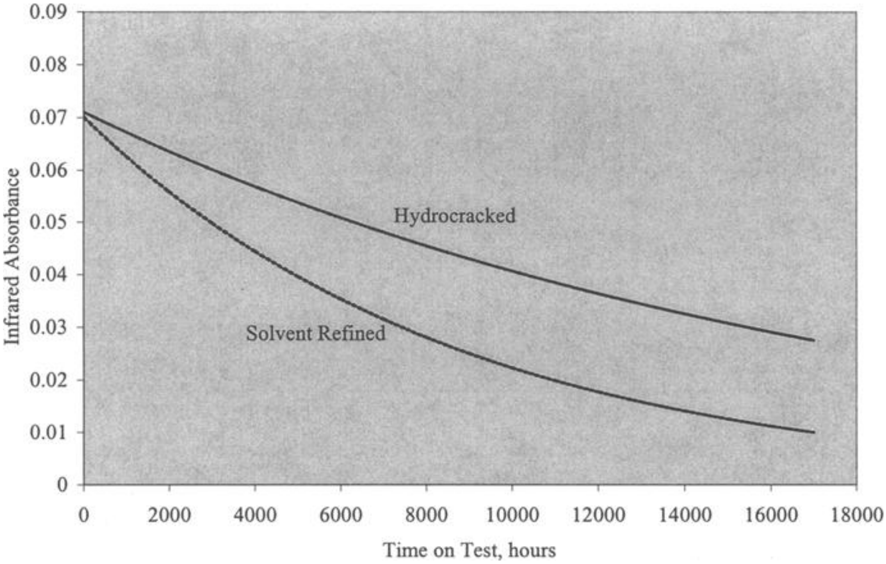

Figure 1 – *Loss of Antioxidant in Bubbling Tube Oxidation Test at 95°C*

Properties of a high quality solvent refined base oil are shown in Table 4. Also shown are the properties of a turbine oil designed with a hydrocracked base oil. Both oils are commercial products, optimized for the specific base oil being used.

Table 4 – *Properties of Steam Turbine Oils (ISO 32 Viscosity Grade)*

	Solvent Refined	*Hydrocracked*
Viscosity, cSt at 40°C	30	32
Viscosity, cSt at 100°C	5.2	5.4
Viscosity Index	100	103
Pour Point, °C	-37	-40
Color (ASTM D1500)	1.0	0.5
Oxidation Control (ASTM D943), hours	3 000	7 500
RBOT Life (ASTM D2272), minutes	700	850
Rust Test (ASTM D665 A&B)	Pass	Pass
Emulsion Characteristics (ASTM D1401)		
- minutes to 40-40-0	10	5

The dramatic increase in the D943 life points out the improved life expectancy that can be obtained by formulating a product to take advantage of hydrocracked base oils. The hydrocracked product also does a better job of shedding the water which is present in steam turbine systems.

Natural Gas Turbine Oil

Gas turbines expose the lubricant to much higher temperatures than in steam turbines. The oil must be able to withstand these hot spots without oxidizing or forming varnish or sludge. The high purity of hydrocracked base oils is a natural fit for this application. A natural gas turbine oil optimized for hydrocracked base oil can provide extremely long life in this application (Table 5). The solvent refined oil in this example is already a premium commercial product compared to most turbine oils, yet the hydrocracked product provides nearly four times the life in the D943 test. (By reducing the sampling frequency, the test was carried out beyond the 10,000-hour limit of the D943 procedure to measure the extent of the performance improvement.)

Table 5 – *Properties of Natural Gas Turbine Oils (ISO 32 Viscosity Grade)*

	Solvent Refined	*Hydrocracked*
Viscosity, cSt at 40°C	30	33
Viscosity, cSt at 100°C	5.2	5.5
Viscosity Index	100	102
Pour Point, °C	-34	-40
Color (ASTM D1500)	0.5	0.5
Oxidation Control (ASTM D943), hours	6 000	22 000
RBOT Life (ASTM D2272), minutes	900	1 900
Rust Test (ASTM D665 A&B)	Pass	Pass
Emulsion Characteristics (ASTM D1401)		
- minutes to 40-40-0	10	5

Both of these products were used in a GE 7EA gas turbine that is part of a cogeneration plant in south Texas. Oil samples are taken monthly and checked for performance. D2272 is used as the primary means to evaluate remaining oxidation resistance. Figure 2 shows the RBOT results for both products. The premium performance and the extended life of the hydrocracked product are obvious.

Conclusion

The high purity of hydrocracked base oils (reduced aromatics and heteroatoms) leads to some unique properties – they are more thermally and oxidatively stable when combined with appropriate additives, they are more fluid at low temperatures, they shed water more quickly, and they respond better to treatment with additives. By taking advantage of these properties, products can be formulated that provide premium performance to turbine systems. R&O oils, steam turbine oils and natural gas turbine oils can all take advantage of hydrocracked technology and improve the efficiency of plant operations.

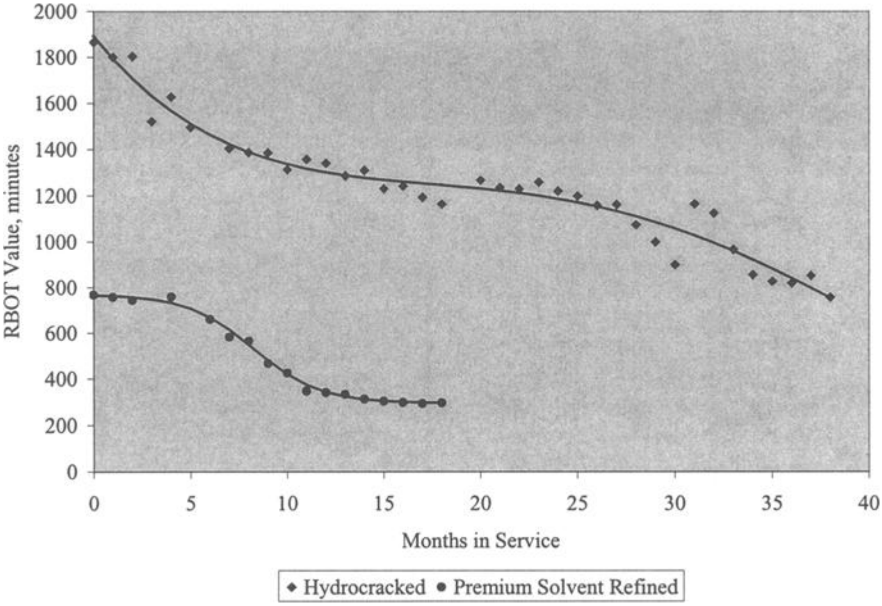

Figure 2 – *Natural Gas Turbine Oils in Service*

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Performance Advantages of Turbine Oils Formulated with Group II Base Oils

Reference: 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., American Society for Testing and Materials, West Conshohocken, PA, 2001.

Abstract: Formulation of high-quality turbine oils with API Group II base oils provides finished turbine oils with numerous performance advantages. When blended with the proper additives, these high-purity base oils provide turbine oils with outstanding oxidation stability, lower sludging tendencies, and improved water separability properties. The exceptional feature of these Group II finished products is their outstanding oxidation stability. The outstanding oxidation stability of the Group II lubricants is due not only to the high-purity base oils, but also to the carefully chosen additive package. The inherent sludging tendency of turbine oils is reduced when changing from Group I to Group II oils. Also, the water separability of these oils is improved when making the same change. Data which highlight these striking performance differences between Group I and Group II finished turbine oils and field test data will be shown.

Keywords: turbine oil, turbine oil additives, lubricant, Group II, oxidation stability, RPVOT, TOST

Base Oils

The American Petroleum Institute (API) has classified base oils [*1*] according to their viscosity index and sulfur and saturates content. As seen in Table 1, Group I oils have sulfur concentrations above 300 ppm (0.03 %) and saturates content of less than 90% while Group II oils have sulfur concentration of less than 300 ppm and saturates level of more than 90%. The saturates content is defined as the amount of paraffins and it can be calculated by subtracting the aromatics percentage from 100. For example, if a base oil contained 5% aromatics, then the amount of saturates would be 95%. The

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primary difference between Group II and Group III oils is the higher viscosity index for the Group III base oils. Poly-alpha-olefin base stocks are defined as Group IV oils and all other base stocks not defined as Group I through IV are defined as Group V oils.

Table 1 – *API Base Stock Classification*

Base Oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	>0.03	and/or	90	80 to 120
Group II	≤0.03	and/or	≥90	80 to 120
Group III	≤0.03	and/or	≥90	≥120
Group IV	All polyalphaolefins			
Group V	All others not included in Groups I, II, III or IV			

Turbine Oils

Gas and steam turbines typically use lubricants in their systems as bearing and gear lubricants and as a hydraulic fluid. In most steam turbines, phosphate ester-based fluids are used as the hydraulic fluid. Turbine OEMs (Original Equipment Manufacturers) have lubricant specifications for turbine oils. All high quality turbine oils meet the viscosity, load-carrying ability, oxidation stability, corrosion protection, foam resistance and water separating ability tests. Among these tests, oxidation stability is among the most important test specifications. A more oxidatively stable oil will provide longer oil life for the end use customer by extending the drain interval.

The turbine OEMs typically use RPVOT (Rotating Pressure Vessel Oxidation Test, formerly known as RBOT) (ASTM D2272) and TOST (Turbine Oil Stability Test) (ASTM D943) as specification tests for turbine oils. The RPVOT test is a fairly high temperature test (150°C) which measures the relative oxidation stability of finished oils and it usually takes about 1 day to complete. The OEM minimum specification for RPVOT results range from 250 to 500 minutes. The TOST test (95°C) also measures the relative oxidation stability of oils, but it typically takes over one year to complete. The OEM minimum specification for TOST ranges from 1000 to 4000 hours.

Outstanding Oxidation Stability

For turbine oils, the greatest advantage Group II finished oils provide over Group I oils is superior oxidation stability. Severe hydroprocessing of feedstocks greatly reduces the aromatic, sulfur and nitrogen-containing “impurities” to give virtually impurity-free Group II base oils. These impurities are responsible for the lower oxidation stability of Group I stocks because they readily oxidize. These impurities oxidize to form benzylic, sulfuric, and nitric acids and other oxidized species. Group II base oils typically contain only trace amounts of these impurities and the finished oils can exhibit outstanding oxidation stability properties when formulated with the proper additives. The superior oxidation stability of Group II finished turbine oils is demonstrated in their RPVOT and TOST values.

Table 2 - *Use of One Additive Package in Different Base Oils*

Test/Oil	Method	Base Oil A	Base Oil B	Base Oil C	Base Oil D	OEM Specifications
Base Oil Type		Group I	Group I	Group II	Group II	-
Turbine Oil Stability Test, Hours	ASTM D943	4256	6636	>10000	>10000	1000 - 4000 minimum
Rotating Pressure Vessel Oxidation Test, minutes	ASTM D2272	980	1025	2295	1698	250 - 500 minimum
Oxidation and Corrosion Test	FTM 791b 5308-7					
Viscosity change, %		17.7	13.7	3.8	1.4	-
Acid number increase		2.8	1.47	0.98	0.06	-
1000 Hour TOST Test, Insolubles, mg	ASTM D4310	37	36.1	25	20	100 max
Water Separability, time to 0 mL emulsion, minutes	ASTM D1401	20	15	10	10	30 max

For gas turbines, such as the General Electric (GE) Frame 7 series, a turbine oil with excellent oxidation stability is very desirable. The GE Frame 7 series has three journal bearings with a center bearing that can be subjected to 500°F. Since a turbine oil also acts as a coolant, it will be subjected to high temperatures from the center bearing and it must be oxidatively and thermally stable. A turbine oil with excellent oxidation stability is necessary in many gas turbine applications.

Data in Table 2 show the effect of using one additive package in a number of different base stocks. As can be seen, the RPVOT and TOST values for the Group I oils are good; however, the Group II oils far exceed the values of the Group I oils and the OEM specification minimums. The reasons for the superior oxidation stability of the Group II finished oils are twofold. First, Group II oils have greatly reduced impurities and this produces a base stock that is inherently more stable. Second, the use of synergistic and/or complementary additives can create oils with extremely high oxidation stability. In other words, formulation of Group II oils with the proper additives is very important.

Another test that can be used to measure the relative oxidation stability of an oil is FTM 791b 5308-7 (Federal Test Method). This method was used as a test in some older specifications, but it is not presently used. However, because it measures the viscosity change and acid number increase, the results will show the relative oxidation stability of different turbine oils.

The FTM data indicates that the Group I finished oils had larger viscosity and acid number increases than the Group II oils. An increase in both of these properties indicates that oxidation has occurred. Hence, the Group I oils are less oxidatively stable than the corresponding Group II oils with the same additive package.

Table 3 shows the effect of using different additive packages in one Group II base stock. The total additive treat levels are within a range of 80 to 120% of a base case level. As one can see, different additive packages have very different oxidation stability results. This demonstrates the importance of how a finished oil is formulated. Use of a Group II oil for any finished oil does not guarantee excellent oxidation stability results.

Table 3 - *Effect of Different Additive Packages in the Same Group II Base Oil*

Additive/Test	RPVOT, minutes	TOST, Hours
Additive Package E	705	5590
Additive Package F	1320	>10000
Additive Package G	735	7800
Additive Package H	494	8434
Additive Package I	1300	6590

Reduced Sludging Tendency

In conjunction with improved oxidation stability, Group II finished turbine oils have reduced sludging tendency when compared against the Group I finished oils. The sludging tendency of a turbine oil is an important performance feature. Sludging tendency is not a turbine OEM specification, but it is a part of a Military specification (MIL-L-17331H (SH)). A lower sludge weight will indicate a lower potential for varnishing and deposit formation with a particular turbine oil. ASTM D4310 is a variation of the TOST test (1000 hours) and it is a requirement for the MIL-L-17331H (SH) specification. After running the test for 1000 hours, the total amount of sludge is measured. A lower sludge weight is a desirable feature and Group II finished turbine oils provide lower sludge weights.

The use of Group II base stocks lowers the sludging tendency of finished turbine oils. Data in Table 2 show the sludge weight (ASTM D4310 results) effect of using one additive package in different base stocks. As can be seen, the Group I finished oils have an overall higher sludge weight than the Group II oils.

The reduced sludging tendency of Group II finished turbine oils can be seen in a couple of commercially available turbine oils. Turbine oils which use Group I, Group II and Group IV (poly-alpha-olefins) were tested. The RPVOT method was used as a test to measure the relative sludging tendency of an oil. A number of oils were subjected to the RPVOT conditions for 600, 900 and 1200 minutes. After each time period, the acid number of the oil and the filterable solids were measured. The solids were filtered onto a pre-weighed filter and rinsed with heptane. The filter and solids were then oven dried and weighed again to obtain the total amount of filterable solids. The data is summarized in Table 4.

Table 4 - *RPVOT Sludge Results of Commercially*[1] *Available Turbine Oils*

		600 Minutes		900 Minutes		1200 Minutes	
Oil/Test	Base Oil Type	AN	Sludge, wt., mg	AN	Sludge, wt., mg	AN	Sludge, wt., mg
Commercial Oil J	Group I	0.08	2	0.24	4	5.1	49.8
Commercial Oil K	Group I	4.53	53.7	-	-	-	-
Commercial Oil L	Group II	0.06	4.6	0.1	5.1	0.17	22.8
Commercial Oil M	Group II	0.05	3.8	0.08	3.5	0.05	5.4
Commercial Oil N	Group IV	0.64	19	0.92	59.8	0.69	117

[1] - Based on 1998 North American formulations

The Group I and Group IV oils had higher sludging tendencies than the two Group II finished oils. Because the end time for one of the Group I (Oil K) oils was less than 600 minutes, one can see the effect of oxidation. This oil had oxidized, had a very high acid number and it produced a large amount of sludge. Both Group II finished oils had relatively stable acid numbers and low sludge weights even at 1200 minutes. The additive packages (Oils L and M) are not the same, but this illustrates the lower inherent sludging tendencies of the Group II finished oils over the Group I products.

The Group IV finished oil exhibited poor results in both acid number and sludge weights. Although the RPVOT end time for the Group IV oil is greater than 1200 minutes, the oil exhibited poor sludge tendency throughout the test and it had a relatively high acid number, too. In this case, the high sludging tendency can be explained by the formulator's choice of additives and base stocks.

Improved Water Separability

When changing from a Group I base oil to the Group II oil, the water separability of the turbine oil is improved. The ability of the turbine oil to "shed" or separate water is a very important property for steam turbines since water can leak into the oil reservoir. Emulsions and/or water are very poor lubricants, so the oil must be able to separate from water. The water separating characteristic of oils can be measured (ASTM D1401). Data shows that Group II finished oils separate faster than the Group I counterparts.

Data (ASTM D1401 results) in Table 2 shows the difference between Group I and Group II finished oils which use the same additive package. On the whole, the times for the Group II oils are shorter than the corresponding times for the Group I oils. Group II base oils have better water separability response to this additive package than the corresponding Group I oils. A shorter time is more desirable since the oil is separating from water in a quicker manner.

Field Test Data

When introducing a new or reformulated turbine oil, most lubricant companies will field test the product in a challenging application. Because of the hot center bearing design, the General Electric Frame 7 gas turbine is a good choice to evaluate the performance of a turbine oil. A Group II finished turbine oil was placed into a GE Frame 7B/E peaking unit in North America. The turbine's previous oil was another Group II product with good oxidation stability (RPVOT = 350 minutes; TOST = 5000 hours). The previous oil was used and replaced by the plant after about 40000 hours. The new oil was monitored over a long period of time and it is still being monitored.

The new oil was monitored for over 40000 hours and it has performed well with no problems. A number of physical and performance properties of the oil were monitored and the data is summarized in Table 5. Overall, the oil is still in very good condition and suitable for continued use. As evidenced by the RPVOT value at 40353 hours, the oil still has additives to protect against oxidation.

Color, acid number and RPVOT values are indicators of oil oxidation. Over time, the field test oil's oxidation indicators were very stable. As an oil ages and approaches the end of its useful life, it will turn darker in color. The darker color is due to oxidized by-products from the additives or oil itself. The field test oil started with a light color (L1.0) and increased to only L3.5 after over 40000 fired hours. Since the oil was not oxidized, the color increase can be explained by the expected oxidation of the anti-oxidants. The acid number of an oil will dramatically increase when the anti-oxidant additives are depleted. The field test oil's acid number is almost a straight line over the monitoring period. By itself, a stable acid number is an indication that the oil has not started to oxidize and form acidic by-products.

The RPVOT method is a good monitoring test for in-service oils. When oils are monitored on a regular and meaningful basis, one can essentially predict when the oil should be drained and replaced. The field test oil's RPVOT values were tracked over the 40,000+ hour time period. Over time, the oil maintained its oxidation stability and the last RPVOT value (40353 hours) shows that the oil is still in good condition. ASTM D4378 recommends consideration of oil changeout when an in-service oil has a RPVOT value that is 25% of the fresh oil. The field test oil is still above that level and, considering all of the other properties, it is in very good condition. Continued monitoring of the oil's RPVOT will allow this customer to predict when the oil should be changed.

The field test oil has performed very well with no reported varnishing, deposit and wear issues. The Group II field test oil has already extended the oil life from about 40000 to well over 40000 fired hours. Continued monitoring of the oil's RPVOT will allow further extension of this oil's useful life.

Table 5 - *Group II Turbine Oil from a GE Frame 7B/E Field Test*

Fired Hours	ASTM Method	0	500	1001	1500	2500	3500	4500	5500	6500	7500	9500	11500	13500	40353
Color	D1500	L1.0	L1.0	L1.0	1	L1.5	L1.5	L1.5	1.5	L2.0	L2.0	L2.0	L2.0	L2.0	L3.5
Viscosity, 40C, cSt	D445	30.04	30.18	30.21	30.22	30.22	30.24	30.24	30.3	30.5	30.59	30.5	30.51	30.55	32.06
Acid Number, mg KOH/g	D974	0.05	0.06	0.05	0.05	0.07	0.06	0.05	0.06	0.06	0.05	0.06	0.05	0.05	0.05
RPVOT, Minutes	D2272	2020	2215	2250	2275	2268	1641	1497	1538	1708	2163	1432	1652	1364	742
Wear Metals,[1] ppm	ICP	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Other Elements,[2] ppm	ICP	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

[1] - Copper, iron, tin

[2] - Aluminum, barium, boron, calcium, chromium, lead, magnesium, molybdenum, nickel, phosphorus, silicon, sodium, titanium, zinc

Summary

Formulation of high-quality turbine oils with API Group II base oils provides finished turbine oils with numerous performance advantages. When blended with the proper additives, these high-purity base oils provide turbine oils with outstanding oxidation stability, lower sludging tendencies, and improved water separability properties. The outstanding oxidation performance of the Group II lubricants is due not only to the high-purity base oils, but also to the carefully chosen additive package. With the proper experience, a formulator can develop an oil with outstanding oxidation stability. A decrease in relative sludging tendency and shorter water separability time of turbine oils are two added improvements when changing from Group I to Group II oils. Lastly, laboratory tests notwithstanding, actual use of a turbine oil in an application is the ultimate test to prove its performance. A Group II finished turbine oil has been in service for over 40000 hours and it is still giving satisfactory performance in the turbine.

References

[1] American Petroleum Institute Publication 1509.

Jo Ameye,[1] Robert E. Kauffman [2]

Antioxidant Analysis for Monitoring Remaining Useful Life of Turbine Fluids

Reference: Jo Ameye, Robert E. Kauffman, "**Antioxidant Analysis for Monitoring Remaining Useful Life of Turbine Fluids**," *Turbine Lubrication in the 21st Century, ASTM STP 1407*, W.R. Herguth and T.M. Warne, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2001

Abstract: In this study we measured the remaining useful life of a wide range of turbine lubricants by detecting directly the remaining activity and performance of phenolic and amine antioxidants, known as primary antioxidants. We applied a patented (linear) voltammetric technique. First we evaluated the accuracy of the voltammetric response (vs. weight %) for phenolic (BHT) and amine (PANA) types of antioxidants. The next step of the program included antioxidant performance testing using laboratory oxidation tests. The voltammetric test data were then correlated with other widely used analytical methods (RBOT, FTIR, and DSC). These tests enabled us to understand the performance of mixed antioxidant systems and their importance in the remaining useful life of the new generation of turbine lubricants.

Finally and in order to understand the chemical role of antioxidants in real life conditions we monitored several industrial steam and gas turbine lubricants (N. America and Europe) with voltammetric analyses to observe the antioxidants' depletion trends. Voltammetric analysis correlated well with the RBOT (as per ASTM D-2272), and standard physico-chemical analysis methods (TAN, viscosity, color, ...). These results show that antioxidant monitoring adds valuable information to RBOT and DSC measurements for the new type of turbine lubricants. This will allow the user to enhance the management of the oil on-site; to detect abnormal equipment/usage and consequently to improve the planning of maintenance actions resulting in a more efficient oil management.

Keywords: antioxidants, voltammetry, RBOT, oxidation control, amines, phenols

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Introduction

In order to meet the demands of the industry turbine oil base stocks have continuously improved, both through processing and synthesis. They parallel the development of performance additive packages. Environmental and performance requirements are the main drivers for this evolution. The direct consequence of the commercial and environmental pressure results in a second remarkable development: the power generating industry has significantly improved the thermal efficiency of its industrial equipment. Combining gas and steam turbines (combined cycle operation) improved the efficiency from an average of 30-35% for a single cycle equipment to between 50 and 60%. As a direct consequence of this advanced technology lubricant specifications became stricter e.g. controlling oxidation under the conditions of high temperatures representative of typical gas turbine operating conditions. During the normal operation of gas turbines, the temperature of the oil film can exceed 140 to 150°C.

For both these developments the goal is to obtain a lubricant with higher thermal and oxidative stability, or to create a lubricant with a minimal oxidative degradation. Typical results for lubricants with poor oxidation protection/control are:

- Sludge formation /filter blockage
- Oil thickening / increased viscosity
- Formation of deposits/oxidation products such as lacquers/varnishes etc...
- Increased acidity

These operating problems can be prevented by the combination of good quality base oil, with a supplemental antioxidant package. Antioxidants added alone or in synergistic combinations extend the operating life of the oil by improving its " oxidation stability". During their use in the lubrication systems of turbines, the oxidation inhibitors (antioxidants, AO) will deplete to a certain critical level at which point the fluid will start to degrade / polymerize at an accelerated rate. At that point important changes in the physical properties of the base stock occur. The oil or lubricant is no longer able to protect the equipment, and its useful life is over. There is a growing interest in methods predicting oil change measuring antioxidant concentration during the lubricant lifetime. Monitoring the onset and the propagation of oxidation will lower operating costs (e.g. downtime costs, equipment loss), and allow users to detect abnormally oxidized and degraded lubricants.

The basic mechanism of oxidative degradation *[1]* and the role that different antioxidants play, begins with the formation of reactive compounds, better known as free radicals, hydroperoxides and peroxides. These reactive compounds will then propagate into oxygenated hydrocarbons, such as alcohol, acids, and sludge. The antioxidants act in 2 ways: by removing radicals (primary antioxidancy) or by decomposing hydroperoxides to form non-reactive products, which do not participate in further oxidation of the lubricant (secondary antioxidancy). The current commonly used primary antioxidants are the phenolic and amine types; the secondary antioxidants are usually sulfur or metal containing additives.

This paper presents research on the relationship between the remaining useful life of lubricants and antioxidant concentration, detected by using an electrochemical analytical technique, based on cyclic voltammetry. First we will present laboratory studies demonstrating the accuracy of the cyclic voltammetric-based method for phenol and amines antioxidants. We will also establish the correlation between the remaining antioxidant concentration with oxidation tests (Rotating Bomb Oxidation Test -RBOT, Differential Scanning Calorimetry - DSC) for different types of turbine lubricants.

In the second part of the research, data collected from the field are compared with standard physical property measurements (viscosity, total acid number, color and water) and RBOT-values.

Experimental

Fresh lubricating oils

The fresh lubricating oils evaluated during this study were obtained from the equipment operators (power stations), as well as commercial lubricant suppliers. The base stock oils were polyol ester-based oils (jet engine oils) and hydrocarbon-based turbine oils, supplemented with phenolic BHT (Butylated Hydroxy toluene also known as DBPC) and/or aminic PANA (Phenyl-α-NaphthylAmine) and DPA (Di-alkylphenylAmine).

Voltammetric method

The method for evaluating the remaining useful life of the oil is mainly based on voltammetric analysis *[2]* of the lubricant sample. Voltammetric techniques are electroanalytic methods in which a sample is mixed with an electrolyte and a solvent, and placed in an electrolytic cell. Data are obtained by measuring the current through the cell as a function of the applied potential. The test results are based on current, voltage and time relationships at the cell electrodes.

The cell consists of a fluid container with a small, easily polarized microelectrode, and a large non-polarizable reference electrode. The reference electrode should be massive compared to the microelectrode so that its behavior remains essentially constant with the passage of small current: it remains unpolarized during the analysis period. Additional auxiliary electrodes can be added to the electrode system to eliminate the effects of resistive drop for high resistance solutions. In 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. The data recorded during this oxidation reaction can then be used to determine the remaining useful life of the oil type.

A typical current-potential curve produced during the practice of the voltammetric test is illustrated in figure 1. 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 (figure1), the electro-active species (such as substituted phenols) begin to oxidize at the microelectrode surface, producing an anodic rise in the current. As the potential is increased, 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 (figure 1).

In this study the voltammetric method was performed with a commercially available voltammograph equipped with a glassy carbon-working electrode, a platinum wire electrode, and a platinum wire auxiliary electrode. The oil samples (400μl) were diluted in an ethanol/electrolyte mixture. This extracted the antioxidants into the solvent phase. The voltage of the auxiliary electrode was scanned from 0 to 1.5 V at a rate of 0.2 V/second. As the potential increased, the antioxidants oxidized at the carbon electrode surface. The oxidation released electrons to the electrode, causing current, which was linearly related to the additive concentration in the solution (Figure 1). The peaks produced by the voltammetric method (the oxidation wave) were then used to evaluate the remaining additives of the used oil samples. The peak of a zincdialkyldithiophosphate (ZDDP) additive is followed by an amine (PANA), and then by a phenol (BHT) (Figure 1). The new oil was used as the 100% standard and the solvent was used as the 0% standard. The measurements of the used lubricant samples were expressed as percentages remaining additives. The repeatability of the percent-remaining additive measurements is between 2.5 and 4% RSD *[3-5]*

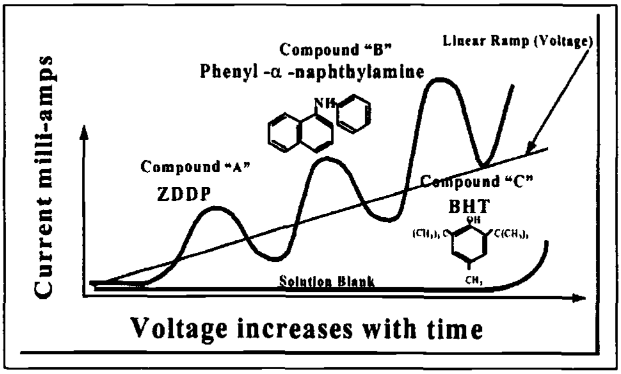

Figure 1 - *Cyclic Voltammetry – Voltage vs. Current for different antioxidants e.g. ZDDP (Zincdialkyldithiophosphate), PANA and Phenol.*

When comparing the voltammetric procedure to existing oil oxidation test methods, such as RBOT, DSC, FTIR, the following differences are apparent:

- Ease in use: the test procedure consists of sampling the oil with a pipette, mixing it with the 5ml prepared solvent vial, inserting the probe, and measuring;
- Test method requires a very small oil sample volume (200 – 400 μl);
- No chemical expertise is required;
- Portable technology, allowing on-site analysis;
- Quick test method (less than 5 minutes), which can be used for field analysis.

Oxidation test methods

The Rotating Bomb Oxidation Test (RBOT) in accordance with the ASTM Test Method for Oxidation Stability of Steam Turbine Oils by Rotating Bomb (D 2272) was used to estimate the oxidation stability of turbine oils. Differential Scanning Calorimetry (DSC) (at atmospheric pressure with 50-ml/min oxygen, 200°C hold temperature) was also applied to measure the oxidation stability for used turbine oils.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a film of oil (10 μL) between two potassium bromide plates. The FTIR analyses were performed to monitor the depletion of the phenolic antioxidants (3650 cm^{-1}) versus time.

Precision of the technique for detecting antioxidants in turbine lubricants

For this part of the study we used a mineral base oil (Group II) in which antioxidants (supplied by a major additive company) were added with increasing concentration, to determine:

a) The capability of the cyclic voltammetry to detect amine (PANA) and phenol (BHT) antioxidants;
b) Calibration plots of the cyclic voltammetry for amines and phenols from oil samples prepared with concentration of 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4 and 4,5 wt.% antioxidants. No other additives were present in the oil.
c) All tests were measured in triplicate, by two independent laboratories, and the average value of the peak height value was used.

A selected oil volume of 200μl of the prepared standards was added to the electrolytic test solutions, mixed, and tested by voltammetry. For the amine and phenol detection we used 2 different electrolytic test solutions, for which we refer to the patent *[2]:*

- Test solution 1: acetone based solvent with a neutral electrolyte
- Test solution 2: ethanol based solvent with a basic electrolyte

As the previous experiment *[5]* has shown, both test solutions have good detection capabilities. We included them both in this precision test. The resulting data are presented in Figures 2, 3, 4, and 5. The antioxidant concentration by weight percentage was plotted on the x-axis. The voltammetric response in arbitrary units was plotted on the y-axis.

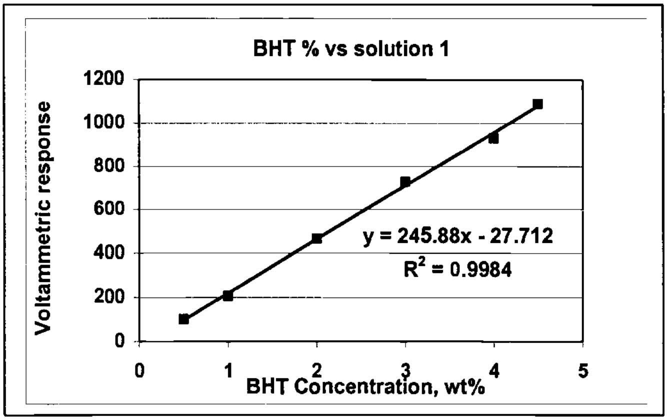

Figure 2: *Correlation BHT% with voltammetric peak response for test solution 1*

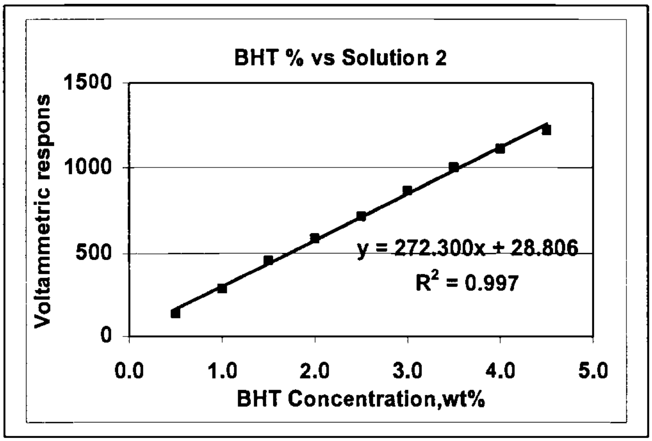

Figure 3: *Correlation of BHT% with voltammetric peak response in test solution 2*

The data (Fig. 2-5) show that both test solutions can be used to detect the BHT and PANA antioxidants, with correlation factors higher than 0.98.

A similar excellent correlation was demonstrated with mixtures of aryl amines and phenol mixtures in a previous publication *[5]*.

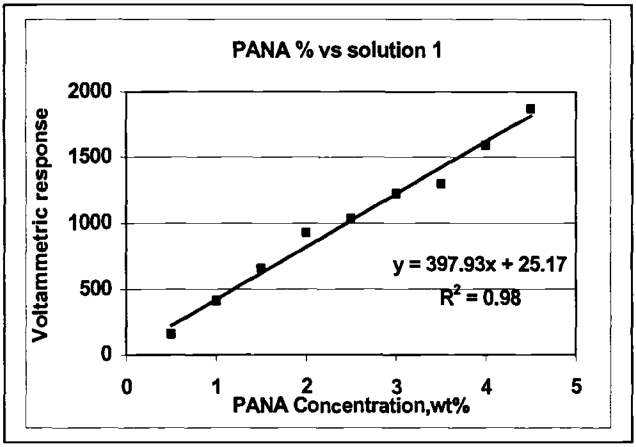

Figure 4: *Correlation PANA% with voltammetric peak response in test solution 1*

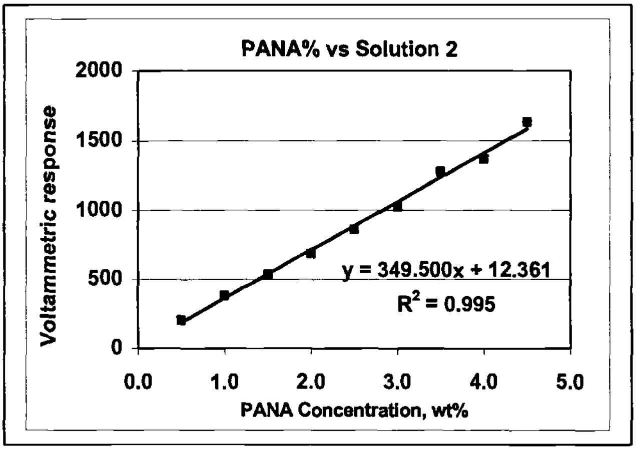

Figure 5: *Correlation PANA% with voltammetric peak response in test solution 2*

To confirm the above graphs, an oil company blended an ISO 32 grade turbine oil, with 2,6 di-tertbutyl phenol, with increasing concentration from 250 till 4000 ppm. There was an excellent correlation between the voltammetric response and phenolic antioxidant concentration (Figure 6).

In the above figure 6 voltammetric response is expressed both for the highest additive peak number (RUL Number), as well as the total area (RUL area). The total area under the voltammogram calculates the total antioxidant concentration, whereas the additive peak number specifically focuses on 1 type of antioxidant.

In her research of the oxidation potentials of a wide range of additives and antioxidants Amy Clough reported that the oxidation potential (E_{ox}) of compounds does not have an absolute magnitude; the value depends on the measuring conditions *[7]*. For example E_{ox} values of phenols were measured in a mixture of acids/alcohol which was a particularly favorable medium for the oxidation of the phenolic functional groups. Oxidation potential depends on the number, size and position of the groups attached to the aromatic ring of the phenols. She also reported that E_{ox} values of other compounds, such as phenates and sulfurized olefins/polysulfides, were generally higher than those of phenols, indicating that they were somewhat more difficult to oxidize. No research work has yet been reported on voltammetric response for other secondary antioxidants such as sulfur – or selenium-containing antioxidants.

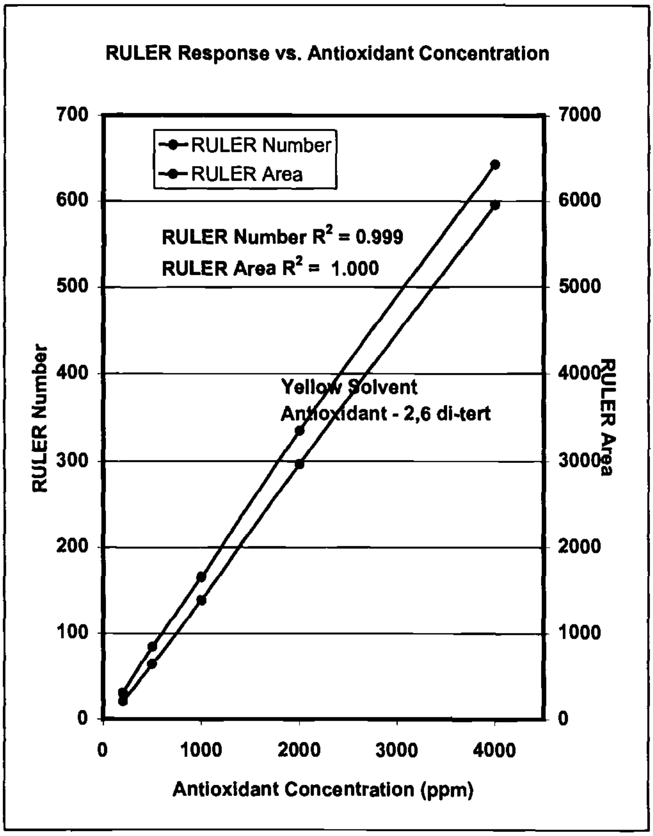

Figure 6: *correlation antioxidant % with voltammetric peak response in test solution 2*

Correlation study between oxidation test and cyclic voltammetry

Analysis of Jet Turbine Oil using Oxidation Test (DEF STAN 05-50 Part 61 Method 9)

The oxidation method used was Defence Standard 05-50 Part 61 Method 9. This involves two different procedures *[8]*. The first is referred to as "Temperature Parameters

- Oxidative Stability". The second is referred to as "Effective Life - Oxidative Stability", We will present the test data from the second procedure. The turbine oil used for this test is a polyol ester base oil manufactured for the latest generation of turbine engines (High Thermal Stability -HTS oils). With its specific mixture of aromatic amines, as an antioxidant package, this HTS turbine oil has an improved high thermal-oxidative stability. This is a great improvement since the jet engine oils of earlier generations.

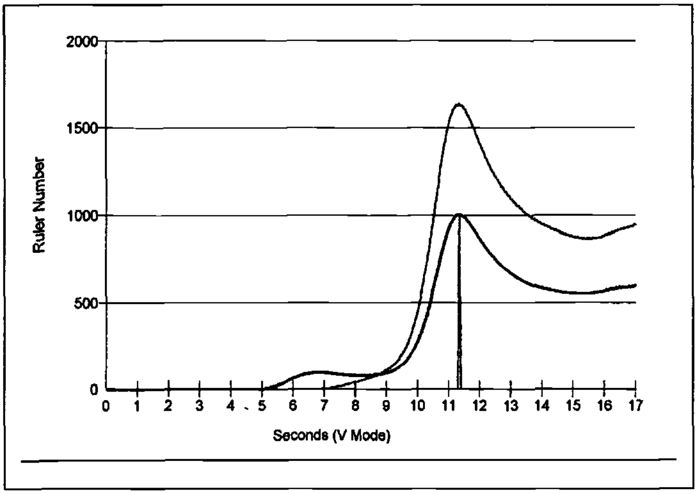

Figure 6a: *voltammogram HTS jet turbine oil*

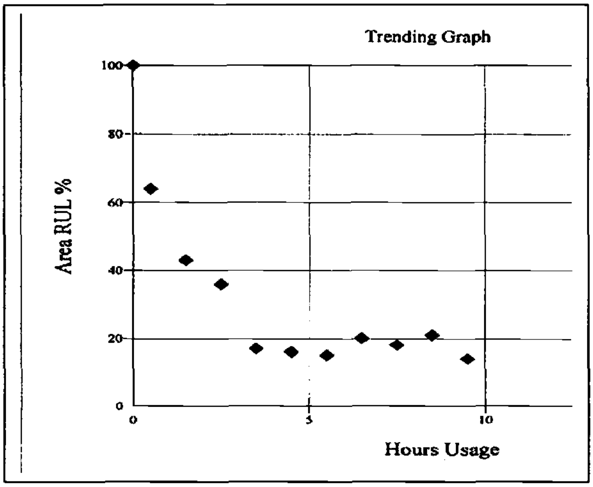

Figure 6b: *trending Graph AO Depletion Turbine oil*

Figure 6a shows a typical voltammogram from the HTS jet turbine oil: the main antioxidant (aromatic amine) appears at 11.5 seconds. The graph of a used (oxidized) oil shows the appearance of dimers & trimers (of the primary antioxidants) before the antioxidants, at 6-8 seconds.*[8]* In order to determine the contribution of the dimers & trimers to the remaining useful life of the jet oil, the voltammogram calculates the total area under the voltammetric response (area RUL%) (Figure 6b).

Effective Life - Oxidative Stability

The procedure for Effective Life - Oxidative Stability is as following *[9]*: a weighed volume of oil contained in a boiling glass tube is inserted into a heating block. Water-saturated air is bubbled through the sample maintained at a constant temperature of 250°C. After measuring the volatilisation loss, the sample is restored to its original weight by adding fresh lubricant. Its viscosity, acidity increase and insolubles content were then determined. Samples taken after the above tests were analyzed by voltammetry using 100µl of test oil in the test solution 1 (Figure 6a). The time at which the same parameters (TAN increase etc.) reached the critical points was determined: a volatilisation loss of 15% w/w; an acidity increase of 1.0 mg KOH/g; a viscosity increase of 15%; an insoluble content of 0.05% w/w and the formation of a gel (solidus).
The samples were heated to a 250°C for 0.5, 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5 hours.

Results - The RUL% of the samples falls rapidly to a minimum at 3.5 hours of testing, (Figure 7). Make-up oil is used in order to make viscosity and TAN determinations resulting in a gentle rise in RUL% of the samples from 3.5 to 9.5 hours. The viscosity and TAN increases almost linearly until 9,5 hours.

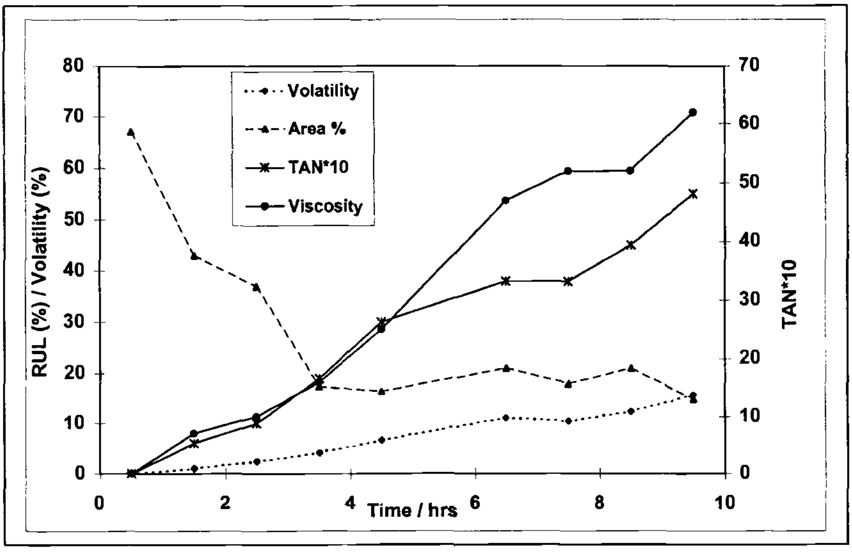

Figure 7: *Aircraft Turbine Oil Effective Life with remaining antioxidant %, volatility, viscosity (@40°C), TAN vs. Test Duration at 250° C test temperature*

Discussion - When the oil has less than 20% RUL the antioxidant becomes ineffective, leaving the base oil open to oxidative degradation. This stage was reached after 3.5 hours and from this point onwards the base oil was relatively unprotected. Both the TAN and viscosity increases reached their critical limits between 2.5 and 3.5 hours.

Analysis of Steam Turbine Oil Following Oxidation Test

In this part of the study, analysis was performed on a ISO VG 32 mineral steam turbine oil with an R&0 -package. The new oil was analyzed by the voltammograph, and a package of amines (diaphenylamines) and phenols was detected. The first additive peak showed the amines, and the second additive peak the phenolic antioxidants (Figure 8).

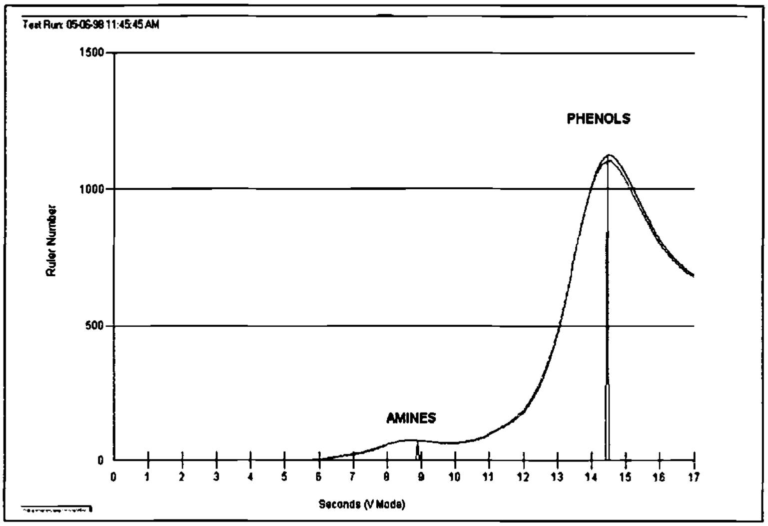

Figure 8: *voltammogram for ISO VG 32 turbine oil, with in the x-axis the time of analysis, and the Y-axis the voltammetric response as arbitrary units.*

Data were obtained from a RBOT test performed on the above-described ISO VG 32 steam turbine oil. Four oil samples were collected from 4 multiple RBOTs that were run and terminated at the times shown in table 1. These samples were analyzed by voltammetry for the detection of total antioxidant concentration. Figure 9 and Table 1 show the depletion trend of total antioxidant concentration, detected in both test solutions (solution #1 & # 2), as well the % remaining RBOT life.

Table 1 – *RBOT test results vs. Remaining AO%*

Sample ref	RBOT (min)	Remaining % AO Test solution 1	Remaining % AO Test solution 2
New oil	2008	100	100
1	1708	98	55
2	1408	58	23
3	1104	48	6
4	808	46	10

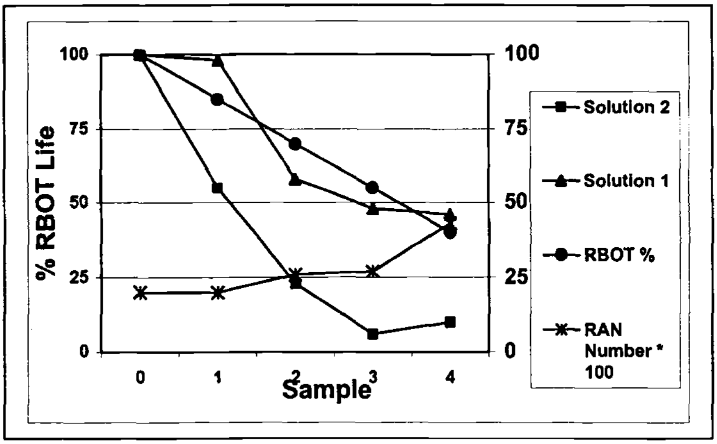

Figure 9: *correlation of RBOT values with voltammetric data for oxidized turbine oils*

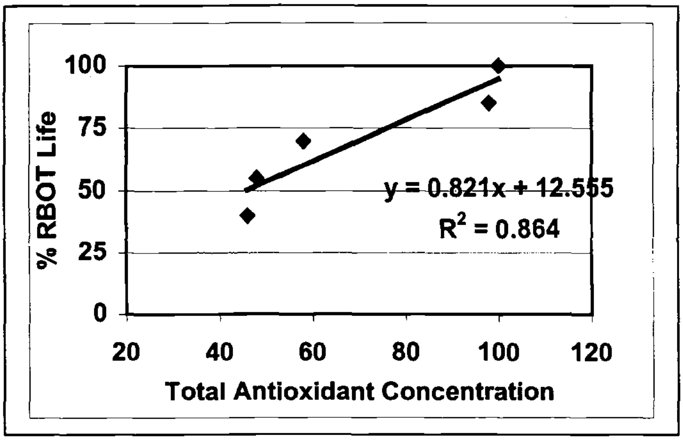

Figure 10: *correlation graph between RBOT and total antioxidants concentration by voltammetry in test solution 1.*

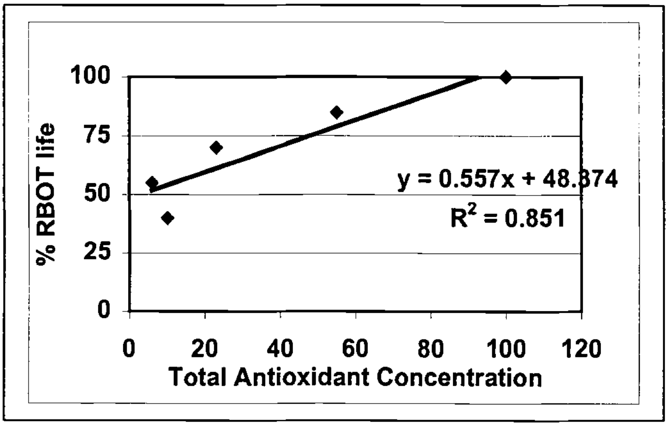

Figure 11: *correlation graph between RBOT and total antioxidants concentration by voltammetry in test solution 2.*

For this mineral-based turbine oil the correlations between RBOT and total antioxidants concentration by voltammetry in test solution 1 and 2 were 0.86 and 0.85 (Figures 10 &11). These values, based on previous research *[6]* are within expectations. The question however, could be asked why the antioxidants have different depletion rates. As voltammetric analysis has the capacity of differentiating antioxidant depletion rates, the above data were analyzed again from that perspective. Also, the acidity increase (measured by voltammetric Ruler Acid Number, expressed in mg KOH/ ml oil) *[10]* started accelerating when the remaining additive percentages fell below 40-50%. This could be due to 2 phenomena:

- Consumption of basic antioxidants.
- Increase of oxidation rate and products.

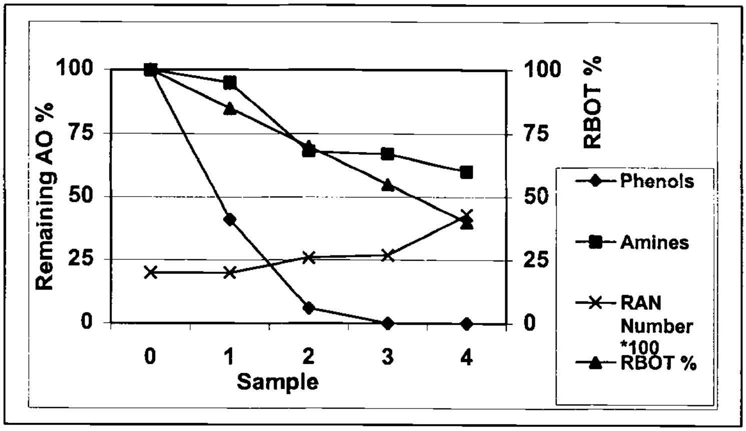

Figure 12: *Individual antioxidant depletion vs. RBOT shows RBOT more dependent on amines than phenols.*

The data in Figure 12 indicate the phenols that had become depleted in the first 10 hours.

Previous research on Dry-TOST test for hydraulic oils confirmed the same trend *[5]*, but the total acid number started to increase much faster once amine levels were reduced to 40% of the remaining antioxidant. Earlier experiences from field data *[3]* also indicate the difference in antioxidant depletion mechanism between steam and gas turbines. BHT, used commonly as antioxidant in steam turbine oil, is consumed, both by evaporation and by oxidation. Aromatic amines typically used in gas turbine oil and subjected to much higher temperatures than conventional steam turbine oil, have a different depletion rate (Figure 12). Bearing this difference in antioxidant depletion mechanism in mind, the capability of voltammetry to show the difference in depletion rates between antioxidants represents a complementary advantage over RBOT and DSC.

Research study data on ISO VG 32 turbine oil– RULER vs. DSC

A DSC oxidation test was performed on all the collected oil samples from the RBOT test. It was expressed as the Oxidation Induction Time (OIT minutes). The DSC test was performed at atmospheric pressure, with an oxygen flow of 50 ml/min, and at a hold temperature of 200°C. The temperature ramp rate was set at 20.0 C/min. First the RBOT results were correlated to the DSC results. This resulted in a correlation factor of 0.923 for the data shown below in table 2.

Table 2 – *Results of RBOT vs. DSC for oxidized oil samples*

Sample	RBOT %	DSC OIT
New oil	100	10.04
1	85	6.63
2	70	5.53
3	55	4.53
4	40	3.23

For the correlation with voltammetry and RBOT, we needed to determine the OIT of the base stock, which is 0.5 minutes. Comparison of the DSC OIT with the depletion trends of the antioxidants showed that the amine depletion rate has 2 different trends (Figure 13):

- For concentrations of phenols > 20%; the amines and DSC values have the same trend.
- Once phenol concentration is below 20%; the DSC values show more severe oxidation.

It is interesting to note that the acid number started to increase for oil samples with low phenol concentration. This is probably the result of lack of radical catchers.

As for the RBOT values, the individual antioxidant depletion rates have been correlated to the DSC values (Figures 14 and 15).

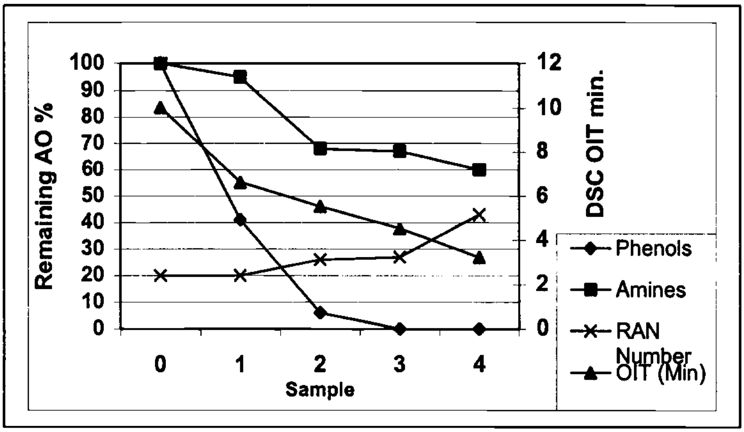

Figure 13: *Individual Antioxidant depletion rate (RUL%) vs. DSC OIT (minutes)*

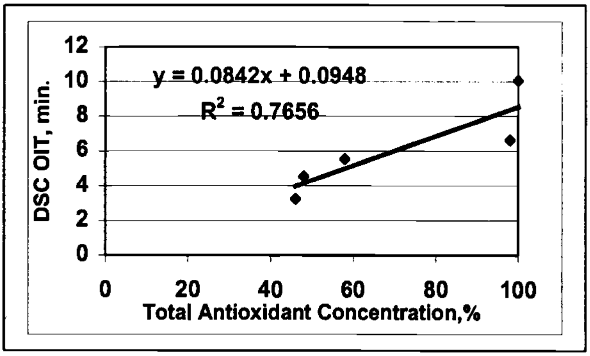

Figure 14: *correlation graphs for DSC OIT and Total Antioxidant Concentration by voltammetry for test solution 1*

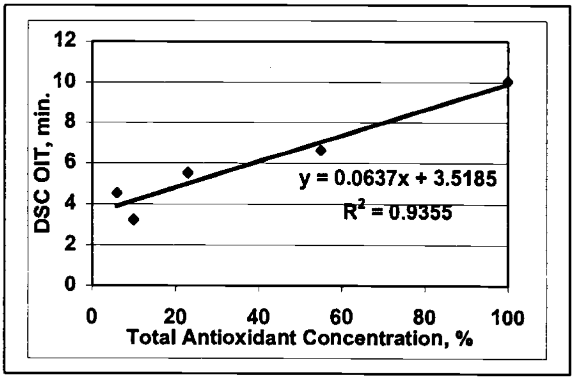

Figure 15: *correlation graphs for DSC OIT and Total Antioxidant Concentration by voltammetry for test solution 2*

In order to compare the depletion trends of amine and phenolic antioxidants all the oil samples analyzed by RBOT, voltammetry and DSC, were also analyzed by FTIR.
FTIR data showed the phenol depletion (3650cm^{-1}), and oxidation increase (1750 – 1650 cm^{-1}) for the new oil and the used oil. Combined spectra of the 4000-3000 cm^{-1} band (Fig 16) for the four oil samples illustrate the depletion of the phenol additive (3650 cm^{-1}) versus time. Earlier publication *[11]* also described the good correlation between voltammetry and amine antioxidants by FTIR.

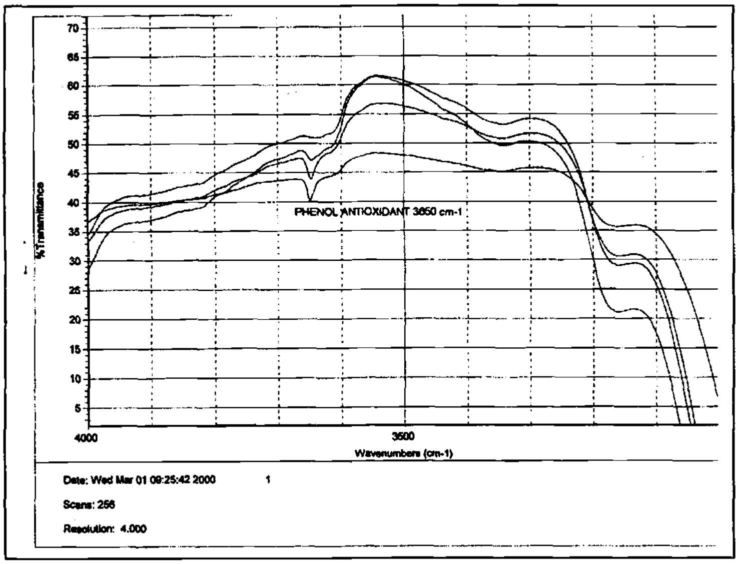

Figure 16: *FTIR spectra for the series of 4 used oil samples*

Used oil analysis from field oil samples

Field practical case 1

In this part of the program, measurements were taken from a power station in Europe, with Frame-9 Gas turbines for a total output of 2000 MW. Each turbine is equipped with a 35,000 liter oil reservoir and uses a mineral based turbine oil. The power station measures every 6 months the following parameters: water, viscosity, RBOT, voltammetric analysis for antioxidants, color and ISO cleanliness level.
The turbine fluids are now more than 2 years in service. Their characteristics/specifications for the voltammogram, detecting broad peak of aromatic amines as antioxidants are shown in Figure 17.

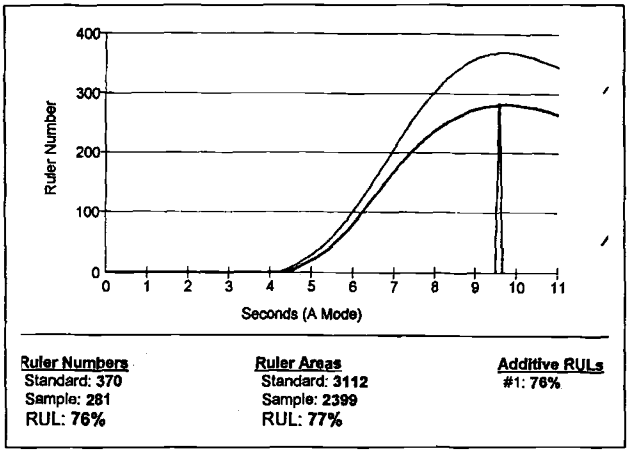

Figure 17: *Voltammograph of industrial gas turbine lubricant*

The voltammogram shows no phenolic antioxidant. This is a logical consequence of volatility and reactivity of phenols in the higher temperature environment. Table 3 summarizes the characteristics of the new oil.

Table 3: *characteristics new gas turbine oil ISO VG32*

Measurements	New Oil
TAN (mg KOH/g)	0.07
Color	L 2.0
RBOT (mins.)	> 1500
Viscosity (40°C) mm2/s	32,1
Water (%)	< 0.05
RUL % Amines	100%

Every two months the power station analyzed samples with the voltammetric equipment, to determine their remaining % antioxidant. They complemented their 6 months analysis with the antioxidant data. Figure 18 summarizes all the analytical data for one of the five turbines, during the last two years of service. Figure 19 presents only the trending graphs of the antioxidants for the 5 gas turbines.

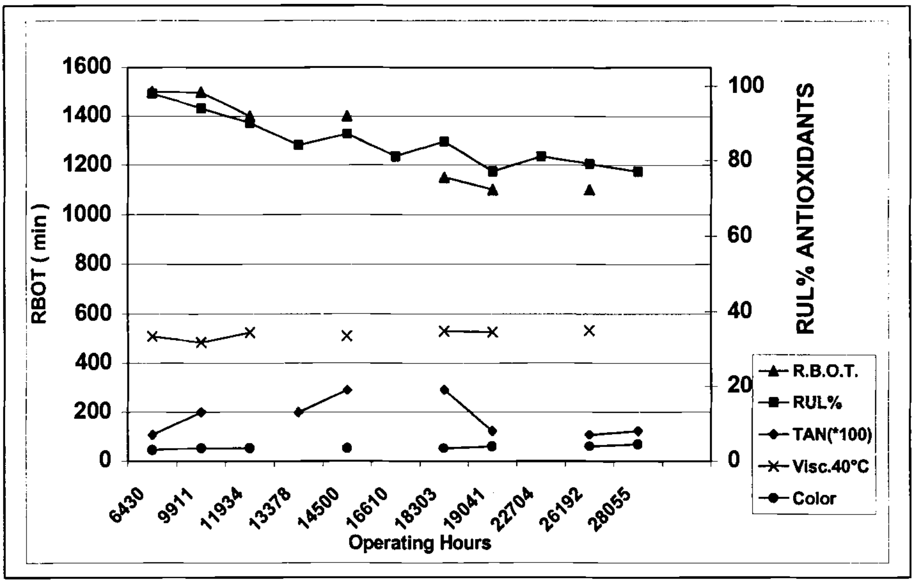

Figure 18: *analytical data for gas turbine oil in service on GT 2*

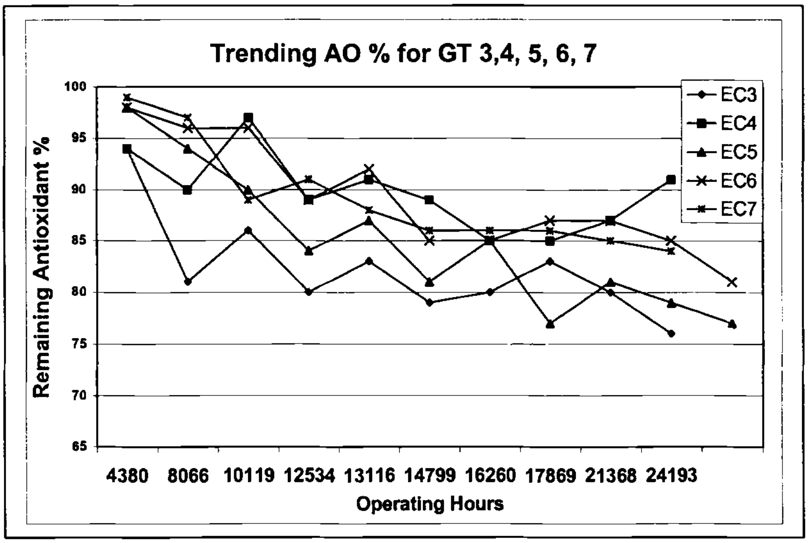

Figure 19: *trending graphs for antioxidants on 5 operational gas turbines*

It is important to note that antioxidant trending by voltammetry and RBOT (as well DSC) gives similar results. From the operator's (power station) point of view, the voltammetric field results could be used to screen oils for RBOT. When the antioxidant concentration stays above 50 % and the total acid number remains below the oil company specifications RBOT is not needed. This will save the end user money and time.

The 2-years data showed that the parameters (viscosity, color and water) remain relatively stable. The AO concentrations suggest that the fluctuations are probably caused by top-ups of fresh oil.

Field practical case 2

To finalize this research regular oil samples were assembled from different North-European power stations over a period of 6 months. The oil samples from different oil suppliers are used in various steam and gas turbines. For the 35 oil samples, RBOT and the remaining antioxidant were measured by the power station or a central laboratory. The laboratory supplied the fresh oil RBOT data. A good correlation can be observed between the antioxidants remaining and the remaining RBOT life (Figure 20). The summary of the information on all oil samples of the North-European power stations is listed in the appendix.

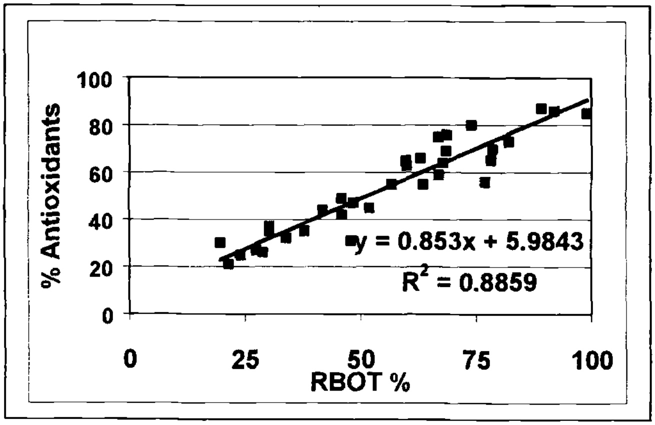

Fig. 20: *correlation graph for field oil samples between RBOT and remaining antioxidant concentrations*

The correlation holds well for a wide variety of oil manufacturers and different turbines. We emphasize the added value of voltammetry for the new generation of turbine fluids:

- If the oil has a high RUL, the oil is good.
- If RUL % is low, confirmation by RBOT measurement is necessary.

There is a slight difference between the RBOT values and the remaining antioxidant concentration. This can be explained by the fact that RBOT detects the total antioxidant capacity of the lubricant, including the natural antioxidancy of the base stock. The above data show however, that two important factors must be considered:

- New hydrotreated base stocks, as well as synthetic base stocks, have a much lower natural antioxidancy. This will be of less influence on their remaining useful life.
- Existing procedures e.g. ASTM Test Method for In Service Monitoring of Lubricating Oil for Auxiliary Power Plant Equipment (D 6224), advise to consider oil change when the warning limit for turbine fluids reaches the value of 25% remaining RBOT . This is in line with voltammetric analysis.

Conclusions

Laboratory and field data both show there is a good correlation between RBOT, DSC and antioxidant analysis by voltammetric technique. Voltammetric analysis has the additional benefit to differentiate the depletion rates for different antioxidant. This is very valuable information for the new generation of turbine fluids (e.g. re-additization).

The antioxidant detection by voltammetry proves its highest value for jet turbine lubricants, which operate at the highest temperatures. It is a predictive technique that detects abnormally operating engines before the viscosity and total acid number increase. In the case of industrial turbine lubricants, field experience shows the complementary features of voltammetry with standard analysis programs. For the new generation of turbine fluids, in combination with higher load factors of equipment, the voltammetric analysis of antioxidants will result in a quick and easy understanding of oxidation processes.

Voltammetry complemented by RBOT (DSC) also provides the user information on which antioxidant depletes faster. Voltammetric analysis can be performed on site, with a minimal time and sample size. Therefore it can be used to monitor the oil more frequently and thereby detect abnormally operating conditions (accelerated rate of antioxidant depletion) at an earlier stage.

The results show that there is good correlation between voltammetric analyses and RBOT measurements. Further research will improve the correlation between voltammetry, RBOT and other field tests. It will give a better insight of the effects of different types of antioxidants on the test results of the various techniques.

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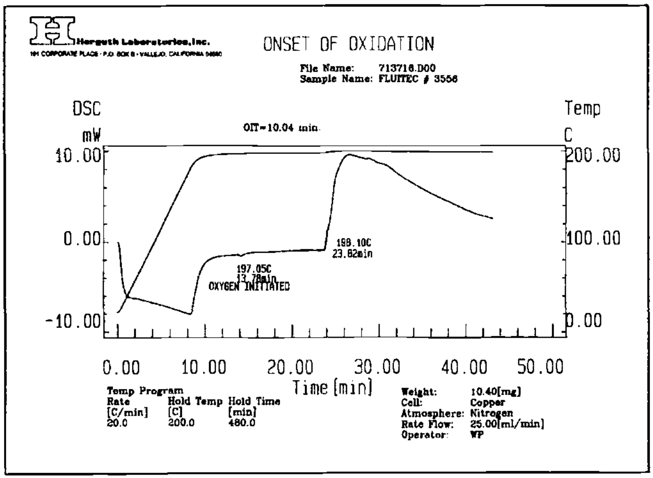
Appendix

1) DSC printouts



Herguth Laboratories, Inc.
101 CORPORATE PLACE · P.O. BOX 8 · VALLEJO, CALIFORNIA 94590

ONSET OF OXIDATION

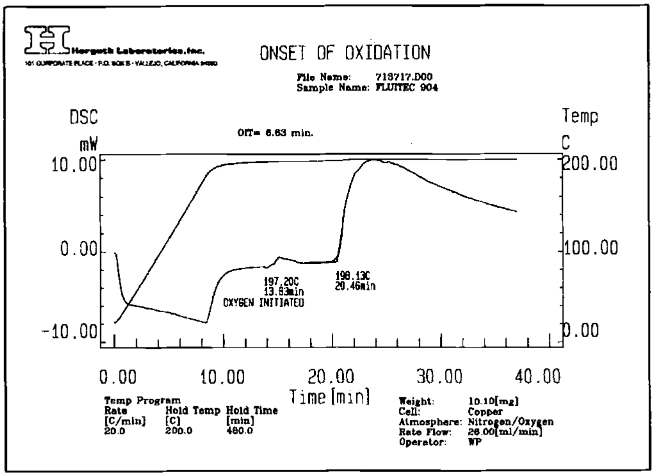
File Name: 713716.D00
Sample Name: FLUITEC # 3556

OIT=10.04 min.

Temp Program		
Rate [C/min]	Hold Temp [C]	Hold Time [min]
20.0	200.0	480.0

Weight: 10.40[mg]
Cell: Copper
Atmosphere: Nitrogen
Rate Flow: 25.00[ml/min]
Operator: WP

DSC test new oils



Herguth Laboratories, Inc.
101 CORPORATE PLACE · P.O. BOX 8 · VALLEJO, CALIFORNIA 94590

ONSET OF OXIDATION

File Name: 713717.D00
Sample Name: FLUITEC 904

OIT= 6.63 min.

Temp Program		
Rate [C/min]	Hold Temp [C]	Hold Time [min]
20.0	200.0	480.0

Weight: 10.10[mg]
Cell: Copper
Atmosphere: Nitrogen/Oxygen
Rate Flow: 28.00[ml/min]
Operator: WP

DSC test used oil
(sample 1)

Journal ID	Date	RBOT %	RUL%	Oil
1918.9.07 QFA	21-01-99	29	26	Castrol
2093.9.37 QFA	02-09-99	46	49	Castrol
2003.9.23 QHI	07-06-99	60	63	Shell
1912.9.06 QSÆ	04-02-99	63	66	Shell
2069.9.30 QSÆ	26-07-99	64	55	Shell
1985.9.20 SH	11-05-99	21	21	Texaco
2145.9.45 SH	09-11-99	20	30	Texaco
2140.9.44 RFV	02-11-99	69	69	Shell
2041.9.29 HKV	03-05-99	28	27	Mobil
2208.9.52 SVHO	16-12-99	24	25	Mobil
2002.9.23 RKV	04-06-99	30	37	Texaco
2143.9.45 SH	05-11-99	30	35	Texaco
2122.9.43 QHØ	15-10-99	92	86	Shell
1990.9.20 DIV	20-05-99	89	87	Texaco
2073.9.34 SVSB3	23-08-99	82	73	Texaco
2209.9.52 DIV	24-12-99	49	47	Shell
2121.9.43 SH	12-10-99	34	32	Texaco
2171.9.50 SVSB3	08-12-99	69	76	Texaco
2172.9.50 SVSB3	08-12-99	79	70	Texaco
2047.9.29 NVVB3	21-07-99	67	75	Castrol
2079.9.35 NVVB3	03-09-99	38	35	Castrol
2080.9.35 NVVB3	03-09-99	74	80	Castrol
1981.9.19 SVSB3	07-05-99	99	85	Texaco
2048.9.29 NVVB3	21-07-99	52	45	BP
2168.9.49 NVVB3	01-08-99	77	56	BP
2049.9.29 NVVB3	21-07-99	46	42	BP
2169.9.49 NVVB3	01-08-99	42	44	BP
2050.9.29 NVVB3	21-07-99	48	31	BP
2090.9.37 DIV	16-09-99	57	55	Shell
2091.9.37 DIV	16-09-99	78	65	Shell
2092.9.37 DIV	16-09-99	67	59	Shell
2043.9.29 HKV	15-07-99	60	65	Texaco
2046.9.29 HKV	03-05-99	68	64	Shell
2005.9.23 DIV	25-05-99			Texaco