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OPTIMIZING THE THERMO-OXIDATION STABILITY OF GAS TURBINE OILS

Abstract

The reliable and trouble-free operation of the gas turbines is highly dependent upon the lubricating system and the lubricating oil performance. Recently the typical operating temperatures of turbine oils have been rising as modern gas turbines in power generation become more efficient. At the same time gas turbine oils are increasingly required to have longer service life. In order to fulfil all these requirements the current turbine oils need to possess adequate thermo-oxidation stability. However, as new quality of gas turbine oils have been introduced in turbine systems, new challenges appeared in regard of sludge, varnish and deposit formation. These contaminants and lubricating oil related problems led to downtimes, outages and extra maintenance costs. Due to clarify the reasons and backgrounds, extensive investigations and studies of the given thermo-oxidation stability problems are required for a better understanding of the complex phenomena.

1. Introduction

The modern gas turbines have lubrication needs that are different from the lubrication of other type of turbo-machines, such as water and steam turbines.

As the demands rise base stock and additive selection are becoming increasingly more important to fulfil the desired key features. Successful formulation balance is also required to design robust gas turbine oil that can meet the challenges of a severe operating environment. In recent time new "high performance" turbine oils have been introduced and commercialized with so desired, believed and declared "extreme high thermo-oxidation stability". However, now new serious claims and discrepancies are arising regarding to the frequent appearance of the sludge, varnish and deposit in many gas turbine applications.

Recently, a lot of articles and reports have been published on this sludge and varnish formation issue [1] [2] [6] [9] [10] [11], seeking the adequate problem

solutions and way outs to avoid it. Nevertheless, all these contributions, investigations and industrial efforts have not yet resulted the definitive solutions, overall consensus and satisfactory answers to this complex problem. Due to these facts, further investigations, extensive studies of the given thermo-oxidation stability problems are required for a better understanding of the phenomena.

This paper will review the current situation of lubrication of the gas turbines and will discuss the authors' viewpoints and considerations on reasons of the sludge and varnish formation. The significance of the balanced turbine oil formulation via a proper selection of base stock quality, types of antioxidant additives and their treat rates in relation to the high thermo-oxidation stability, as well as its bench testing will be also discussed and emphasized.

A better understanding of the exact backgrounds that occur those thermo-oxidation stability claims, it will be feasible to design and harmonize the gas turbine oil performance with the operation conditions, as well as to reduce the sludge and varnish formation potential

2. Current market situation and industrial trends

The turbo-machines and their lubrication

In the power generation there are three main principal types of turbo-machinery that have gained their major role and importance, widespread acceptance and common popularity: water, steam and gas turbines. Due to their high efficiency and flexibility in the heavy-duty operation regimes a greater than ever market share has been achieved specially by the gas and combined cycle turbines [1] [2] [4].

Table 1 - Overview of turbine oil operation conditions

	Water	Steam	Gas
Critical turbine components	bearings guide vanes control system	bearings control system	bearings gears control system
Speeds, rpm	50-600	>3000	3000-7000
Oil sump temp., °C	40-60	45-65	50-95
Hot spot peaks, °C	75-90	80-150	150-280
Unfavorable impact	(water) air	(steam) air	air high temp.
Oil service life, thousand hours	100-250	50-150	20-30

Each of the three turbine types has own typical regimes and representative operation conditions. These different turbo-machines are characterized by a wide variety of speeds, mechanical loads and lubricating oil temperatures. The turbo-machinery design and construction, the operating conditions, as loads, operating temperatures, oil makeup and contaminants belongs to the main factors, determining the turbine oil performance requirements and its service life.

The general overview of the turbine oil operation condition is shown in the Tab. 1 [5].

Gas turbine oil requirements

As shown above in Table 1, the gas turbine applications have the most severe operation conditions for turbine oil. Elevated sump temperature and high hot spot peaks represent the uniqueness of overall gas turbine oil challenges. This unfavourable impact of much higher operation temperatures call for distinguishing oils with much higher thermal and oxidation resistance and robustness.

Furthermore, there are strong efforts to ensure a longer, more extended, but trouble-free operation of gas turbines. An adequate lubricating oil quality should be responsible to ensure and perform that desired longer service life and the reliability of the gas turbines operation [1].

Table 2 - The new ISO 8068 (September 2006)

TSA	Steam turbine for normal (low) temperature
TGA	Gas turbine, for normal (low) temperature
TSE	Steam turbine for normal (low) temperature with EP
TGE	Gas turbine for normal (low) temperature with EP
TGB	Gas turbine, B = higher temperature
TGSB	Gas + steam Turbine, higher temperature
TGF	Gas turbine, higher temperature with EP
TGSE	Gas turbine + steam, higher temperature, with EP
TGCH	Gas turbine for high temperature formulated from synthetic base oils
TGCE	Gas turbine for high temperatures used in aircrafts
THA	Turbine for normal temperature operating in the boundary/mixed lubrication regime
THE	Turbine for normal temperature operating in the boundary/mixed lubrication regime with EP additives
TSD	steam Turbine, fluid based on phosphate ester = fire resistant
TGD	gas Turbine, fluid based on phosphate ester = fire resistant
THCH	Turbine, fluid environmentally acceptable based on PAO (almost AWHF: HEPR)
THCE	Turbine, fluid environmentally acceptable based on Esters (almost AWHF: HEES)

Standardization and specification development activities

In regard to match these severe operation requirements, in recent time new or revised industrial standards and turbine oil specifications have been introduced [1] [2]. The latest issue of the international standard ISO 8068 is shown in T. 2 [2] [12].

More severe thermo-oxidation stability requirements have resulted changes and definition of more detailed turbine oil specifications, distinguishing the standard (water and steam) and gas turbine application areas. The development and the progress of standardization activities have not been stopped with the creation of international and national specifications. In the meantime there have been also introduced or revised several new Original Equipment Manufacturers (OEM) specifications and guidelines of turbine oils. Especially the gas turbine oils have been recently specified in distinctive product standard with individual performance requirements for thermo-oxidation stability [2].

Gas turbine oil formulation trends and bench testing

Turbine oil formulators and manufacturers have responded by using non-conventional base stocks with extremely increased antioxidant additive treat rates. Correspondingly, enhanced type of turbine oils have been appeared and commercialised to satisfy these lately specified demands on better thermo-oxidation stability.

As main test criteria of thermo-oxidation stability were employed same bench test methods as measured by ASTM D 2272 Rotating Pressure Vessel Oxidation Test (RPVOT) and ASTM D 943 Turbine Oil Stability Test (TOST) as in evaluation of the traditional R & O (Rust and Oxidation Inhibited) and conventional formulated turbine oils (see Table 3 and 4) [1].

Table 3 – Comparison of main physical and chemical characteristics in specifications of gas turbine oils (I)

Parameter	Test method	DIN 51515-2 L-TG	ASTM D 4304 TYP III (draft)	ISO/DIS 8086 TGB/TGSB
Viscosity class	ISO 3448	32 / 46	32 / 46	32 / 46 / 68
Viscosity index min.	ISO 2909	90
Air release, min max.	ISO 9120	5	5	5 / 5 / 6
Forming (tendency/ stability) max. - Seq. I °C @ 24 °C, ml/ml - Seq. II °C @ 93 °C, ml/ml - Seq. III °C @ 24 °C after 93 °C, ml/ml	ISO 6247	450/0 100/0 450/0	50/0	450/0 50/0 450/0
Water content, m% max.	ISO 12937	0,015	0,02	0,02
Water separability - Time to 3 ml emulsion @ 54 °C, min max. - separation (steam), sec, max.	ISO 6614 DIN 51589-1	... 300	30 ...	30 ...
TAN, mg KOH/g max.	ISO 6618	report	0,2	report
Cleanliness at delivery state, class max.	ISO 4406	20/17/14	-/17/14	-/17/14
Flash point (COC), °C min.	ISO 2719	160 / 185	200 / 200	200 / 200 / 200

In fact, the recent gas turbine oil developments of oil companies have concentrated on the satisfaction and fulfilment of required extremely high RPVOT/TOST values

only, but not on the real-life operation conditions. The validations of methodology and the evaluation of fleet discrepancies have not been taken into account.

3. Sludge and varnish formation – as critical issue

Fleet experiences

In spite of detailed, strict and distinguishing gas turbine oil standards, there have been occurred frequent and serious problems, related to sludge and varnish formation phenomena. Recently the sludge and varnish formation has become the most serious oil related problem. It can appear even in so called and so declared “high performance” gas turbine oils, and also very often related with use of high quality non-conventional base stocks [6] [9] [10] [11]. In many cases the sludge and varnish formation in servo valves has been shown to cause the valves to stick. In other cases caused by varnish and deposits in turbine oil circuits include decreased oil flow rates, increased wear rates and potentially a change in lubrication regimes from hydrodynamic to boundary.

Table 4 – Comparison of thermo-oxidation test requirements in specifications of gas turbine oils (II)

Parameter	Test method	DIN 51515-2 L-TG	ASTM D 4304 TYP III (draft)	ISO/DIS 8086 TGB/TGSB
Oxidation stability @ high temperature (72 h @ 175 °C) - viscosity change max. - Acid number change max.	ASTM D 4636 according to "alternative procedure 2"	...	report report	...
Metal specimen weight change, mg/cm ² - steel - aluminum - cadmium - copper - magnesium			± 0.250 ± 0.250 ± 0.250 ± 0.250 ± 0.250	
Oxidation stability ("TOST") - time for TAN to 2 mg KOH/g min. - 1000-h TOST sludge, mg max. - 1000-h TOST TAN, mg KOH/g max.	ISO 4263-1 ASTM D 4310 ASTM D 4310	3000	3500/3000/250 0	3500/3000 200 report
RPVOT, min min.	ASTM D 2272	800	750	500
Modified RPVOT, % min.	ASTM D 2272	85	85	85

Other problems caused by varnish in turbine oil systems include reduction of cooler performance, increased bulk oil temperatures, prematurely plugged filters and strainers, and plugging of small oil orifices [10] [11]. Most routine and standardized oil analysis tests do not correlate to sludge and varnish problems in the field. New standard test methods have to be developed and applied to evaluate or to quantify the oil's tendency to form varnish.

Reasons behind the sludge and varnish formation

The cause of sludge and varnish formation is varied. However, most of the factors include extreme thermal and oxidative stresses from elevated operating temperatures, cyclic or peaking duty cycle operations of the gas turbines, as well as the use of less solvent non-conventional base stocks and certain additive chemistries [6]. No doubt that the use of non-conventional base stock qualities can guarantee much better thermo-oxidation stability, as the conventional mineral oils Group I. Nevertheless, those deeply refined oils definitively demonstrate a poorer solvency and a reduced polar component tolerance. In regard to fulfil the required high level of TOST / RPVOT values in product standards currently higher additive treat rates, especially that of aminic antioxidants, should be necessary to employ. In regard to the limited solvency of non-conventional base stocks and the vulnerable thermal stability of aminic antioxidants, the high dosage treat rate of antioxidants is not a preferable choice in fighting against sludge and varnish formation. The high treat rate of antioxidants can cause itself additive dropout, sludge and varnish at an early stage.

4. Focussing on sludge and varnish formation control**How to avoid the sludge and varnish**

Several similar studies [6] [10] [11] have revealed that the sludge and varnish formation is usually the result of a complex string of unfavourable circumstances. This complex problem can be solved only in close cooperation via successive, harmonized and systematic actions and efforts of OEMs, machinery operators as well as turbine oil manufacturers

Firstly, the Original Equipment Manufactures (OEM's) should contribute, creating new, more favourable future machinery designs and lubrication circuit constructions, reducing the extreme high thermal peaks on turbine oils. Furthermore, the attention and awareness of turbine machinery operators should be concentrated also on these problems. They have to be able to monitor, detect and recognize the sludge and varnish formation tendency during the whole service period. An oil condition monitoring program should be part of regular maintenance including a combination of on-site inspections and off-site oil analysis tests. While there is no direct standard test method to quantify the sludge and varnish formation potential, the support of an advanced oil laboratory is required.

Currently, many power plants and gas turbine operators utilize electrostatic type filtration (e.g. Kleentek, Isopur) [11]. Many publications have reported good results in reducing the sludge and varnish formation potential. However, all these extra equipment and manipulation expenditures mean an extraordinary increase of maintenance costs for the operators. The authors of given paper has performed extensive studies to validate the potential options to find optimal and feasible ways of lubricant manufacturers to reduce risk of the sludge and varnish formation.

The lubricant manufacturers have the best opportunities to develop new, more efficient standard and bench testing methods, as tools for oil performance

evaluation, and also for condition monitoring to predict the sludge and varnish formation potential. This more advanced oil testing methodology should perform better evaluations of thermo-oxidation stability and overall capabilities of gas turbine oil, giving better correlations with the real life. As above reported, a gas turbine oil formulation balance plays itself an ultimate role, as a preventive measure to minimize the risk of the sludge and varnish formation. ("The best care is prevention...!") A balanced gas turbine oil formulation means a formulation design via optimization and harmonisation of base stock quality and solvency as well as the right selection of antioxidant types and their treat rate.

5. Oil formulation considerations

How to balance the oil formulation

Quality of lubricant base stock predestined fundamentally the thermo-oxidation resistance and aging characteristics. Therefore the solvent refined base stocks Group I can hardly fulfil the modern heavy-duty gas turbine performance requirements [6] [9]. Without an effective antioxidant, which is non-volatile and thermally stable, even the non-conventional base stocks will be oxidized quite rapidly. Part of antioxidants can be lost by vaporization or become ineffective as a result of high temperatures. The proper treat rate and chemical selection of antioxidants are key issues for the design of the thermal stability and aging resistance and for the reduction of the sludge and varnish formation potential.

Table 5: Base stock categories according to ATIEL/API

<u>Group I</u> Saturates < 90 % Sulphur > 0,03 % 80 < VI < 120	<u>Group II</u> Saturates > 90 % Sulphur < 0,03 % 80 < VI < 120	<u>Group III</u> Saturates > 90 % Sulphur < 0,03 % VI > 120
<u>Group IV</u> Polyalphaolefins (PAO)		<u>Group V</u> Others

Dilemma of using non-conventional base stocks

The non-conventional base stocks are advantageous because of much higher oxidation and thermo-oxidation stability, in comparison with conventional base stocks Group I. They have a quite homogenous hydrocarbon structure (see Table 5), nearly full absence of aromatic, hetero-aromatic constituents - therefore low sludge and varnish formation potential.

The non-conventional base stocks have an excellent additive response for a comparable performance level; a lower additive treat rate is required. Nevertheless all these non-conventional base stocks have lower solvency, resulting an earlier sludge formation and additive dropout, if use the commonly high treat rates and antioxidant types.

Significance of proper solvency

The solvency features of the given and employed base stocks are a crucial issue [8]. A limitation of base stock solvency can cause real-life problems. High treat rates of some polar functional additives without additional surfactants make the formulation instable. The solvency is very seldom an investigated phenomena in the laboratory testing, nevertheless a critical matter in field and for the general performance of most industrial oils. The determination of the aniline point can provide approximate information about the solvency of a given base stock. The determination of the aniline point will be according to ISO 2977 (ASTM D611) [8]. The typical aniline points of different type of base stocks are shown in Table 6 [8].

Table 6 - Aniline point of different base-stocks

Type of base stock ISO VG 32	Aniline point °C
Naphthenic	56-59
Paraffinic Group I	99-102
Group II	114-118
Group III	124-126

The solvency characteristic is related to the aromatic nature of the oil. It is determined by the temperature at which there is a complete miscibility between aniline and the oil. With a higher aromatic content has the given oil a lower aniline point.

Selection and proper balance of antioxidants

There are a huge number of different chemical sorts of antioxidants that can be selected and employed for gas turbine oils [7] [9]. A proper formulation balance requires a selection of two or more chemical type of antioxidants with synergetic potential and multifunctional character, finding out the ways to reduce the overall additive treat rates. Lower treat rates of antioxidants can decrease the additive solubility weakness in highly non-polar base stocks, and also minimize the probability for additive dropout, sludge and deposit formation.

The individual components of employed antioxidant additives and their chemistry must be carefully selected and have low volatility, good thermal stability and adequate solubility in the base stocks used in the desired gas turbine oil formulations.

The hindered phenolic antioxidants are very effective types at moderate sump oil temperatures. Nevertheless they have high sublimation and volatility potential. This type of antioxidant is not enough effective as a single antioxidant to control the high temperature stability of the gas turbine oils.

The aminic antioxidants are very effective types to boost RPVOT / TOST values, especially in non-conventional base stocks. Therefore, they are widely used and definitive constituents in current turbine oil formulations. Nevertheless at higher treat rates they can cause additive dropout and form insoluble at elevated temperatures.

Using mixed antioxidant additive systems

The antioxidant system used for gas turbine oil is based upon a unique, synergetic combination of primary and secondary antioxidants, which exhibit good solubility and allow the use of lower treat rates [6] [9]. Synergies have been found when an optimal ratio of primary antioxidant or free radical scavengers are added to the combination of hindered phenols and alkylated diphenylamine antioxidants. Further optimization can be achieved with the addition of phosphorus or sulphur type secondary antioxidants or peroxide decomposers. This synergetic antioxidant effects differ from base stock to base stock [7].

It should be noted that in the industrial practice rather the ready-made turbine oil packages will be employed, offered by different additive suppliers. The formulations, based on such full packages have gained a broad use. Only, few of lubricant manufacturers make themselves extra efforts in regard to optimize the chemical composition of additive ingredients and using single components. However, a balanced, self-tailored and optimal ratio or component combination is important in reducing additive treat rates and in design of a correct turbine oil composition.

6. Necessity of new bench testing procedures

Shortcomings of the current bench testing

All used and specified key bench test methods are required to correlate with real-life operating condition or they have to be more severe of it.

The current turbine oil thermo-oxidation bench testing methods are shown in T. 7 [1].

The test method ASTM D 2070 has been introduced earlier for evaluation of hydraulic fluids. The test temperature of 135 °C seems not to be high enough to evaluate the extremely high stresses on gas turbine oils. The other two tests TOST / RPVOT used for gas turbine oils, as they were introduced for the water and steam turbine application. Nevertheless, the operation regimes and performance requirements of these turbine oils are very different. Currently, in case of "high performance" gas turbine oils the TOST test procedure takes a long time (e.g. more than 10.000 hours) and it does not cover the critical temperature and required performance range.

Some antioxidants have their performance disadvantages and weaknesses (intensive volatility, dropout, thermal instability) even above the specified values of TOST (95 C) and that of RPVOT (150 C). It is in the range of 150-190 C. The gas

turbine oils should have distinctively high thermo-oxidation stability, at right elevated temperatures and without presence of water. The currently used higher antioxidant (or additive package) levels generate not only higher TOST / RPVOT values, but as side effect, they induce also a higher sludge formation potential. These critical features cannot be simulated and evaluated with the current praxis.

Table 7 - Turbine oil thermo-oxidation bench testing methods

Test method	CM-A ASTM D 2070	TOST ASTM D 943	RPVOT ASTM D 2272
Oil sample volume	200 g	300 mL	50 g
Water content	none	60 mL	5 mL
Metal catalysts	Cu rod Fe rod	Cu coil Fe coil	Cu coil
Air / Oxygen	air (no flow)	oxygen, 3 L/h	90 PSI oxygen
Temperature	135 °C	95 °C	150 °C
Test duration	168 hours	ca. 3.000-10.000+ hours	ca. 10-40 + hours
Evaluation criteria	sludge rod rating	dTAN	pressure drop

New recommended bench testing

The currently used bench tests are not able to fulfil the state-of-the-art bench testing requirements, in evaluation of the sludge and varnish formation tendency [10] [11]. As mentioned above, the adequate bench test procedures of thermo-oxidation stability should have to simulate the real operation conditions and their results should have to correlate with real-life turbine oil conditions. The current real-life needs require that the desired bench test procedures should be focussed on evaluation of the solubility of base stocks, thermal stability of functional additives at elevated temperatures, as well as the overall sludge and varnish formation potential of gas turbine oils.

There are three candidate methods under development progress that will be considered and recommended in future for the evaluation of the sludge and varnish formation tendency (see Table 8):

1. A rapid screening test of thermal stability, solvency and antioxidant dropout will be a modification and adoption of MAN Turbo in-house test [13].
2. An evaluation of sludge formation potential in presence of copper coil can be carried out with the modified Baader aging test adopting DIN 51554 [14].
3. A high temperature oxidation stability test is an in-house test adopting CEC-L-48-A-00, method B test apparatus [15].

Involving several industrial partners there are broad ongoing studies and running experimental program aimed at developing new qualifying methods. A large number of test series will be carried out and experimental data base will be generated.

Table 8 - New recommended bench testing

Test method	MAN Turbo in-house	Modified Baader DIN 51554	in-house HTOST (CEC-L-48-A-00)
Oil sample volume	150 mL	60 mL	100 mL
Water content	-	-	-
Metal catalysts	-	Cu coil	-
Air / Oxygen	-	air (no flow)	air, 5 L/h
Temperature	120/150/180 °C	150 °C	160 °C
Test duration	48 hours	168 hours	(96-)192 hours
Evaluation criteria	screening for sludge	sludge, dTAN, dSaponification, Cu coil	dKV, dTAN, dFTIR (oxidation, AO)

7. Conclusions

The gas turbines have become an important role in market share in the modern power generation.

The thermo-oxidative stability of gas turbine oils is a key performance parameter.

Different origin, structure and features of base stock categories determine and impact their solubility and solvency against antioxidants, polar degradation products and submicron particles. Advanced gas turbine oil formulations should be in future based on non-conventional base stocks Group II/III.

Balanced mixture of hindered phenolic and aminic antioxidants should be used to control oxidative degradation and aging either at moderate elevated and high oil temperatures. The total treat rate of antioxidants should be reduced and optimized to the base stock performance level and its solubility.

There are no any existing widely accepted and adequate practices evaluating the sludge and varnish formation potential at high temperatures. Nevertheless, the sludge and varnish formation potential should be also evaluated and specified.

New testing procedures should be introduced and tailored to the distinctive performance requirements of gas turbine oils, depending on severity of operational conditions.

Solving thermo-oxidation problems of gas turbine oils is furthermore a challenge for oil formulators OEMs and machinery operators as well.

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