ASTM, Dec. 05 –
"Turbine Oil Oxidation Symposium"

Oxidation and Testing of Turbine Oils Symposium

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

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Introduction

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

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

Brief History

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

Figure 1 – Varnish Formation on Inlet Guide Vane (IGV) Valve from a Gas Turbine

Sludge and Varnish Defined

Lubricants degrade in different ways, and the products of this degradation are essentially referred to as sludge and varnish. These products are generally unstable in the oil and, as such, are looking for a place to deposit or simply separate from the bulk oil. In certain instances, deposits form on machine surfaces at the exact location where the oil has degraded, for example, thermal degradation known as hot surface coking. In other cases, the oil degrades in one location but the insoluble degradation products are carried elsewhere by the moving fluid forming deposits on surfaces.

Over time, some deposits can thermally cure to a tough enamel-like coating. Other types of deposits, generally in cooler zones, remain soft or gummy. Sludge is not always black or even dark. It may appear clear and grease-like, similar to petroleum jelly. The following are examples of where sludge and varnish might occur in turbine lube oil and hydraulic control systems[2]:

- Black crusty deposits on mechanical seals
- Gold adherent films on spool valves in EHC hydraulic systems
- Charcoal-like deposits on babbitt sleeve bearings
- Gooey-brown mayonnaise on oil filters
- Black scabby deposits on thrust-bearing pads (Figure 2)
- Carbonaceous residue of servo strainers

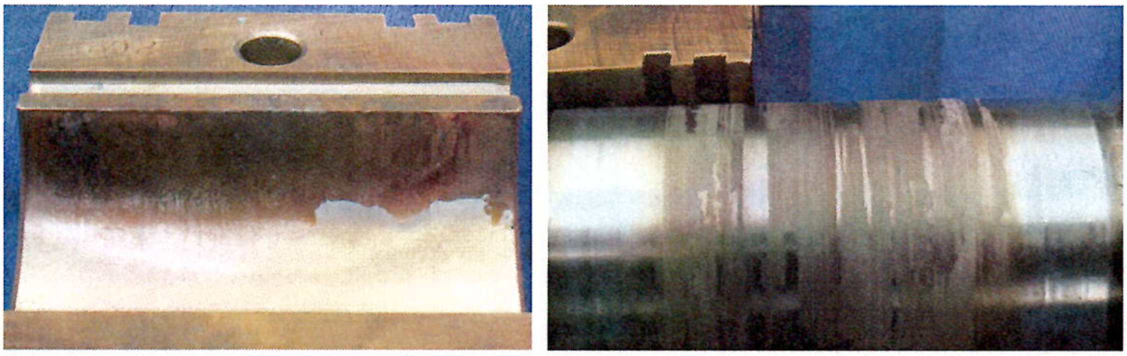

Figure 2 – Varnish Formation on Plain Bearing and Shaft
Courtesy of Cerestar Deutschland

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

Other types of sludge and varnish-induced failures include plugged orifices, damaged mechanical seals, plugged discharged ports, journal-bearing wear (disrupted hydrodynamic film production), premature plugging of oil filters and impaired oil cooler performance. [2]

In turbine applications where reliability is demanded and operating conditions are stressful, there is a need for incipient advisories that report developing varnish potential. Such risk-prone machines are especially pronounced in high-pressure, servo-controlled hydraulic systems operating in continuous and high-duty service. Factors that compound the risk of valve stiction in hydraulic systems include the following:

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

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

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

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

Formation of Sludge and Varnish

Sludge and varnish are insoluble materials typically formed as a result of either deterioration reactions in oil or contamination of oil, or both. Varnish is typically distinguished as a thin, insoluble, nonwipeable film deposit whereas sludge is soft and tacky and can move about the system. A simplistic illustration of varnish formation is shown in Figure 3.

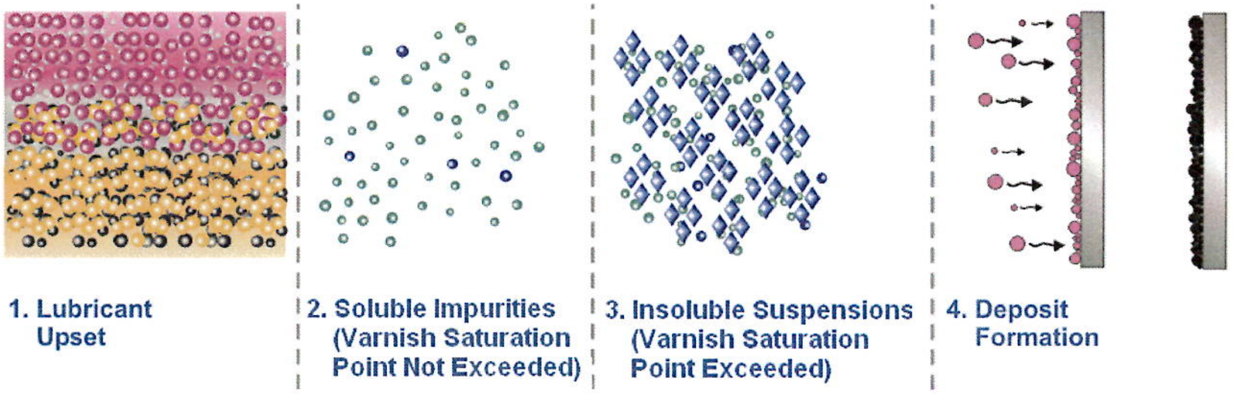

Figure 3 – Varnish Formation Stages

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

Degradation Methods and Analysis

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

Bulk Oil Oxidation

Oxidation causes degradation of the bulk oil over time. Under mild machine operating conditions and clean environment, oxidation will occur gradually. However, elevated temperature plays a significant role in accelerating the oxidation process – the general rule of thumb is that for every 10°C (18°F) increase in operating temperature, the rate of oxidation doubles (Arrhenius Rate Rule). Water, metals such as iron or copper particles and aeration also act as catalysts to speed up this process.

As the rate of oxidation increases, oxidation by-products develop and coalesce into insolubles in the oil (as previously discussed), resulting in sludge and varnish in the system. Oil that degrades through oxidative pathways typically produces metal carboxylates, carboxylic acids and similar oxide transformation products. Depending on the nature of the oxidation process and the formulation of the oil, the tendency and severity of sludge production can vary. The base oil type and the refining process influence this as well. For instance, naphthenic base oils, normally high in aromatic compounds, tend to more quickly form hydroperoxides, which are sludge precursors.

Thermal and Compressive Base Oil Degradation

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

Regardless of the means of entrainment, the forcing function that leads to sludge and varnish is in place. From here, the failure can proceed along one of two pathways. Both involve adiabatic compression in either the load zone of a lubrication system or the pressured zone of a hydraulic control system. Adiabatic compression is what occurs when air bubbles travel from low pressure to high pressure. The air bubble compresses rapidly (implosion), resulting in intense entrapment of the heat and extreme rise in temperature locally in the oil. The temperatures reached (typically greater than 1,000°F) are often more than sufficient to thermally degrade the oil.

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

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

Electrostatic Discharge

Studies have been conducted on the effects of static discharge in hydraulic systems since at least the 1970s.[6, 7] Static discharge is a form of localized thermal degradation as discussed earlier. Recently, much attention has been directed to the potential role of fluid electrification and static discharge as a prominent contributor to sludge and varnish formation in turbine systems.[8, 9, 10, 11]

Electrostatic charge generation occurs in fluids systems as a result of internal molecular friction and electric potential between the fluid and machine surfaces (particularly where no boundary films develop, such as the interstices of an oil filter). The magnitude of the static charge within the oil will depend on many factors, however grounding of the machine itself has little impact toward mitigating charge propagation. This is because the oil is nonconductive and effectively self-insulates the charged fluid zones from grounded surfaces. Once these charges build up in the working fluid zones, including reservoirs, the subsequent static discharging, similar to lightning strikes through the fluid, may cause localized thermal-oxidative oil degradation. The most obvious noticeable effect may be an audible noise (clicking sound) as the discharge occurs by spark-arcing internally within the system. Less noticeable effects include migration of the electrical charge downstream (streaming currents) of the filter, causing damage to system components and the filter itself when the charge suddenly dissipates to nearby grounded surfaces.

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

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

Table 1 – Acid Number (AN) for Turbine Oil Exposed to Static Charges After Zero, Six and Nine Months in Storage

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

1. Higher Combustion Temperatures – In response to higher combustion temperatures, flow rates in the lubrication and control system have increased proportionally. The increased flow translates to higher molecular frictional energy and corresponding electrification of the oil (charge accumulation).

2. Low Oil Conductivity – Turbines oils have exceptionally low polar constituents in their additive system and base oil(s) compared to nearly all other types of lubricants.

3. Low Moisture Levels (<100 ppm) – Moisture contamination is polar and conductive. The hot environment of gas turbine lubricants drives off both free and soluble water which keeps the oil's dielectric constant low (higher risk for static discharge).

4. Low Level of Entrained Air – New Group II turbine oils have excellent air release and foam suppression features. Such air handling performance is generally good for quality lubrication, except where static discharge is concerned. In other words, the lower the aeration, the higher the risk.

5. Cleanliness – Turbine oils are increasingly being filtered to achieve higher magnitudes of fluid cleanliness. This purification of the oil is good from the standpoint of wear reduction and fluid health, except where static discharge risks occur. Particle contamination is generally conductive and contributes to the bulk conductivity of the oil (lower risk of static discharge). According to one study, particle contamination equivalent to an ISO 18/15 was sufficient to dissipate static charge buildup in contrast to low contaminant levels of ISO 13/10 or cleaner, which led to strong discharges.[11] Compounding the problem is the fact that fine filtration intensifies the internal molecular friction that generates the static charge within the oil, that is, the finer the filter pore size, the more pronounced the problem.

Sparking Locations – discharging is more likely to occur in high-pressure differential zones (such as in filter elements) and at sharp edges of pipe submerged in oil in the reservoir.

Analysis Techniques for Monitoring Sludge and Varnish

Analytical techniques for measuring sludge and varnish vary depending on the failure mechanism. These methods fall into three categories, according the stage of contaminant or degradation product they target. The first stage is a precursor condition. Specifically, it relates to the properties (contaminants) that give an oil a propensity to form oxides and other oil breakdown products. Stage two is a transitory stage. Typically, it consists of soluble oxides and other dissolved impurities that might later synthesize to form insolubles. The condition that aids the transition from stage two (oxide soluble) to stage three (oxide insoluble) may be cold oil temperature or simply a supersaturated state (a concentration of oxides in excess of the varnish saturation point).

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

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

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage) – *Root causes that propel the fluid into the next stage*	Measurable Oxidation Root Causes: 1. Particle contamination 2. Wear debris 3. Water contamination 4. Antioxidant additive depletion	1. Various laboratory particle counting methods (optical, pore blockage and microscopic) 2. Elemental analysis, ferrography, ferrous density analysis 3. Various laboratory methods including Karl Fischer and FTIR 4. Methods include FTIR, RPVOT, RULER, and HPDSC
Stage Two (transitory stage) – *The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* oxidation products to form: 1. Carboxylic acids, formic acids, etc. 2. High-density resins, polymers, etc. 3. Chromophoric compounds (color bodies)	1. FTIR (1730 cm^{-1}), AN 2. Coagulated oxide insolubles 3. Spectrophotometry, patch colorimetry
Stage Three (attack stage) – *More advanced oxidation phase where significant risk of varnish, corrosion and impaired lubrication is present*	The presence of both *soluble* and *insoluble* oxidation products to form: 1. Metal carboxylate soaps and sludge 2. Suspended oxide insolubles 3. Rising oil viscosity	1. Analysis of sludge (bottom sediment, organic filter sediment, etc.) by elemental analysis, FTIR (1,730 cm^{-1}), GC/MS 2. Ultracentrifuge, patch test, patch colorimetry 3. Viscometry

Table 2 – Methods for Analyzing Oxidation-induced Sludge and Varnish

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage) - *Root causes that propel the fluid into the next stage*	Measurable Root Causes: 1. Impaired air-release properties 2. Cross contamination (mixed lubricants) 3. Contamination with polar impurities (dirt, water, oxides, etc.)	1. Air release tests, (ASTM D3427) 2. FTIR, elemental analysis, etc. 3. Various standard lab tests for such impurities
Stage Two (transitory stage) - *The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* thermal degradation products: 1. Nitric oxides 2. Chromophoric compounds (color bodies) 3. Localized thermal failure conditions	1. Thick-cell (500 μm) FTIR for nitration (1,639 cm^{-1}) 2. Spectrophotometry, patch colorimetry 3. Pattern testing (combining above tests with RPVOT, AN, viscosity, etc.) to differentiate from bulk oil degradation
Stage Three (attack stage) - *More advanced degradation phase where significant risk of varnish is present*	The presence of both *soluble* and *insoluble* thermal degradation products to form: 1. Suspended high molecular-weight nitric oxides and similar resinous insoluble compounds 2. Sludge and deposits	1. Ultracentrifuge, patch test colorimetry, coagulated insolubles 2. Analysis of sludge (bottom sediment, organic filter sediment, etc.) by elemental analysis, FTIR, GC/MS

Table 3 – Methods for Analyzing Thermal Degradation-induced Sludge and Varnish

Stages of Failure	Conditions of the Fluid to be Tested	Corresponding Analytical Method
Stage One (precursor stage) - *Root causes that propel the fluid into the next stage*	Root causes: 1. Exceedingly dry oil 2. Exceedingly clean oil 3. Unoxidized oil 4. Drop in oil conductivity	1. Karl Fischer, dew point meters 2. Particle counters (various), total insolubles 3. AN, RPVOT, FTIR (1,730 cm^{-1}) 4. Conductivity meters, dielectric breakdown testers, dielectric constant meters, etc.
Stage Two (transitory stage) - *The beginning of base oil degradation and increasing risk of varnishing formation*	The presence of *soluble* thermal degradation products: 1. Chromophoric compounds (color bodies) 2. Localized thermal failure conditions	1. Spectrophotometry, patch colorimetry 2. Pattern testing (combining above tests with RPVOT, AN, Viscosity, etc.) to differentiate from bulk oil degradation[*]
Stage Three (attack stage) - *More advanced degradation phase where significant risk of varnish is present*	The presence of *soluble* and *insoluble* thermal degradation products: 1. Suspended high molecular-weight similar resinous insoluble compounds 2. Sludge and deposits 3. Gas evolution	1. Coagulated total insolubles 2. Analysis of sludge (bottom sediment, filter sediment, etc.) by elemental analysis, FTIR (1,730 cm^{-1}), GC/MS 3. Flash point, gas chromatography for acetylene and other gases[*]

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

Table 4 – Methods for analyzing Static Discharge-induced Sludge and Varnish

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

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy – As oxidation increases, common reaction by-products are carbon-oxygen double bonds, also called the carbonyl group. Carbonyl peaks on FTIR spectra in the 1,740 cm^{-1} region (Figure 4)[4], easily identifying oxidation. As oxidation increases, the absorbance peaks will also increase in this region. Additionally, phenol inhibitors used as antioxidants in the oil show peaks around 3,650. [12, 13] Changes in this peak are also noteworthy.

Because thermal degradation can occur without significant amounts of oxygen, different degradation by-products are often observed. So the 1,740 cm^{-1} peak is less likely to be significant. Instead, the by-products of thermal base oil degradation show up in the 1,600 to 1,640 cm^{-1} region – also known at the nitration peak due to the nitrogenous by-products [4]. This is more pronounced using a thick cell (500 µm path length) spectrometer.

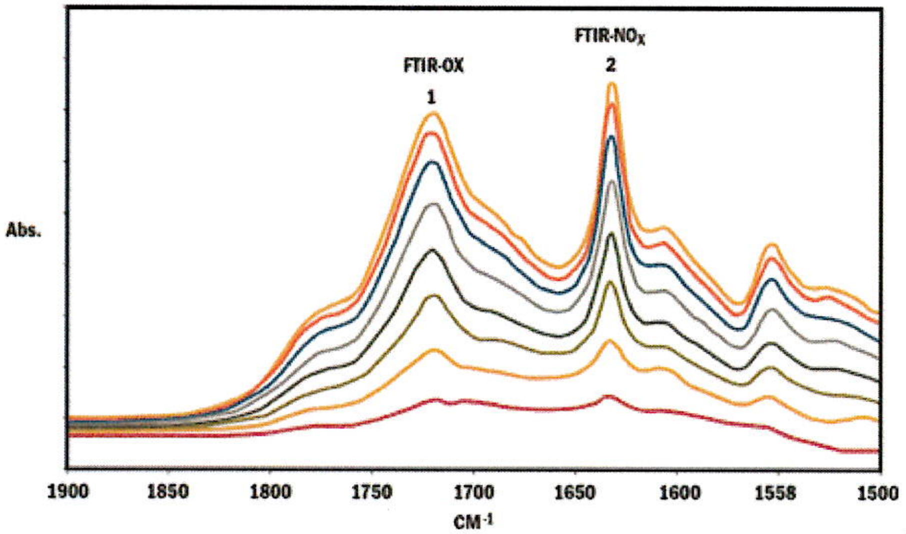

Figure 4 – FTIR Example Spectrum Showing Oxidation Peak Around 1,740 cm^{-1} Range

Acid Number (ASTM D974 or D664)

As the number of acids increase due to the oxidation process, acid number will increase accordingly. In large turbine systems, an acid number change as low as 0.3 to 0.4 above the new oil baseline is often sufficient to condemn an oil.[5]

Rotating Pressure Vessel Oxidation Test (ASTM D2272)

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

Viscosity (ASTM D445)

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

Flash Point (ASTM D92)

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

Gas Chromatography (GC)

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

Patch Colorimetric Test

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

Recent Changes in Oil Formulations in Turbine Applications

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

When impurities form in the oil, regardless of the root cause, the ability of the base oil to keep these compounds in soluble suspension will directly affect the likelihood and rate of varnish formation. Because of the highly pure nature of the Group II base oils, they present greater risk of varnish formation once degradation has occurred because they have a more limited ability to solubilize polar impurities such as water, oxides, carbon resins, dirt and similar contaminants.

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

Conclusion

A number of theories on the degradation methods have been discussed in this paper. A serious and frequently occurring cause is static discharge in turbine oil systems. Further aggravating the problem is the poor solubility of Group II mineral oils compared to Group I oils. In order to differentiate between the failure mechanisms and assess varnish potential severity, turbine owners should consider a variety of tests to monitor the oxidative or chemical degradation of their turbine oils, such as the following:

- FTIR
- RPVOT
- RULER (cyclic voltametry)
- Patch colorimetry
- Ultracentrifuge
- Coagulated insolubles
- Acid number

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