The Root Cause of Varnish Formation

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INTRODUCTION

It has long been established that thermal stressing of lubricating oil results in its oxidation. It is also known that the byproducts of oil oxidation lead to the formation of varnish in hydraulic control and lubricating oil systems. Dr. Akira Sasaki, former Managing Director, Kleentek Corporation, conducted a groundbreaking study on the root causes of varnish formation in gas turbine oil. Specifically, his study examined the hydraulic control and lubricating oil filters of a gas turbine to determine what role they played in the formation of varnish, and the reasons for spark discharges that result from static charge buildup within the system. The research included the examination of a GE Frame 9FA gas turbine that was experiencing severe varnish effects. Although the subject of review involved a gas turbine, the conclusions do have relevance to both gas and steam turbine systems, as well as hydraulic control and lubricating systems in general.

GAS TURBINE APPLICATIONS – THE MOST SEVERE CASE

The severity of the operating environment for gas turbine oil has significantly increased through the years as turbine developments to improve efficiency and minimize capital cost have led to elevated firing temperatures (hence higher operating oil temperatures) and the use of a common oil reservoir, often combining the turbine's bearing oil with the control oil. In some cases, this single oil reservoir may also supply the sealant for compressed gases (such as hydrogen) and provide hydrostatic lift oil while the turbine is on turning gear. These severe operating conditions - particularly the high cyclic nature of operation and very high temperatures — cause varnish generation. Although steam turbines and other hydraulic applications may have less severe operating conditions, the formation of varnish is still a problem.

TURBINE PROBLEMS CAUSED BY VARNISH



Figure 1 – Varnish on a bearing (left). Stuck valve due to varnish (top). Varnished pencil filter (bottom).

After oxidation of the oil and the evolution of "free radicals" into a combined form that constitutes varnish, these sticky deposits adhere to the metal surfaces of the oil loop — piping, valves, heat exchangers, strainers, filters, and other sensitive equipment. In turn, this growing film catches other fine particulates on the sticky surface, which continues to build up around the particulates, forming an abrasive, destructive surface. Research has also shown that deposits of polymerized oil oxidation products play a role in the deterioration of gaskets and mechanical seals. Other potential problems caused by varnish in turbine systems include:

- Restriction and sticking of moving mechanical parts, such as servo or directional valves.
- Increased component wear due to varnish's propensity to attract dirt and solid particle contaminants.
- Loss of heat transfer in heat exchangers, increased friction, heat and energy due to varnish's thermal insulation effect.



- Auto-catalytic deterioration of the lubricant.
- Plugging of small oil flow orifices and oil strainers.
- Reduction in filter efficiency and potential filter plugging.
- Journal-bearing failure.
- Increased maintenance costs due to cleanup and discard of oil.

MAIN ROOT CAUSE OF VARNISH: HEAT

No matter how robust the oil additive package for oxidative and thermal stability, there is always a point where the varnish contamination level in the oil exceeds the capability of the inhibitors. Higher operating temperature or increased levels of harmful catalysts (e.g., water and wear metals), accelerate the oxidation of the oil and severely challenge the effectiveness and durability of antioxidant additive packages.

It is observed that for every 10°C (18°F) increase in operating oil temperature, the rate of oil oxidation doubles (Arrhenius rate rule). However, oxidation of oil, and hence the formation of varnish, is not slowed as much as expected when the oil temperature is kept below 60°C (140°F). Reason: Other causes of intense heat, beyond the heat generated within the turbine bearings, exist within the oil circuit. One cause of hot spots in the oil is "micro-dieseling" the implosion of entrained air bubbles when the oil passes through a high-pressure pump in the hydraulic circuit — that creates a local oil temperature in excess of 1000°C (over 1800°F), more than hot enough to cause oxidation of oil molecules.

Another cause of hot spots is the generation of spark discharges. The power generation industry's shift to synthetic and glass filter media has created unexpected side effects due to the combination of tighter filter pore sizes to remove fine sediment with very high filter flux rates (flow rate per unit area) to reduce capital cost. The result is significant static charge buildup within the oil system.



Figure 2 – Spark discharge within an oil reservoir.

These spontaneous discharges (lasting nano seconds) can generate sparks with temperatures greater than 10,000°C (over 18,000°F) — which is hotter than the surface of the sun. This intense heat caused by static discharges literally "cooks" the oil, creating oil molecule fragments that deplete antioxidant additives. A video of the filter spark discharge test conducted by Dr. Sasaki can be found at www.kleentek.com/video.asp.

Although filter manufacturers are conducting research to mitigate the static charge effect of synthetic and glass media, additional research has shown that places in the oil circuit where there is metal-on-metal contact can also generate a significant static charge that leads to spark discharges.

Even gas turbines that drive peaking units having very low operating hours are still vulnerable to oil oxidation and varnish formation. Experience with gas turbines shows that the practice of rolling the turbines with the turning gear two to four hours each week minimizes rotor bowing and keeping the lube oil circulating at all times maintains high reliability and availability. But with those benefits comes the undesirable side effect of furthering lube oil oxidation and varnishing.

SPARK DISCHARGE IN OIL FILTERS

Dr. Sasaki looked at the voltage potential generated by oil flow through various common filter medias used in turbine oil filtration — the most prevalent being a tight-pore glass media composite.



The electrically isolated test assembly configured to see if a charge is produced within the filter when grounded and un-grounded is shown in *Figure 3*.



Figure 3 – Filter spark discharge test assembly.

The hose on the right of the small tank supplies oil to the pump (seen in the background), which then delivers oil to a filter cell assembly (inlet marked by the flow transmitter mounted on a tee at the inlet to the filter). The outlet of the filter cell is directed through a hose back to the tank, closing the oil flow circuit. The wire leading from the left side of the filter cell is connected to one side of a gap electrode assembly while a ground wire leading from the other electrode in the glass beaker heads off to the right of the assembly. The glass beaker is filled with ISO VG32 oil and the "stick" extending out of the small tank is a thermometer for monitoring the oil temperature. The gap between the electrodes that are immersed in the beaker of oil



Figure 4 - Measured oil potentials.

measures 1mm. The complete assembly is mounted on a poly-tetrafluoro-ethylene base with vinyl hoses to electrically isolate the system, so any charge produced within the filter cell could be measured at the outside wall of the filter cell.

The two most startling observations from this experiment (*Figure 4*) are that the oil filter generates a greater voltage potential when it is grounded than when electrically isolated and that the generation of these high voltages, and resultant spark discharges, can occur quite quickly and frequently. Dr. Sasaki consistently found voltage potentials exceeding 10 kilovolts and that the magnitude of the voltage potential caused by static charge buildup is directly related to the flux rate through the filter media. A high flux rate creates very high voltages resulting in more powerful and frequent spark discharges while a low flux rate yields lower voltages.

In his analysis of the hydraulic and lubricating oil filters on a GE 9FA large frame gas turbine, Dr. Sasaki observed that the oil flow through these two circuits is decidedly different in two key process parameters:

- The oil flux rate (flow per unit filter area) through the lubricating oil filter is dramatically higher than in the hydraulic control oil filter.
- The oil flow through the lubricating oil filter protecting the turbine bearings is continuous while the oil flow through the hydraulic control oil filter is very infrequent (occurring only when a control device is adjusted), leading to cooler oil in the hydraulic lines.

The significance of these disparate conditions is that the high flux lubricating oil filter contributes by frequent spark discharges to the creation of oxidized oil byproducts that form varnish and the hydraulic filter system provides the cooler, more sedate environment where these varnish molecules can combine and become a substantial fouling problem for the critical hydraulic control devices.



The results of the study clearly show that spark discharges in oil do cause oxidation of the oil and that the magnitude of this oxidation is affected by the frequency of spark discharges.

Dr. Sasaki's research also involved studying oil that is subjected to varying frequencies of spark discharges followed by isolation from light at room temperature over a period of months. His findings reveal that there is an auto-catalytic process that continues the oxidation of the oil (and hence varnish formation), even when the conditions that directly cause oxidation (such as heat and oil wear) are removed. (*Table 1*)

TABLE 1 – TURBINE OIL ACID NUMBER, MG KOH/G							
Number of Spark Discharges	0	500	2000	3000			
AN – Just after Spark Discharges	0.08	0.08	0.08	0.08			
AN – After 6 Months	0.08	0.09	0.36	0.59			
AN – After 9 Months	0.08		0.40	0.74			

The results of this test work shows that spark discharges in oil do cause oxidation of the oil, that the magnitude of this oxidation is affected by the frequency of spark discharges, and that there is an auto-catalytic process that continues the oxidation of oil (and hence varnish formation) even when the conditions that cause oxidation (such as heat) are removed.

PROCESS OF AUTO-CATALYTIC OIL OXIDATION

Regardless of the cause of the start of oil oxidation (high operating temperatures or spark discharge), once sufficient oil molecules have broken down into free radicals and wear metal ions, such as iron and copper, are present, a self-perpetuating reaction that continues the degradation of oil molecules may start. The impact of this chain reaction depends on the degree to which the anti-oxidant (AO) additives have been consumed. Left unchecked, this auto-catalytic oxidation process will accelerate and ultimately overpower the AO additives. The sequence of reactions that form an auto-catalytic process is shown below.

Lubricant Auto-Catalytic Oxidation Process:

Let Metal (Iron and Copper) catalyzed chain initiation

Dissolved oxygen reacts with oil molecules, creating free radicals R• and HOO•

$\circ RH + O_2 \twoheadrightarrow R \bullet + HOO \bullet$	(1)
\circ 2RH + O ₂ → 2R• + H ₂ O ₂	(2)

Iron ion is both oxidized in #3 and reduced in #4 for a net balance

• Fe^{3+} + ROOH → Fe^{2+} + ROO • +H⁺ (3)

• Fe^{2+} + ROOH → Fe^{3+} + RO• +HO⁻ (4)

Copper ion is both reduced in #5 and oxidized in #6 for a net balance

 $\circ \operatorname{Cu}^{2+} + \operatorname{ROOH} \rightarrow \operatorname{Cu}^{+} + \operatorname{ROO} \bullet + \operatorname{H}^{+}$ (5)

 $\circ \operatorname{Cu}^{+} + \operatorname{ROOH} \rightarrow \operatorname{Cu}^{2+} + \operatorname{RO} \bullet + \operatorname{HO}^{-}$ (6)

 $\hfill\square$ Chain propagation and branching

Free radicals R• of #8 reaction feeds #7 reaction

 $\circ \mathsf{R} \bullet + \mathsf{O}_2 \to \mathsf{ROO} \bullet \tag{7}$ $\circ \mathsf{ROO} \bullet + \mathsf{RH} \to \mathsf{ROOH} + \mathsf{R} \bullet \tag{8}$

ROOH breaks down into two radicals

ROOH → RO• + HO•	(9)
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The two products of reaction #9 react with oil molecules to create new free radicals R• that feed reaction #7 above along with alcohols (ROH) and water

 $\circ \text{ RO} \bullet + \text{ RH} \to \text{ ROH} + \text{ R} \bullet$ (10) $\circ \text{ HO} \bullet + \text{ RH} \to \text{ H}_2\text{ O} + \text{ R} \bullet$ (11)

What then follows are:

- \circ Formation of aldehydes and ketones \rightarrow Volatiles result
- Condensation reactions → Higher molecular weight polymers are produced
- Sludge and deposit formation → Insolubles and varnish formed



TABLE 2 -	EFFECTS OF MET	AL CATALYSTS A	ND WATER ON O	IL OXIDATION		
Sample #	Catalysts	Water	Time (h)	TAN		
1	Nil	Nil	3500	0.17		
2	Nil	Exist	3500	0.90		
3	Fe	Nil	3500	0.65		
4	Fe	Exist	400	8.10		
5	Cu	Nil	3000	0.89		
6	Cu	Exist	100	11.20		
Reference: Tribology Series - "Practical Performance of Lubricants," Saiwai Publisher						

Table 2 demonstrates the relationship between the presence of metal catalysts and water versus oil oxidation as measured by the total acid number (TAN).

Note that the oil samples shown in *Table 1* after spark discharges and left for months in a controlled environment did not have free or emulsified water present or significant levels of wear metals (it was new oil), yet the TAN value increased for the 3000 spark discharge/9-month sample. If you combine the harmful effects shown by Dr. Sasaki that occur from spark discharges in oil filters and oil circulation systems with the addition of a continuing supply of wear metals and water, the rate of oil oxidation in lubrication and hydraulic systems can be very challenging for antioxidant additives.

INEFFECTIVENESS OF CURRENT OIL ANALYSIS TESTS

Most oil analysis tests (such as the Rotating Pressure Vessel Oxidation Test, RPVOT) do not reliably indicate the true varnish forming potential of an oil sample, and often cannot detect this condition unless the oil already has a high enough varnish level to be detected, thus serving only as a confirmation of the existence of formed varnish. Research has shown that the application of traditional oil test methods as an early warning for the onset of oil varnish is either ineffective or provides limited information. Tests such as Fourier Transform

Infra-Red (FTIR) can detect the oil oxidation byproducts that are precursors for varnish formation as a "present" or "not present" finding, but do not quantify the condition, which would provide an expression of the degree of vulnerability. The continuing development of colorimetric methods appear to provide a relatively inexpensive means for both early detection of varnish issues and a way of quantifying the condition across time to chart the system trend. This method (for example. the Quantitative Spectrophotometric Analysis, or QSA test offered by Analysts, Inc.) provides a rating number that can be compared to a relative scale to determine the degree of vulnerability to the varnish problem and help to evaluate equipment and methods that seek to reduce varnish.

PREVENTING, SOLVING & REVERSING THE VARNISH PROBLEM ELECTROSTATICALLY

Conventional oil cleaning methods include strainers, centrifuges, vacuum dehydrators, and mechanical media filtration. These methods are effective in removing water and hard contaminants, along with some larger soft contaminants. But removing varnish and the byproducts of oil oxidation that lead to the formation of varnish require the removal of the insoluble sub-micron size soft oxidation products. The best method demonstrated to be effective in accomplishing this is continuous electrostatic oil cleaning, which addresses contamination well beyond conventional means.





Figure 5 – Electrostatic collection process.



Figure 6 – Varnished servo valve before and after 45-days of electrostatic cleaning.

Operation of an electrostatic oil cleaning system on the oil leads to a lower concentration of oxidized oil byproducts, which in turn dissolves the formed varnish on the surfaces of the oil circuit as the oil tries to reestablish the equilibrium relationship between formed varnish and its precursor, the oxidized oil byproducts. As the electrostatic oil conditioner continues to remove the oxidized oil byproducts, the natural response of the fluid system to maintain the equilibrium continues to dissolve formed varnish until it is no longer present.

The mechanism by which an electrostatic oil conditioner removes naturally charged contamination, such as sub-micron sized oxidized oil by products, is shown in *Figure 5*. Varnish that has formed (the soft, sticky contaminate) is by its nature polar (e.g., zero net charge, but having charge distribution within the particle that creates positive and negative charged poles), but is still removed by the system by a process called di-electrophoresis. A more detailed description of this process is provided in the "How It Works" section at www.Kleentek.com. *Figure 6* shows a varnished servo valve before and after 45 days of continuous electrostatic cleaning, demonstrating that formed varnish dissolves and is removed by the system when there is continual removal of the oxidized oil byproducts.

Continuous, on-line electrostatic oil cleaners offer the best means of preventing varnish from interfering with the reliable operation of your equipment.

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