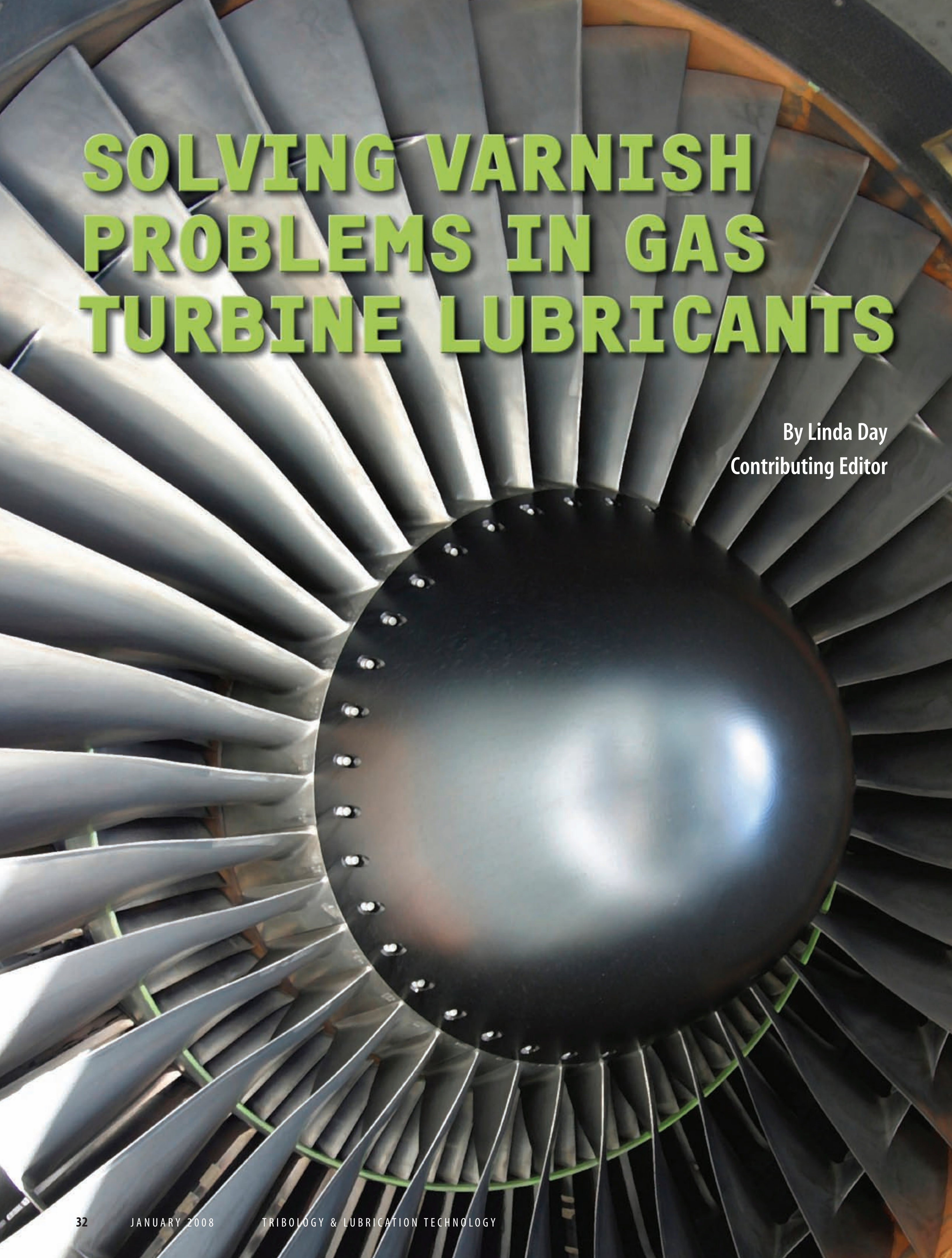

SOLVING VARNISH PROBLEMS IN GAS TURBINE LUBRICANTS

By Linda Day
Contributing Editor

If you've been plagued by the sludge and varnish issues raised by new base oils, take heart.

Editor's Note: *This subject of this month's feature article was conceived by STLE's Power Generation Industry Council.*

Oxidation and varnish have been recognized as problems since the Civil War, but only in the last few years has the problem reached epidemic proportions in power generation and other gas-turbine applications.

"The new turbines that have come on-line in the last five years are designed to put out more energy from smaller equipment," says Dave Wooton of Wooton Consulting, "and that means more stress on the unit and the lubricant." But increasing stress is not the only contributor to the problem. In the same time frame, turbine users have switched their turbines from base-load to peaking and from Group I base oils to Groups II and III.

"A lot of people blame the new base oils for the problems," says Wooton, "but I'm not one of them. I do believe the new formulations were put together improperly when these oils first came out, because lubricant manufacturers weren't accounting for the different chemistry of the base-stocks. But there are many other problems as well."

Regardless of source, Wooton notes that a little varnish can cause a big headache: "If a valve sticks just a little, the computer controlling the unit shuts it down, and the trip-out cost can be $30,000-$100,000 or more." (*see Figure 1*)

Article highlights:

- *Investigating the causes of varnish.*
- *A closer analysis into oxidation and formulation issues.*
- *Probing the effects of lightning.*

Figure 1. A valve stuck with lubricant varnish.

Causes of varnish

The problematic nature of Group II oils is aptly expressed by the "Chinese Curse:" *May you live in interesting times*. These oils can be more resistant to varnish or more prone. Group I oils typically have much higher concentration of aromatics (typically in excess of 10%), which tend to oxidize quickly. Because of their purity, Group II oils are inherently much more stable, but without aromatics they are also much poorer solvents. And that means that oxidation byproducts that do form tend to drop out of solution and form varnish more easily. The situation is further complicated by the fact that most power generation gas turbines nowadays are peaking units that allow plenty of time for varnish to form in cool oil when the unit isn't running.

Chevron introduced the technology to make modern Group II oils, and STLE member Dr. Mark Okazaki, the Chevron senior staff scientist who formulated the company's turbine oils, is well aware of the problems: "We had a chance to use Group II oils before everyone else, and so we found out what some of the issues are," Okazaki says. "First off, certain Group I additives don't work well with Group II base oils because of the lower solvency. You have to take a new approach."

And even the best additive systems available today can't always prevent the problem. Okazaki and others point to oxidation and static discharge as the two main causes of sludge and varnish, along with several other potential root causes:

- **Micro-dieseling.** It's possible for small entrained air bubbles in the oil to get compressed and heated enough to explode and burn the oil.

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- **Incompatible oils and additives.** In some cases, changing to a Group II oil without testing the compatibility with the previously used Group I oil can cause decomposed and/or fresh additives left over from Group I to drop out or react in unexpected ways with the Group II additives.
- **Contamination with chemicals.** The preservative fluids used to protect new equipment from corrosion may not be compatible with the turbine oil—turbine oils are typically ashless (no metals), and the metals in some preservative and flushing fluids (typically calcium) can react with the acidic components of the turbine oils to form an insoluble soap.
- **Contamination with cleaning fluids.** This is a special problem in the paper industry, where machinery may be sprayed with lye to clean it.

A closer look at oxidation and formulation

"Varnish is the hot issue in gas turbines," says STLE member Greg Livingstone, director of fluid technology for EPT, Inc., (Environmental Power Technologies) in Calgary, Alberta, Canada, a company that markets filtration equipment to remove varnish-forming components. "It's easy to predict oxidation in Group I formulations because it proceeds in a predictable, gradual and linear fashion, and you have proven tests to monitor it. But Group II formulations go along fine with no signs of breakdown until suddenly you're in total failure mode." (*see Figure* 2)

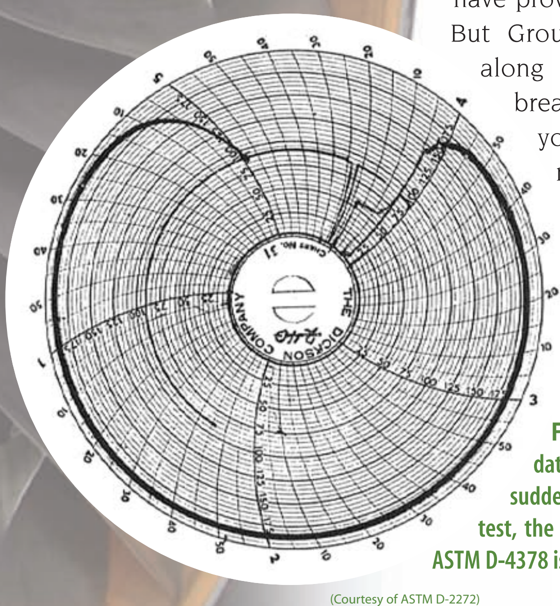
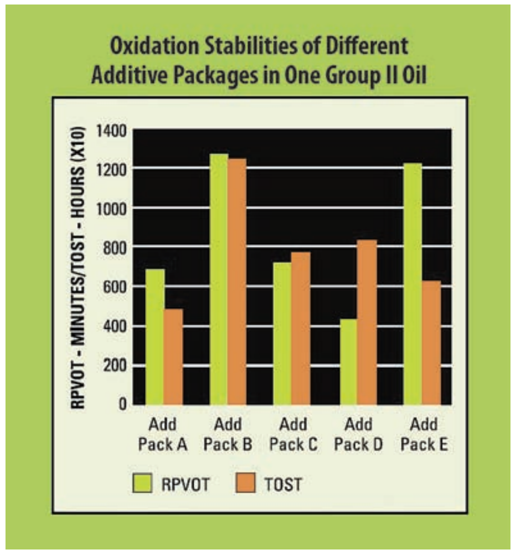


Figure 2. An RPVOT chart of oxidation in a Group II oil shows how suddenly degradation occurs. In this test, the RPVOT residual ratio limit by ASTM D-4378 is 25%.

(Courtesy of ASTM D-2272)



(Courtesy of *Lubricants Magazine*, September 2005, available at **www.lubricantsuniversity.com**)

Figure 3. Oxidation stabilities of different additive packages in one Group II oil. In order to have RPVOT and TOST results on the same scale, the TOST result must be multiplied by 10. For example, the real result (TOST) for additive package A is about 5,000 hours, not 500. Note that RPVOT and TOST may yield dramatically different results.

The two main types of antioxidant additives are phenols, good for temperatures up to about 130 C, and amines for temperatures above that. If phenols get too hot, they polymerize and turn into sludge themselves. Amines also have a tendency to polymerize and turn into varnish when they themselves oxidize.

The excellent high-temperature performance of amines can sometimes be misleading: Many accelerated tests for oxidation stability are run at high temperatures where amines perform well, but this may not reflect actual performance in the real world. Phenyl alpha naphthyl amine, or PANA, is a good example. "A significant amount of PANA gives the oil an extremely high RPVOT value (ASTM D2272, a measurement of the oil's resistance to oxidation)," Livingstone says, "but when it depletes, it can form *tons* of varnish and sludge—it actually catalyzes the reaction. The OEMs don't restrict the heavy use of this additive, and many of the oil companies use it because even though it increases varnish potential, it gives great oxidation stability (*see Figure* 3). It's tough for the end-user to find out about PANA, because the oil companies may not want to reveal their formulations." According to Mark Okazaki, PANA is not necessarily a problem when used in small concentrations and in combination with other antioxidants such as phenolics.

As it turns out, one of the best ways to keep amine additives working is to make sure that phenolic additives are also present. "Phenols will rejuvenate and regenerate the amines and keep them from depleting," says Livingstone. "As soon as the phenols are gone, that's when problems appear to start."

Livingstone strongly recommends monitoring oil condition using the RULER, invented by STLE member Dr. Robert Kauffman with the University of Dayton (Ohio) Research Institute and Fluitec, the company that manufactures and markets the tool.

"The RULER analyzes the types and amounts of antioxidants present, not the quality of the antioxidant" says Kauffman. "But once you can see depletion patterns, you can correlate that with the oxidation patterns of the oil and the varnish tendencies. When you understand the depletion mechanism, you can better understand how to stop the secondary reactions that cause the problems. The tool is useful because it's small and portable, and it's predictive rather than reactive." (*see* Figure 4)

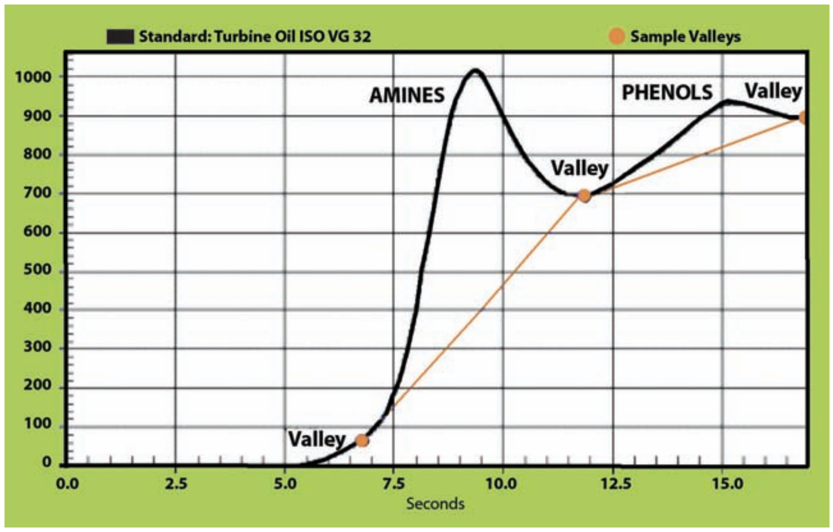
Kauffman differentiates between sludge and varnish, which he says form via different mechanisms. "Some of the amines will polymerize and make sludge, especially if they aren't sterically hindered," he says, "but sludge isn't as bad as varnish because it isn't as sticky—it can plug filters and tight clearances, but it doesn't tend to stick to bearings."

Kauffman believes that varnish is related to the depletion of particular antioxidants. When antioxidants start to lose their capabilities, typical free radical polymerization takes place, but the polymers that used to stay in solution now drop out because of the lower solvency of Group II oils.

"The oil in the turbine really gets beat up," Livingstone says. "Some bearings get hotter than 500 F (260 C), so the oil has all this oxidative stress with extremely high flow rates. Then the same oil can go into a different loop to activate the hydraulic circuits, and this is where the major contaminants precipitate out."

In support of this scenario, Livingstone notes that turbine systems with separate sumps for the turbine section and the hydraulic section suffer far fewer varnish problems than units with a combined sump.

Of course, oxidation degradation is only one problem—there's also lightning.



(Courtesy of Fluitec)

Figure 4. The RULER provides a chart showing the amount of amine and phenolic antioxidants. Comparing a standard with a sample of the current oil provides a measure of the oil's properties. When phenols drop, amine antioxidants can become part of the problem instead of part of the solution.

The trouble with lightning

You can watch lightning in the sky during a thunderstorm—and in some cases you can also watch it in the oil reservoir of a gas turbine. (*see* Figure 5 or you can check out an amazing video at **www.kleentek.com/video.asp**).

It used to be that clicking noises emanating from the housing was thought to indicate air hammering. But when people began pulling out burnt filter elements, it became apparent that something else was going on. STLE fellow Dr. Akira Sasaki of Kleentek in Japan, widely regarded as the guru of this subject, first clarified the damaging nature of static discharge in gas turbine lube oils. His research using GE gas turbines (which have separate filters for the hot turbine section and the cooler hydraulic section) revealed sparking damage and burned oil on the *inside* of turbine filters, and varnish collecting on the *outside* of hydraulic filters. Figure 6 (*see page* 36) shows microphotographs of sparking damage to the nylon filter element, and Figure 7 (*see page* 36) shows off microscopic nylon balls that static discharge creates. Although Sasaki has found localized temperatures up to 20,000 C in the heart of the spark, he explains that the real problem is sparking, which cracks lube oil molecules and creates free radicals that polymerize to varnish. "Once free radicals are produced, auto-oxidation of the oil will not stop unless there are reasonable amounts of oxidation inhibitors present," he says.

Most experts agree that static electricity is

(Courtesy of **www.Kleentek.com/video.asp**)

Figure 5. A look inside the oil reservoir of this turbine reveals a lightning storm of static discharge that causes severe oxidative damage to the lube oil.

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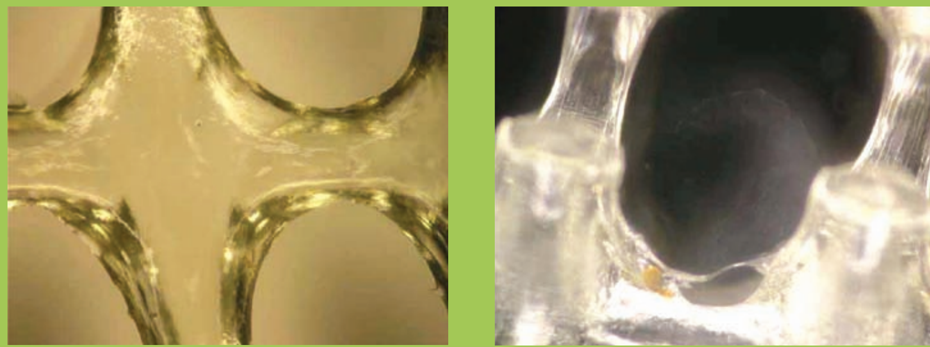

Figure 6. The effect of static discharge in the filter: On the left, a microphotograph of normal nylon filter mesh from a gas turbine, and on the right is the same mesh after damage from static discharge.

(All photos courtesy of Dr. Akira Sasaki, Kleentek)

Figure 7. This microphotograph shows the fine balls of nylon produced by spark discharges of static electricity.

created by the high-speed flow of hot oil through the tiny pores of the filter element. The problem has been exacerbated by more severe operating conditions in the newer turbines and the increasing use of synthetic filter elements that are naturally less conductive than natural fibers such as cellulose. STLE member Dr. John Duchowski, director of technology development for HYDAC Filtertechnik GmbH (now poised to introduce its first charge-reduction filter element) feels that Group II base oils also contribute to the problem in that they do not have the relatively large amounts of heteroatomic species that are present in Group I oils; these species could help carry the charge away. Okazaki, however, feels that operating temperatures are also important: "The high operating temperatures of gas turbine oils drives out residual water that might conduct electricity," he says, "and low conductivity is vastly more important than the base oil used."

In any case, the static charge that builds up in the filter can arc there (causing the damage noted by Sasaki) or float downstream in the oil.

"The charge in a dielectric medium such as turbine lube oil tends to flow like clouds across the sky," says Duchowski. "You don't have lightning over the entire sky, but from cloud to cloud and eventually to ground. If you have a lot of clouds spread over the entire sky, then no one cloud builds up enough charge to cause lightning. So our first approach to the problem is to create a filter element that dissipates the charge evenly across the entire surface

(Courtesy of Dr. John Duchowski and HYDAC)

Figure 8. The "lightning" that occurs on a filter element is localized when it occurs.

(*see Figure* 8).

"But if that's all you do," he continues, "the total amount of charge is still there, and an equal and opposite amount of charge ends up going downstream, where it finds the nearest ground and maybe damages other system components. If the charge doesn't find a ground, it goes back to the reservoir and creates a lightning storm. The best approach is first to eliminate the arcing in the filter, because the damage it causes is very dramatic, and second, to guide the charge out of the entire system right at the filter housing. Matthias Schwender, who's the manager of our filter media development group, has led the effort to develop a new filter element to do that."

The 100% solution

If all of these problems sound daunting, take heart. According to Greg Livingstone, it is possible to prevent all damage from gas turbine lubricant varnish.

"Our philosophy at EPT is holistic," he says. "It's like links in a chain—as soon as you have a weak link, the chain will break and you'll have varnish. If you do just one or two things, that won't work. You have to do it all."

Livingstone's program involves the following:

1. Choose a good oil. According to Livingstone, OEMs have only general specs for turbine oils, and all the lube oils on the market meet the specs. "It's ironic," he says, "varnish is the No. 1 failure mode of turbine oil, one of the highest-profile issues that turbine oils have ever had, yet the OEMs have no good language in their specs for resistance to sludge and varnish. Today's standardized ASTM tests don't really address the problem."

There's hope for standardized tests in the future: Chevron's Mark Okazaki is heading an ASTM group to develop a new varnish test based on the Mitsubishi Heavy Industries' Dry TOST test (a 500-hour test of resistance to varnish formation), and Andrea Wardlow of ExxonMobil is spearheading the effort to develop a cycling test that would measure varnish tendencies in a hot/cold cycling environment.

Meanwhile, it's best to choose an oil based on field experience. "Just because an oil performs well in a lab doesn't mean that it will perform in the actual application," says Okazaki. "I know of one oil that was never field tested, and when the customer used it, the RPVOT dropped 50% within the first year. That should never happen."

According to Akira Sasaki, Japanese oil makers say that their gas turbine lubricants have no varnish problems. For the benefit of gas turbine users in other countries, he wishes these oil makers would publish papers about why this is so.

2. Monitor oil condition. According to Livingstone, regular oil monitoring is essential. In addition to use of the RULER, he also recommends patch tests such as Quantitative Spectrophotometric Analysis, or QSA, developed by Analysts, Inc. QSA is designed to isolate, identify and measure the specific degradation byproducts responsible for the formation of sludge to yield a Varnish Potential Rating (VPR). Because the degradation of Group II formulations oils isn't linear, regular monitoring is essential to catch degradation before it becomes suddenly catastrophic.

3. Minimize sparking. "A lot of the OEMs have duplex filters so that you can change on the fly, but no one ever changes on the fly," says Livingstone. Instead, he recommends that oil be run through both banks of filters, cutting the flow rate in half and greatly reducing static charge. Better yet, invest in charge-reduction filter elements.

4. Maintain the oil. Since the worst varnish problems happen in the hydraulic system when the oil cools, the ideal solution is a turbine with separate oil systems. Failing that, every effort should be made to keep the oil warm when it gets to the hydraulic system, either by adjusting control software to stroke the valves regularly, or by heat-tracing the lines.

Up to a certain point, varnish can be "rejuvenated." Sasaki has tested oils by cleaning them, leaving them at room temperature for 14 days, filtering and noting the color of the filter pad. Fresh oil with sufficient oxidation inhibitors will leave the filter white after 14 days, but if the inhibitors have been depleted, the filter will be yellow to brown. Partially used

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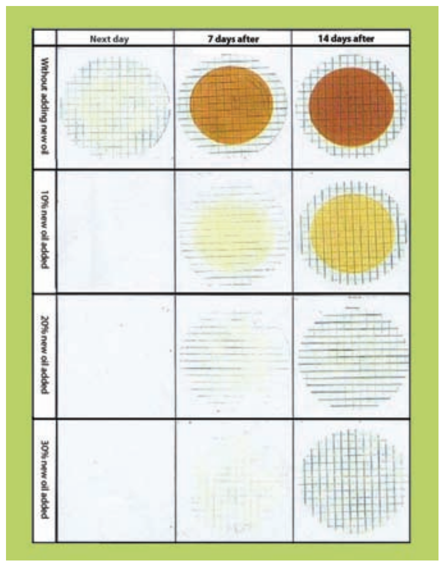

(Courtesy of Dr. Akira Sasaki, Kleentek)

Figure 9. This filter test run by Dr. Akira Sasaki shows results for oil used for 16,200 hours over 7.5 years. The TAN was 0.14 for the new oil and 0.31 for this used oil. The oil was cleaned, then allowed to sit at room temperature. The three columns represent the amount of oxidation after 1, 7 and 14 days. The four rows represent the unadulterated used oil, and the used oil with 10%, 20% and 30% virgin oil added.

For more information:

The following is a list of some useful Web sites and references (*see page* 38) submitted by contributors to this article:

Web sites:

- **www.cleanoil.com** (site for EPT)
- **www.fluitec.com**
- **www.hydac.com**
- **www.kleentek.com**
- **www.lubricantsuniversity.com**, a Chevron site also connecting to *Lubrication Magazine*.
- **www.wooton-consulting.com**

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oil that would normally leave the filter brown can be rejuvenated by the addition of 10% to 30% of the same brand of virgin oil (*see Figure 9 on page* 37). At a point where "the base oil is no longer healthy," rejuvenation doesn't work and the oil must be replaced.

5. Remove contaminants. "We advocate using technology that will remove both soluble and insoluble contaminants," says Livingstone. "It's tricky because when you strip away soluble contaminants, you have to be extremely careful not to take additives with them. EPT uses ion-charged bonding, ICB, to remove soluble contaminants in a narrow band of chemistry.

"Insoluble contaminants can't be removed through normal filtration because they are sub-micron-sized particles," he continues. The way to remove those is through an electrostatic oil cleaner. Both EPT and Kleentek have these. This is the last line of defense to remove contaminants before they settle out and form varnish."

Success. Simply put: "If you go through all five major steps, you will eradicate your varnish problem," says Livingstone. "It will go away."

And you'll be able to return to less interesting times.

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References

1. Yano, A., Watanabe, S., Miyazaki, Y., Tsuchiya, M. and Yamamoto, Y. (2004), "Sludge Formation During the Oxidation Process of Turbine Oils," *Tribology Transactions*, **47** (1), pp. 111-122.

2. Wooton, D.L., "The Lubricant's Nemesis—Oxidation Part I," *Practicing Oil Analysis Magazine*, March-April 2007, p. 26.

3. Wooton, D.L. "The Lubricant's Nemesis—Oxidation Part II," *Practicing Oil Analysis Magazine*, May-June 2007, p. 34.

4. Livingstone, G.J., Prescott, J. and Wooton, D., "Detecting and Solving Lube Oil Varnish Problems," *Power Magazine*, August 2007.

5. Sasaki, A., Uchiyama, S. and Yamamoto, T. (1999), "Generation of Static Electricity During Filtration," *Lubrication Engineering*, **55** (9), p. 14-21.

6. Sasaki, A., Uchiyama, S. and Yamamoto, T. (1999), "Free Radicals and Oil Auto-Oxidation Due to Spark Discharges of Static Electricity," *Lubrication Engineering*, **55** (9), p. 24-27.

7. "Practical Approaches to Controlling Sludge and Varnish in Turbine Oils," William Moehle and Vincent Gatto, Albemarle Corp; Dave Wooton, Wooton Consulting and Greg Livingstone, EPT Inc., NORIA LE2007, Louisville, Ky., May 2007.

8. "Residue Analysis on RPVOT Test Samples for Single and Multiple Antioxidants Chemistry for Turbine Lubricants," Andy Sitton, Focus Laboratories; Jo Ameye, Fluitec and Robert Kauffman, UDRI, ASTM JAI, December 2005, ASTM Turbine Oil Symposium, Norfolk, Va.

9. "Physical, Performance and Chemical Changes in Turbine Oils from Oxidation," Greg J. Livingstone, Brian T. Thompson, and Mark E. Okazaki, *Journal of ASTM International*, December 2005, Joint Oxidation and Turbine Oil Symposium, Norfolk Va.

10. ASTM D-6971–Standard Test Method for Monitoring of Amine and Phenolic Antioxidants in Non-Zinc Containing Turbine Oils by Linear Sweep Voltammetry (RULER).