Approximately one in three large industrial gas turbines (GTs) shows signs of oil varnishing. Because this condition affects the availability and reliability of GTs, the original equipment manufacturer (OEM) recommends the use of varnish removal systems. Despite this, varnish-related turbine outages remain a significant issue for the industry.

The primary reason varnish is an ongoing problem is that strategies aimed at correcting or mitigating varnish-related problems are often misdirected, resulting in less than ideal outcomes. The following is a summary of an article published in Combined Cycle Journal to improve understanding of varnish by discussing its specific cause and how various mitigation alternatives work to minimize operational impacts.

**VARNISH FORMATION**

ASTM D7843-12 defines lubricant varnish as a thin, hard, lustrous, oil-insoluble deposit composed primarily of organic residue. It is most readily defined by color intensity and is not easily removed by wiping.

Varnish begins its life as a soluble/dissolved product before converting to particulate form and depositing on metal surfaces. As such, varnish is a shape-shifter; it can be “insoluble” (particulate – conventionally recognized form) or dissolved (soluble) in the fluid.

An understanding of lubricant solvency is the key to understanding the mechanism by which varnish deposits are formed and, more importantly, the mechanism by which they can be removed.

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LUBRICANT SOLVENCY

Under normal operating conditions, turbine lubricants oxidize producing polar molecules (varnish precursors) from non-polar ones (mineral oil base stocks). These polar precursors represent the starting point of the varnish life cycle. As a result, lubricants in service are a complex combination of base stocks, additives, contaminants and breakdown products.

A lubricant’s solvency is defined as its ability to dissolve these distinct components. Everything in the oil has a finite solubility, which is affected by numerous factors (see next section). This solubility determines if a particular molecule will remain dissolved or if it will precipitate to form a potentially damaging deposit (Fig. 1).

Factors affecting lubricant solvency

The following factors play a role in determining the solubility of varnish precursors in lubricants.

Molecular polarity

Although varnish precursors produced by oxidative oil degradation are polar, they possess a finite solubility in a lubricant’s non-polar mineral oil matrix. Degradation products that are more polar will be correspondingly less soluble. The most basic concept of solvency is that “like dissolves like.”

Contaminant levels

Lubricants have a finite capacity to dissolve other molecules (e.g. additives, contaminants and varnish precursors). As the oil degrades and oxidation products accumulate, the solvency of the fluid decreases accordingly. Beyond a certain point (saturation point), the fluid can no longer dissolve additional varnish precursors and varnish will begin to precipitate as a solid.

Temperature

As temperature decreases, so too does the solubility of varnish and its precursors. This process is responsible for the formation of varnish deposits in cooler regions of a turbine’s lubricant circulation system. Because metals are more polar than the lubricant’s base stock, the precipitated polar varnish prefers to adhere to the metal and form potentially damaging deposits. When the level of varnish precursors in a lubricant is near the fluid’s saturation point, varnishing in cooler regions is very likely to occur.

Fig 1: Varnish is shown here in its deposited form
THE VARNISH CYCLE

The typical varnish formation cycle in a gas turbine involves the following three steps (Fig. 2).

1. Oxidation is a chemical reaction between the lubricant base stock and oxygen in the air. When a new fluid is put in service, it is exposed to higher temperatures and experiences an increase in oxidation rate. Oxidation products build up in the lubricant over time, but remain dissolved at operating temperatures until they exceed the fluid's saturation point.

2. As the oil moves from hotter regions within the system to cooler ones, its temperature falls and the solubility of varnish precursors decreases. These precursors begin to precipitate from solution in the form of particulate. This precipitation of varnish is a physical change and not a chemical reaction.

3. Once formed, varnish particles collect and form deposits, preferentially coating metal surfaces. These deposits are often the cause of unit trips or fail-to-start conditions. Like precipitation in Step 2 above, this process is a physical change.

While the chemical reaction that leads to the formation of varnish precursors (Step 1) is irreversible, the physical changes (Steps 2 and 3) which lead to the formation of varnish deposits are reversible. Therefore, once varnish particles/deposits form, they can be reabsorbed if the solvency of the lubricant is increased. Successful varnish mitigation strategies use this fact to their advantage.

TESTING FOR VARNISH

Due to the potential for costly turbine downtime associated with varnishing, it is critical to test lubricants for varnish potential. Varnish potential testing, also called MPC (membrane patch colorimetry, ASTM 7843, Fig. 3) is recommended by ASTM to be performed quarterly at a minimum. Other collaborative tests, like patch weight, may be helpful in determining oil condition.
It is important to follow the ASTM method, otherwise MPC results may vary significantly depending on the length of time the oil sample was “aged,” or stored. MPC values generally increase during storage or when exposed to ultraviolet (UV) light as oxidation reactions initiated from when the lubricant was in service continue to occur. This highlights the necessity of using varnish removal systems on a continuous basis – oil reservoirs with accumulated break-down products can continue to form varnish when the turbine is not operating.

STRATEGIES TO COMBAT VARNISHING

Most modern turbine lubricants are made with API (American Petroleum Institute) Group II mineral oil base stocks, which contain an antioxidant additive package. The chemistry of Group II base stocks makes them more oxidatively stable than the traditional Group I base stocks (Fig 4).

Antioxidants

Antioxidants are added to the lubricant as a built-in varnish mitigation strategy. These additives commonly comprise two classes of chemicals: phenols and amines. These chemical additives are sacrificial and will oxidize more readily than the oil base stock. Unfortunately, both phenols and amines are consumed as they oxidize. Once the additives are consumed, the rate of fluid degradation accelerates, returning to that of the non-additized base stock (Fig. 4). Antioxidants limit the rate of oxidative degradation and, therefore, delay varnishing, but they cannot prevent it.

When the lubricant inevitably oxidizes and varnish precursors are formed, varnish removal systems are necessary to prevent degradation products from accumulating to the point where varnishing occurs. There are two main types of varnish removal systems: those based on the removal of suspended particles and those based on the removal of soluble varnish and its precursors.

Suspended particle removal systems

Depth filtration, Balanced Charge Agglomeration (BCA™), electrostatic oil cleaning or combinations of these techniques are advanced forms of particulate removal. Since solvency decreases at lower temperatures (favoring the formation of particulates), the maximum benefit using these systems is achieved when the turbine is not operating and the lubricant is at ambient temperatures. Therefore, these systems are of more use when employed periodically, during outages; they are less effective when used continuously during turbine operation. When used during normal turbine operation, these systems are incapable of removing soluble varnish and its precursors.

To overcome this limitation, oil coolers can be used to accelerate the varnish formation cycle and precipitate particulate from the lubricant immediately before it passes through the varnish removal system. However, cool oil is more viscous making it difficult to pass through these filtration systems. The oil cannot be cooled to the temperatures required for complete removal of all soluble varnish. Therefore, lubricant solvency is never improved to the point where existing varnish deposits can be re-dissolved into the fluid.

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**Soluble varnish removal**

Soluble Varnish Removal (SVR™) systems use specialized Ion Charge Bonding (ICB™) ion exchange resins that contain billions of polar sites capable of adsorbing soluble varnish and its precursors (Fig. 5). Conventional ion-exchange resins function by exchanging one chemical for another. Unlike these resins, which essentially exchange one contaminant for another, ICB™ resins are engineered to adsorb the entire contaminant without returning any other to the fluid.

A key benefit of the ICB™ adsorption principle is that harmful oxidation products can be removed at any operating temperature, meaning that SVR™ systems can be used continuously. The continuous removal of soluble varnish ensures that degradation products do not accumulate in the lubricant, eliminating the risk of varnish formation during normal turbine shut down cycles. Moreover, the continuous removal of soluble varnish produces a lubricant with extremely high solvency.

Since the physical changes that resulted in the formation of varnish particles and deposits are reversible, the high solvency of the SVR™-treated lubricant forces varnish already present on turbine surfaces back into the soluble form where it can be adsorbed and removed. With all the remaining oxidation by-products removed, the varnish formation cycle is halted.

**SUMMARY**

Varnish particles and deposits are created from reversible physical changes that begin with soluble oxidation products and end with varnish deposits. For these changes to be reversible, the chemistry of the deposits has to be similar to the chemistry of the lubricant from which the deposits originated. Once fluid solvency has been increased (by removing soluble varnish at normal operating temperature), deposits will simply dissolve back into the fluid and be removed.

**ADDITIONAL RESOURCES**

1. Combined Cycle Journal: Lubricant Varnishing and Mitigation Strategies
2. MPC Varnish Potential Testing White Paper
3. SVR™-1200 Varnish Removal System

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