

What is Varnish?

Varnish formation

Lubricant varnish is defined per ASTM D02.C01 WK27308 as a thin, hard, lustrous, oil-insoluble deposit, composed primarily of organic residue, and most readily definable by color intensity. It is not easily removed by wiping with a clean, dry, soft, lint-free wiping material and is resistant to saturated (light hydrocarbon) solvents. Its color may vary, but it usually appears in gray, brown, or amber hues. Varnish begins its life as a soluble degradation product before converting to an insoluble particulate form. The process responsible for the deposition of particulate varnish is reversible.

Lubricant solvency

Under normal operating conditions, turbine lubricants are subjected to oxidation, which produces polar molecules, the varnish precursors, from lubricant mineral-oil base stocks. These polar species represent the starting point of the varnish life cycle. As a result, lubricants in service are a complex combination of base stocks, additives, and contaminants.

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 variables (molecular polarity, contaminant levels, temperature, etc). When the solubility of a molecule is low, the lubricant cannot dissolve those components which then release from the fluid to form deposits. However, when the solubility of a molecule is high, the lubricant will have a high capacity to dissolve it, avoiding the formation of varnish deposits.

Contaminant levels

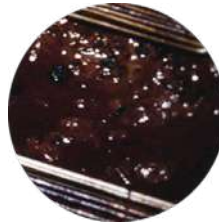
As the oil degrades and oxidation products accumulate, the solvency of the fluid decreases accordingly. Beyond the saturation point, the fluid can no longer dissolve additional varnish precursors formed by continuing oxidation and varnish will begin to precipitate from the solution.

Temperature

Oil temperature directly affects the solubilities of all the species dissolved within it. As temperature decreases, so too does the solubility of varnish and its precursors. Because metals are more polar than the lubricant's base stock, the precipitated polar varnishes prefer to adhere to the metal and form potentially damaging deposits. When the level of varnish precursors in a lubricant is at (or near) the fluid's saturation point, varnishing in cooler regions is very likely to occur.

Types of varnish

The images below depict four different formations of varnish as they can appear in different types and locations throughout a lube system. While this list is not comprehensive, the types listed below are among the most commonly seen.



Varnish can be soft and gooey (Sludge)



Varnish can be hard and brittle (Lacquer)



Varnish on reservoir ceiling (Stalactites)



Varnish deposits on reservoir floor (Plated)

Testing for varnish

Varnishing can cause costly turbine downtime. An easy solution to combat this is to determine the lubricant's potential for varnish formation. Two of the most widely adopted techniques are QSA[®] (quantitative spectrophotometric analysis) and the standardized MPC (membrane patch colorimetry, ASTM 7843).

Both methods can produce results which vary significantly depending upon the length of time during which the oil sample was "aged." Indeed, longer sample aging periods produce higher MPC values, suggesting that degradation of lubricants continues in the sample bottle. For this reason, the ASTM MPC method suggests all samples be incubated at room temperature for 72 hours after being heated to 140°F (60°C) for 24 hours. This well-defined and standardized aging time has provided inter-laboratory consistency and improved testing repeatability.

The Varnish Cycle

It all starts with oxidation.

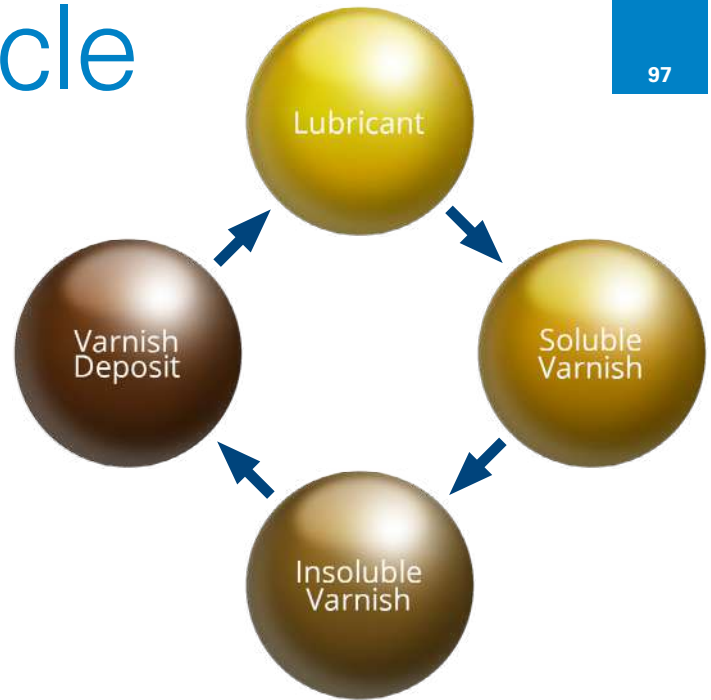
Oxidation is an unavoidable chemical reaction between the lubricant base stock and oxygen present in the air surrounding it. Oxidation increases as the operating temperature rises, but the by-products remain dissolved.







When oil moves from hotter regions within the system to cooler ones, the fluid temperature decreases and these precursors begin a physical change to precipitate from solution in the form of soft particulates.

Once formed, varnish particles agglomerate and form deposits which preferentially coat metal surfaces within the reservoir and on components like valves. These deposits are often the cause of unit trips and fail-to-start conditions.

In most cases, however, once varnish deposits form, they can be reabsorbed into the fluid and broken down if the solvency of the lubricant increases.

The table below breaks down the stages in the process of varnish formation along with the approximate fluid color corresponding to each stage.



 <p>Oxidation</p>	<p>Oxidation is the root cause of the problem. It creates free radicals resulting in acids, alcohols, esters and lactones. Anti-oxidant (A0) additives are designed to neutralize the products of oxidation. As oxidation occurs, the phenol and amine additives are depleted. The products of oxidation become the building blocks of varnish.</p>
 <p>Polymerization</p>	<p>Polymerization occurs as the by-products of oxidation and additive reactions combine to create longer chain molecules with higher molecular weight. These molecules have lower solubility and are polarized. The rate of molecular polymerization is a function of temperature (as a catalyst) and the concentration of oxidation by-products (free radicals).</p>
 <p>Solvency</p>	<p>Solvency describes fluid's capacity to hold the varnish producing molecules in solution (dissolved). Solubility is directly affected by temperature. As more oxidation by-products are generated, the fluid approaches its solubility saturation point beyond which no additional polymerized molecules can be held in solution.</p>
 <p>Precipitation</p>	<p>Precipitation occurs once the solubility threshold (saturation point) has been crossed or if there is a drop in temperature which reduces the solubility of the fluid. As additional oxidation by-products (free radicals) are generated, they become insoluble and precipitate out and are free to form varnish deposits.</p>
 <p>Agglomeration</p>	<p>Agglomeration begins as insoluble sub-micron soft particles (~0.08 micron) that have precipitated out of solution bond to form large particles (1.0 micron). These agglomerated soft particles remain insoluble, remain polarized, and maintain a higher molecular weight than the fluid itself.</p>
 <p>Varnish Formation</p>	<p>Varnish forms as the polarized oxidation by-products come out of solution, agglomerate and collect on metal surfaces. The surfaces where varnish typically forms include cool zones, low flow and low clearance areas. Why? This is where solubility diminishes, precipitation starts and agglomeration goes on undisturbed. Deposit formation also occurs locally in the reservoir and on components where hot spots in the fluid or sparking lead to varnish, such as on reservoir walls and filter elements.</p>

Typical Fluid Condition

Strategies to Combat Varnishing

There are two main types of varnish removal systems: those based upon the removal of suspended (insoluble) particles and those based upon the removal of soluble varnish and its precursors.

Anti-oxidant packages, generally consisting of phenols and amines, are usually added to the lubricant as a built-in varnish mitigation strategy. Anti-oxidants limit the rate of oxidative degradation and, therefore, delay varnishing. But these AO packages fail in that they cannot prevent it indefinitely. Although both phenols and amines have anti-oxidant activity on their own, they function more efficiently in concert with one another. While the specific identities and amounts of the anti-oxidants employed varies with different lubricant formulations, the mechanism by which they enhance fluid lifetime remains the same. AO levels deplete continuously which means the fluid needs to be replaced once all AO additives have been consumed.

Insoluble Varnish Removal

Charge agglomeration, electrostatic oil cleaning, or combinations of these techniques are advanced forms of particulate removal. These techniques remove fine particulates that are suspended within the fluid including insoluble varnish particles. However, these technologies are only helpful once the insoluble particles form. Soluble varnish and soluble varnish precursors are able to return to the turbine and become varnish deposits as seen on the components to the right.

Soluble Varnish Removal

Soluble Varnish Removal (SVR™) systems use specialized Ion Charge Bonding (ICB™) resins that contain billions of polar sites capable of adsorbing soluble varnish and its precursors. This adsorption relies on a preferential molecular interaction between the polar varnish molecules and the polar sites present within the resin. Just as insoluble by-products prefer metal surfaces to being suspended in the fluid, soluble by-products prefer ICB resin than to remain dissolved within the fluid.

Conventional ion-exchange resins function by exchanging one chemical for another. ICB resins are engineered to adsorb the entire contaminant without returning any others 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 and its precursors 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 insoluble varnish particles and deposits are reversible, the high solvency of the SVR treated lubricant forces insoluble varnish already present on turbine surfaces back into the soluble varnish form where they can be adsorbed and removed. With all the remaining oxidation by-products removed, the varnish formation cycle is completely stopped.

Varnish particles and deposits are created from reversible physical changes that begin with soluble oxidation products and end with insoluble 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. Normally, 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.

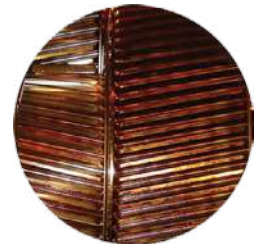
Varnish deposits on filter element (GE Frame 6B)



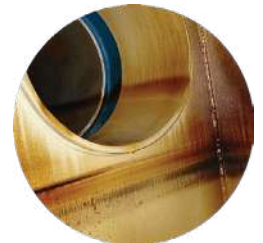
IGV valves and fuel control valves are typically the first problem components



Varnish on load gear (Frame 6)



Lube oil reservoir coated (Varnish Deposits)



Filter element cross section (Lacquer Varnish Deposits, Support Tube)

