

Why Varnish Removal Fails: The Soluble-Insoluble Varnish Equilibrium

Hobbs, Matthew G.
EPT, 4772 50th Avenue S.E. Calgary, AB, Canada
mhobbs@cleanoil.com

Dufresne Jr., Peter T.
EPT, 4772 50th Avenue S.E. Calgary, AB, Canada
pdufresne@cleanoil.com



1. Abstract

Varnish is produced by breakdown of hydrocarbon lubricants. Its deleterious impact on equipment performance and reliability is well-documented. Varnish has traditionally been defined as an insoluble deposit, however, it also exists in an often-overlooked soluble state. While soluble varnish forms as the result of an irreversible chemical reaction, the conversion between soluble and insoluble varnish is often a physical process; importantly, this process is reversible. Like other interconvertible states of matter, the relative amount of soluble and insoluble varnish in a system is dictated by a dynamic equilibrium.

Numerous oil treatment strategies have been developed to mitigate the harmful effects of varnishing. In order to be successful, these strategies must address the effect that their use will have on the soluble-insoluble varnish equilibrium. Most rely on filtration, which focuses on the removal of insoluble varnish particles. Unfortunately, these systems have little impact on varnish's soluble form; once they remove insoluble varnish, soluble varnish persists and will re-establish an equilibrium leading to the formation of new particles/deposits. Filtration, therefore, addresses only half of the varnish problem. Resin-based soluble varnish removal (SVR) systems are engineered to remove dissolved varnish at the molecular level. As the soluble-insoluble varnish equilibrium is re-established, insoluble varnish then begins to re-dissolve. SVR systems exploit the soluble-insoluble varnish equilibrium and provide a total solution by removing both varnish states. Their use can, therefore, mitigate the risks associated with lubricant breakdown.

2. Introduction

2.1. The Varnish Problem

Varnish, produced by lubricant degradation, causes increased wear, filter plugging, restricted flow, poor heater/cooler performance and valve sticking in a variety of industrial applications [1]. Gas turbines (GTs) are especially sensitive to varnish-induced valve sticking which causes costly unit trips and fail-to-start conditions.

Given the criticality of GTs, it is astonishing to discover that 40% of power plants surveyed reported experiencing varnish-related problems [2]. Indeed, the largest GT supplier in the world anticipates that all users will experience varnishing over time [3].

2.2. Varnish Potential Evaluation

The MPC (membrane patch colorimetry) test has been adopted as an industry standard for the assessment of an oil's potential to form harmful varnish [4]. The test involves passing an in-service lubricant sample through a fine (0.45 μm) filter patch and quantifying the color of the organic residue (varnish) left behind. Darker, more intensely colored residues are indicative of degraded oil with a high potential for varnishing (Figure 1).

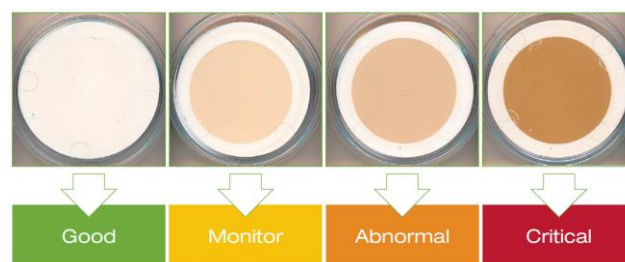


Figure 1: Varnish Potential Assessment by Membrane Patch Colorimetry.

Since hydrocarbon-based lubricants can continue to breakdown after a sample is drawn, the standard MPC test method requires that all samples be subjected to a 24 hour heating period and 72 hour incubation period away from all light. This ensures that all samples have been “reset” to a similar starting point prior to analysis. Although these steps necessitate a 96 hour wait, they are required in order to obtain reproducible and useful evaluations of a fluid’s varnish potential.

2.3. Defining Varnish

Varnish has traditionally been defined as a “thin, hard, lustrous, oil insoluble deposit, composed primarily of organic residue” [4]. While this definition has gained widespread industry acceptance, it focusses only on the insoluble end product of lubricant breakdown. While these insoluble deposits provide the most obvious evidence of a varnishing problem, varnish actually begins its life cycle as an oil-soluble degradation product [5].

Soluble varnish initially forms as the result of chemical breakdown of the lubricant. Whether formed by oxidation, thermal degradation or another pathway, varnish formation involves a chemical transformation. These reactions are irreversible and unavoidable. From the moment that oil is put into service, it begins to breakdown. The use of modern lubricant base stocks and additives can decrease the rate of degradation but they cannot eliminate it.

Once soluble varnish has formed, it can undergo a further conversion to generate the more widely-recognized insoluble varnish phase. This conversion is often a physical process and is, therefore, potentially reversible.

3. The Soluble-Insoluble Varnish Equilibrium

The soluble and insoluble forms of varnish constantly interconvert as part of a dynamic system. As with all other matter, there is a balance between these 2 phases. Under constant conditions, every equivalent of soluble varnish which converts to insoluble varnish is balanced by an equivalent of insoluble varnish which converts to its soluble form. In chemistry, this is referred to as a *dynamic equilibrium* since the individual species present convert from one form to another but the net amount of each remains unchanged.

Thermodynamics dictates that all systems strive to reach this type of balance. Any change in conditions which upsets it, therefore, produces a shift in the equilibrium until a new balance is reached.

3.1. Equilibrium Example: Water

The evaporation of water provides an everyday example of this behavior (Figure 2). At room temperature (20°C), liquid water is in equilibrium with water vapor in the atmosphere above; for every liquid water molecule which evaporates, a vapor molecule condenses and the volume of liquid water remains unchanged.

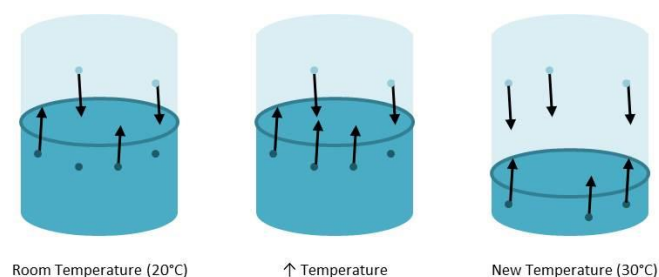


Figure 2: Evaporation and Condensation of Water – An Example of Shifts in Dynamic Equilibria.

When conditions change, however, this equilibrium is upset. Raising the temperature, for example, forces more water to evaporate. This decreases the volume of liquid but increases the amount of water vapor in the atmosphere above. As the vapor concentration increases, there is an increased likelihood of condensation, returning the water to its liquid phase. Eventually, the liquid and the vapor reach a new dynamic equilibrium and for every molecule which evaporates, another condenses. The result of this change in temperature is a new system which features less liquid and more vapor.

In the example above, the less-condensed gaseous water phase was favored as temperature increased. Indeed, the equilibrium between 2 phases generally shifts to favor the more disperse whenever temperature is increased. Since phase changes are physical and reversible, the corollary is also true: decreases in temperature will favor the more condensed state.

3.2. Equilibrium Example: Varnish

Like water and its vapor, the soluble and insoluble forms of varnish are phases in equilibrium with one another.

Soluble varnish is relatively disperse while insoluble varnish is condensed. The relative amount of varnish present in either state is, therefore, strongly temperature-dependant.

In GT applications, lubricants are subjected to high temperatures. Typical GT oils encounter temperatures as high as 120°C at the bearing while aero-derivative GT oils are subjected to even more extreme conditions (>300°C) [6]. At these temperatures, the more disperse soluble state of varnish is favored. Once the oil begins to cool elsewhere in the system, however, the varnish equilibrium shifts towards the insoluble state (Figure 3). Therefore, cooler areas (reservoir, transfer lines, valves etc.) are more prone to varnish deposition. In peaking plants, the problem is especially severe since the entire lubrication system is allowed to cool during non-peak periods. During a shutdown, any surface wetted by lubricant will be prone to varnish deposition as the entire system cools.

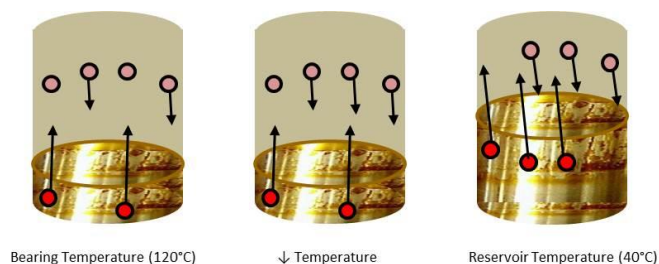


Figure 3: Shift in the Soluble-Insoluble Varnish Equilibrium as Oil Temperature Decreases.

To demonstrate the temperature-dependence of the soluble-insoluble varnish equilibrium, we split an oil into 2 equal aliquots (Figure 4). Having been subject to the rigors of service in a GT, this oil contained varnish. Half the oil was left “as received” while the varnish was removed from the other half. Both samples were then heated to 50°C. At this temperature, both appeared clear and bright as the varnish present in the “as received” sample was soluble. As the samples were allowed to cool, however, the varnish equilibrium shifted and the “as received” sample became cloudy and opaque. By contrast, the varnish-less sample remained clear and bright at the lower temperature. The cloudiness observed in the “as-received” sample was the result of fine insoluble varnish particles precipitating from solution. The fact that the varnish-less sample remained clear

demonstrates that the oil itself was not prone to wax formation which could produce a similar effect.

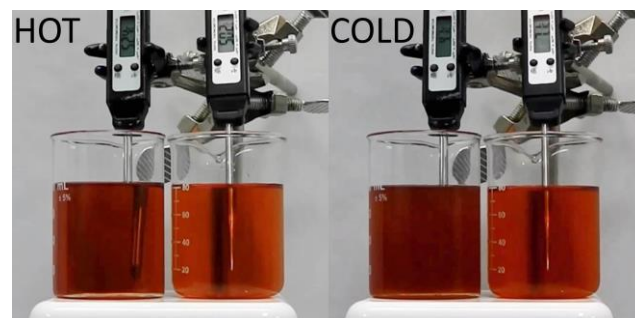


Figure 4: Change in Appearance of Oil Containing Soluble Varnish (Left Beaker) and Oil Without Soluble Varnish (Right Beaker) as Temperature Decreases.

4. Varnish Removal Strategies

When varnish exists in a system, both soluble and insoluble varnish will be present; their relative amounts are dictated by a dynamic equilibrium. Successful varnish-removal strategies must, therefore, account for the effect that they will have on this equilibrium in order to completely remove varnish in all of its forms.

4.1. Filtration/Particulate Removal

The majority of varnish removal systems rely upon particulate filtration to remove the insoluble varnish formed in Step 2 of the varnish life cycle above (Figure 5). In this manner, they aim to prevent the formation of varnish deposits. Depth filtration, agglomeration, electrostatic oil cleaning or combinations of these techniques are common examples of particulate removal systems which have been applied to this end. For these technologies to be effective, varnish must already have formed and be present in its insoluble state.

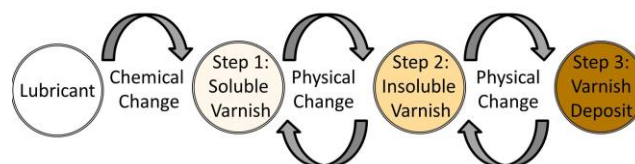


Figure 5: Equilibria Involved in the Varnish Life Cycle.

These technologies have no effect on soluble varnish which is dissolved and passes readily through the mechanical filters employed. This soluble varnish will then seek to re-establish equilibrium with its insoluble counterpart. In doing so, there will be a net conversion of

soluble varnish to its insoluble form. Indeed, so long as soluble varnish persists, insoluble varnish will continue to deposit; especially in regions where cooler conditions further promote varnishing.

Particulate removal systems are well-suited for the removal of insoluble contaminants and the improvement of oil cleanliness. This has a well-documented beneficial impact on equipment reliability and lifetime [7]. Nevertheless, these systems are ill-suited to solving varnish problems since they are unable to remove varnish in both its soluble and insoluble states. Indeed, their use amounts to an effective half-measure.

4.2. Resin-Based Soluble Varnish Removal

Soluble varnish removal (SVR) systems use specialized resins that contain billions of sites capable of adsorbing soluble varnish at the molecular level. This adsorption relies on a preferential interaction between the varnish molecules and the sites present within the resin. SVR systems interrupt the varnish life cycle at its earliest stage and prevent soluble varnish from accumulating in the lubricant and eventually forming harmful varnish particles and/or deposits. These systems are ideally suited to continuous use during turbine operation since the soluble contaminants that they remove are prevalent at operating temperatures. When soluble varnish is continuously removed, the insoluble varnish feedstock cannot accumulate and the risk of varnish deposition in cooler areas is essentially eliminated.

While the competing particulate removal systems are unable to remove both the soluble and insoluble states of varnish, resin-based systems exploit the equilibrium that exists between these 2 phases to remove all varnish. This includes not only the varnish present in the lubricant but also suspended varnish particles and varnish which may have previously deposited out on equipment surfaces.

Whenever 1 phase of a 2 component equilibrium system is removed, the equilibrium shifts to compensate and favors the formation of the removed phase. This occurs due to the natural preference for balance in an equilibrium system. In chemistry, this positive feedback phenomenon is referred to as Le Châtelier's principle [8]. When soluble varnish is continuously removed, its equilibrium with the insoluble varnish phase is upset. In

an effort to restore balance, the equilibrium shifts to favor the removed soluble phase so that both phases can, once again, be present in equilibrium. As a result, insoluble varnish particles and deposits will begin to dissolve back into the lubricant forming soluble varnish. These newly soluble species are then removed by SVR systems prompting additional varnish particles and/or deposits to re-dissolve. In this manner, SVR creates a positive feedback cycle which leads to the complete removal of varnish in all of its forms (Figure 6).

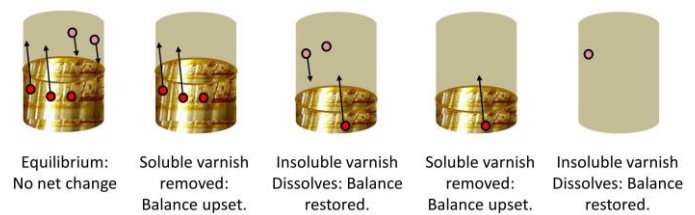


Figure 6: Complete Removal of Soluble and Insoluble Varnish by Positive Feedback with Resin-Based Oil Treatment.

5. Case Study: Filtration vs. Resin







A user recently experienced downtime as the result of repeated actuator sticking problems in their hydraulic system. Subsequent analysis confirmed that their fluid possessed an elevated MPC varnish potential and varnish was determined to be the root cause of their actuator problems.

5.1. Varnish Removal by Filtration

In an effort to address this problem, new high efficiency (0.8 μm absolute) filters were installed. To monitor the performance of their new filters, the user performed modified on-site MPC testing which omitted the 96 hour wait required by the standard. This was done so that real-time results could be obtained to gauge the effectiveness of the new filter media. Samples taken prior to and following the installation of the new filters suggested that they were effective varnish-scavengers as evidenced by the apparent 92% decrease in real-time MPC varnish potential (Table 1).

When duplicate samples were sent to a lab for MPC analysis according to the standard method, however, dramatically different results were obtained. Indeed, once the lubricant was heated to 60°C for 24 hours and allowed to incubate at room temperature for 72 hours, the obtained results suggested that the new filters had no

Table 1: Filtration vs. Resin-Based Varnish Removal Effectiveness.

MPC Method	Test Location	60°C Heating Period (hours)	20°C Incubation Period (hours)	Initial Patch Photo	Filtered Patch Photo	Initial MPC ΔE	Filtered MPC ΔE	Change
Real Time	On-Site	0	0			36.0	3.0	- 92%*
ASTM D7843-16	Lab	24	72			22.1	22.1	- 0%
ASTM D7843-16	Lab	24	72			22.1	3.2	- 86%

impact on the oil’s varnish potential. We note that amber bottles were used to keep the oils away from all light following sampling.

The discrepancy between the results obtained on-site (in real-time) and those obtained by the lab (following the required 96 hour wait) are the result of the soluble-insoluble varnish equilibrium. On-site, insoluble varnish was removed by the high efficiency filters. The remaining soluble varnish passed through these filters as well as the membrane filter patch employed for MPC analysis. A misleading near-zero MPC varnish potential was, therefore, obtained.

During lab analysis, however, the sample was aged for 96 hours as required by the MPC standard. During this time, the soluble varnish still present re-established a new soluble-insoluble equilibrium. These results demonstrate the importance of removing soluble varnish. If soluble varnish is allowed to persist, it will re-establish equilibrium with its insoluble analog. The above results also highlight the importance of following the established MPC test method. Modifications of this method which omit the required 96 hour wait may not allow the soluble varnish content of the lubricant to be established.

5.2. Varnish Removal by SVR

Surprised by the results of the lab analysis, the user opted to install a resin-based SVR system to remove the soluble varnish which their high efficiency filters could not. MPC testing was again performed prior to and following SVR installation. Based on the failure of previous on-site modified MPC tests, all subsequent MPC analyses were conducted in a lab according to the established method. The results obtained in this manner demonstrate that SVR efficiently removed all forms of varnish from lubricant, decreasing its varnish potential by a dramatic 86%. At the low MPC ΔE observed following SVR treatment, the risks associated with lubricant varnishing are effectively mitigated; most significantly, the user has reported no actuator sticking problems since their SVR system was put in place.

As a result of their ability to remove both soluble and insoluble varnish by exploiting equilibrium, resin-based systems provide a total solution to the varnish problem, mitigating the risk of varnish-related failure.

6. Conclusion

Despite its prevalence and significant impact on equipment performance/reliability, current definitions of lubricant varnish remain incomplete. Indeed, these definitions emphasize the insoluble end product of

varnishing but fail to account for the fact that soluble varnish plays an equally important role.

Soluble varnish forms in the first stage of oil breakdown as the result of irreversible and unavoidable chemical degradation. Once formed, soluble varnish accumulates within the fluid, establishing a dynamic equilibrium with its more recognized insoluble analog. Throughout the varnish life cycle, the soluble and insoluble forms of this contaminant exist in a temperature-dependent dynamic equilibrium with one another. At higher temperatures, the more dispersed soluble varnish phase is favored while the more condensed insoluble phase is favored at lower temperatures. Varnish-removal strategies must account for their own effect upon the soluble-insoluble varnish equilibrium in order to be effective.

The majority of varnish-removal strategies employ particulate-removal technologies (filters, depth media, electrostatics etc.). These systems all function on the basis of mechanical filtration; they remove insoluble varnish but leave its soluble analog behind. While their use remains beneficial, they do not address the entire varnish problem. Indeed, they eliminate the insoluble effect but not the soluble cause of varnishing problems. By failing to remove soluble varnish, these systems allow the soluble-insoluble varnish equilibrium to be re-established and varnish problems may persist.

Resin-based strategies employ specialized polar media to remove soluble varnish at the molecular level. Such soluble varnish removal systems exploit the soluble-insoluble varnish equilibrium via positive feedback (Le Chatelier's Principle). Indeed, the removal of soluble varnish shifts the varnish equilibrium to drive the removal of insoluble varnish. By removing soluble varnish, resin-based systems provide a total varnish solution.

The prevalence and potential economic impact of varnishing in industrial applications is so significant that many original equipment manufacturers (OEMs) recommend the use of varnish removal systems to mitigate risk. It is, therefore, vital that users employ varnish-removal strategies which will be effective in light of the dynamic equilibrium that exists between the soluble and insoluble forms of varnish.

7. References

- [1] Atherton, B., Discovering the Root Cause of Varnish Formation. Machinery Lubrication, March 2007 (Tulsa, OK) Pub. Noria Corporation (2007).
- [2] Hannon, J., Wardlow, A., Vanquish Varnish to Improve Gas Turbine Reliability. Combined Cycle Journal, 2011 Outage Handbook (Las Vegas, NV) Pub. PSI Media Inc. (2011).
- [3] GE Customer Technology Services, Lube Oil Varnishing. General Electric Technical Information Letter, TIL1528-3, Pub: General Electric (2005).
- [4] ASTM D7843-16: Standard Test Method for Measurement of Lubricant Generated Insoluble Color Bodies in In-Service Turbine Oils using Membrane Patch Colorimetry. Book of ASTM Standards (West Conshohocken, PA) Pub. ASTM International (2016).
- [5] Dufresne Jr., P., Hobbs, M. G., MacInnis, G., Lubricant Varnishing and Mitigation Strategies. Combined Cycle Journal, Fourth Quarter 2013, 34 – 40, (Las Vegas, NV) Pub. PSI Media Inc. (2014).
- [6] Hannon, J., How to Select and Service Turbine Oils. Machinery Lubrication, July 2001 (Tulsa, OK) Pub. Noria Corporation (2001).
- [7] Williamson, M., Setting Targets for Oil Cleanliness: A Simplified Approach. Lubrication Excellence 2007 (Tulsa, OK) Pub. Noria Corporation (2007).
- [8] Daintith, J. (Ed.), Le Chatelier's Principle. A Dictionary of Chemistry - 6th Edition (Don Mills, ON) Pub. Oxford University Press (2008).