Lubricant Varnishing and Varnish Mitigation

M. G. Hobbs [1], P. T. Dufresne Jr. [1]

[1] EPT, 4772 50th Ave. S.E. Calgary, AB, Canada.

ABSTRACT

Varnish is an organic residue produced by irreversible chemical degradation of mineral oil lubricants. Varnish can lead to numerous equipment problems including: filter plugging, restricted oil flow, poor heat transfer, valve sticking, fail-to-start conditions and costly unit trips.

Varnish has traditionally been defined as an insoluble deposit, however, varnish also exists in an often-overlooked soluble state. While varnish forms as the result of an irreversible chemical reaction, the conversion between soluble and insoluble varnish is a physical equilibrium process dependent upon temperature; importantly, this process is reversible.

Due to the costly nature of varnish-related failures and their prevalence, numerous strategies have been developed to mitigate the effects of varnishing. Most varnish removal technologies focus on the removal of the most obvious signs of varnishing: insoluble particles/deposits. Unfortunately, these particle removal systems have no effect upon varnish in its soluble form; once they have removed particulate varnish, soluble varnish persists and continues to deposit. Soluble varnish removal (SVR) systems provide the only means of removing varnish in both its soluble and insoluble states.

Keywords: Contamination Control, Varnish, Gas Turbine, Equilibrium, Soluble Varnish Removal (SVR) Systems.

INTRODUCTION

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. Gas turbines (GTs) are especially sensitive to varnish-induced valve sticking which causes unit trips and fail-to-start conditions. The lost production arising from 1 such event can easily cost a typical GT operator up to $480,000 US per day.

Given the magnitude of these potential losses, it is astonishing to discover that approximately 40% of the 192 power plants surveyed by Exxon Mobil reported experiencing varnish-related problems [1]. Indeed, the largest GT supplier in the world (General Electric, GE) anticipates that all users will experience varnishing over time [2]. For this reason, GE recommends the use of varnish removal systems to mitigate the risk associated with lubricant varnishing in the power generation industry.

In response to this need, a variety of varnish removal systems are now available. These systems generally operate in 1 of 2 ways; most employ technologies which specialize in the removal of particulate (insolubles) while others focus on the removal of dissolved (soluble) species. Since the mechanism of varnish removal differs between systems, so too does their effectiveness.

VARNISH REDEFINED

Varnish has traditionally been defined as a "thin, hard, lustrous, oil insoluble deposit, composed primarily of organic residue" [3]. 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 in a different form/phase as a soluble oil degradation product.

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

THE SOLUBLE - INSOLUBLE VARNISH EQUILIBRIUM

Throughout its lifetime, the soluble and insoluble forms of varnish 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 individual species present convert from 1 form to another but the net amount of each remains unchanged.

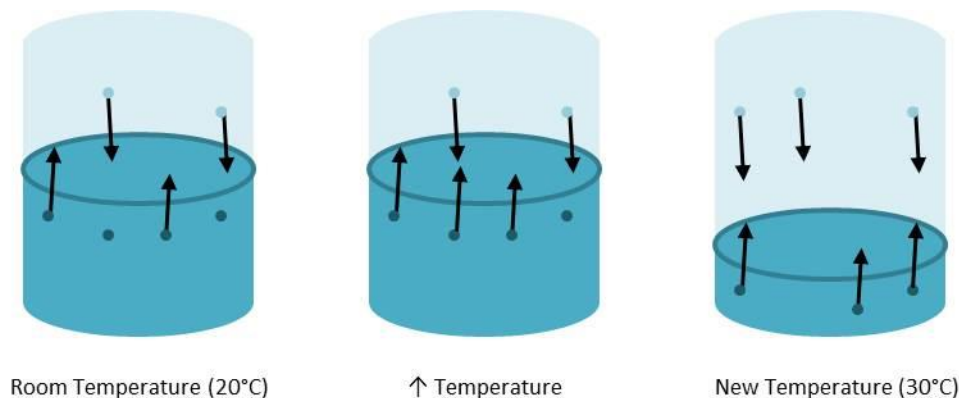Room Temperature (20°C)   ↑ Temperature   New Temperature (30°C)

Figure 1: Example of the dynamic equilibrium between liquid water and its vapor under different conditions. Left: At room temperature, every liquid molecule that evaporates is replaced by a vapor molecule. There is no net change in the amounts of liquid and vapor present. Center: As conditions change (application of heat), the rate of evaporation becomes greater than the rate of condensation. The equilibrium position shifts as liquid evaporates faster than it can be replaced. There is a net change as vapor levels increase and liquid levels decrease. Right: Eventually, the vapor phase becomes saturated and the rate of condensation increases to match the rate of evaporation. A new dynamic equilibrium favoring more vapor and less liquid is reached. There is no further net change.

All systems strive to reach this type of balance, therefore any change in conditions which upsets it produces a shift in the equilibrium until a new balance is reached. The evaporation of water provides an everyday example of this behavior (Figure 1). 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 water vapor molecule condenses and the volume of liquid water remains unchanged. When conditions change, however, this equilibrium is upset. Raising the temperature by 10°C, for example, forces more water to evaporate. This decreases the volume of liquid but increases the amount of water vapor present in the atmosphere above. As the concentration of water vapor increases, there is an increased chance that vapor molecules will encounter one another and condense, returning to the liquid phase. Eventually, the liquid and the vapor reach a new dynamic equilibrium and for every molecule which evaporates, another condenses. The result of the change in conditions (temperature) is a new system which features less liquid water and more water vapor. Phase changes like this are physical in nature and are, of course, reversible. If the temperature is dropped back to 20°C, the water vapor will begin to condense at a greater rate than the liquid can evaporate until the original equilibrium (and concomitant volume of liquid water) is restored.

Like water and its vapor, the soluble and insoluble forms of varnish are 2 phases in equilibrium with one another. The relative amounts of varnish present in either state depend strongly upon the temperature of the system. An understanding of the effect of temperature upon the soluble – insoluble varnish equilibrium is, therefore, key to developing a strategy to effectively combat varnishing in different applications.

THE EFFECT OF TEMPERATURE UPON THE VARNISH PHASE EQUILIBRIUM

Normally, matter exists in 1 of 3 phases: solid, liquid solution or gaseous vapor. The principle difference between these 3 phases is the spacing (and, therefore, interaction) between adjacent molecules/atoms. Solids are the most highly condensed phase and experience the strongest interaction between neighboring constituents. Gases, on the other hand, are the most dispersed phase and experience the weakest interactions between individual atoms/molecules. Liquid solutions are intermediary.

In the example above, the less-condensed gaseous phase of water was favored as the temperature of the system increased. This resulted in liquid evaporating and levels of water vapor increasing. This occurs because the increased temperature increases the energy of the molecules within the system and disrupts the interactions between them; as the interactions weaken, the constituent water molecules grow more distant and a more dispersed phase is produced. Indeed, for this reason, the equilibrium between 2 phases will shift to favor the less condensed one whenever temperature is increased. Since phase changes are physical in nature and reversible, the corollary is also true: decreases in temperature will favor the more condensed state of matter.

In GT applications, lubricants are subjected to high temperatures. Typical GT lubricants encounter temperatures as high as 120°C at the bearing while aero-derivative GTs lubricants are subjected to even more extreme conditions (>300°C) [4]. 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 begins to shift towards the insoluble state (Figure 2). As oil cools, the rate at which soluble varnish becomes insoluble increases. Therefore, cooler areas (reservoir, transfer lines, valves etc.) are more prone to varnish deposition. In peaking plants where GTs are not operated continuously, the problem is especially severe since the entire GT lubrication system is allowed to cool during non-peak periods. During a shutdown, any GT surface wetted by lubricant will be prone to varnish deposition as the entire system cools.

Bearing Temperature (120°C)   ↓ Temperature   Reservoir Temperature (40°C)
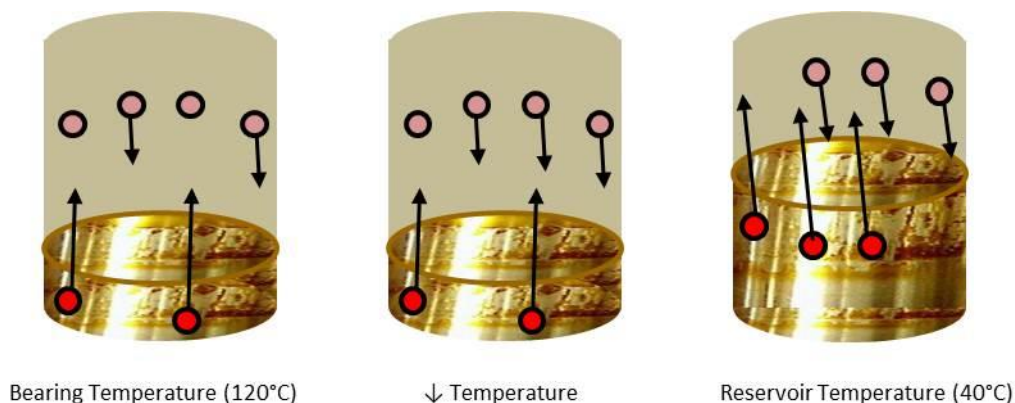
Figure 2: The dynamic equilibrium between the soluble (top) and insoluble (bottom) states of varnish. Left: At high temperatures, the more disperse soluble state is favored. Center: As the lubricant's temperature decreases, the lubricant's solvency decreases and the more condensed insoluble state is favored. The equilibrium shifts and varnish deposits at a greater rate than it dissolves. Right: As the levels of insoluble varnish increase, eventually a new dynamic equilibrium is reached and no further net change occurs.

SATURATION, EQUILIBRIUM AND THE VARNISH LIFE CYCLE

At any given temperature, a lubricant only has a finite ability to dissolve soluble varnish. A solution is said to be saturated once soluble varnish levels reach that capacity. At the saturation point, a lubricant is unable to dissolve

additional varnish. Since the equilibrium which dictates the relative levels of soluble and insoluble varnish is temperature-dependent, so too is the saturation point of a lubricant. As the temperature is increased, the equilibrium shifts to favor the less condensed soluble phase of varnish. Consequently, the lubricant's saturation point is increased when its temperature is raised. When the temperature is decreased, on the other hand, so too is the lubricant's saturation point. Lubricant saturation and thermal equilibria all play key roles in the life cycle of varnish (Figure 3).
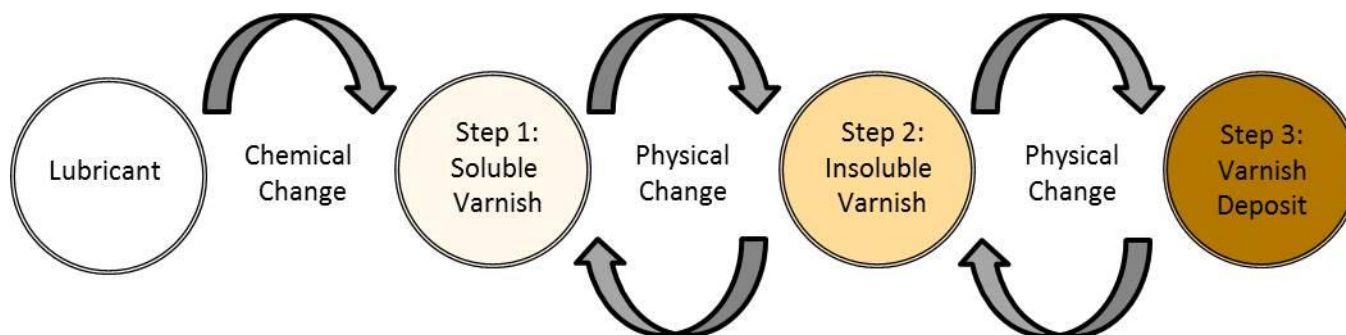

Figure 3: The varnish life cycle. Soluble varnish forms as the result of an irreversible chemical reaction. Subsequent physical changes lead to the formation of insoluble varnish (particulate) and varnish deposits. Unlike the chemical change that leads to soluble varnish formation, the physical changes that lead to deposition are reversible.

During service, lubricants chemically degrade in an irreversible manner, producing soluble varnish which accumulates in solution (Step 1). As soluble varnish builds up, the lubricant's saturation point is eventually reached. Beyond this point, any additional varnish which is produced will be insoluble since the capacity of the lubricant to hold varnish has been exceeded. Therefore, continued degradation of an already saturated lubricant produces insoluble varnish particles (Step 2) which can eventually agglomerate to produce deposits (Step 3). As discussed above, the phase changes between soluble and insoluble varnish are physical in nature and, therefore, reversible. The relative levels of soluble and insoluble varnish present are subject to temperature-dependent equilibria. As a result, even once varnish is deposited, conditions can be changed to shift the equilibrium position and favor the return of the deposits to a dissolved soluble state. As we shall see below, the ability to manipulate this equilibrium is the key to completely removing varnish and effectively mitigating the risks associated with lubricant varnishing.

The vast majority of lubricant breakdown events (oxidation, thermal etc.) occur in the hottest areas of a system. The high temperature of these "hot spots" is sufficient to warm the lubricant and increase its capacity to dissolve soluble varnish. As the lubricant-varnish solution then cools in other areas, the saturation point of the oil decreases accordingly. Although the lubricant may have been able to accommodate the soluble varnish levels present when warm, the levels present often exceed the lubricant's capacity in cooler areas. When the concentration of soluble varnish in a fluid exceeds its saturation point, the lubricant is said to be supersaturated; soluble varnish will convert to insoluble varnish and deposits until its levels drop to those which can be accommodated at that particular temperature. If nothing is done to address the levels of soluble varnish present at lubricant operating temperatures, varnish will continue to precipitate and deposit in cooler regions.

FIGHTING BACK: PARTICULATE VARNISH REMOVAL SYSTEMS

The majority of the varnish removal systems currently available rely upon particulate filtration to remove the insoluble varnish formed in Step 2 of the varnish life cycle above. In this manner, they aim to interrupt the varnish life cycle and 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 have already formed and be present in its insoluble state. These technologies have no effect on soluble varnish which is dissolved and passes readily through the mechanical filters employed.

Since the formation of insolubles is favored at lower temperatures, the maximum benefit obtained using particulate removal systems is achieved when the turbine is not operating and the lubricant is at ambient temperatures. These systems are, therefore, of more use when employed periodically, during outages; they are less effective when used continuously during turbine operation since soluble varnish is favored over insoluble varnish at operating temperatures.

Regardless of the temperature at which particulate varnish removal systems are operated, they do not remove soluble varnish. Since the lubricant still contains dissolved varnish, insoluble varnish can continue to deposit in other regions where cooler conditions influence the varnish equilibrium and favor its harmful, insoluble form. Particulate removal systems are well-suited for the removal of insoluble contaminants and the improvement of oil cleanliness. These systems are useful tools for maintaining low particle counts which decreases wear and has a well-documented beneficial impact on equipment reliability and lifetime [5]. Nevertheless, they are ill-suited to solving varnish problems since they are unable to remove varnish in both its soluble and insoluble states.

EXPLOITING THE EQUILIBRIUM: SOLUBLE VARNISH REMOVAL SYSTEMS

Soluble varnish removal (SVR) systems use specialized Ion Charge Bonding (ICB™) media that contain billions of sites capable of adsorbing soluble varnish. This adsorption relies on a preferential interaction between the varnish molecules and the sites present within the ICB™ media. 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 also 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 levels present remain well-below the lubricant's saturation point meaning that the risk of varnish deposition in cooler areas or during a shutdown is essentially eliminated.

While the competing particulate removal systems are unable to remove both the soluble and insoluble states of varnish, SVR 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 varnish which may have previously deposited out on equipment surfaces.

Soluble Varnish Continuously Removed By SVR System

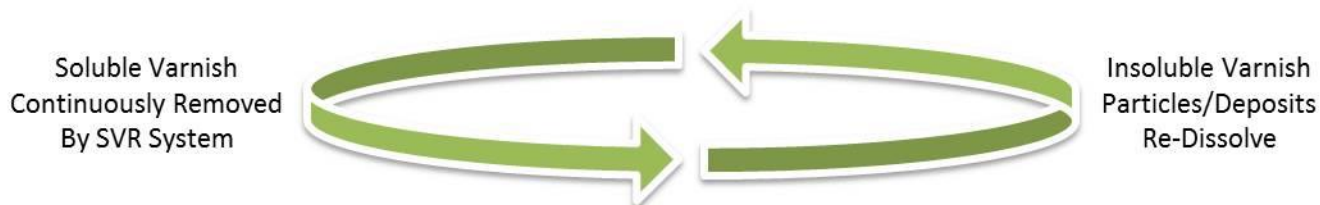Insoluble Varnish Particles/Deposits Re-Dissolve

Figure 4: The use of SVR systems produces a positive feedback loop within the soluble – insoluble varnish equilibrium resulting in the complete removal of varnish from the system.

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 and is well-established [6]. When soluble varnish is continuously removed, the soluble varnish levels present within the lubricant fall well below the fluid's saturation point. The lubricant, therefore, has an improved capacity to hold additional soluble varnish; the solvency of the lubricant is said to be improved. Since soluble varnish is being 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 high solvency lubricant forming soluble varnish. These newly soluble species are continuously removed by SVR systems prompting additional varnish particles and/or deposits to dissolve. In this manner, SVR creates a positive feedback cycle which leads to the complete removal of varnish in all of its forms (Figure 4).

SVR™ CASE STUDY

As a result of their ability to remove both soluble and insoluble varnish by exploiting the equilibrium between the two, SVR systems provide an effective tool with which the risk of varnish-related failure can be mitigated. While the above sections provide insight into the mechanism by which SVR systems function, the goal of this section is to present a practical case study highlighting the effectiveness of these systems, both for restoration and for on-going maintenance of lubricants and systems subject to varnishing problems.

Plant A is a 620 MW gas-fuelled generating station. The lubricant in Plant A's primary GT had been in-service for 8 years and had a long history of high varnish potential as determined by membrane patch colorimetry (MPC) testing according to the industry-accepted method (ASTM D7843) [3]. Following a series of varnish-related failures, the varnish potential of the lubricant was found to be critically high (MPC ΔE = 44.6) indicating that an extremely high level of varnish was present within the fluid. With a 23,500 L (6,200 US gallon) reservoir, the complete replacement of this degraded lubricant would have proven to be a costly venture. Moreover, the replacement of the fluid would necessitate a shutdown resulting in further costs associated with lost production. In an effort to improve the condition of the lubricant during continued operation, maintenance staff at the plant made the decision to install an SVR™ system. Following SVR™ installation, the varnish potential of the lubricant was monitored weekly (Figure 5).
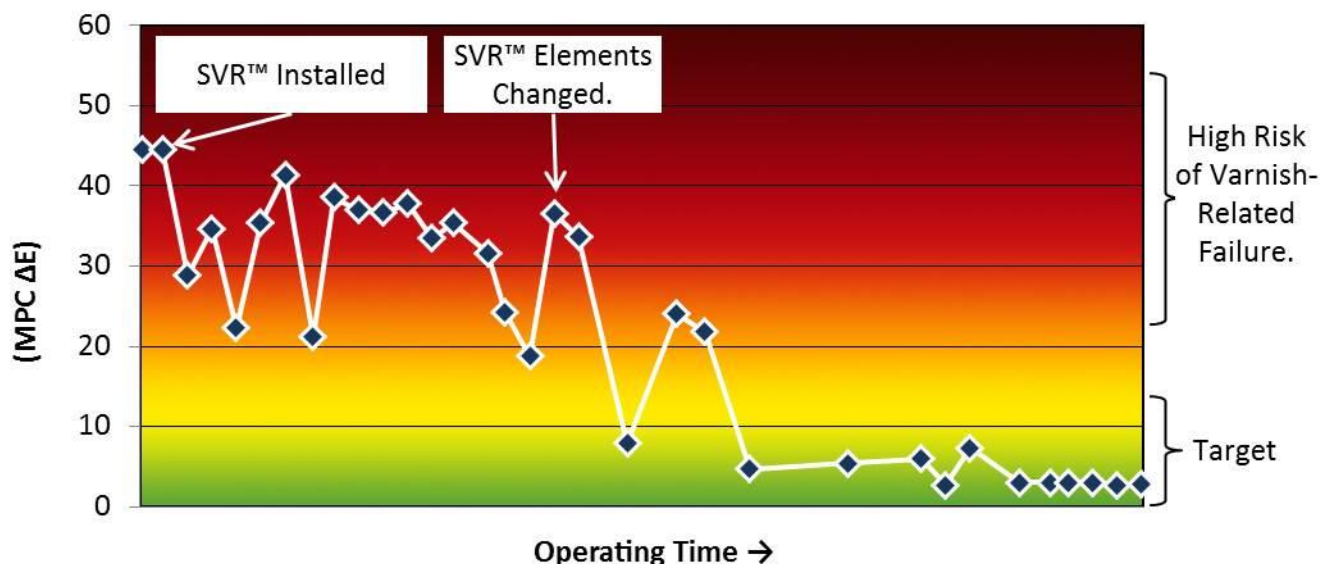

Figure 5: Varnish potential (MPC ΔE) of the in-service lubricant at Plant A following SVR™ system installation.

During the initial period following SVR™ installation, the lubricant's varnish content fluctuated over a reasonably high range of MPC ΔE values. Regardless of fluctuations between individual measurements, an overall downward trend in the fluid's varnish content was nevertheless apparent. The significant fluctuations are the result of the complex equilibria between the soluble and insoluble forms of varnish present within the system. Following SVR™ installation, soluble varnish levels immediately drop improving the lubricant's solvency and upsetting the varnish equilibrium. As the system strives to restore equilibrium, insoluble varnish already present begins to re-dissolve in the high solvency lubricant causing spikes in the fluid's varnish content. Once dissolved, however, the SVR™ system continues to remove the soluble varnish leading to an overall downward trend in MPC ΔE. This pattern of fluctuating lubricant varnish content is characteristic of systems which contain significant levels of insoluble varnish deposits; it is referred to as the "restoration stage".

As the continuous removal of soluble varnish drives the overall varnish content of the system steadily downwards by positive feedback, varnish deposits gradually disappear and the varnish content of the lubricant begins to stabilize. Fluctuations in MPC ΔE become less frequent and severe until they disappear all-together. At this stage, insoluble varnish has been eliminated and the SVR™ system is effectively removing any soluble varnish present

as it forms. This stage is characterized by very low varnish potentials and is referred to as the "fluid stability stage". The low varnish levels present during this stage make the risk of varnish-related failure extremely low. At Plant A, the restoration stage was completed and fluid stability was achieved following 4 month of SVR™ treatment. With the continued operation of the SVR™ system since this time, the plant has not encountered any further issues relating to lubricant varnishing.

CONCLUSION

Soluble varnish forms as the result of irreversible and unavoidable chemical degradation of lubricants. Modern turbine oil formulations are designed to limit oxidative degradation, however, they cannot eliminate it. Once formed, soluble varnish accumulates within the fluid until its saturation point is reached. Beyond this point, varnish undergoes a reversible physical change to an insoluble form, precipitating from the lubricant as harmful particles and deposits. This is the process responsible for varnishing problems. Throughout the varnish life cycle, the soluble and insoluble forms of this contaminant exist in a temperature-dependent equilibrium with one another. At higher temperatures, the more disperse soluble varnish phase is favored while the more condensed insoluble phase is favored at lower temperatures.

The prevalence and potential economic impact of varnishing in GT applications is so significant that original equipment manufacturers (OEMs) recommend the use of varnish removal systems to mitigate risk. These removal systems can be categorized as either particulate removal systems or soluble varnish removal (SVR) systems.

Particle removal systems function on the basis of mechanical filtration removing insoluble varnish but leaving its soluble analog behind. Since the soluble form of varnish is favored at GT operating temperatures, these systems are most effective during shutdowns and are ill-suited to continuous use during GT operation. These systems cannot remove soluble varnish; they eliminate the effect (insoluble varnish) but not the cause (soluble varnish) of varnishing problems.

SVR systems employ positive feedback to exploit the equilibrium between the soluble and insoluble forms of varnish. Unlike particulate removal systems, SVR systems are effective at turbine operating temperatures, meaning that they can be employed continuously. This makes these systems ideally suited for lubricant restoration or maintenance. By removing soluble varnish, SVR systems effectively put a stop to the varnish life cycle.

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