

The Emerging Problem of Lubricant Varnish



Greg Livingstone,
Fluitec International



David Oakton,
OilCare Ltd

Abstract

Lubricating oils are undergoing more changes today than at any time in recent memory. This has been driven by the switch to more advanced base stocks which require new additive chemistries, along with increased equipment performance duties and extreme lubricant operating conditions. These are among the factors that have contributed to the emerging problem of lubricant 'varnish' deposits caused by oil degradation. Varnish is a sticky residue that leads to valve malfunction, blocked flow lines, premature filter blockage, increased bearing friction, nuisance oil leaks etc. All of which are leading to reliability problems across many industries. This article highlights how lubricant varnish is formed, what problems it can cause and how to test the new generation oils for their tendency to form varnish deposit. It will then discuss the proactive methods and technologies available for solving varnish deposit problems.

NEW TECHNOLOGY LUBRICANTS

Many types of lubricating oils and hydraulic fluids are being formulated differently today than they were a decade ago. Industry's drive towards globalisation and efficiency improvements has set off a chain of events impacting on all aspects of operation.

Manufacturers are demanding faster, smaller, more efficient machines. Although the OEMs deliver, the upgrade in machine technology typically means more stress on the lubricant. The OEMs have strengthened their specification, demanding that the lifeblood of their equipment has oxidatively stable oils that can be used longer, at higher temperatures, in smaller spaces and with

Group	Sulfur (Wt %)		Saturates (Wt %)	Viscosity Index
I	>0.03	And/or	<90	80-119
II	<0.03	And	>90	80-119
III	<0.03	And	>90	>120
IV	Polyalphaolefins (PAO)			
V	All stocks not included in Groups I-IV (Pale Oils & Non-PAO Synthetics)			

Table 1 API base stock classification

the ability to withstand a wide range of contaminants. These new demands cause the oil companies to change their formulation chemistries to meet more demanding specifications. The oil companies first meet these new demands by making changes to their lubricant's base stock. Newer synthetic chemistries are increasing the energy efficiencies and solving problems that wouldn't be feasible with mineral oil base stocks. However, the biggest change has been the global adoption of more advanced mineral oil base stocks. The American Petroleum Institute classifies different base stocks into the five different categories outlined in Table 1.

Group I base oils are manufactured by solvent extraction, solvent or catalytic de-waxing, and hydro-finishing processes. The oils are more polar in nature due to their remaining soluble impurities. These polar species lead to a higher solvency than other paraffinic base stocks and a higher natural oxidative stability compared to other base stocks.

Group II base oils are manufactured by hydrocracking and solvent or catalytic de-waxing processes. Fully formulated Group II lubricants have superior antioxidant properties since virtually all hydrocarbon molecules are saturated. They typically have a water-white colour.

Group III base oils are manufactured by special processes such as isohydromerization or severe hydrocracking. These oils are extremely pure and so are non-polar and often require the addition of an ester or aromatic compound to increase solvency to a sufficient point to hold additives in solution. These fluids also have the lowest natural oxidative stability. However they have the capability to achieve the highest oxidative stability for fully formulated lubricants.

Informally, oil manufacturers have created two new categories to further distinguish mineral oils, viz. Group I+ and Group II+.

The shift from Group I to Group II and III oils has resulted in a significant change in formulation strategies due to the strong influence that base oil has on the type of additives used. Consequently these new generation oils degrade differently from the traditional formulated lubricants. Instead of degradation occurring in relatively linear predictable fashion, many of the newer lubricants maintain higher oxidation stability for longer, but then fail very quickly. It is the failure of the lubricant that can lead to the formation of varnish deposits.

THE CAUSES OF OIL DEGRADATION AND VARNISH

The chemical composition of varnish can be extremely varied. Hence it is defined more by its appearance than by its

chemistry. Typically, sludge is considered to be resinous and easily wiped from surfaces, whereas varnish has a more cured, shiny, appearance and the deposits are not easy to wipe from a surface.

Varnish is primarily caused by the continual process of oil degradation, commonly termed oil oxidation (the loss of electrons from the molecules in the lubricant). Virtually everything is susceptible to degradation from the presence of oxygen and the process is accelerated by the higher temperatures typical of modern oil systems. Antioxidants are formulated into modern lubricants in order to inhibit the oil oxidation mechanism and so extend the lubricant life. However, these antioxidants are gradually consumed, leading to an eventual increase in the oxidation process.

There are other common types of lubricant degradation. Sometimes the oil will react with water in a process known as hydrolysis. Thermal degradation is also a significant form of fluid degradation in many applications, where rapid oil ageing occurs in the absence of oxygen. Incompatible contaminants, including different additive formulations or base oils can react to form precipitates, gels and deposits. For example, some ester-based oils will react negatively with mineral oils, producing significant deposits. Also, acidic rust inhibitors are incompatible with basic rust inhibitors, creating flocculants upon mixing.

The resulting varnish deposits can cause a wide range of reliability concerns. Varnish impacts on the precision of servo-valves, affecting equipment such as is found in robotic manufacturing, in plastic injection moulding, in modern controls on the majority of the world's largest power generation facilities and in the steering of naval vessels. It can also cause premature bearing and gear wear in compressors, turbines and paper machines – and finally,



Figure 2 Significant deposits on a heating element due to extreme temperatures

varnish can develop in inconvenient places, clogging up oil flow lines and reducing the heat transfer ability of heaters and coolers.

Figure 1 shows sludge on the bottom of an oil reservoir. You can see where the return oil line is as it disperses the sludge. You can also see the formation of more tenacious deposits where the fluid level is. These deposits are typically referred to as bathtub rings and are more difficult to remove, even though the chemistry of the sludge is similar.

Figure 2 shows the formation of significant deposits on the heating elements inside a reservoir. The high wattage heater contributed to rapid oil degradation and encouraged deposit formation

THE FORMATION OF VARNISH

Oxidation is the initiating process of varnish formation. At this point, the soluble oxidation products will condense and polymerise together forming higher molecular weight objects referred to as oligomers. Depending upon their concentration, chemistry and temperature, these oligomers will eventually reach the saturation point of the fluid. After the solubility point has been reached, the contaminants will precipitate out of solution and form insoluble particles. These particles are also called soft contaminants and have a median size of approximately 0.08 microns. These soft contaminants are polar and attracted to each other in the non-polar environment of modern lubricating oils. They are also attracted to metal surfaces by the high permanent dipole moment. This process leads to sludge formation in reservoirs and in low-flow parts of the system along with

high friction varnish deposits on moving parts (see Figure 3).

One interesting thing to note about the varnish life cycle diagram is that there is a double-arrow between the solubility-precipitation-agglomeration-varnish formation stages. This indicates that in many cases these reactions are reversible. In other words, it is possible for varnish that has already been deposited in a system to be removed and re-absorbed back into the oil and

then for these particles to become dissolved again into the fluid. This is true with organic degradation products. Inorganic degradation products such as depleted zinc dialkyl dithiophosphate (ZnDDP) – a common anti-wear that also functions as a secondary antioxidant – are not able to go back into solution and immediately form deposits upon their creation. In the case

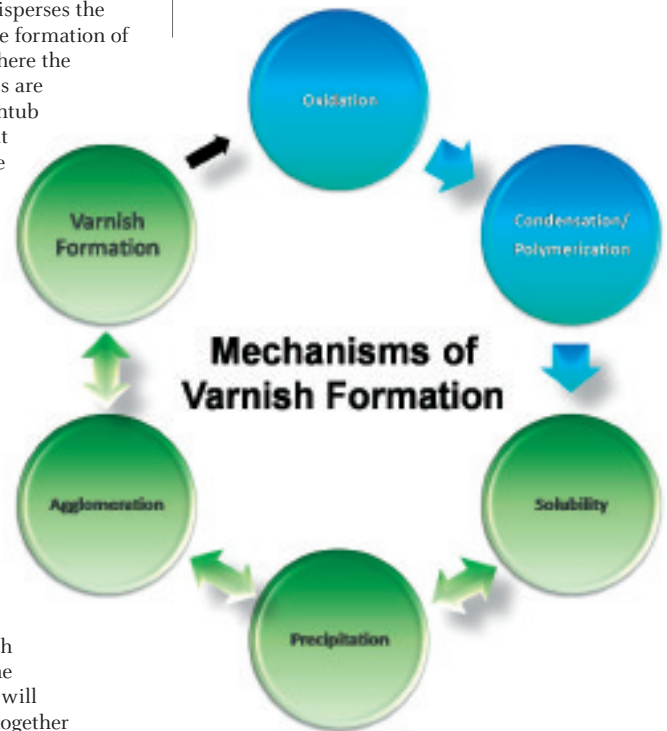


Figure 3 The varnish life cycle, showing the typical stages from oxidation to varnish formation

of ZnDDP these deposits are inorganic sulphates and phosphates and can readily come out of solution upon depletion. The small black arrow pointing from the varnish stage to the oxidation stage represents the possibility that varnish can be a catalyst of further oxidation.

RETHINKING OIL ANALYSIS

For the last half century oil analysis has been the primary tool for detecting incipient lubricant failure. There has been a rising challenge however to the use



Figure 1 The formation of both sludge and varnish in a hydraulic oil reservoir

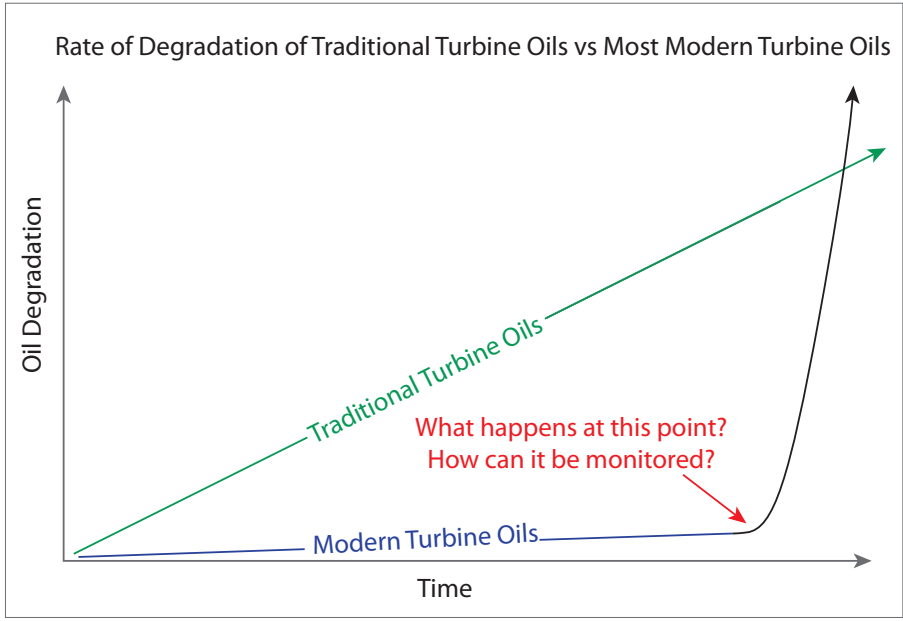


Figure 4 The criticality of choosing the correct oil analysis tests when monitoring today's lubricant formulations.

of traditional testing methodologies for predicting the point of lubricant failure and subsequent formation of deposits. Many research papers have highlighted that tests such as those for viscosity, acid number and ISO (or NAS) particle count are not able to predict early lubricant degradation and the formation of deposits. This is for a couple of reasons. Firstly, the polar products formed from lubricant degradation are mostly sub-micron in size – undetectable with routine analysis. Secondly, many of today's new lubricant formulations no longer degrade in a linear fashion, making it more challenging to predict when the lubricant will begin to rapidly develop deposits. The non-linear degradation of modern lubricants is related to the antioxidant selection as well as the oxidative stability of Group II and III base oils. Once the antioxidants have been depleted, Group II and III oils have less natural oxidative stability than Group I oils, and hence degrade extremely quickly. As a result, the majority of standard oil analysis tests provide no warning as to when the lubricant will start to rapidly degrade and generate deposits. *Figure 4* above illustrates how traditional lubricants degrade compared to most modern lubricant formulations.

It is well understood that as a lubricant is exposed to thermal and mechanical stresses its antioxidant package depletes. There are two ways to monitor the depletion of these important additives. Firstly, antioxidants can be indirectly monitored using oxidative stress tests such as Rotating Pressure Vessel Oxidation Test (RPVOT; ASTM D-2272) or High Pressure Differential Scanning Calorimetry (ASTM D-6186). Secondly, antioxidants can be measured directly using Fourier Transform Infrared or Linear Sweep Voltammetry

(ASTM D-6971), otherwise known as the RULER test.

There has been a rising concern with oil analysts about using oxidative stress tests like RPVOT on modern lubricant formulations utilising complex antioxidant systems. Experience strongly suggests that the precision of this test has dropped considerably compared to the precision statement in the ASTM D-2272 standard (which quotes a repeatability of 12% and a reproducibility of 22% for oils with values less than 1,000 minutes. Many new lubricants have test values higher than 1,000 minutes.) The repeatability and reproducibility of the test is generally accepted to be between 30-50%. A recent survey at an international

standards institute reported a 39% reproducibility result. Poor repeatability and reproducibility of the RPVOT test has made it much more challenging for data analysts to interpret the results. *Figure 5* illustrates some of the challenges in determining an end-point to the RPVOT test with modern lubricants and shows the difference between the RPVOT results with a traditionally formulated lubricant and those with many modern formulations. Oil B represents the RPVOT results of many modern turbine oils. There is not a universal understanding of the end-point of the test, even though ASTM determines the end-point to be at 175 kPa. This is one of the contributing factors to decreasing precision standards for RPVOT.

Directly monitoring individual antioxidants has been demonstrated to be a very good predictive method for monitoring antioxidant depletion and provides a more thorough understanding of how fluids degrade. FTIR analysis is a powerful tool for identifying molecular changes in lubricants as they degrade. The RULER test is specifically engineered to track individual antioxidants and, unlike FTIR, is not influenced by other additive components. It identifies the type of antioxidants in the oil and by comparing the results to the new oil, facilitates determination of the remaining antioxidant as a percentage of the new oil benchmark. An example of RULER results is given in *Figure 6* opposite.

Once the antioxidants in a lubricant start to degrade, the first physical impact on the lubricant is the generation of extremely small, sub-micron, contaminants. These may consist of degraded base oils, but at the early stages of development often consist of the degraded antioxidants. Clearly, tests such as ISO particle count, which measures particles greater than

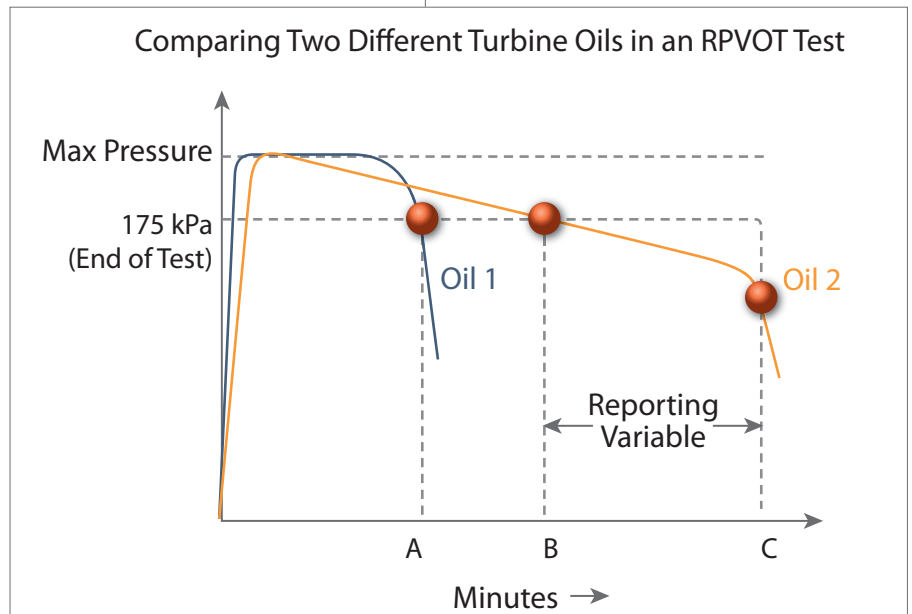


Figure 5 The challenges in reporting RPVOT results with some modern formulations

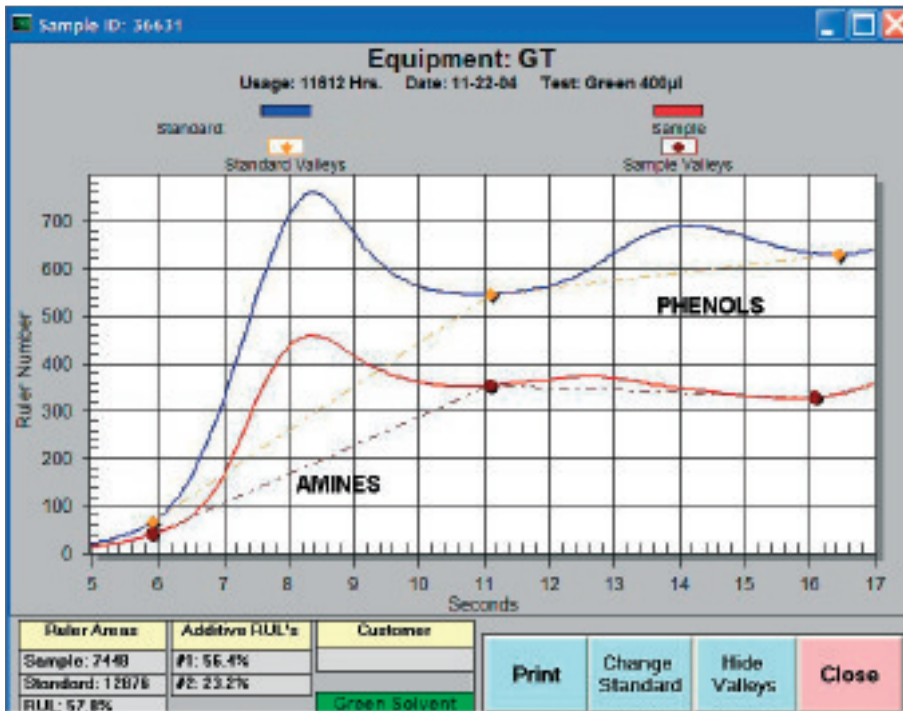


Figure 6 Results from the RULER instrument. The red line is the used sample and the blue line is the new oil reference sample. (It can be seen that one of the primary antioxidants, phenols, is at 23% of the new oil reference while another, amines, is at 56%)

4-microns and above, are not able to detect these particles. Other tests such as measuring the gravimetric weight of the insolubles, or ultra-centrifuging, have shown promise but are also influenced by larger contaminants.

The test that has shown the most promise in identifying degradation by-products is referred to as Membrane Patch Colorimetry (MPC). This is a relatively straight forward test. Fifty millilitres of oil sample are mixed with an equal amount of solvent (usually petroleum ether) and filtered through a 0.45 micron 47mm diam. membrane patch. The colour of the patch is then analysed with a spectrophotometer and the total amount of colour is reported. Most laboratories report the result as CIE LAB DE, the same scale that is currently used in the draft standard being developed

by ASTM.

Figure 7 shows a couple of examples of patches and their corresponding MPC value.

The RULER and MPC tests are complementary. RULER identifies the depletion of the antioxidants and provides critical insight as to when a fluid will start to exponentially degrade. MPC measures the formation of these degradation products, allowing users to predict when deposits will start to settle out in their lubricating system. These two tests are appropriate tools to use for predicting the creation of deposits in modern lubricant formulations, and at the same time provide opportunities for proactive remedial steps.

REMOVING THE CONTAMINANTS THAT CAUSE LUBRICANT VARNISH

A decade ago, there wasn't a vendor in the industry that claimed to have a 'varnish solution'. As varnish became recognised as a key factor in impacting reliability in manufacturing and power plants some existing technologies refocused their product specification sheets to say 'varnish removal systems' instead of sub-micron particulate removal. This has led to the introduction and commercialisation in recent years of over

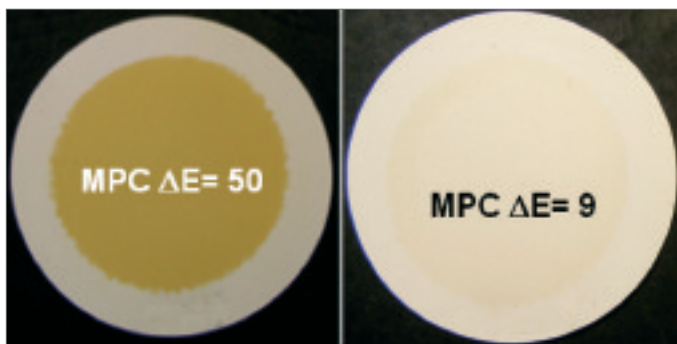


Figure 7 Example patches and values from the Membrane Patch Colorimetry (MPC) test. (A value of 50 would be cause for concern in any servo-valve application and suggests that the lubrication system is already coated in varnish. A result of 9 would be considered normal.)

a dozen new technologies that claim to 'solve' the varnish problem. Most perform well. However, there is not one technology that is able to provide the solution to all problems.

The success of a varnish mitigation system in adequately removing sub-micron contaminants and freeing a system of varnish concerns is determined by the chemistry of the contaminant, the temperature of the fluid that is to be treated, and the sizing of the varnish mitigation system.

Oil degradation products can be either organic or inorganic and either soluble or insoluble in nature. When the degradation products consist of depleted metallic-based additives, such as ZnDDP, the deposits are inorganic and have difficulty remaining in solution. These contaminants require a technology that can efficiently remove sub-micron contaminants.

If the oil degradation products are organic in nature they typically consist of degraded antioxidants such as phenols and amines, and often oxidised base oil. These degradation products are initially soluble but, depending on their size and solubility in the oil they can transit in and out of solution. Experiments have shown that typically these types of contaminant have a 'melting' point between 40°C and 50°C. When the oil is at 50°C, more of these organic soft contaminants will be in solution. However, if the oil cools in parts of the system (such as servo valve lines) then more degradation products will come out of solution and form varnish. Clearly, the filtration technology required for these types of contaminant depends upon the temperature of the fluid that is being treated, because most technologies that claim to be 'varnish mitigation systems' can only remove insoluble degradation products.

Typically, varnish mitigation systems are 'kidney-loop' filtration systems, which circulate the oil to and from the oil reservoir at relatively low flow rates. As with other contamination control technologies their sizing is critical; such systems must be able to remove oil degradation products at a rate that is quicker than their rate of production.

TYPES OF VARNISH MITIGATION SYSTEMS

The following is an overview of the various types of varnish mitigation systems available in the market today.

Electrostatic Liquid Cleaners (ELC)

Utilising electrostatic forces to attract polar contaminants, these devices work by passing the oil over a series of anodes and cathodes. Negatively charged particles are attracted to a positive collection zone and positively charged particles to a negatively charged zone through a process

known as electrophoresis. Neutral particles are attracted by the deformation of the electrical field through a process known as dielectrophoresis. Electrostatic oil cleaners require a non-conductive environment to function and are sensitive to small amounts of water contamination. They are effective devices for removing sub-micron insolubles, including insoluble oil degradation products.

Charge Agglomeration (CA)

A process similar to electrostatic liquid cleaners, but in this case the particles are charged with electrostatic forces and forced to agglomerate in size. The charge on the particles does not relax within the confines of the filtration equipment, meaning that agglomeration occurs when the oil returns to the lubrication system. When the sub-micron particles agglomerate to multi-micron sized particles, they are removed through conventional mechanical filtration. Agglomeration units have the same sensitivity to water as electrostatic oil cleaners.

Depth Media Filters (DM)

Depth media filters can filter particles down to approximately three microns in size. However, many of these filters are also constructed with a polar, cellulose, media. In these cases the polar oil degradation products are attracted to the polar nature of the media and adsorb onto the fibres. These units are effective at removing smaller amounts of polar sub-micron contaminants that are in suspension. However, if the oil is heated to above the melting point of the contaminants all of the filtered oil degradation products will melt back into solution, re-contaminating the fluid.

Electrophysical Separation Process (ESP)

This patent-pending technology was designed to remove organic soft contaminants from the lubricants. Utilising a selective absorptive filtration media, the unique attribute of this technology is its ability to remove oil degradation products that are both in insoluble and soluble. It does not impact on other additive components in the formulation, nor is the filter media affected by water or other contaminants.

Most of these technologies work very well, however their limitations are in their application. The key is to understand what technology is best for what application. Table 2 lists some variables to consider when selecting an appropriate varnish mitigation technology.

Electrostatic technologies are clearly superior when attempting to remove insoluble oil degradation products. When dealing with R&O oils which produce organic degradation products, temperature

Type of Oil	Nature of Degradation Products	Temp	Recommended	Not Recommended
Hydraulic and other ZDDP-based oils	Insoluble	<40°C	ELC & CA	ESP & DM
		>40°C		
Non-Zinc Hydraulic Oils	Insoluble	<40°C	All Technologies	DM
	Soluble	>40°C		
Turbine, Compressor & other R&O	Insoluble	<40°C	All Technologies	DM
	Soluble	>40°C		

Key Electrostatic Liquid Cleaner – ELC; Charge Agglomeration – CA; Depth Media Filter – DM; Electrophysical Separation Process – ESP

Table 2 Recommended varnish mitigation systems based on the chemistry of the contaminants and temperature of the fluid

becomes a large consideration (see Figure 8).

If, during an outage, removal of oil degradation products from in-service lubricants is required, and the oil can be cooled for many days, all of the technologies will work, with various degrees of success. However, the additional ability of the ESP technology to remove the soluble products has distinct advantages. If the soluble oil degradation products are removed before they have the chance to form varnish deposits then perhaps this is a step closer to a true varnish mitigation system.

SUMMARY

Lubricant varnish is an emerging problem for modern hydraulic and lubricant formulations, increasing maintenance, production and energy costs while decreasing plant reliability. This problem has coincided with a dramatic change in oil formulations, focussing on Group II and III base oils. Varnish is caused by fluid degradation, the leading contributor being oxidation.

A contributing factor in these new deposit problems is that traditional oil analysis tests have not provided appropriate warning signs for incipient lubricant degradation and the creation of degradation products, which cause varnish. Incorporating oil analysis tests such as the RULER, which monitors the depletion of antioxidants, and MPC, which measures the creation of varnish-forming oil degradation products, has been shown to forecast varnish potential earlier than other oil analysis tests. Upgrading routine oil analysis tests to incorporate these technologies will allow a manufacturing

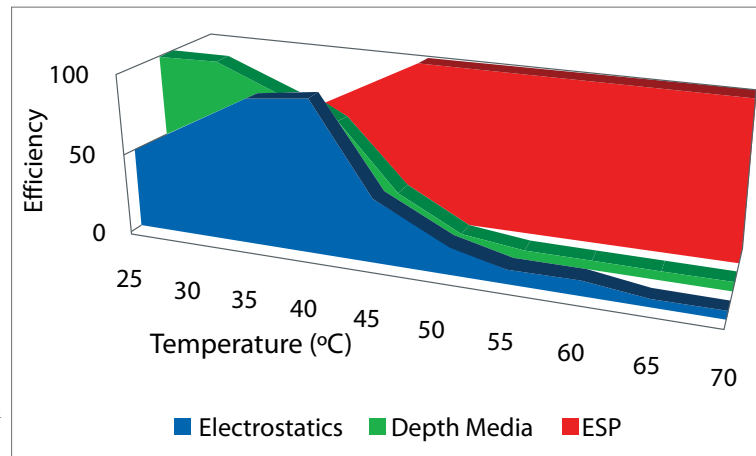


Figure 8 The relative efficiency of various varnish mitigation technologies depending on the temperature (°C) of the fluid

plant to achieve optimum life of lubricants along with improved plant reliability.

When the varnish potential of a hydraulic oil or lubricant increases beyond normal values a new generation of contamination control technologies is required to remove these sub-micron contaminants. Electrostatic liquid cleaners are an effective technology for removing sub-micron contaminants in hydraulic oils. However, the ability to remove even the oil soluble oil degradation products by employing ESP technology can take varnish mitigation to a new level.

The combination of improved oil analysis and the most appropriate varnish mitigation system to suit the specific application should provide valuable payback in the form of increased oil life, greater plant reliability, improved product quality etc. In selecting the most appropriate varnish mitigation system a deep understanding of the lubricant, its environment and its operating regime is required. What may be good for one system may not be for the next. As stated at the beginning, lubricating oils are undergoing more changes today than at any time in recent memory. Therefore, we must change the way we manage these lubricants in order to achieve optimum performance. ✨