

WHITE PAPER

Managing Rotating Equipment Lube Oils in the Ammonia & Nitric Acid Industry

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BACKGROUND

Compressors are an important machinery asset in the production of fertilizers and are integral in their ammonia and nitric acid production lines. Reliable compressor performance is dependent upon having a high quality, well maintained lubricant. These compressor lubricants are placed under a lot of thermal stress and may be exposed to process gases, which can cause rapid fluid deterioration. These chemical changes in the lubricant manifest themselves into mechanical challenges in the compressor set, such as vibration, bearing temperature increases and valve sticking in hydraulically manipulated controls.

This paper examines the nexus between these chemical changes in the fluid and mechanical impacts to the machinery. Furthermore, best-practice condition monitoring strategies and maintenance actions are suggested for integration into a fertilizer plant's reliability program.

LUBRICATION REQUIREMENTS FOR COMPRESSOR SETS IN THE FERTILIZER INDUSTRY

Compressors are an integral part of the manufacturing process for urea, nitrogen, nitric acid and ammonia within fertilizer plants. These compressors are typically centrifugal or axial in design, requiring a high-quality Rust and Oxidation inhibited (R&O) oil typically categorized as an ISO VG32. The compression of gases such as ammonia, nitrogen, carbon dioxide, oxygen or nitrogen sometimes results in their migration through seals and into the lube oil system, which can have deleterious effects.

Both lubricants and their applications continue to evolve. Industry's drive towards more globalization and efficiency improvements have set off a chain of events, impacting all aspects of an operation. The industry is demanding faster, smaller, more efficient machines. The Original Equipment Manufacturer (OEM) responds, delivering a more compact, efficient machine, however in most cases, this results in placing higher thermal and mechanical stress on the lubricant. In the case of compressor oil, the fluid is now expected to perform at higher temperatures, in small capacity systems, for longer periods of time and in the presence of many potential contaminants.

Oil manufacturers have responded by reformulating their products to meet these new demanding specifications. The most consequential change to lubricant formulations over the last two decades is the use of more highly refined base stocks, such as API Group II and III.



Fully formulated Group II and III lubricants have superior oxidative resistance because virtually all hydrocarbon molecules are saturated. A drawback of Group II formulated lubricants is reduced solubility. This often requires the use of a solubility enhancer, or cosolubilizer, in order to keep the additive package in solution. As the oil degrades, the reduced solubility properties mean a limited ability to keep oil degradation products in solution.

Over the last couple of decades, the combination of the new generation of lubricants and the increased operational conditions of industrial compressors, has resulted in new oil degradation mechanisms. During maintenance overhauls, operators often report that compressor bearings or gearboxes are coated with a dark brown/amber deposit, or oil reservoirs have more problems with foaming control. These oil-derived deposits are commonly known as varnish.

Varnish is typically defined as a thin deposit in a lubrication system that is difficult to remove by wiping and comprised primarily of organic residue. The chemical composition of varnish can be extremely varied and can be classified by chemistry and degradation mechanisms. Typically, sludge is considered an easy to wipe, gooey substance that also contains moisture. Varnish has a more cured, shiny appearance and not easy to wipe.

Varnish is primarily caused by the continual process of oxidation, and which is accelerated by temperature and various metallic components, and gaseous catalysts. Virtually everything is susceptible to degradation due to the presence of oxygen, lubricants not excluded. Antioxidants are formulated into modern compressor oils because they are more reactive species than the base oil. The oxygen more readily reacts with the antioxidants, who sacrifice themselves to protect the base oil and significantly extend the life of the oil.

In addition to oxidative stress, high temperature thermal events may also be a contributing mechanism for fluid degradation. Thermal degradation is created by high temperature events without the influence of oxygen, such as Micro-dieseling or Electrostatic Spark Discharge (ESD).



¹ Livingstone, G. Wooton, D. (January 2013) "Lubricant Deposit Characterization", Oil Doc 2013 Conference Proceedings, Rosenheim, Germany



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OVERVIEW OF VARNISH-RELATED PROBLEMS IN COMPRESSORS

Rotating equipment require lubricants to perform in a hydrodynamic lubrication regime with a film thickness between 20-30 microns. Interactions between gas ingression and lubricants can create new degradation pathways. Compressor oil degradation causes the formation of polar products that interact with white metal bearing surfaces (i.e. Babbitt), forming deposits.

These deposit formations can have mechanical consequences, such as:

- Increased Vibration
- Bearing temperature excursions
- Control valve hysteresis or sticking
- Bearing deposits
- Gearbox deposits and accelerated wear

THE IMPACT OF VARNISH ON BEARINGS

Varnish formation on compressor bearings has a consequential impact on a fertilizer plant's reliability program. It can be responsible for wiping a bearing, shutting down the compressor and all associated production processes. The financial impact can be from a few tens of thousands of dollars to well over a million dollars.

The two consequences of bearing deposits are:

- 1. Temperature excursions,
- 2. Increased bearing wear.

Vibration analysis is a powerful condition monitoring tool and compliments oil analysis as foundation technologies in a reliability program. The direct link between deposit formation and vibration signals continues to be an evolving area of study, but there is clear evidence that there is a correlation between the two.

Varnish acts as an insulator, preventing the oil from performing one of its primary functions: cooling. The greater degree of deposit formation, the more insulation on the bearing resulting in a corresponding increase in bearing temperature.

There appears to be a direct link between certain axial and radial bearing temperature



excursions and deposit formation. The figure below shows a typical vibration signal on a bearing due to deposits. This is characterized by sawtooth pattern with small, sharp peaks that grow in amplitude over time.



Figure 1: Bearing temperature increase in a compressor

It is also possible to see a correlation between vibration signals and temperatures, as shown in Figure 2.



Figure 2: Increases in axial bearing temperatures (red) are correlated to increases in vibration signals (green)





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In some cases, it is also possible to see a correlation between rotor position and temperature increases.





Figure 4 illustrates the relationship between deposit film thickness, bearing temperatures and rotor position.



Figure 4: Illustration suggesting the impact that varnish deposits have on bearing temperatures and rotor position.

When the force to move the rotor becomes greater than the film strength of the deposit, the varnish layer is "wiped" off. This is seen as a sharp drop in temperature, explaining the formation of the sawtooth-like appearance of the vibration signal. The other phenomena caused by deposit formation on bearing surfaces is an increase in wear.



As polar degradation products are attracted to the highly finished, white metal surfaces of bearings, the bearing surface is altered. Microscopic views of varnish deposits show an irregular surface. Varnish essentially creates additional asperities on the metal surface, making it more challenging for the lubricant to maintain its film under high loads. Occasionally, the hydrodynamic film will crack, causing a temporary collapse, creating metal-to-metal contact. This occurs most frequently in the highest load zone of the bearing.

Hydro-dynamic film collapse, causing metal-to-metal contact creates further surface asperities, increasing the chance of film collapse in the future. Metal-to-metal contact also results in extremely high temperatures, which can instantly carbonize the oil film creating additional bearing deposits of a different chemistry.



Figure 5: Deposit formation on a bearing, showing surface damage at its highest load zone.





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THE IMPACT OF VARNISH ON CONTROL VALVES

Varnish deposits are sticky in nature. This will impact the performance of control valves, which rely on clean, deposit-free lubricants to function as designed. Often, oil flow to parts or all of the control valve is intermittent. This results in the oil cooling in temperature, allowing degradation products to come out of solution, forming on the internals of the valve. The formation of deposits in valves has been shown to cause valve lock due to resulting high levels of static friction . In some control systems, the energy input of a valve Sasaki, A., "Hydraulic Valve Problems Caused by Oil Oxidation Products" Hydraulic Failure Analysis: Fluids, Components and System Effects, ASTM STP 1339, G.E. Totten, D.K. Willis and D. Feldmann, 2001.

2 Sasaki, A., "Hydraulic Valve Problems Caused by Oil Oxidation Products" Hydraulic Failure Analysis: Fluids, Components and System Effects, ASTM STP 1339, G.E. Totten, D.K. Willis and D. Feldmann, 2001.

Valve that are sticky due to oxidation products are can be identified by the increased amount of energy required to move the valve.

Besides loss of hydraulic control, valves that are coated with varnish are often considered to be malfunctioning and are prematurely replaced. Although this may immediately solve the valve sticking issue, the newly replaced valve will be quickly coated with varnish, causing reoccurring issues.



Figure 6: A Failed valve coated with varnish deposits.

COMPRESSOR OIL CONDITION MONITORING STRATEGIES

The operator of a compressor unit is acutely aware of the need for realizing optimum reliability and availability of this asset. Monitoring the condition of the lubricant by selecting the correct tests and analysing the fluid at the right intervals helps the operator know if the fluid is suitable for service. It is also the primary tool to identify incipient lubricant failure, allowing the operator to take proactive actions. Guidance on oil condition monitoring strategies is often provided by OEMs, international standard bodies and lube oil experts.

As the formulation of both compressors and their lubricants have evolved, so too have the tests required to monitor them. Traditional oil analysis methods, such as viscosity, elemental spectroscopy, acid number, particle count and water can still provide some value, however they cannot be reliably used for detecting fluid failure. This is for two reasons. First, the polar products formed from lubricant degradation are less than a micron in size – undetectable with routine analysis. Second, 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.

One of the contributing factors to a modern oil's non-linear degradation is the fact that Group II and III oils have a lower natural oxidative stability compared to Group I oils:

RPVOT (ASTM D2272) API Group I Base oil: 85 mins RPVOT (ASTM D2272) API Group II Base oil: 30 mins

The lower oxidative stability of the base oil means that when the antioxidants degrade, the base oil has little ability to resist further degradation and will fail rapidly.

In order to understand fluid failure and remaining useful life, it is therefore useful to augment standard oil analysis tests with more advanced testing methodologies.

The health of a lubricant's antioxidant system will largely determine the life of the oil. Directly monitoring individual antioxidants has demonstrated to be a very good predictive method to monitor antioxidant depletion and provides a more thorough understanding of how fluids degrade.





The RULER is specifically engineered to measure and trend individual antioxidants. Unlike other testing methodologies that can detect antioxidant molecules, like FTIR, the RULER is not influenced by the presence of other additive components. An example of a RULER test can be seen below:

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Figure 7: RULER directly measures the health of individual antioxidants, revealing the health of the lubricant. The red line is the used sample and the blue line is the new oil reference sample. One can see that one of the primary antioxidants – phenols, are 6.6% of the new oil reference while another primary antioxidant – amines, are 76.3% of the new oil reference.

Once the antioxidants in a lubricant start to degrade, the first physical impact to the lubricant is the generation of extremely small, sub-micron degradation products. These contaminants may consist of degraded base oil molecules, but at the early stages of development, most often consist of the degraded antioxidants.

The most common test method to detect oil degradation products is Membrane Patch Colorimetry (MPC), conforming to ASTM D7843. Other tests such as



measuring the gravimetric weight of insolubles or ultracentrifuges have shown promise, but may also be influenced by larger contaminants.

The MPC test is a relatively straight forward procedure. Fifty milliliters of sample are mixed with an equal amount of solvent (usually petroleum ether) and filtered through a 0.45-micron patch. The color of the patch is then analyzed with a spectrophotometer and the total amount of color is reported. The results are reported on the CIE LAB Δ E color scale, examples of which can be seen below:



Figure 8: Example Patches and values from the Membrane Patch Colorimetry (MPC) test. A value of 50 would be considered critical, warranting immediate action. A result of 9 would be considered acceptable.

Other test methods that may also be of value in a compressor oil analysis program are:

1. FTIR analysis. The Fourier Transform Infrared (FTIR) practice is a refined infrared spectroscopy method, which can be used to monitor molecular changes in the fluid, potentially identifying its mode of degradation.

2. Particle count – Cleanliness of compressor oil can be determined by particle counting, most often by an automatic optical particle counter. In some formulations, the increase of the 4-6µm contaminants may also suggest the presence of soft contaminants.

3. Air Release – Measuring the fluid's ability to dissipate air bubbles can be of value if the lubricating oil is also expected to provide hydraulic work, such as moving a value or lifting a bearing shaft.





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4. Elemental Spectroscopy by ICP –can identify wear in various machinery components, such as Babbitted surfaces.

In all of the above test methods, it is important to have a correct oil sampling interval. The most common sample periodicity for compressors is every 3 months. Oil sampling frequency shall also be adapted to the function of the condition of the oil.

Finally, with this compressor oil monitoring matrix, the main objective is to establish a trend for the individual oil parameters. Variations from fluid condition trends may be further investigated for root cause determination.

A SOLUTION TO REMEDY COMPRESSOR OIL VARNISH DEPOSITS

Fluitec has developed a solution to manage deposits already formed in lubricating systems and prevent their further development by use of a solubility enhancer. This technology is referred to as **Solvancer™**.

A solubility enhancer should only be considered under the following conditions:

- 1. The solution must be added to the machine while operating.
- 2. It must be compatible with in-service oil and other system materials.
- 3. It can't affect the oil's interaction with contaminants, inhibit corrosion, anti-wear performance and must work under intense monitoring.
- 4. Doesn't give into oxidative stress.
- 5. Usage of this solubility enhancer eliminates the need to install ANY other mitigation system.
- 6. Works even under extreme oxidative conditions and doesn't even produce deposits when burnt.

Solvancer[™] technology was developed after an exhaustive categorization of the various deposit chemistries found in compressors. Three essential properties were studied in this categorization exercise: polarity, hydrogen bonding and dispersive forces. Solvancer[™] is optimized taking these three characteristics into account to ensure that lube oil deposits are quickly dissolved back into the lubricant.

Solvancer[™] is added a treat rate between 3 and 5% to an in-service lubricant. It has no adverse effects on the performance of the fluid and goes to work immediately dissolving deposits, and preventing further varnish from forming.

The case study below shows both the immediate and long-term impact of adding Solvancer[™] technology to an in-service compressor. This graph shows a 1-year temperature trend, before and after adding Solvancer[™]. The temperature spike dropped within one hour of adding it to the system has been maintained at a low level ever since.



Figure 9: The impact of adding Solvancer[™] technology to an compressor's bearing temperature.

CONCLUSIONS

Reliable compressor operation is essential for fertilizer plants. These fluids are under increasing levels of thermal stress and may be exposed to gas ingression causing further acceleration to its failure. The result of compressor oil degradation are polar degradation products that form as varnish deposits on bearings, valves and other lube system components. The impact of these deposits in a bearing are temperature excursions and bearing wear. In a hydraulically controlled valve, the impact of deposits are valve sticking and locking.

It is possible to monitor the health of these fluids, and their potential to develop varnish, by RULER and MPC tests. One solution to the formation of deposits in compressor oils is the use of a solubility enhancer. Fluitec has developed its Solvancer[™] technology, specifically for this application. It has been shown to provide immediate relief to systems suffering from varnish and long-term deposit control protection for components susceptible to failure from varnish.



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