ADDITIVE DEPLETION: IMPACT ON USEABLE OIL LIFE AND EQUIPMENT WEAR

Pentair

Abstract
Additives are introduced into lubrication and hydraulic oils in order to minimize the rate of wear occurring in costly manufacturing equipment. A failure of the oil used to provide a suitable level of protection can result in excessive wear, increased maintenance costs, and also an increased likelihood of very expensive, unexpected plant downtime. The results of recent testing of traditional anti-wear additives show that in the presence of moisture contamination, there is the potential for degradation of the additives. This degradation is such that changes occur in the chemical makeup of the additives, so that they may no longer be suitable for anti-wear protection.

In this paper, we will demonstrate how this chemical breakdown is dependent on the moisture content of the lubricant. We also introduce a new technology for oil conditioning that is able to prevent moisture contamination from affecting the oil. We will demonstrate that successfully maintaining a low moisture status prevents the degradation of the oil and its additives, and measurably decreases equipment wear.

Introduction
In the process of designing a specific lubricating or hydraulic fluid, sophisticated and costly additive chemistry is employed. The intention is to ensure that the fluid will provide characteristics that are suited to the applications of the machinery, as specified by the equipment manufacturers. Some of the most common additives are designed to minimize wear, control viscosity, prevent oxidation, and minimize the impact of water on machinery. It is well understood that continued use of oil in a degraded condition will cause significant and costly damage to equipment. Historically, plant operators and oil suppliers have used periodic oil sampling to monitor the level of specific elemental compounds, and when certain threshold limits are reached, condemn the fluid.

The actual maintenance cost for equipment repair and replacement is a significant portion of a facility’s annual operating budget. In a paper recently published by Strategic Asset Management at the TAPPI Fall Technical Conference, a formula for estimating the potential for savings associated with improved maintenance techniques was presented. The formula is based on the Replacement Asset Value (RAV) of the equipment within the facility. The current industry norm for maintenance expenses is an RAV of 4.5–7.5%. This means that for every $1MM of replacement value for an asset, a facility would be expected to spend $45–75K per year on maintenance. With optimal maintenance tools and techniques, it is believed that it is possible to attain an RAV value of 1.5–2.5% – a saving of $30–50K per year (for each $1MM of asset value). These savings would represent a reduction in maintenance costs of up to 66% per year.
Utilization of a purpose-specific, advanced oil-conditioning technology enables operators to maintain oil with the intended additive content, ensuring optimal fluid quality. By doing this, it is possible to drastically reduce the rate at which these additives are consumed, thereby extending the usable fluid life and ensuring that equipment is properly protected. In applications where equipment has very high replacement value, the savings potential can be remarkably high.

Experimental tests were conducted on both hydraulic and lubrication oils to assess the impact of the presence of water on the degradation of additives. Additional measurements were made to assess the impact of lubricant moisture content on equipment wear, as assessed by wear metal levels.

**Impact of Water on Hydraulic Oil Anti-Wear Additive Degradation**

A hydraulic oil and vane pump circulation system was used to investigate the mechanism through which anti-wear additives can break down. A test was run to determine the effect water has on the degradation of anti-wear additives in hydraulic oil. Two tests were performed using the same procedure. The first involved maintaining the system with a water concentration of 1,000 ppmw (0.1%), while the second involved maintaining the system at a very low water concentration (<50 ppm) using an ULTIDRITM oil-conditioning system.

**Case 1 – Wet Hydraulic Oil: Water Concentration of 1,000 ppm**

In the first test, water was injected into the system and allowed to circulate with the oil. Oil analysis was used to monitor the rate of anti-wear additive depletion due to degradation and the intermediate compounds that are created during the degradation process. The concentration of metal in the oil, an indication of equipment wear, was also measured.

The general configuration of the apparatus is shown in Figure 1.

**Test Procedure Overview:**

1) The system was filled with new ISO 68 hydraulic oil and recirculated in a closed loop.

2) A pressure control valve was used to maintain a constant 500 psig pump discharge pressure. The oil then passed through a heat exchanger and was returned to the reservoir.

3) The reservoir maintained oil temperature at 140°F.

4) Once the system had stabilized, water was injected into the oil with a target content of 1,000 ppm. Water content was monitored using the inline moisture analyzer and additional water injected on a scheduled basis to maintain the target level.

5) Oil samples were collected and analyzed for anti-wear additives (ZDDP complexes) using infrared spectroscopy (FTIR) and phosphorus nuclear magnetic resonance (31P-NMR) technologies. The FTIR results provided evidence that the anti-wear additives were degrading and the 31P-NMR was used to quantify the degree of degradation and the type and amount of degradation products formed.
A plot of the NMR data for the experiment is shown in Figure 2. In the top spectrum (new oil), peaks indicating the primary and secondary anti-wear complexes are clearly visible. The primary additive has been identified as an overbased ZDDP complex typically consisting of 4 ZDDP molecules, while the secondary additive has been identified as neutral ZDDP.

After 1,500 hours, most of the primary ZDDP complex has been depleted, as is evident from the reduction in the peak area. The decomposition pathway of the primary ZDDP complex typically involves the formation of the neutral ZDDP molecules, which can then undergo further decomposition reactions. Concurrent with the reduction in the primary and secondary anti-wear compounds, thermal and hydrolysis degradation products (associated with copper) have clearly appeared in the samples.

In the 2,000-hour sample, it can be seen that the primary and secondary anti-wear compounds have decreased in concentration even further. In addition, the degradation compounds continue to accumulate.
Case 2 – Dry Hydraulic Oil: Water Concentration of <50 ppm

A second test was simultaneously performed using the same circulation configuration and test procedure. In this situation, an ULTIDRI™ oil-conditioning system was also incorporated into the system to continually condition a slipstream of the oil being circulated. This oil-conditioning system ensured that all of the oil within the circulation system was continually maintained in a very dry state (<50 ppm). The same testing of the oil was performed as in the “wet oil” case.

Figure 3: Dehydrated Hydraulic Apparatus

Figure 4 shows the NMR spectra for this test. The peak areas of the primary and secondary anti-wear compounds demonstrate a very minor decrease when compared to the wet case (see Figure 2). This would confirm that by continually eliminating moisture from the oil and controlling potential for ingestion, both primary and secondary anti-wear compounds will be maintained in very high concentrations – close to that of the original oil.
In addition, it can be noted that no hydrolysis-related degradation by-products have been formed at all. This lack of hydrolysis by-products would be directly attributed to the lack of free or dissolved water in the fluid.

In Figure 5, the total concentration of the primary and secondary anti-wear complexes for the wet and dry systems are compared.

<table>
<thead>
<tr>
<th>Elapsed Time</th>
<th>&lt;50 ppm Water Concentration</th>
<th>1,000 ppm Water Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anti-Wear Concentration</td>
<td>Percent Remaining</td>
</tr>
<tr>
<td>New Oil</td>
<td>72</td>
<td>100%</td>
</tr>
<tr>
<td>1,500 Hours</td>
<td>48</td>
<td>66%</td>
</tr>
<tr>
<td>2,000 Hours</td>
<td>48</td>
<td>67%</td>
</tr>
</tbody>
</table>

**Figure 5: Total Anti-Wear Concentration**

In Figure 6, the total concentration of the decomposition products formed by the hydrolysis and thermal mechanisms for the dry and wet systems are compared.

<table>
<thead>
<tr>
<th>Elapsed Time</th>
<th>&lt;50 ppm Water Concentration</th>
<th>1,000 ppm Water Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Decomposition Products</td>
<td>Decomposition Products</td>
</tr>
<tr>
<td>New Oil</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1,500 Hours</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td>2,000 Hours</td>
<td>13</td>
<td>47</td>
</tr>
</tbody>
</table>

**Figure 6: Total Decomposition Products**

As the data shows, if the oil is maintained in a very dry state (<50 ppm moisture), the depletion rate of the anti-wear complexes is significantly slowed, and the rate of generation of decomposition products is greatly reduced. Additionally, comparison of the data at the 1,500-hour and 2,000-hour elapsed time for each case shows that the degradation rate in that period was significantly less in the dry oil system.

**Metals Analysis by ICP**

As additives are depleted from a lubricant, the fluid begins to lose its intended ability to protect the equipment within the process. Induction Coupled Plasma (ICP) analysis can be used to monitor the presence of metals in the oil. The presence of these metals is an indicator that material is being lost by equipment during its use. Samples from the aforementioned hydraulic tests were evaluated in this manner for the presence of metals. Copper was found to be the primary wear metal generated.
As shown in the graph, both the amount of copper and its rate of accumulation within the hydraulic oil was significantly greater when moisture was present in the oil. After 2,000 hours of testing, the system with moisture contained 108 ppm of copper versus <1 ppm for the system operated with an ULTIDRI™ system for continuous dehydration.

In addition to wear metals, oil analysis programs often use elemental analysis, such as ICP, to gather data regarding the status of additive compounds. During the course of these tests, samples from the hydraulic testing were evaluated for phosphorus and zinc using conventional ICP analysis, and the results compared to those from NMR testing. The results of tests run on the wet oil (1,000 ppm) are shown in Table 8.

<table>
<thead>
<tr>
<th>Elapsed Time</th>
<th>ICP Phosphorus (ppm)</th>
<th>ICP Zinc (ppm)</th>
<th>NMR Total Anti-Wear Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Oil</td>
<td>282</td>
<td>380</td>
<td>100%</td>
</tr>
<tr>
<td>1,000 Hours</td>
<td>317</td>
<td>400</td>
<td>NA</td>
</tr>
<tr>
<td>1,500 Hours</td>
<td>288</td>
<td>361</td>
<td>40%</td>
</tr>
<tr>
<td>2,000 Hours</td>
<td>325</td>
<td>399</td>
<td>33%</td>
</tr>
</tbody>
</table>

Based solely on the ICP results for the phosphorus and zinc compounds, it would appear that the anti-wear additives within the oil had remained intact throughout the test period. However, the NMR data indicates that the anti-wear compounds had been degraded to levels far below that of new oil. After 2,000 hours, only 33% of the combined anti-wear complex in the wet system remained usable.

This discrepancy is the result of the ZDDP complex being consumed. As the additive is consumed, it breaks down into other compounds, which will be comprised of phosphorus or zinc, along with other elements. As a result, the apparent content of these elements remains close to the original oil, even though they no longer provide the system with the same degree of protection from wear.
Impact of Water on Lubricating Oil Anti-Wear Additive

Two additional tests, again using both a wet and a dry oil, were performed to investigate the impact of water on the anti-wear additives used in lubricating oil and its impact on equipment wear. The test apparatuses were similar in configuration to those used in the tests described previously (see Figure 9). In the first test, paper machine lubrication oil was used and a water concentration of 1,000 ppm maintained. In the second test, the same oil was continually dehydrated to maintain <50 ppm water concentration, again using an ULTIDRI™ oil-conditioning system.

Case 1 – Wet Hydraulic Oil: Water Concentration of 1,000 ppm

Water was injected into the oil, maintaining a concentration of 1,000 ppmw of water within the circulating system.

The operating conditions for the test are shown below:

- Oil Type: Paper Machine
- Grade: ISO 220
- Discharge Pressure: 25 psig
- Reservoir Temperature: 135°F

![Figure 9: Lube Oil Test Apparatus](image)

Figure 9 shows the NMR spectra for the lube oil system contaminated with water after 2,000 hours of operation. The largest peaks represent the primary anti-wear compound, a phosphorus-based additive. According to the lubricant manufacturer, this compound is a proprietary, advanced anti-wear additive, as opposed to ZDDP. By comparing the size of the peak and the area contained, it can clearly be seen that the anti-wear compound remaining in the oil has been significantly depleted.

![Figure 10: NMR Data – Wet Lubricating Oil (1,000 ppm)](image)
Case 2 – Dry Hydraulic Oil: Water Concentration of <50 ppm

A second test was simultaneously performed using the same circulation configuration and test procedure. In this case, an ULTIDRI™ oil dehydration system was incorporated into the system to continually condition a slipstream of the oil being circulated, ensuring that the oil was maintained with less than <50 ppm moisture content.

Figure 11: NMR Data – Dry Lubricating Oil (<50 ppm)

Figure 11 shows the NMR spectra for the lube oil system water after 2,000 hours of operation with the ULTIDRI™ oil-conditioning system in operation. In this case, it can be noted that the anti-wear compound exhibits little to no measurable depletion.

<table>
<thead>
<tr>
<th>Elapsed Time</th>
<th>&lt;50 ppm Water Concentration</th>
<th>1,000 ppm Water Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anti-Wear Concentration</td>
<td>Percent Remaining</td>
</tr>
<tr>
<td>New Oil</td>
<td>51</td>
<td>100%</td>
</tr>
<tr>
<td>2,000 Hours</td>
<td>47</td>
<td>92%</td>
</tr>
</tbody>
</table>

Figure 12: Anti-Wear Concentration

The tabulated data for anti-wear additive depletion (Figure 12) shows that in the system that remained dehydrated (<50 ppm moisture), 92% of the original additive content remained after 2,000 hours. In the system with water contamination, nearly 1/3 of the anti-wear compound had already been consumed.
ICP analysis was utilized to determine the rate of wear metal generation for the lubrication systems. In this case, both copper and lead showed measurable increases during the course of the test.

![Figure 13: Copper Content in Lube Oil](image)

The data in Figure 13 once again indicates that in the presence of moisture, the rate of copper transferring from the process system into the oil is greatly accelerated. After 2,000 hours, the copper content of the oil was 34 ppm compared to <1 ppm for the oil with continual dehydration.

![Figure 14: Lead Content in Lube Oil](image)

In Figure 14, it can be seen that over the course of the test, measurable amounts of lead became entrained in the oil. After 2,000 hours, the oil was found to contain 5 ppm of lead versus 0 ppm for the dehydrated system.
**Experimental Conclusions**

In both lubrication and hydraulic circulation systems, the NMR data clearly indicates that process operation with high water concentrations in the fluid produces significantly increased degradation of the anti-wear additives. This results in a reduction in the useable life of the oil, requiring an earlier condemnation of the oil.

Additionally, the data from the ICP wear metals analyses confirms the deleterious wear effects associated with system operation while moisture contamination exists within the oil. This excessive wear metal content strongly suggests a reduction in overall equipment component life.

**Continuous Oil Conditioning**

The net result of operating with lubricants in a sub-optimal condition is an increase in overall maintenance requirements and expenses. As noted earlier, in most plants there is a potential saving of up to 66% of the annual maintenance budget, and optimal oil conditioning helps make that possible. With these experiments, the NMR and other data have shown that if the oil remains in a dry condition, the rate of anti-wear additive depletion is quite minor, while wear metal generation remains undetectable. These results further reinforce the well-accepted industry objective of keeping oil clean, dry and cool at all times.

A variety of devices are commonly used in an effort to reduce the water content of oil. Systems such as centrifuges and coalescers can remove free water and a portion of the emulsified moisture, but cannot remove any dissolved moisture and have limited utility in higher-viscosity fluids. For the removal of all water, including dissolved moisture, facilities can utilize vacuum dehydration technologies. Unfortunately, due in part to the size, complexity and cost, these systems tend to be reserved for only the most valuable or critical equipment, or are expected to be shared among numerous pieces of equipment.

ULTIDRI™ oil-conditioning technology for dedicated filtration-dehydration systems has been developed by Pentair, with each ULTIDRI™ system specifically engineered for a given application. The specific oil type, viscosity grade, reservoir volume and operating temperature are considered in the system design. The design also carefully considers the amount of moisture removal needed, given the degree of new moisture ingress relevant to the application. This engineered-solution approach enables users to have systems sized for each and every piece of equipment in the facility.

The systems are fully scalable, based on moisture removal requirements of the application, and consist of a circulation pump, an inlet particle filter, a contactor for the removal of moisture, a pressure control valve, and all required valves and instrumentation.

The scalability assists in minimizing the overall cost of ownership. The systems are then dedicated to a specific reservoir and run continuously, without interruption. This ensures that the oil within the process is continually at its optimal condition, with moisture...
and other contaminants removed as they enter the fluid. This filtration-dehydration technology has been successfully utilized in numerous industries, including: Power Generation, Pulp & Paper Production, Power Transmission, Metal Fabrication, Gas Compression, and Mobile Equipment. The technology is suitable for any application where lubrication or hydraulic fluids are employed.

Oil is continually circulated through the system. The first stage of the ULTIDRI™ oil-conditioning system is a high-efficiency particulate filter. This advanced coreless particle filter element provides exceptionally high particle removal efficiency (i.e. B1 = 1,000) combined with extended element life for optimal filtration economics. By using the particle filter, the foil conditioning system is able to increase the overall particulate filtration effectiveness, lowering the process ISO cleanliness code.

The second stage of the ULTIDRI™ system is the oil dehydrator. In the dehydrator, the principles of mass transfer will cause the moisture to diffuse from regions of higher activity (the oil) to regions of lower activity (a vacuum or dry air stream). Once the moisture is transferred into the dry air stream, it can be simply exhausted from the process. In order to maximize mass transfer rates and optimize the separation process, the filter-dehydrator system begins by ensuring that the air stream to be used contains the lowest possible moisture content. This can be achieved by using either an on-board vacuum generator or a point-of-use membrane air dryer using compressed air from an on-board compressor or from a conventional plant air source. By continually ensuring the presence of extremely dry air, the mass transfer function of the dehydrator is capable of removing virtually all of the moisture within the oil – including all free and emulsified water, and dissolved water down to 25 ppm.

With the ULTIDRI™ oil-conditioning system technology, it is economically feasible to continually condition lubrication and hydraulic fluids, attaining ISO cleanliness codes of 12/9 or better, and dissolved water content of less than 50 ppm. Because of the technology’s unique design scalability, it can be used on systems from less than 50 gallons to more than 10,000 gallons in total volume, regardless of oil viscosity.

Summary

Ingression of moisture into lubrication and hydraulic fluids has the potential to very quickly degrade the specialized anti-wear additives that have been incorporated into these fluids to provide a suitable level of equipment protection. Once these chemical compounds have been consumed or destroyed, costly wear to equipment will result. Through continuous oil dehydration and conditioning, it is possible to remove the harmful contaminants as soon as they enter the process, preventing them from damaging equipment and necessitating the replacement of the oil. Dedicated ULTIDRI™ oil-conditioning systems can be incorporated into all new and existing process systems, enabling operators to continually remove all types of contaminants, extending oil life and reducing overall maintenance requirements and costs.

References

1) Analyzing/Quantifying Your Company’s Asset Management Opportunity and Selling the Program to Management – James W. Davis, Strategic Asset Management Inc.

Acknowledgements

David Wooton, Ph.D. – Wooton-Consulting